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The references for the testimony entitled “Pam Castle Opposition Testimony – Burden of PFAS” all have “PFAS Pam Castle – “ at the start of the file names. The reference citation style in the testimony is a common one used in scientific publications – the Name-Year citation style. The file name for each begins with “PFAS Pam Castle – “ followed by the author names and publication year as written in the citations.

List of files in folder entitled “Castle PFAS Leachate”

Testimony

Pam Castle Opposition Testimony – Burden of PFAS

References Cited

PFAS Pam Castle – Andrews et al 2023

PFAS Pam Castle – Brendel et al 2018

PFAS Pam Castle – Costello and Lee 2024

PFAS Pam Castle – Fenton et al 2021

PFAS Pam Castle – Heimovaara and Wang 2025

PFAS Pam Castle – Kumar et al 2023

PFAS Pam Castle – Lang et al 2017

PFAS Pam Castle – Lenka et al 2021

PFAS Pam Castle – Lin et al 2024

PFAS Pam Castle – Neill and Megson 2024

PFAS Pam Castle – Tolaymat et al 2023

PFAS Pam Castle – Vierke et al 2011

PFAS Pam Castle – Wang et al 2024

Commissioners Wyse, Malone and Shepherd,

Thank you for considering this testimony in making your decision about the application to expand Coffin Butte landfill. I am writing to urge you to deny LU-24-027 – I strongly oppose this expansion. As I sat through the planning commission hearings, it became clear to me that the burden of dealing with the PFAS in Coffin Butte Landfill was not fully appreciated. I have a Master's degree in pharmacology/toxicology, taught college biology and genetics for 20 years, and have access to the scientific literature through my college's library. It seemed important to provide some background about why the PFAS in both landfill gas and leachate are such a vexing problem. While it is common practice to dispose of landfill leachate by mixing it with municipal wastewater and processing them together, it is not an appropriate way to dispose of leachate. Wastewater treatment plant (WWTPs) processes do **not** mitigate PFAS contamination.

The only solution to the issue is to make less leachate and landfill gas (the two major routes by which PFAS move from landfills to the environment) by reducing the quantity of material being landfilled, reducing the amount of organic matter that is landfilled, by disposing of municipal solid waste in landfills in dry environments like Columbia Ridge Landfill in Gillam County Oregon, and to appropriately handle landfill leachate separately from municipal wastewater. The operators of Coffin Butte Landfill must treat leachate on site, mitigating PFAS prior to release into the environment or transporting to WWTPs rather than foist this problem on municipalities.

Expanding the landfill will increase the amount of PFAS, fugitive landfill gas, and landfill leachate Benton County must contend with. This comes at environmental and economic costs, likely **far greater** than any modest up-front economic gains. The planning commission spent endless hours assessing thousands of documents and participating in 20 hours of public hearings to arrive at their decision to deny the application for expansion. Please honor their sound reasoning, great attention to detail, and thoughtful assessment of whether the application met the CUP criteria by upholding the denial of LU-24-027 by the planning commission.

PFAS background

- **PFAS are per- and polyfluoroalkyl substances** – there are thousands of these molecules.

- Carbon-fluorine bonds are very strong and take a great deal of energy to break. That makes PFAS molecules persistent and is why they are referred to as “forever chemicals” – they take a long time to break down and, as a result, **accumulate in the environment.**

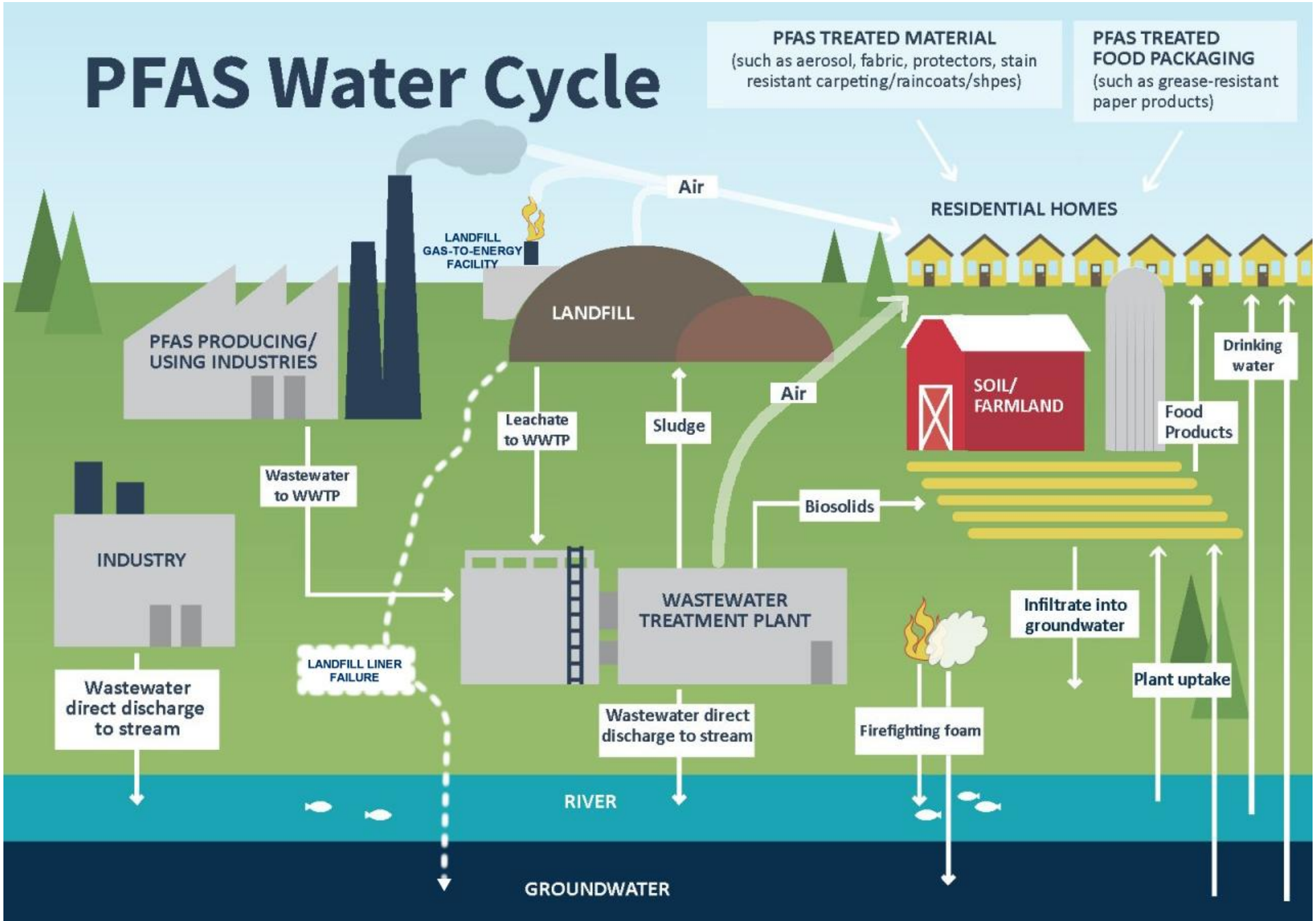
- PFAS have been used in firefighting foams, in nonstick cookware coatings, in products such as shampoo and dental floss, in water-resistant food wrappers and food packaging, on rainproof and stainproof clothing and carpets, cleaning products, sealants…

- It has long (since at least 1961) been known by some (due to industry suppression of internal research) that **PFAS constitute a health hazard for animals and humans**. Their GenX replacements are also known to be toxic.

- It has taken a very long time for agencies to develop rules regarding PFAS in water, soil, air, etc., but regulatory agencies are **slowly** catching up. We should expect that we will continue to see new rules and their enforcement with regard to drinking water, biosolids, landfill leachate, industrial waste disposal, etc.

    - It takes too long for agencies to issue guidance and to hold businesses accountable, if we wait for them to do so on issues like PFAS, the damage will be done. They are too slow.

How are humans and other organisms exposed to PFAS?



This figure was modified from the original EPA figure to include the movement of PFAS into the air via landfill gas and into groundwater via landfill leachate leakage. It is a bit difficult to see the representation of PFAS entering the air from the landfill.

Why should we care about PFAS?

PFAS present human health risks. The following is from the EPA.

“Current peer-reviewed scientific studies have shown that exposure to certain levels of PFAS may lead to:

- Reproductive effects such as decreased fertility or increased high blood pressure in pregnant women.
- Developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, or behavioral changes.
- Increased risk of some cancers, including prostate, kidney, and testicular cancers.
- Reduced ability of the body’s immune system to fight infections, including reduced vaccine response.
- Interference with the body’s natural hormones.
- Increased cholesterol levels and/or risk of obesity.”

https://www.epa.gov/pfas/our-current-understanding-human-health-and-environmental-risks-pfas

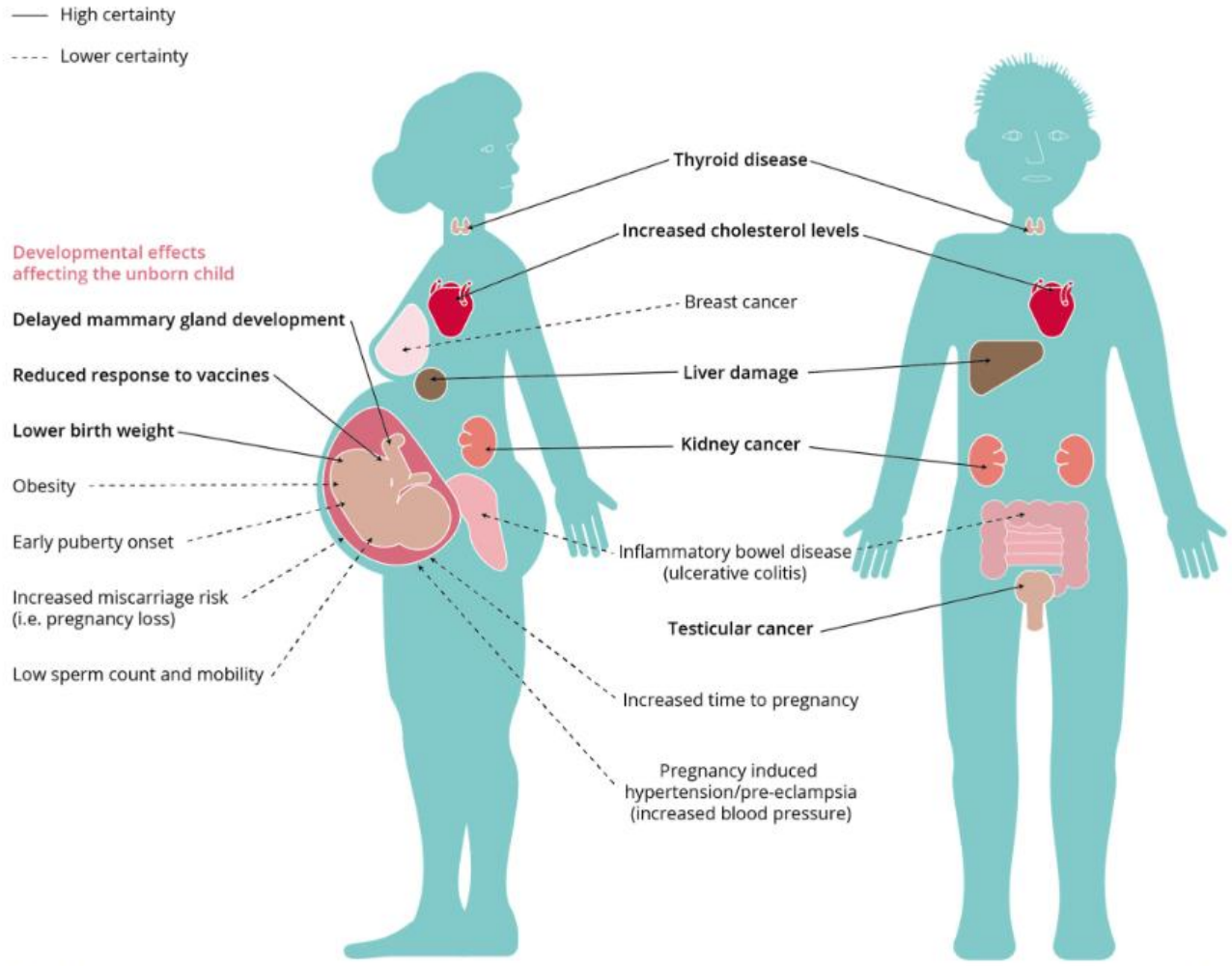


FIGURE 1: Effects of per- and polyfluoroalkyl substances on human health. Used with permission from European Environment Agency (2019). Original sources for this figure: National Toxicology Program (2016), C8 Science Panel (2012), IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (2017), Barry et al. (2013), Fenton et al. (2009), and White et al. (2011b).

From Fenton et al. 2021

<u>Andrews et al. 2023 highlights</u>:

- PFAS are detected in wildlife globally.
- **There is concordance between findings on PFAS health effects in wildlife and humans**.

Plants also bioaccumulate PFAS and exhibit metabolic and phytotoxic responses

Costello and Lee (2024) found:

- “Land application of PFAS-containing media results in plant uptake of short-chain PFAS into plant components that are consumed by humans, utilized as fodder, or land-applied. Long-chain compounds typically sorb to or are taken up into plant roots and largely remain in the roots while short-chain compounds have a higher propensity to translocate into plant shoots.”

- “Also in lettuce, PFOS and PFOA altered amino acid metabolites, dipeptides, fatty acids, lipids, phytol, purine nucleosides, phenolic antioxidants, and flavonoids, as a result of stress responses to DNA injury, photosynthesis inhibition, and impact to energy metabolism.”

- That plant enzymes were found to convert precursor molecules into more bioavailable PFAS.

Summary:
Plants bioaccumulate PFAS from soil and those PFAS have been shown to disrupt cellular processes. In addition, plants can convert PFAS into forms that are more disruptive to biological processes.

Landfill leachate composition is complex and contains:

- Water from precipitation as well as deposited waste and the decomposition of that waste.
  - Coffin Butte Landfill receives a great deal of rainfall adding to this component of leachate.*
- Organic materials from food and landscape waste, animal waste, paper, etc.
  - Coffin Butte Landfill has been documented to receive animal carcasses like cows from Tillamook county, increasing its organic material burden.
- Inorganics like ammonia, sulfates, heavy metals, etc.**
- Xenobiotics like pesticides, industrial chemicals, pharmaceuticals (Wang and Qiao 2024) and PFAS (Neill and Megson 2024).**

*As water percolates through the landfill matrix, contaminants are leached out of the landfill contents. Limiting the amount of water passing through the landfill contents limits the contaminants released by the contents. Landfills should be in dry climates.

**Items like batteries, televisions and other electronics that have been disposed of at Coffin Butte Landfill contribute to the levels of these contaminants.

Processes that occur in landfills can convert precursor molecules into PFAS (Tolaymat et al. 2023).

Landfills in wet climates produce more PFAS-laden leachate

- Lang et al. (2017) found that even though they contained only 47% of the total landfill waste, landfills in wet regions of the US (>30” precipitation/year) generated 79% of the leachate formed.

- In the US, <1% of PFAS released into leachate at landfills does so in arid climates (Lang et al. 2017).

- Coffin Butte Landfill is sited terribly due to the large amount of rainfall it receives.

For some leachate components, even very low concentrations are of high importance.

Table 1
Composition of municipal solid waste leachate [32,33].

Components	Range	Unit
pH	7.29–8.61	mg/L
COD	580–1821	mg/L
BOD	76–701	mg/L
Total suspended solids	191–740	mg/L
Volatile suspended solids	72–329	mg/L
Total nitrogen	95–401	mg/L
Organic nitrogen	29–46	mg/L
Ammonia nitrogen	66–364	mg/L
Total phosphorus	1.4–15.7	mg/L
Magnesium	126–419	mg/L
Calcium	192–430	mg/L
Chlorides	490–1190	mg/L
Volatile dissolved solids	1248–2175	mg/L
Total dissolved solids	2969–6384	mg/L
Cadmium	0.022–0.13	mg/L
Zinc	0.22–0.435	mg/L
Chromium	0.05–0.08	mg/L
Mercury	0.005–0.017	mg/L
Ethylbenzene	2.4–89	µg/L
Xylene	9.3–225	µg/L
Toluene	0.3–182	µg/L

"Landfill leachate contains a variety of micropollutants, including synthetic compounds like- phthalic acid esters (PAEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs), pesticides, microplastics (MPs), per- and **polyfluoroalkyl substances (PFAS),** cleaning detergents, microplastic, steroids, etc. [22,54]. *Despite being in very lower concentrations (µg L− 1 to ng L− 1 or even lower), micropollutants still significantly adversely affect ecosystems, the economy, and humans [55].*" (Kumar et al. 2023)

During the April 29 Planning Commission hearing, the applicant attempted to downplay the environmental and health risks associated with PFAS by stating that they were measured in parts per trillion (ng/L), describing this as a "trace" amount. The sheer volume of leachate and, as indicated by Kumar et al.(2023), the low concentrations required to cause harm, mean that their concentration in parts per trillion are of concern. The applicant also appeared to suggest that the fact that it takes work and expertise to measure PFAS was an excuse for not doing so. That is part of the cost of operating a business that concentrates PFAS – they've trucked them in from around Oregon, they have the responsibility to prevent their spread in the environment. Monitoring is required.

Wastewater treatment plant processes are not designed to remove PFAS

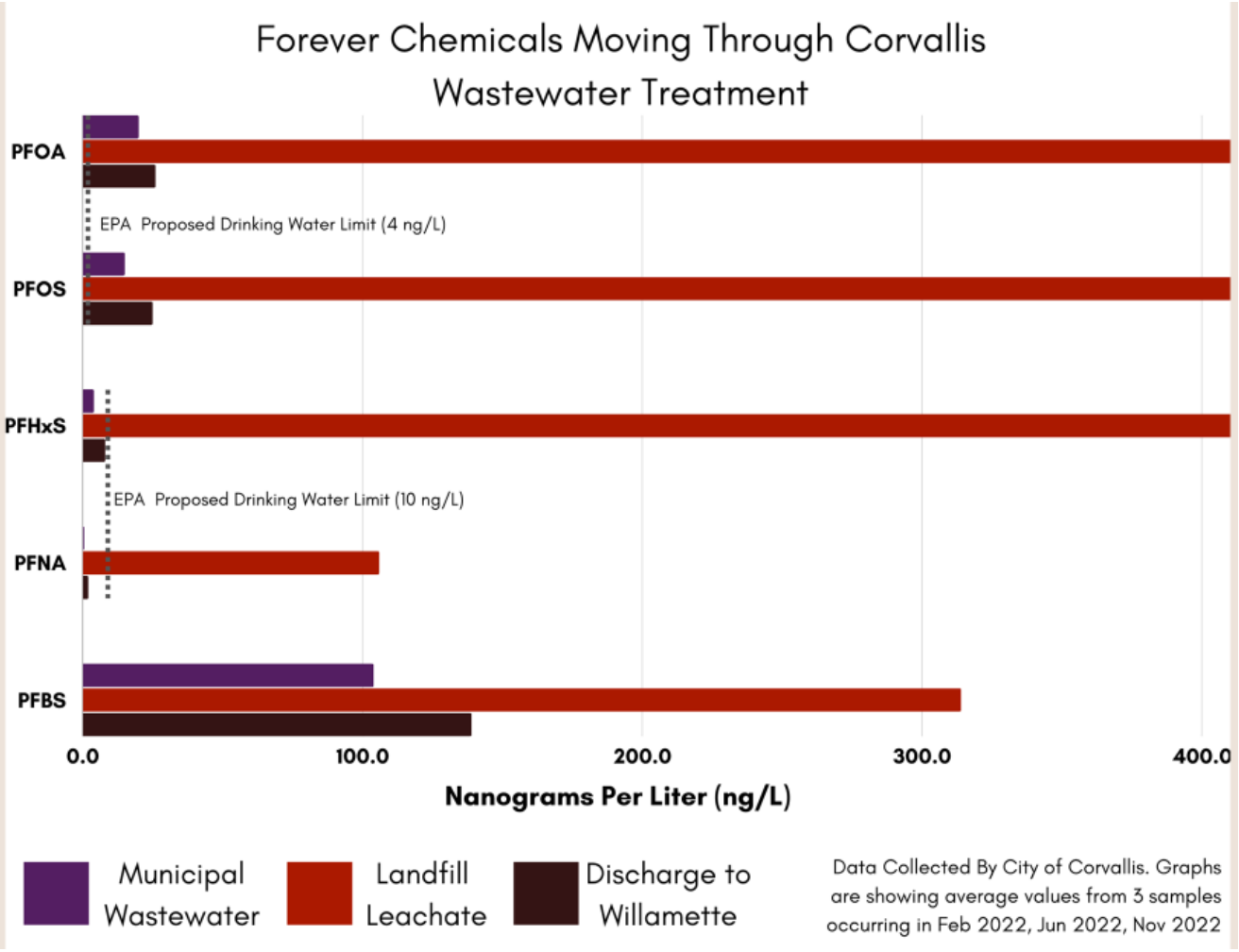
- A 2023 review summarizes the problem with treatment of leachate at wastewater treatment plants as “the treatment of ammonia and COD relies on chemical or biological oxidation, which do not effectively treat PFAS but often have the unintended effect of transforming precursor PFAS to terminal PFAS” (Tolaymat et al. 2023).

- The biological processes used to mitigate organic matter can convert precursors into PFAS resulting in higher PFAS levels in effluent compared to influent (Lenka et al. 2021).

- Short-chain PFAS are generated (Lenka et al. 2021) and are highly mobile and extremely persistent (Brendel et al. 2021).

Most of the PFAS moving through the Corvallis WWTP comes from Coffin Butte Landfill leachate. The same could be said for probably any WWTP receiving landfill leachate.

Landfill leachate is especially high in PFAS

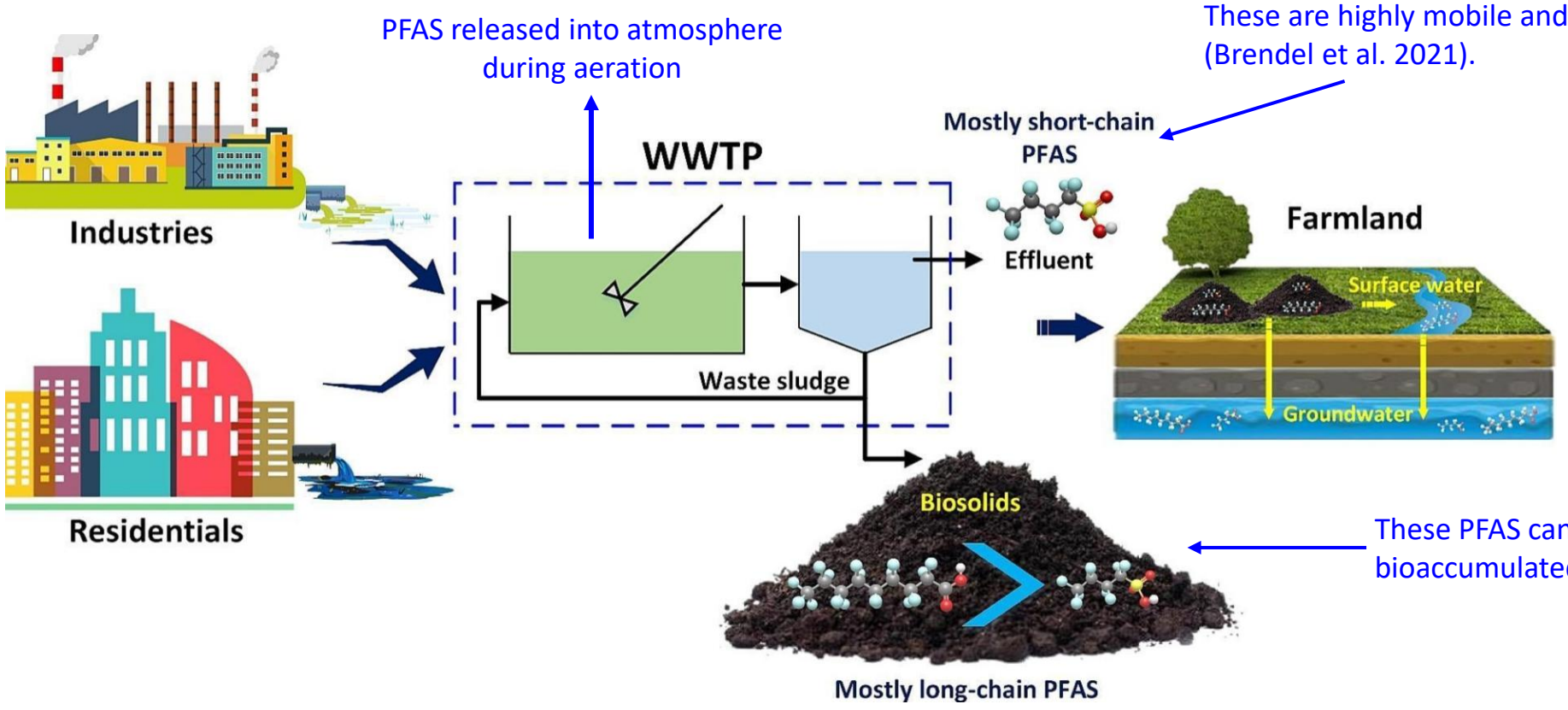


It is important to note that the PFAS not discharged to the Willamette River in effluent have not been destroyed. Instead, they are in the biosolids applied to local properties and in the air around the WWTP. Fortunately, Corvallis has said no more leachate, but it will now likely be trucked to Salem or Albany. This means CBL will continue to pollute communities with PFAS and it is impossible to know the damage already done to our own.

Summary of why landfill leachate should not be disposed of with municipal wastewater

WWTPs do not treat PFAS (Tolaymat et al. 2024) and those PFAS leave the WWTP via effluent (to the Willamette River or wherever the effluent is released), via aerosols at aeration tanks and via biosolids applied to soils. In short, PFAS from the landfill are distributed into the environment where they persist (Behnami et al. 2024).

The Corvallis and Salem WWTPs rely heavily on aeration (biological oxidation), a process that results in airborne PFAS and conversion of precursor to PFAS. We are fortunate that Corvallis has said no more, but the problem still exists, RS will pass the buck to another town.



It IS possible to treat leachate and remove the PFAS but…

- Since the various harmful components of leachate require different treatments, a treatment facility that does this while removing PFAS requires the design, building and operation of a coordinated, nuanced treatment system (Wang and Qiao 2024). Otherwise, they risk generating *more* PFAS.

- "PFAS treatment technologies have advanced significantly in recent years, demonstrating promising applicability for commercial use. Despite this progress, challenges remain, including high energy consumption, high-maintenance requirements for high-strength matrices, reduced performance in the presence of background contaminants, and the production of harmful byproducts" (Sabba et al. 2025).

- The landfill operators have shifted the PFAS burden onto Corvallis, Salem, Benton County, and Marion County by sending leachate to WWTPs and by not preventing the escape of PFAS-laden fugitive landfill gas. The operators of Coffin Butte Landfill must build a treatment facility to remove PFAS from leachate on site. This is their problem to solve. They have chosen to concentrate PFAS from around Oregon at Coffin Butte Landfill knowing that its wet location causes it to produce a great deal of PFAS-laden leachate, they must deal with the result of the choice to continue to concentrate PFAS in an inappropriately-situated landfill.

PFAS from landfills enter surface water and groundwater

- Direct leakage of leachate:
  - Although geomembrane liners have a 98% collection efficiency, imperfections allow approximately 1.2 billion L of municipal solid waste landfill leachate to enter groundwater directly every year (Tolaymat et al. 2023).
- WWTP effluent:
  - PFAS are not eliminated or mitigated at WWTPs. Millions of gallons of leachate have passed through the city of Corvallis' and Salem's WWTPs each year and the PFAS in the leachate that do not migrate with the biosolids or aerosolized during aeration into enter the Willamette River with WWTP effluent.

PFAS from landfills are spread to soils and air

WWTP Biosolids:

PFAS from landfill leachate enter the environment when the biosolids are spread on local fields. Lenka et al.'s 2021 review stated:

- "The occurrence of PFAS in biosolids and its consequences are often overlooked (Letcher et al. 2020), although biosolids and sludge from secondary treatment are notable routes for PFAS emission into the environment (e.g. groundwater, soil, vegetation etc.) (Ebrahimi et al. 2021, Stoiber et al. 2020, Zhang et al. 2013). PFCAs, PFSAs, precursors (e.g. FTOHs) (Guerra et al. 2014) and novel fluorinated polymers (Letcher et al. 2020) have been detected in biosolids worldwide, including North America, Europe, Africa, Asia, and Australia (Moodie et al. 2021)."

Air:

- It has recently been found that landfill gas (LFG) is a major route of PFAS entering the environment (Lin et al. 2024).

- WWTP processes cause aerosolization of PFAS which then enter the atmosphere (Vierke et al. 2011).

Landfills are a forever problem

“Landfills have historically been the primary waste disposal method in Europe, leading to numerous legacy sites requiring extensive aftercare to safeguard human health and the environment. Long-term aftercare of sanitary engineered landfills requires insight in the risk associated with possible emission of contaminants from the landfill waste body…This is important information for landfill operators and responsible authorities in order to develop approaches for landfill aftercare. Especially because after-care is expected to last for a very long time (up to several centuries)” (Heimovaara and Wang 2025).

The responsible authorities in Benton County must consider this prospect when making decisions about the landfill.

If Benton County approves the application for expansion of Coffin Butte Landfill, it will continue to fail to meet its own goals, guidelines and policies.

- As described previously, PFAS originating at Coffin Butte Landfill are spread to the air, soil and water via several routes.

- Continuing to allow this spread means the county is not meeting the **Benton County Comprehensive Plan policy 6.1.2** that dictates that the county must manage air, water, and land resources to insure their protection, conservation, restoration or enhancement. The same is true for policies **6.1.4** and **6.3.1** which call for the county to consider these types of impacts when making land use decisions and to take steps to minimize degradation of our air, water, and land.

- With regard to landfills and solid waste, comprehensive plan policies **6.5.4** and **6.5.8** direct the county to make sure that our solid waste handling, disposal and storage is safe and environmentally sound – allowing the unmitigated spread of PFAS does not meet the requirements in these two policies.

Allowing this problem to worsen by approving an expansion, is antithetical to everything Benton County and Corvallis purport to represent. Why have these policies at all if they play no role in decision-making?

The expansion does not meet the CUP criteria BCC 53.215(1)

- The possibility of widespread PFAS contamination seriously affects the use of landfill-adjacent properties (and WWTP-adjacent and biosolid application-adjacent properties).

    - The application does not meet **BCC 53.215(1)** since an expansion would mean a worsening of all the PFAS-related issues – more air, soil, and surface and groundwaters will be affected further interfering with the ability of residents to use their properties.

The expansion does not meet the CUP criteria BCC 53.215(2)

- Carrying out the PFAS mitigation required to meet EPA standards when they are defined and enforced will be a further economic burden on Benton County.

  - We know that the landfill operators must maintain a landfill for 30-years after it closes, that is far short of the centuries-long period of after care we know landfills require.

  - Benton County will be faced with a potentially enormous financial bill associated with the contamination and continued production of leachate. Thus, an expansion does not meet **BCC 53.215(2)**.

It is time to do the right thing in Benton County

We have a chance to make a solid-waste handling course-correction and that is likely only if the expansion is denied. A denial of expansion will help prevent further environmental damage and almost certainly save Benton County money in the long run. Benton County's future financial burden associated with dealing with local PFAS contamination could be high – far higher than any fees collected by the county for allowing Coffin Butte Landfill's operation. It is also my opinion that it has suffered a damaged reputation for allowing this problem to continue for so long.

Benton County must deny the application for expansion of Coffin Butte Landfill. The trash being trucked in should be transported by rail to Columbia Ridge Landfill which produces much less leachate due to limited precipitation. The small volume of leachate that is produced stays on site being recirculated as part of their landfilling process. The extraordinarily thick clay layer beneath the landfill provides extra environmental protection. If a leak were to occur, the clay would buffer against the PFAS and other contaminants migrating to groundwaters. Columbia Ridge Landfill produces much less fugitive landfill gas, closing another route by which PFAS enter the environment. In short, Columbia Ridge Landfill truly concentrates and sequesters PFAS and other contaminants while Coffin Butte Landfill concentrates and then distributes PFAS and other contaminants into the environment via LFG and leachate sent to WWTPs. Diverting solid waste to Columbia Ridge Landfill is the appropriate course of action.

I strongly urge you to deny the application for expansion of Coffin Butte Landfill. It does not meet the CUP criteria and it is not right for Benton County and its residents.

Respectfully,

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Discussion

Discussion. Has the human population become a sentinel for the adverse effects of PFAS contamination on wildlife health and endangered species?

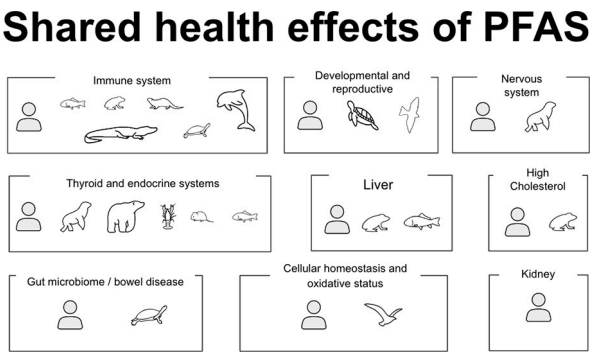
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HIGHLIGHTS

- *Per-* and polyfluoroalkyl substances (PFAS) are global environmental contaminants.
- PFAS are detected in wildlife globally.
- There is concordance between findings on PFAS health effects in wildlife and humans.
- Humans can be regarded as a sentinel species for adverse health impacts of PFAS.
- Wildlife conservation must consider health impacts of chemical contaminants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords
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Wildlife health
Endangered species
Sentinel species
Environmental contamination

ABSTRACT

Global contamination with *per-* and polyfluoroalkyl substances (PFAS) poses a threat to both human health and the environment, with significant implications for ecological conservation policies. A growing list of peer-reviewed publications indicates that PFAS can harm wildlife health and that the adverse effects associated with PFAS exposure in wildlife are in concordance with human epidemiological studies. The correlation of cross-species data supports a unique perspective that humans can be regarded as a sentinel for PFAS effects in other species. The health harms due to PFAS are potentially most concerning for populations of endangered and threatened species that are simultaneously exposed to PFAS and other toxic pollutants, and also face threats to their survival due to habitat loss, degradation of ecosystems, and over-harvesting. Human epidemiological studies on the PFAS doses associated with health harm present a rich source of information about potential impacts on wildlife health due to PFAS. Our analysis suggests that national and international efforts to restrict

Abbreviations: DDT, Dichlorodiphenyltrichloroethane; NHANES, National Health and Nutrition Examination Survey; PCB, Polychlorinated biphenyl; PFAS, *Per-* and polyfluoroalkyl substances; PFBS, Perfluorobutane sulfonic acid; PFCA, Perfluoroalkyl carboxylic acid; PFDA, Perfluorodecanoic acid; PFDoDA, Perfluorododecanoic acid; PFHpA, Perfluoroheptanoic acid; PFHxA, Perfluorohexanoic acid; PFHxS, Perfluorohexane sulfonic acid; PFNA, Perfluorononanoic acid; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonate; PFSA, Perfluoroalkyl sulfonic acid; PFTeDA, Perfluorotetradecanoic acid; PFTrDA, Perfluorotridecanoic acid; PFUnDA, Perfluoroundecanoic acid; POP, Persistent organic pollutant; ppt, parts per trillion; U.S. EPA, United States Environmental Protection Agency.

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[1] These authors contributed equally to the study and should be considered joint first author.

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the discharges of PFAS into the environment and to clean up PFAS-contaminated sites present an opportunity to protect wildlife from chemical pollution and to advance species conservation worldwide.

1. Using humans as sentinels to better understand chemical pollution impacts on the biodiversity crisis

In a classic ecotoxicological approach, monitoring of indicator species such as sensitive bird populations has provided information about the health harms due to bioaccumulative pollutants such as PCBs and DDT, including information highly relevant to human health (Bowerman et al., 2002; Solla et al., 2016). As the global wildlife and biodiversity conservation crisis deepens, there is an urgent need to better protect wildlife from the threats of chemical pollution. One such path towards this goal is to shift the perspective so as to understand how what we know from studies in humans applies to wildlife health. The use of animals as toxicity sentinels has been explored and developed for decades as an approach to protect human health. In contrast to this anthropocentric perspective, more recent frameworks emphasize a One Health approach that considers shared health risk for all species, which may provide better opportunities to protect human and wildlife health simultaneously within a global ecosystem (Destoumieux-Garzon et al., 2018). However, adoption of such frameworks has been slow, with examples so far limited to acute high dose chemical exposures or infectious disease risk. Just a handful of publications to-date explored cross-species extrapolation from humans to animals, which may be appropriate when humans are the most extensively studied exposed population (Beasley, 2009; Rabinowitz et al., 2009; Rabinowitz et al., 2008).

Per- and polyfluoroalkyl substances (PFAS) are recognized as pervasive contaminants associated with harmful effects on the global environment and all species that live on the planet (Evich et al., 2022). We use the term "PFAS" in this Discussion to describe this entire broad class of anthropogenic fluorinated chemicals that have been manufactured globally since the 1950s (Kwiatkowski et al., 2020; U.S. Environmental Protection Agency, 2023a; Wang et al., 2021). Research literature presents overwhelming evidence from studies in humans about the health harms of PFAS exposures. Here we explore the idea that humans can be used as sentinels for wildlife health to enable conservation measures for wildlife and endangered species. Loring and co-authors have previously noted "... the versatility of the word 'sentinel', which generally describes a sentry or guard, but also can be used to refer to the act of keeping watch, as well as the position from which watch is kept" (Loring et al., 2017). Here we adapt this wider epistemological and policy perspective within which we seek to explore the concept of humans as a sentinel species.

A quickening loss of biodiversity threatens species and ecosystems across the globe with significant negative implications both for food security and human health world-wide (World Health Organization and Secretariat of the Convention on Biological Diversity, 2015). Estimates published in 2023 suggest that 48 % of species globally are experiencing population declines, a feature of population dynamics classified as a symptom of potential extinction (Finn et al., 2023). Anthropogenic influences can impact wildlife health, species diversity, and species survival through alteration of physical, biological and chemical composition of terrestrial and aquatic ecosystems (Rillig et al., 2021). In particular, the chemical contamination of the environment with industrial chemicals, pesticides, and a variety of pollutants discharged by the global economy is both a considerable burden (Persson et al., 2022; Sigmund et al., 2022) and a growing peril (Naidu et al., 2021). Yet, the existing frameworks of industrial chemical regulation in individual countries and globally have not yet given sufficient consideration to the impact of toxic chemicals on wildlife and have not yet developed effective approaches to species conservation and wildlife protection in the face of pervasive anthropogenic pollution.

There is a growing recognition that conservation of biodiversity plays a fundamental role in sustaining all aspects of society. The need to address global threats to biodiversity, and action steps for doing so, were outlined in the Kunming-Montreal Global Biodiversity Framework adopted in December 2022 at the 15th meeting of the Conference of Parties to the UN Convention on Biological Diversity. One of the eight primary targets includes reducing pollution risks from pesticides and highly hazardous chemicals "to levels that are not harmful to biodiversity and ecosystem functions and services, considering cumulative effects" (Convention on Biological Diversity, 2022). The Framework emphasizes the need for an integrated whole-of-government and civil society approach to reduce threats to biodiversity and calls for urgent actions to protect biodiversity that should be initiated immediately.

2. PFAS health effects have been extensively studied in humans

The human health effects of PFAS exposure have been well studied in areas of severe local contamination such as the C8 science panel studies in the mid-Ohio River Valley in the United States (Frisbee et al., 2009) and in human studies evaluating health impacts with exposure differentials across the general population. State, federal, and international human health risk assessments for regulatory action on some PFAS have drawn on the vast literature of likely causal associations between PFAS exposure and adverse health effects in humans to establish health protective exposure limits. The U.S. Environmental Protection Agency 2023 toxicity assessment for the proposed drinking water standard for perfluorooctane sulfonic acid (PFOS) in drinking water included 423 epidemiological studies, 45 animal studies, 89 toxicokinetic studies, 22 physiologically-based pharmacokinetic and pharmacodynamic modeling (PBPK) studies and 301 mechanistic studies (U.S. Environmental Protection Agency, 2023a). A similar number of studies were included in the proposed drinking water standard for perfluorooctanoic acid (PFOA) (U.S. Environmental Protection Agency, 2023b). An effort to catalog the studies on health and toxicological effects for PFAS other than PFOA and PFOS identified 1067 studies (505 in people, 385 in animals) for 29 different PFAS compounds (Pelch et al., 2022).

The well-studied link between PFAS exposure in humans and associated health harms along with widespread contamination of wildlife provide an important opportunity to explore the potential for humans to serve as sentinels for PFAS impacts in other species. In this Discussion, our goal is to bring to the attention of the research community and government decision makers the threat PFAS pollution poses to wildlife health, emphasizing that health impacts of globally significant chemical contaminants must be considered in wildlife conservation strategies.

As a result of uncontrolled discharges into the environment, PFAS now pollute water, soil, air and living organisms, and are found in the blood of people around the world (Evich et al., 2022). In the past two decades, research worldwide revealed that exposure to PFAS can cause numerous health harms, as observed in experimental toxicology studies with laboratory animals and in epidemiological studies of highly exposed human populations in the vicinity of contaminated sites as well as in the general population (Fenton et al., 2021; Sunderland et al., 2019). While initial health studies regarding PFAS exposure focused on two most-studied members of this class, PFOA and PFOS, a growing body of scientific research finds that exposure to numerous types of PFAS can harm health (Pelch et al., 2022; Temkin et al., 2020), acknowledging the importance of considering the health impacts of PFAS mixtures (Goodrich et al., 2023).

3. PFAS are detected in wildlife globally

Unlike other classes of industrial chemicals with an identified impact

on wildlife, such as polychlorinated biphenyls (PCBs) that have been phased out from use globally, various types of PFAS continue to be produced, as new fluorochemicals are developed to replace PFOA and PFOS whose use was either phased out or decreased globally. Further, as documented by environmental monitoring studies, there is seemingly no place on the planet untouched by PFAS contamination. A study of the snow on Mount Everest found evidence of PFAS presence, perhaps partially related to PFAS leaching from climbing gear, as well as due to air deposition from the global atmospheric PFAS pollution (Miner et al., 2021).

The manufacturers of PFAS have known for decades that these substances can accumulate in the bodies of living organisms. In 1998, testing by 3M chemical manufacturing company could only find uncontaminated human blood by using archived samples from the Korean War fought in 1950–1953 (3M, 2000). Subsequent testing sponsored by 3M in 2001 documented the ubiquitous presence of PFOS in a global collection of tissue samples for turtles, fish, birds such as bald eagles and albatrosses, and marine mammals such as seals and polar bears (Giesy and Kannan, 2001).

Wildlife are exposed to PFAS through their habitat, such as contaminated waterways (Teunen et al., 2021), as well as their diet (Boisvert et al., 2019). Various PFAS can accumulate in living organisms following exposure to contamination. However, unlike other persistent pollutants, such as organochlorines, PFAS do not tend to accumulate in fat, but rather tend to bind to proteins (Butt et al., 2010). Measurement of PFAS in blood, eggs and other tissues is often limited to a select number of compounds due to analytical capabilities or other limitations in wildlife studies. The set of approximately two dozen PFAS commonly included in various monitoring studies may only account for a fraction of this wide class of chemicals and could underestimate exposure as non-targeted analysis has shown (Barrett et al., 2021; McDonough et al., 2019; Spaan et al., 2020; Wang et al., 2021). Current targeted methods may not be keeping pace with the shifting patterns in global manufacturing of PFAS materials (De Silva et al., 2021).

Hundreds of studies reported the accumulation of various PFAS in animals from a variety of taxa. PFAS are found in wildlife on every continent from manatees in the U.S. state of Florida to fish in Ethiopia and Uganda, flamingos in the Caribbean, whales and dolphins in Hawaii, polar bears across the Arctic, ducks in Australia, sea turtles in Mexico, seafood caught off the coast of Bangladesh and freshwater fish across the United States (Barbo et al., 2023; Vendl et al., 2022; Vendl et al., 2021). For additional resources and visualization of the studies that detected PFAS in the environment, we direct the readers to the U.S. Environmental Protection Agency website (https://echo.epa.gov/trends/pfas-tools) as well as the global map of PFAS contamination in wildlife developed by our organization (Environmental Working Group, 2023, https://www.ewg.org/interactive-maps/pfas_in_wildlife/map/) to view a visualization of a subset of studies documenting this far-reaching contamination.

4. Cross-species extrapolation to assess PFAS toxicity

Current thinking behind traditional toxicity testing is moving towards greatly reducing the use of animals in testing. As alternatives to animal testing, there is now more focus on examining cell-based, computational, and mechanistic approaches to toxicity assessment. Such advanced methods would increase the understanding of biological mechanisms and pathways of adverse effects and their conservation between species and thereby support the research efforts to extrapolate effects across species. For example, the Key Characteristics approach and the Adverse Outcomes Pathways approach (LaLone et al., 2021) offer conceptual frameworks for gathering and utilizing data across species to understand the shared biological linkages that can be used to predict adverse effects (Arzuaga et al., 2019; Germolec et al., 2022; La Merrill et al., 2020; Lind et al., 2021; Rusyn et al., 2021; Smith et al., 2020). Additionally, analytical technologies like transcriptomics and metabolomics which can assess biomarkers of adverse health effects, such as oxidative stress, DNA damage and changes in hormonal levels, are rapidly being developed in laboratory model species and in humans, and are also applied to investigations of wildlife health. Within this framework, researchers can leverage existing data, with a considerable amount of information from humans, as well as generate data from non-lethal and non-invasive sampling methods to predict potential adverse effects from PFAS exposure to a diversity of species.

PFOA, PFOS, and other compounds in the PFAS chemical family have been linked with a broad array of toxic effects in humans and laboratory animals, including harm to the immune system, harm to reproduction and fetal development, changes in the endocrine balance and increased risk of various cancers (National Academies of Sciences, 2022). Here we briefly review the literature on PFAS toxicity in environmental field studies of wildlife, which indicate similar target organ systems and health impacts in wildlife as humans and model organisms, from PFAS exposure (Acosta-Tlapalamatl et al., 2022; Beaulieu and Costantini, 2014; Bedia, 2022). Importantly, while not covered in this review, PFAS exposure has been also shown to affect the health of domesticated animals, including companion pets and livestock (Rock et al., 2023). Published studies, described in more detail below (Table 1), include reports of the impact of PFAS on hormonal levels in polar bears (Pedersen et al., 2016) and hooded seals (Gronnestad et al., 2018); the immune systems and disease resistance in fish (Guillette et al., 2020), alligators (Guillette et al., 2022) and marine mammals (Ishibashi et al., 2008; Kannan et al., 2006; Soloff et al., 2017); and hatching success in birds and emergence success in turtles (Custer, 2021; Custer et al., 2014) (Wood et al., 2021), as well as metabolic alterations associated with PFAS exposure in turtles (Beale et al., 2022), among other effects. Of note, associations with health parameter changes were reported for several different members of the PFAS family, including the sum of more than 20 PFAS, PFOS and other long chain PFAS, as well as new compounds from PFAS class with regional contamination patterns such as Nafion byproduct 2. Table 1 summarizes the health effects in wildlife associated with summed PFAS exposure and/or individual PFAS, while Table 2 indicates the number of studies where each compound was reported in association with these health effects.

It is important to recognize that reports on PFAS and wildlife health published in peer-reviewed scientific literature to date are likely a significant underestimate of all possible impacts of PFAS on wildlife, due to the practical difficulties of carrying out studies in the field as well as ethical and legal considerations protecting the health and survival of already endangered species. The PFAS-associated health effects described in the studies cited in Table 1 are indicative of chemical stressors that can impact both species fitness and survival and therefore can be considered a factor influencing population dynamics, with a potential connection to overall biodiversity loss (Groh et al., 2022). Impacts on the immune, nervous and endocrine systems, reproduction and development and metabolism are reported consistently by the published studies on different taxa.

4.1. Immune system

The immune system is one of the most sensitive targets of PFAS toxicity, as observed by human studies that examined reduced vaccine response and increased susceptibility to infection and disease (Budtz-Jorgensen and Grandjean, 2018; European Food Safety Authority, 2020). Similarly, studies in reptiles, mammals, fish and birds have shown immune system impacts of PFAS exposure. Researchers studying alligator populations in the industrially contaminated Cape Fear River Basin (North Carolina, United States) observed an association between elevated levels of PFAS and altered biomarkers of innate immune activity related to autoimmune response (Guillette et al., 2022). Additionally, an increased incidence of skin lesions and unhealed wounds was observed, which is uncharacteristic for American alligators, and may be similar to the elevated risk of slow-healing wounds associated

Table 1
Recent studies of impacts of PFAS on wildlife health from field studies.

Species	Continent/Region	System affected and findings
Invertebrate and fish		
Crayfish (*Faxonius immunis, F. rusticus, F. virilis*)	North America, (Northern Michigan, USA)	Behavioral impacts Increased exposure to PFAS (sum of 24 compounds) was associated with decreased foraging in crayfish (Coy et al., 2022).
Bluegill (*Lepomis macrochirus*)	North America, (Northern Michigan, USA)	Behavioral impacts Increased exposure to PFAS (sum of 24 compounds) was associated with changes in swim speed (Coy et al., 2022)
Striped bass *(Morone saxatilis)*	North America (North Carolina, USA)	Liver and immune system Elevated PFOS and Nafion byproduct 2 concentrations in serum were associated with altered liver biomarkers. Elevated PFOS was associated with alterations in the immune system in fish (Guillette et al., 2020).
Amphibians		
Black spotted frog (*Rana nigromaculata)*	Asia (Zhejiang province, China)	Liver Higher levels of PFAS, particularly PFOA, PFOS, and 6:2 Cl-PFESA, were correlated with liver biomarkers that indicated disrupted lipid metabolism (Lin et al., 2022).
Reptiles		
American alligator (*Alligator mississippiensis*)	North America (North Carolina, USA)	Immune system Elevated total PFAS (sum of 23) were associated with increased lysozyme activity in serum (an indicator of innate immunity), autoimmune-like traits and increased incidence of skin lesions (Guillette et al., 2022).
Freshwater turtle (*Emydura macquarii macquarii*)	Australia	Immune system Changes in the gut microbiome, gut inflammation and gut metabolic changes were observed in turtles exposed to elevated total PFAS concentrations (sum of 47) (Beale et al., 2022).
Hawksbill turtle (*Eretmochelys imbricata*)	North Pacific Ocean	Reproduction Higher concentrations of PFUnDA and PFTrDA in eggs were correlated with reduced emergence success of the hatchlings (Wood et al., 2021).
Birds		
Arctic black-legged kittiwakes (*Rissa tridactyla*)	Kongsfjorden, Svalbard	Cellular homeostasis and oxidative status Oxidative status markers were correlated with higher plasma concentrations of PFDoDA, PFTrDA, PFTeDA, PFUnDA, PFOS (Costantini et al., 2019).
Tree swallows (*Tachycineta bicolor*)	North America (Minnesota, Wisconsin, Michigan, USA)	Reproduction Decreased hatching success was associated with PFOS concentrations in eggs (Custer et al., 2014).
Arctic black-legged kittiwakes (*Rissa tridactyla*)	Kongsfjorden, Svalbard	Reproduction and endocrine system PFDoDA concentration was related to lower hatching success. PFNA was related to changes in body mass in male kittiwakes and PFTrDA and PFTeDA were related to decreased baseline corticosterone in both sexes (Costantini et al., 2019).
Mammals		
Bottlenose dolphin (*Tursiops truncatus*)	North America (South Carolina, USA)	Immune system PFOS exposure was associated with increased T cell proliferation and proinflammatory cytokine production, a marker of chronic immune activation (Soloff et al., 2017).
Hooded seals (*Cystophora cristata*)	East Greenland	Endocrine system Elevated total PFAS (sum of 8) were associated with changes in both concentrations and ratios of thyroid hormones in mothers and pups (Gronnestad et al., 2018).
Polar bear *(Ursus maritimus)*	East Greenland	Nervous system and endocrine system Higher concentrations of PFAS (both sum of 10 perfluoroalkyl carboxylic acids and sum of 4 perfluorosulfonic acids) in brain tissue were associated with increased levels of steroid hormones in brain tissue (Pedersen et al., 2016).
Bank voles (*Myodes glareolus)*	Europe (Norway)	Nervous system and endocrine system Higher PFAS concentrations (sum of 10 perfluoroalkyl carboxylic acids and 5 perfluorosulfonic acids) in the liver were associated with elevated dopamine levels in the brains and lower testosterone levels in muscle of wild bank voles (Gronnestad et al., 2021b).
Southern sea otter (*Enhydra lutris nereis)*	North America (California, USA)	Immune system Higher concentrations of PFOS and PFOA in the liver were associated with higher rates of infectious disease (Kannan et al., 2006).

with autoimmune disease in humans (Shanmugam et al., 2017). In marine mammals, increased levels of PFOA and PFOS in the liver were significantly associated with disease mortality in sea otters (Kannan et al., 2006), and environmental exposure to PFOS in bottlenose dolphins was associated with immune system dysregulation (Foguth et al., 2020; Soloff et al., 2017). Exposure to PFAS mixtures as well as exposure

Table 2
Studies where specific PFAS exposure was associated, either as individual compound or as a part of the summed PFAS, with the health outcomes in Table 1. Where total PFAS sum was reported, all PFAS within that summation are listed. PFAS names are provided in footnote.

PFAS*	Beale et al., 2022	Costantini et al., 2019	Custer et al., 2014	Coy et al., 2022	Gronnestad et al., 2018	Gronnestad et al., 2021b	Guillette et al., 2020	Guillette et al., 2022	Kannan et al., 2006	Lin et al., 2022	Pedersen et al., 2016	Soloff et al., 2017	Wood et al., 2021	Number of studies listed in Table 1
PFOS	*	*	*	*	*	*	*	*	*	*	*	*		12
PFOA	*			*	*			*	*	*	*			7
PFNA	*	*		*	*	*		*			*			7
PFTrDA	*	*		*	*	*					*		*	7
PFUnDA	*	*		*	*	*					*		*	7
PFDA	*			*	*	*		*			*			6
PFDoDA	*	*		*	*	*					*			6
PFHxS	*			*	*	*		*			*			6
PFBS	*			*		*		*			*			5
PFHpA	*			*		*		*			*			5
PFHxA	*			*		*		*			*			5
PFTeDA	*	*		*		*					*			5

* PFAS reported in 4 studies in Table 1: PFBA (perfluorobutanoic acid). PFAS reported in 3 studies in Table 1: PFPeA (perfluoropentanoic acid), PFDS (perfluorodecane sulfonic acid), 6:2 FTS (6:2 fluorotelomer sulfonate). PFAS reported in 2 studies in Table 1: PFPeS (perfluoropentane sulfonic acid), PFNS (perfluorononane sulfonic acid), PFHpS (perfluoroheptane sulfonic acid), Nafion byproduct 2, 7H-Perfluoro-4-methyl-3,6-dioxaoctanesulfonic acid), N-MeFOSE (N-ethyl perfluorooctane sulfonamido ethanol), N-MeFOSAA (N-Methylperfluorooctane sulfonamidoacetic acid), N-MeFOSA (*N*-methyl perfluorooctane sulfonamide), N-EtFOSE (N-ethyl perfluorooctane sulfonamido ethanol), N-EtFOSAA (N-ethylperfluorooctane sulfonamidoacetic acid), N-EtFOSA (N-ethyl perfluorooctane sulfonamide), HFPO-DA (GenX) (Hexafluoropropylene oxide-dimer acid), FOSA (perfluorooctanesulfonamide), 8:2 FTS (8:2 fluorotelomer sulfonate), 4:2 FTS (4:2 fluorotelomer sulfonate). PFAS reported in 1 study in Table 1: R-PSDA (Formerly Nafion Byproduct 4) (Perfluoro-4-(2-sulfoethoxy) pentanoic acid), PMPA (Perfluoro-2-methoxypropanoic acid), PFPrS (perfluoropropanesulfonic acid), PFPeDA (Perfluoropentadecanoic acid), PFOSA (Perfluorooctanesulfonamide), PFODA (Perfluorooctadecanoic acid), PFO5DoDA (TAFN4) (Perfluoro-3,5,7,9,11-pentaoxadodecanoic acid), PFO4DA (Perfluoro-3,5,7,9-butaoxadecanoic acid), PFO3OA (Perfluoro-3,5,7-trioxaoctanoic acid), PFO2HxA (Perfluoro(3,5-dioxahexanoic) acid), PFHxDA (Perfluorohexadecanoic Acid), PFECHS (Perfluoroethylcyclohexane Sulfonate). PFDoDS (perfluorododecane sulfonic acid), PEPA (perfluoro-2-ethoxypropanoic acid).

NVHOS (1,1,2,2-tetrafluoro-2-(1,2,2,2-tetrafluoro-ethoxy)ethane sulfonic acid), Nafion Byproduct 1 (Perfluoro-3,6-dioxa-4-methyl-7-octenesulfonic acid), Hydro-EVE Acid (2,2,3,3-Tetrafluoro-3-{[1,1,1,2,3,3-hexafluoro-3-(1,2,2,2-tetrafluoroethoxy)propan-2-yl]oxy}propanoic acid), FHxSA (perfluorohexane sulfonamide), FBSA (perfluorobutane sulfonamide).

FASA (perfluoroalkane sulfonamide), ADONA (trade name for 4,8-dioxa-3H-perfluorononanoate), 9Cl-F53B (9-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid), 8Cl-PFOS (Sodium 8-chloroperfluoro-1-octanesulfonate), 8:2 FTCA (8:2 fluorotelomer carboxylic acid), 8:2 DiPAP (8:2 fluorotelomer phosphate diester), 6:6 PFPiA (6:6 perfluorophosphinic acid), 6:2 FTCA (6:2 fluorotelomer carboxylic acid), 6:2 Cl-PFESA (6:2 chlorinated polyfluorinated ether sulfonate), 5:3 FTCA (5:3 fluorotelomer carboxylic acid), 11Cl-F53B (11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid), 10:2 FTS (10:2 fluorotelomer sulfonate), 10:2 FTCA (10:2 fluorotelomer carboxylic acid).

to PFHxS increased parasite infections in different species of frogs (Brown et al., 2021; Lech et al., 2022). The inability to heal from injury or increased susceptibility to disease may impact both individual survival and overall population of a species.

4.2. Nervous system

Several PFAS have been detected in the brains of laboratory animals, humans, as well as environmentally exposed wild animal populations (Foguth et al., 2020; Shang et al., 2023). While the extent of known PFAS impacts on the human nervous system are somewhat limited, evidence from laboratory animal studies, especially for exposures during development and early life, suggest that PFAS, particularly PFOA and PFOS, can harm the nervous system, causing changes in motor activity and function, and impaired learning and memory (Starnes et al., 2022). In wild bank voles caught in a PFAS-contaminated ski area in Norway, higher PFAS concentrations were associated with higher dopamine levels in the brain compared to voles caught from a reference site (Gronnestad et al., 2021a). The study authors exposed mice in the lab to a mixture of PFAS based on the concentrations at the contaminated site and found disruption of dopamine homeostasis (Gronnestad et al., 2021b). In another study, environmental exposure to PFAS in crustaceans (crayfish) and fish (bluegills) was associated with altered behavioral outcomes, including decreased foraging for crayfish, and altered swim speeds in fish (Coy et al., 2022).

4.3. Endocrine system

Studies suggest that PFAS disrupt levels of thyroid hormones in the body in both humans (Kim et al., 2018) and other species with thyroid-dependent development, like amphibians (Flynn et al., 2022). Additionally, PFAS have been implicated in altering circulating levels of reproductive hormones at different life stages in humans and laboratory animals and endocrine-mediated diseases, effects that may be related to the ability of PFAS to bind directly with sex steroid nuclear hormone receptors (Mokra, 2021). In wild bank voles from a contaminated ski area, some associations were observed between PFAS concentrations and lower testosterone in muscle tissue (Gronnestad et al., 2021b). In a study of hooded seal mothers exposed to complex contaminant mixtures, PFAS contributed to hormone disruption and were the most important predictor of thyroid hormone levels (Gronnestad et al., 2018). Levels of perfluoroalkyl carboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs) in brain tissue were associated with increased levels of steroid hormones in the brains of polar bears studied in Greenland (Pedersen et al., 2016). Prolonged periods of exposure to elevated levels of steroid hormones could adversely affect reproduction rates and fetal development.

4.4. Reproduction and developmental

In human studies, PFAS impacts on reproduction and development include preeclampsia, low birth weight, altered breastfeeding duration, reduced fertility among others (Blake and Fenton, 2020; Rickard et al., 2022). For wildlife species, reproductive success is critical, especially for a species population that is threatened or endangered. PFAS exposure, happening at the same time with other anthropogenic pressures, may be contributing to decreased reproduction success in wildlife. In hawksbill sea turtles, a critically endangered species, emergent success was negatively correlated with levels of perfluoroundecanoic acid (PFUnDA) and perfluorotridecanoic acid (PFTrDA) in eggs (Wood et al., 2021). Maternal transfer of PFAS to eggs has been observed in both freshwater and sea turtles (Beale et al., 2022; Wood et al., 2021). A negative association with PFOS in tree swallow eggs and hatching success was observed along with total nest failure in nests with eggs that had PFOS concentrations at or above 150 ng/g (Custer et al., 2014). In contrast, a subsequent study by the same team observed no effects of PFAS exposure on reproduction in tree swallows at another field study site (Custer et al., 2019). It is important to acknowledge that not all published studies detect and report a consistent association of individual PFAS exposures and distinct, measurable adverse outcomes. This diversity of findings could be due to a variety of factors in the population at the site of study, such as site-specific mixtures of PFAS, or the presence of co-occurring contaminants causing or contributing to overall population health effects (Custer, 2021).

4.5. Impacts on metabolism, including liver function and oxidative stress

Blood serum biomarkers can be useful tools indicative of immune and reproductive functions as well as the overall health of populations in wild species where other types of health parameters may be difficult to study. Elevated levels of PFOS were associated with increased activity of blood serum biomarkers indicative of adverse impacts to the liver and immune system in striped bass from the Cape Fear River (North Carolina, United States) (Guillette et al., 2020). In Arctic black-legged kittiwakes, analysis of blood serum biomarkers indicated higher protein oxidative damage and lower plasma antioxidants in birds with higher levels of longer chain PFAS (Costantini et al., 2019). Additionally, freshwater turtle eggs exposed to PFAS contained significantly elevated levels of purine metabolites which may alter eggshell structure and egg physiology and were depleted of lipids needed for growth and development. Overall, higher PFAS exposure may affect egg development and the health of the turtle hatchlings. Analysis of the eggshells showed lower levels of essential calcium and higher levels of lipids and metabolites indicative of weakened physical structure (Beale et al., 2022). In field studies in black spotted frogs, associations were found with PFOS, PFOA and 6:2 Cl-PFESA and lipid metabolism-related indices suggesting that PFAS exposure may disrupt lipid metabolism in frogs collected from a contaminated industrial site (Lin et al., 2022). While changes in lipid metabolism, endocrine system, and immune defense may not be immediately lethal to an individual animal's health, these changes in biomarkers indicate significant alterations in hepatic, endocrine and immune systems, with a potential to contribute to overall population decline (Shi et al., 2023).

5. Shared health concept

There is strong concordance between adverse health effects observed in epidemiological research in humans and in wildlife studies in association with PFAS exposure (Fig. 1), supporting an argument that humans can be regarded as a unique sentinel species for the identification of the potential health harms from PFAS to other species. Distinctly, the amount of data available from epidemiological studies as well as humans' large population, geographic spread, and widespread health monitoring make *Homo sapiens* potentially a true global sentinel for the impacts of toxic chemicals on biological organisms. Future research will provide more information on the species differences in sensitivity to individual PFAS and to the overall load of combined exposure to PFAS as a class. Meanwhile, just as wild or domesticated animals have been both regarded and used as early warning sentinels for the impacts of toxic chemicals, humans can also serve in this role, especially for PFAS health harms to other animals, since similar levels of PFAS have been measured, for example, in seals, dolphins, dogs, horses, alligators and humans.

We posit that the mobility of humans does not preclude their potential as a sentinel species. Of note, epidemiological studies that can provide valuable information for cross-species extrapolation about PFAS effects between species were conducted for populations that have stayed in their local area for a long time, such as the C8 health study (Frisbee et al., 2009), the Faroes island study of PFAS effects on the vaccine response (Grandjean et al., 2012), and worker health studies (Olsen et al., 2003). Further, in general population exposures, published data suggest that a significant portion of overall PFAS exposure is due to local

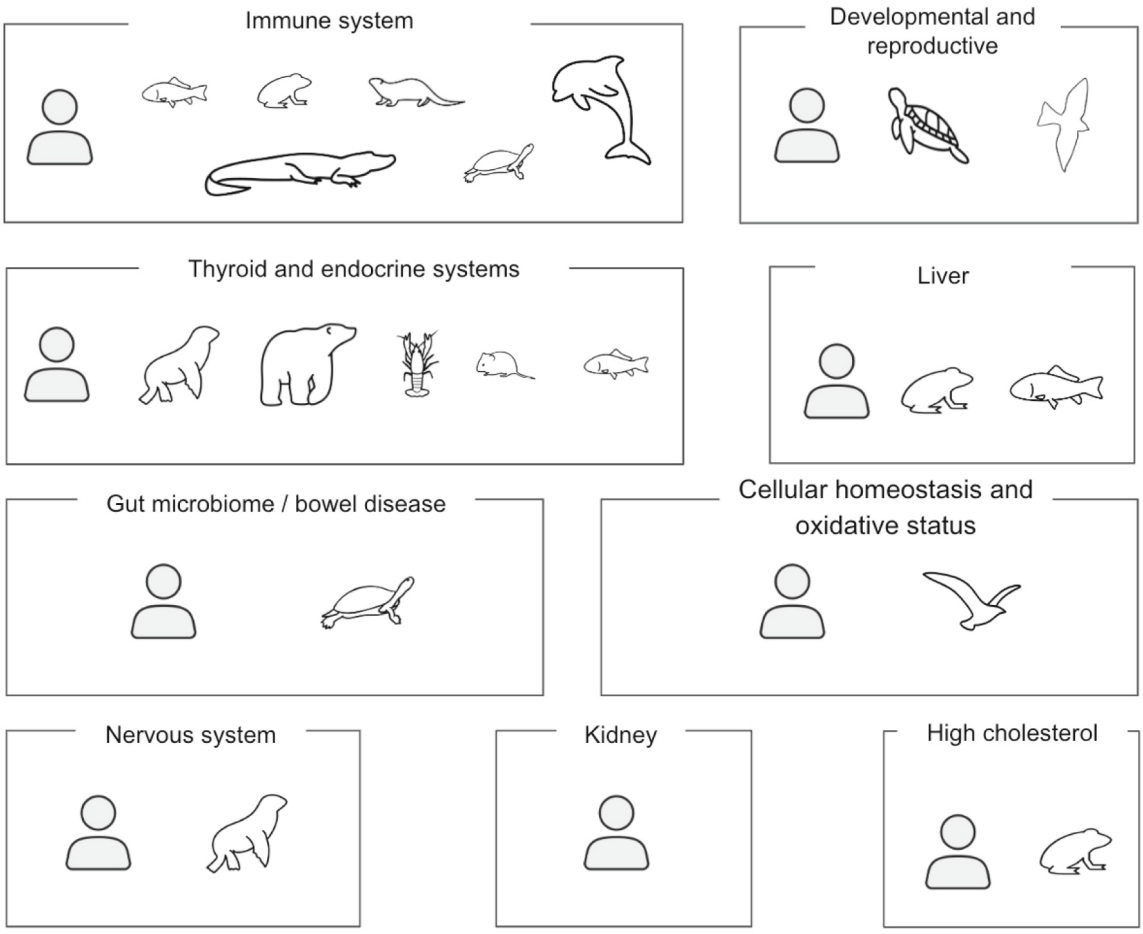


Fig. 1. Adverse health effects on organ systems and biomarkers observed in association with PFAS exposure in epidemiological research and wildlife studies. Individual wildlife study references are included in Table 1. Immune system: *Homo sapiens,* Striped bass *(Morone saxatilis),* American alligator (*Alligator mississippiensis*), Black spotted frog (*Rana nigromaculata),* Southern sea otter (*Enhydra lutris nereis),* Freshwater turtle (*Emydura macquarii macquarii*), Bottlenose dolphin (*Tursiops truncatus*). Developmental and reproductive system: *Homo sapiens,* Hawksbill turtle (*Eretmochelys imbricata*), Tree swallows (*Tachycineta bicolor*). Nervous and endocrine systems: *Homo sapiens*, Crayfish (*Faxonius immunis), Bluegill (Lepomis macrochirus),* Hooded seals (*Cystophora cristata*), Polar bear *(Ursus maritimus),* Bank voles (*Myodes glareolus)*. Liver: *Homo sapiens*, Black spotted frog (*Rana nigromaculata),* Striped bass *(Morone saxatilis)*. Gut microbiome/bowel disease: *Homo sapiens*, Freshwater turtle (*Emydura macquarii macquarii*). Cellular homeostasis and oxidative stress: *Homo sapiens*, Arctic black-legged kittiwakes (*Rissa tridactyla*). Thyroid: *Homo sapiens*, Hooded seals (*Cystophora cristata*). Kidney: *Homo sapiens*. High cholesterol: *Homo sapiens*, Black spotted frog (*Rana nigromaculata)*.

exposures, through dietary patterns and locally contaminated drinking water supplies (Sunderland et al., 2019). Migratory species of birds, large mammals and reptiles such as aquatic marine turtles can carry out annual journeys of distance, difficulty and diversity of geographic areas that may be well out of range for most humans on the planet. Finally, and irrespectively of whether a "sentinel" or "comparison" populations are localized or mobile, the atmospheric transport of PFAS and global contamination have put all species and populations at risk of PFAS exposures.

Conceptualizing humans as a sentinel species for other animals is supported by the One Environmental Health approach that views human health, wildlife health and ecosystem health as one (Perez et al., 2018). Given the extent of global PFAS contamination (Cousins et al., 2022) and the ubiquitous PFAS exposure of nearly all biota on the planet, this interconnected approach is needed to understand and confront the universal threat to human health and to global biodiversity from PFAS exposure. Further, a translation of the concept "humans as sentinels" to environmental risk assessment points to the value of using human data where available to aid the development of policy measures for protecting wildlife populations.

Examples of the cross-species extrapolation approach comparing human and wildlife health data already exist in the literature. Some of the highest levels of PFAS reported globally in marine mammals have been measured in bottlenose dolphins from the Charleston, South Carolina (U.S.) urban coast and have been compared to levels in humans that have been exposed occupationally (Fair et al., 2010; Fair et al., 2012). Levels of PFOS ranged from 49 ng/g in plasma from dolphins in Bermuda to 1171 ng/g in dolphins near Charleston, South Carolina from a 2005 study (Houde et al., 2005). Mean PFOS levels in serum in workers at a 3 M facility were reported to be 1.32 ppm, equivalent to 1320 ng/g (Olsen et al., 2003). Comparing human exposure with exposure for bottlenose dolphins may be useful because of dolphin's longevity, top-predator status and high site fidelity in an urban area (Fair et al., 2019). Published studies linked immune system dysregulation in dolphins with exposure to PFOS (De Guise et al., 2019; Fair et al., 2014; Soloff et al., 2017). Nevertheless, a substantial gap in data availability is evident when comparing the number of health studies conducted on wild animal populations to studies in humans. Given the availability of hundreds of studies in humans, epidemiological data could serve as the basis for conservation risk assessments and the development of conservation policies for other mammals or species where such data are lacking.

Available data suggest that the adverse health effects observed in humans due to PFAS exposure are relevant and applicable to all animal

species generally, and across the globe. The health impacts documented in wildlife, as detailed in Table 1, are similar to adverse health endpoints with likely causal associations to PFAS exposure in humans (Agency for Toxic Substances and Disease Registry (ATSDR), 2021) (EPA 2023B). Further, the graphical representations in Fig. 1 and Fig. 2 highlight both reported and anticipated health effects due to PFAS exposure in wildlife and correlate the measured PFAS levels in the blood of wildlife from the studies in Table 1 with the PFAS levels in humans that have documented health impacts.

While the concordance in types of health impacts observed in humans and other species point to the value of cross-species extrapolation for this analysis, the uncertainties associated with dose-response curves for adverse effects in PFAS in different species remain a scientific challenge. In Fig. 2, the circulating concentrations of PFAS do not represent the probability of the frequency of occurrence of specific health effects. Rather, Fig. 2 documents the fact of global PFAS contamination in wildlife at levels that in many circumstances are vastly greater than concentrations shown in epidemiological studies to impact human health parameters. In parallel, Table 2 documents the co-occurrence of different PFAS compounds measured in wildlife health studies, pointing to the relevance and necessity of both assessing and mitigating against the adverse effects of PFAS mixtures.

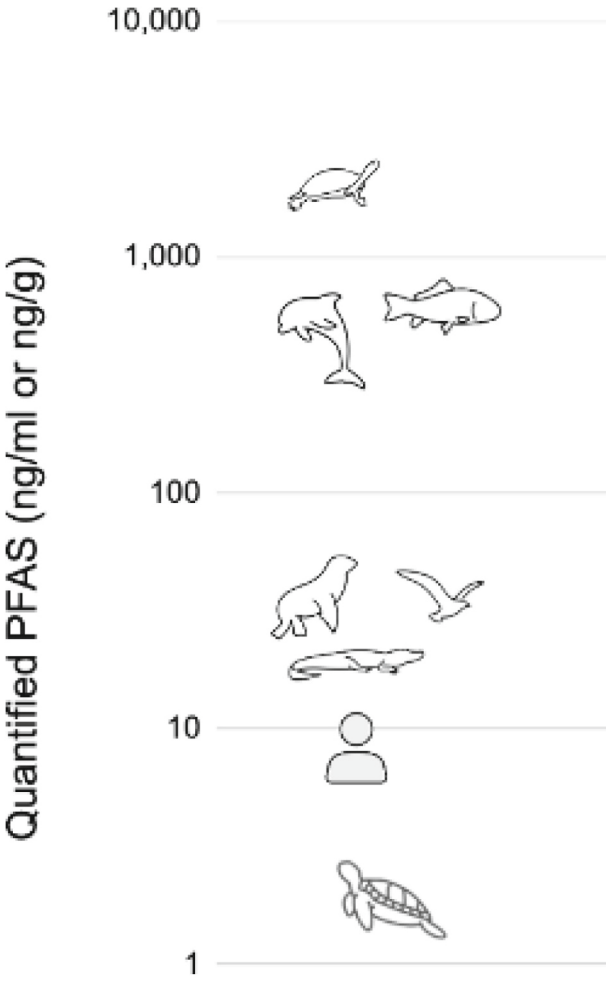


Fig. 2. Concentration of PFAS in animals in studies documenting health impacts from exposures, as detailed in Table 1, compared to the median levels in the U.S. population for 2017–2018. PFAS concentrations are cited according to how they were reported in original references. From lowest to highest: Hawksbill turtle (*Eretmochelys imbricata*, 1.74 ng/g median PFAS in plasma with a median of 31 ng/g in eggs), human (*Homo sapiens*, 16.7 ng/ml median PFOS in serum), American alligator (*Alligator mississippiensis,* 18.6 ng/ml median total PFAS in serum), Arctic black-legged kittiwakes (*Rissa tridactyla*, 39.9 ng/g mean PFAS in plasma), Hooded seals (*Cystophora cristata*, 40 ng/g median PFOS in plasma), Striped bass (*Morone saxatilis*, 551 ng/ml median total PFAS in serum), Bottlenose dolphin (*Tursiops truncatus*, 571 ng/g median PFOS in plasma), Freshwater turtle (*Emydura macquarii macquarii*, 1992 ng/ml average total PFAS in plasma). Frequency of associations of different PFAS compounds with reported health effects in different studies is shown in Table 2, with most associations reported for PFOS.

For practical reasons, the number of studies linking specific health effects in wildlife with PFAS exposure remains limited. Nevertheless, the published literature clearly demonstrates that exposure to PFAS in the environment and elevated levels of PFAS in animals' bodies are associated with changes in key health parameters, such as hormonal levels, immune function, reproduction, and growth of the young, which have also been observed in controlled toxicological studies in laboratory animals as well as human epidemiological cohorts. Changes in these health indicators have significant relevance to individual animal's reproduction and survival and the overall health and stability of wildlife populations and ecosystems.

Available data do not allow a definitive assessment of whether humans are the most susceptible species to the toxic effects of PFAS exposure, or whether other species, including species shown in Fig. 1 and Fig. 2 have a more sensitive population-level dose-response relationship for PFAS. For a read-across or cross-species extrapolation approach, uncertainties remain in the context of exposure of life-histories across species that may vary drastically. Further, exposures may differ, especially for aquatic species that may be exposed simultaneously to numerous contaminants during developmental phases and throughout their life. Yet, given the dramatic and tragic rate of the disappearance of endangered species and shrinking of wildlife populations globally, all measures should be taken to consider pollution reduction as part of the essential framework for protecting threatened and endangered species, and a cross-species extrapolation approach holds, in our view, valuable potential for both research and policy.

It is important to acknowledge the difficulty of conducting wildlife health studies in general, especially in endangered species, as well as the appropriate ethical barriers and legal restrictions on conducting lethal sampling of wildlife. These practical considerations preclude a comprehensive assessment of the full scope of PFAS impacts on wild animals' health. Additionally, given the reality of global PFAS contamination of the environment and wildlife, identifying a true, uncontaminated reference population generally proves impossible, since even samples of animals collected from the geographic sites without known sources of industrial discharges still contain PFAS (Beale et al., 2022). All these factors make it especially urgent and timely to use a read-across or cross-species extrapolation approach so as to draw on all available data to assess potential damage to the ecosystems and specific animals due to PFAS contamination, and to develop and implement measures to prevent such damages.

Scholars and environmental advocates across the world are raising the alarm on the critical state of anthropogenic pollution and its effects on human health globally (Cousins et al., 2022; Groh et al., 2022). As emphasized in previous reports, the planetary boundary for chemical pollution has likely been crossed (Persson et al., 2022). Yet, with the human population continuing to grow, we can anticipate the continued increase of chemical manufacturing and with it, the potential for growing pollution levels in the environment. Given this reality, both regulation and minimization of environmental discharges of industrial chemicals are essential measures for protecting human and wildlife health as well as for wildlife and endangered species conservation on our planet. Protection of a sentinel species from a particular toxic chemical impact would begin the process to protect all species on the planet. In this process, it is especially important to consider the cyclical nature of

PFAS pollution (Stoiber et al., 2020), so as to ensure that remediation policies and practices do not end up shuffling the PFAS pollution load from one site to another. Systematic approaches to tackling the PFAS contamination crisis should be the focus to protect both humans and wildlife.

Summarizing our argument, we posit that the use of human data as a sentinel approach can serve as a foundation for ecological conservation policies that are urgently needed now. While PFAS exposures of humans may be conceptually similar to PFAS in large mammalian carnivorous species such as dolphins and polar bears, the similar health effects in different taxa are documented (Table 1, Fig. 1). Building on this concordance of recorded health effects, future research of the mechanistic basis for toxicological outcomes due to PFAS exposure can provide a framework for extrapolation across species as well as potential explanations of variability (Celander et al., 2011; LaLone et al., 2021). Finally, while human epidemiological data might not provide a full set of information relevant to the environmental impacts of PFAS contamination, this corpus of data is the most extensive dataset on a single species that is currently available and it can shed light on a wide variety of toxic effects elicited by PFAS.

6. Research needs

Contamination of living organisms around the globe with anthropogenic environmental pollutants, such as persistent organic pollutants or POPs, has been known for decades. Top predators in terrestrial and aquatic food webs often carry the heaviest body burden of such pollutants, even decades after regulatory action restricting the manufacturing of these persistent substances (Kean et al., 2021; Travis et al., 2020). In co-occurrence with chlorinated and brominated contaminants, PFAS have emerged as ubiquitous pollutants with planetary-wide impact (Cousins et al., 2022). Most species, including species included in the International Union for Conservation of Nature Red List, are exposed to the PFAS family of chemicals that, as human epidemiological evidence indicates, may compromise basic life functions critical to survival of individuals and populations: the ability to reproduce and to resist disease and injury.

Animals in the wild are exposed to PFAS through the water, air, soils and sediments, and the food chain. Those species also face habitat loss, over-harvesting and other anthropogenic threats to their survival. PFAS exposures are potentially most concerning for endangered and threatened species populations that are simultaneously exposed to a mix of toxic pollutants (Routti et al., 2019). With widespread wildlife exposure to mixtures of PFAS and other persistent organic pollutants, additional research on the health impacts of these chemical mixtures is urgently needed. The chemical concentrations of individual pollutants or pollutant mixtures varies in different geographic sites for both people and different wildlife species. It remains to be investigated what might be potential limits on the concordance of adverse health effects of exposure to similar pollutants in humans and in wildlife species. Further studies on characterizing the exposure, dose-response relationship, and toxicological outcomes in various species remain necessary. Yet, such data limitations should not preclude prompt, coherent and comprehensive action on protecting the wildlife species populations that still remain on this planet. A consideration of humans as sentinel species is a promising approach that would be refined with the generation and dissemination of new research studies.

Additional research needs to apply the question of chemical pollutant impacts on population dynamics and trends in population health, which is an under-investigated topic to date. For example, the documented detrimental effects of PFAS exposure on the immune system can make species susceptible to other stressors. Additionally, large aquatic animals that suffer injuries from plastic pollution could potentially face reduced resistance to infections due to their body burden of PFAS. Together, the cumulative pressures of chemical exposures, habitat loss and climate change may act jointly, exacerbating the loss of biodiversity. As habitat loss increases, species are increasingly living closer and closer to human populations (Simkin et al., 2022). The density of the human population has been observed to correlate with the levels of PFAS measured in wildlife living in close proximity (Guillette et al., 2022; Wood et al., 2021), indicating both elevated PFAS exposure and degraded habitat quality. As documented by numerous studies, the current loss of species and the rate of species loss is unprecedented (IPBES, 2019; Isbell et al., 2022) and understanding the role of chemical exposures in this global extinction will be critical for attempting to conserve biodiversity (Mueller et al., 2023).

We hope that future research will also focus on developing models to characterize specific adverse health effects such as reproductive harm in wildlife, thus facilitating environmental health assessments while avoiding any lethal sampling of wildlife populations (Finn et al., 2023). We look forward to the greater acceptance of the importance of biomarker effects in ecotoxicology studies and the application of the toxicological read-across and cross-species extrapolation concepts for developing effective policies for species conservation. Positively, recent emphasis on reducing animal testing and efforts to focus on cross-species extrapolation and new approach methodologies to leverage existing toxicity data (LaLone et al., 2021) may help to protect all species. These efforts align with the One Health approach and point out the connectedness of all species that share the planetary environment. Methods that focus on examining molecular, cellular and organ-level changes can be more predictive compared to whole-organism endpoints, which reduces animal testing and broadens the possibilities for extrapolating toxicological data across a variety of species.

7. Recommendations

Analysis presented in this article supports the call for an integrated government and society approach to reduce threats to biodiversity due to PFAS pollution and for urgent actions to advance species conservation that should be initiated immediately:

1. Biodiversity conservation policymakers need to consider chemical pollution reduction as part of the essential framework for protecting threatened and endangered species.
2. In situations where a direct wildlife health study may be impractical or not appropriate due to endangered species status, a read-across and cross-species extrapolation approach incorporating all available data sets can aid policy measures to protect wildlife populations anthropogenic contaminants.
3. Where available, human epidemiological studies should be included as one of the sources of reference data for developing policies for species conservation. The epidemiological dataset for PFAS presents a compelling case study for such an approach.
4. International measures controlling PFAS pollution and preventing future discharges of PFAS into the environment are essential for protecting both human health and global biodiversity.
5. Protection of wildlife populations from PFAS pollution has the potential to contribute to ecosystem stability and sustainable development goals connected with ecosystem functions and services.
6. Industrial chemical registrations and approvals should be developed and implemented to prevent adverse impacts of PFAS on critical habitats, wildlife populations, and endangered species, by ending ongoing releases to the environment and capturing PFAS in discharges from manufacturing plants, wastewater treatment plants, landfills, and other types of commercial and residential PFAS discharges.
7. More research is needed to develop technologies for assessing and remediating PFAS contamination in the environment and for the cleanup of contaminated sites.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Short-chain perfluoroalkyl acids: environmental concerns and a regulatory strategy under REACH

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Abstract

Background: Short-chain PFASs (per- and polyfluoroalkyl substances) are widely used as alternatives to long-chain PFASs. Long-chain PFASs become gradually regulated under REACH (EC No. 1907/2006) and other international regulations, due to having persistent, bioaccumulative and toxic properties and/or being toxic for reproduction. The increasingly used short-chain PFASs are assumed to have a lower bioaccumulation potential. Nonetheless, they have other properties of concern and are already widely distributed in the environment, also in remote regions. The REACH Regulation does not directly address these emerging properties of concern, complicating the implementation of regulatory measures. Therefore, this study illustrates these environmental concerns and provides a strategy for a regulation of short-chain PFASs within REACH.

Results: Short-chain PFASs have a high mobility in soil and water, and final degradation products are extremely persistent. This results in a fast distribution to water resources, and consequently, also to a contamination of drinking water resources. Once emitted, short-chain PFASs remain in the environment. A lack of appropriate water treatment technologies results in everlasting background concentrations in the environment, and thus, organisms are permanently and poorly reversibly exposed. Considering such permanent exposure, it is very difficult to estimate long-term adverse effects in organisms. Short-chain PFASs enrich in edible parts of plants and the accumulation in food chains is unknown. Regarding these concerns and uncertainties, especially with respect to the precautionary principle, short-chain PFASs are of equivalent concern to PBT substances. Therefore, they should be identified as substances of very high concern (SVHC) under REACH. The SVHC identification should be followed by a restriction under REACH, which is the most efficient way to minimize the environmental and human exposure of short-chain PFASs in the European Union.

Conclusion: Due to an increasing use of short-chain PFASs, an effective regulation is urgently needed. The concerns of short-chain PFASs do not match the "classical" concerns as defined under REACH, but are not of minor concern. Therefore, it is of advantage to clearly define the concerns of short-chain PFASs. This might facilitate the following restriction process under REACH.

Keywords: REACH, SVHC, PFASs, Candidate list, Restriction, Regulation, Per- and polyfluoroalkyl substances, PFAAs

Background

Some representatives of per- and polyfluoroalkyl substances (PFASs) are highly stable organic compounds, due to the C–F bond being one of the strongest in organic chemistry [1]. Compared to hydrocarbons, PFASs have enhanced technical properties, such as a higher surface activity and better dielectric properties, and possess at the same time a higher thermal stability, an increased chemical resistance and a physiological inertness [2]. Due to these properties, PFASs are well suited for manifold applications and have been used extensively in various industrial and consumer applications since the 1950s, e.g., impregnation of textiles, paper, hard metal plating,

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in paints, the production of fluoropolymers, etc. [3, 4]. During the production and life cycle of the products, a certain fraction of PFASs is inevitably emitted into the environment (e.g., [5]). Many commonly used PFASs can degrade under environmentally relevant conditions to perfluoroalkyl acids (PFAAs), regarded as final degradation products (e.g., [6]). Besides the direct emission of PFAAs, e.g., from production and life cycle of certain fluoropolymers, indirect emissions via degradation of the precursor substances are of high relevance regarding the global emissions [7]. Also, side-chain fluorinated polymers, in particular the group of side-chain fluorotelomer-based polymers, were shown to be degraded to PFAAs under environmental conditions in the range of decades to centuries [8] and are therefore considered to be precursors. As highly persistent final degradation products of many other PFASs, PFAAs are a relevant group regarding environmental and human exposure, even though being a small substance group within the whole PFASs group, consisting of at least 3000 substances [9].

The concern of possible risks of PFAAs to the environment and human health was broadly unrecognized until the turn of the millennium, when two groups of PFAAs, long-chain perfluoroalkyl carboxylic acids and long-chain perfluoroalkane sulfonic acids, have been shown to be ubiquitously present in biota and humans (e.g., [10, 11]). Since becoming aware of the ubiquitous distribution and the hazardous properties (see [12]) of long-chain PFASs (i.e., long-chain PFAAs and their precursors), voluntary measures of manufacturers and regulatory action have been taken place to reduce the emissions. Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) are listed as persistent organic pollutant (POP) under the Stockholm Convention and perfluorooctanoic acid (PFOA) and related precursors are proposed as POP. Under the European Chemicals Regulation (REACH EC No. 1907/2006), several long-chain perfluoroalkyl carboxylic acids (C_8–C_{14}) and the long-chain perfluorohexane sulfonic acid are identified as substances of very high concern (SVHC) and included in the REACH candidate list. In the EU restriction, proposals for the perfluoroalkyl carboxylic acids on the candidate list are in progress, but only implemented for PFOA its salts and related substances up to the present. In summary, global measures to ban long-chain PFAAs of concern are ongoing and need to be continued.

With the regulation of long-chain PFASs and due to voluntary measures, non-regulated PFASs have been more extensively used as alternatives. Information of these replacements are not easily accessible, however, it is known that short-chain PFASs (i.e., short-chain PFAAs and respective precursors, see Fig. 1 for terminology) are important and broadly used alternatives [13]. Due to historical emissions mainly as unintended by-products during the manufacturing of long chain PFASs in the past, short-chain PFASs are already present in environmental compartments [7, 14]. The replacement of long-chain PFASs with short-chain PFASs and in general other PFASs is highly criticized [15–17], as short-chain PFASs have also relevant properties of concern.

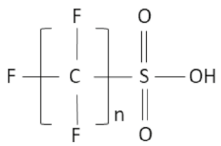
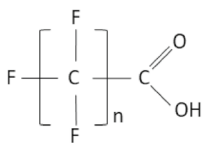
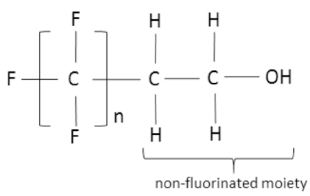
Perfluoroalkane sulfonic acids Long-chain: n ≥ 6 Short-chain: n < 6 Example short-chain representative: PFBS (n = 4)	
Perfluoroalkyl carboxylic acids Long-chain: n ≥ 7 Short-chain: n < 7 Example short-chain representatives: PFBA (n = 3), PFHxA (n = 5)	
Example of short-chain precursors 4:2 fluorotelomer alcohol (n = 4) 6:2 fluorotelomer alcohol (n = 6)	

Fig. 1 Terminology of per- and polyfluoroalkyl substances

Long- and short-chain PFAAs were originally distinguished, since short-chain PFAAs are assumed to have a lower bioaccumulation potential and improved environmental properties compared to long-chain PFAAs [3, 18]. However, short-chain PFAAs are as persistent as long-chain PFAAs have different, but not less alarming properties of concern, and are already widely distributed in the environment [e.g., 19–27]. The awareness of these concerns needs to be raised to obtain a fast regulation of short-chain PFASs. Therefore, this study (i) summarizes and highlights the concerns of short-chain PFAAs, (ii) investigates the need for a regulation and (iii) provides a strategy for how a regulation could be implemented in REACH.

Results and discussion

Uses and sources of environmental exposure

According to the publicly available information on REACH registrations, short-chain PFAAs, e.g., PFBA (perfluorobutanoic acid), PFBS (perfluorobutanesulfonic acid) and PFHxA (perfluorohexanoic acid) have not been registered so far. The last registration deadline under REACH for substances which are manufactured or imported between one and 100 tons per year is 31 May 2018. However, registration obligations do not include substances in imported articles. In contrast to the short-chain PFAAs, various short-chain precursor substances are registered in high tonnages (> 100 tons per annum) and are mainly used for manufacturing polymers. Those polymers may most likely have wide dispersive uses. In general, short-chain PFASs can substitute long-chain PFASs in manifold applications [28]. Therefore, they are used comparably to long-chain PFASs in many consumer products and industrial applications requiring inert or repellent characteristics. Due to a partially limited technical performance in comparison with long-chain PFASs, higher amounts of short-chain PFASs are usually used in compensation (e.g., in wax and polish) [28]. During the production and life cycle of the products, inevitably releases of short-chain PFASs into the aquatic and terrestrial environment occur [29]. There are vast amounts of applications, but only scarce information on uses of short-chain PFASs. Additionally, the degradation of side-chain fluorinated polymers might contribute significantly to emissions of short-chain PFASs in the long-term, as demonstrated by an environmental fate modeling analysis by Li et al. [30]. Besides degradation of the polymers in the long-term, non-bound residues can easily reach the environment and may thus contribute to future releases [29, 30]. Due to the hundreds of various precursors, assessing the uses of all precursors is nearly impossible. The Swedish Chemicals Agency [4], the Norwegian Environment Agency [31] and the Danish Ministry of the Environment [32] provided detailed information on the use of short-chain PFASs to the extent possible. In the following, information for some use areas is summarized.

In recent years, surfactants in foam-based fire-fighting agents, used to extinguish flammable liquids or gases, shifted from long-chain PFASs (mainly C8-based) to short-chain PFASs (mainly C6-based). The stability and surface-active properties of PFASs enable a film formation on top of burning liquids, extinguishing the fire and preventing burn back. Nowadays, a number of foam-based fire-fighting agents contain short-chain PFASs. The use of fire-fighting agents results in direct contaminations of the environment when there is no possibility of collecting the fire water and subsequent disposal [33, 34].

Textiles, leather, carpet, apparel, and upholstery are desired to be oil, water and dirt repellent. For some papers and food contact materials, greaseproof properties are required. Therefore, these items can be impregnated with side-chain fluorinated polymers, consisting of non-fluorinated carbon backbones connected to short-chain PFAS side-chains such as fluorotelomer alcohols.

Short-chain PFASs are furthermore used for example as mist suppressing agents in hard metal-plating [35], in the electronic industry due to insulating and water repellent properties [36], in cosmetic products to make the products oil and water repellent [37], in paints and inks to improve wetting, smoothness and flow [36], in medical devices [4] and the oil production [32].

Overview of concerns of short-chain PFAAs

This section specifies concerns attributed in general to short-chain PFAAs. The properties of concerns only attributed to certain PFAAs or precursor substances are not addressed. However, precursors share the common concern of degradation to short-chain PFAAs as final degradation products. It is therefore possible to include precursors in a regulation of short-chain PFAAs (see "Strategy for regulation of short-chain PFASs under REACH").

Short-chain PFAAs are extremely persistent

Based on the high energy of the carbon–fluorine bond [2], it can be assumed that short-chain PFAAs are extremely persistent similar to the persistence of long-chain PFAAs [38, 39]. They do not undergo abiotic or biotic degradation at all under environmental conditions and are considered highly stable transformation products in which several precursors ultimately degrade into [13, 40]. This extreme persistence is regarded as an incalculable hazard itself, as short-chain PFAAs will stay in the environment for decades to centuries [41]. The possible risks of such extremely persistent organic fluorochemicals for humans and the environment have been

emphasized by leading scientists [16, 17]. Each released PFAS molecule remains in the environment, meaning that it is impossible to reverse exposure. Thus, levels of these substances will most probably increase over time in certain compartments. As a consequence, long-term effects on humans and wildlife may be possible in the future, when certain effect thresholds are reached.

Short-chain PFAAs have a low adsorption potential and are very mobile

The determination of the physicochemical properties of short-chain PFAAs requires, due to the unusual substance properties, specific methods. Estimates of the physicochemical properties are available (PFBS, PFBA and PFHxA [42, 43]: logK_{ow} (neutral form) = 2.82–4.6, water solubility > 20 g/L, logK_{oa} = 6–6.7, pK_a < 1, log-K_{oc}: 2.7–3.6), showing that short-chain PFAAs are very mobile, which is also confirmed by their environmental distribution [44, 45]. Due to this mobility short-chain PFAAs effectively reach water bodies which is of special concern regarding human exposure: Drinking water resources are highly sensitive to contamination with short-chain PFAAs [19, 46]. Due to the low adsorption potential, short-chain PFAAs will not bind to particles and stay mainly dissolved in the water phase.

In a larger scale, once emitted short-chain PFAAs can only hardly be removed from water

Long-chain PFAAs can be removed from water with activated carbon filters. However, this is not as effective for short-chain PFAAs due to the low adsorption potential [47]. Hence, at a large scale short-chain PFAAs can only hardly, if at all, be removed from the environment with the main methods available today [46, 48, 49]. Some promising methods are very costly and just applied at a laboratory scale [50]. The absence of effective measures on a larger scale is problematic in particular with regard to contaminated drinking water reservoirs. Since short-chain PFAAs are not expected to degrade chemically and biologically, the concentrations in contaminated areas will only decline with a further spatial distribution, provided that no further release occurs.

Short-chain PFAAs have the potential for long-range transport. Already today, short-chain PFAAs are monitored in remote regions and show a wide spread distribution in biotic and abiotic compartments

Due to the high mobility caused by the high aqueous solubility and relatively low adsorption potential of short-chain PFAAs, they have a higher potential for long-range transport compared to the long-chain homologues [43]. Additionally, volatile precursors are likely to be transported to remote regions via the atmosphere and then being degraded to short-chain PFAAs. Monitoring data show that already today short-chain PFAAs are present in remote areas [20, 51, 52] and have a wide spread distribution in biotic and abiotic compartments. Table 1 shows examples of monitoring data from Europe. In a few cases, increasing concentrations of short-chain PFAAs in the environment and biota are already observed; for example, for PFBS in dolphins from the South China Sea [53], for PFHxA in water samples near a fluoropolymer production plant in Japan [54] and for PFBA in snow from remote regions in the European Alps [25, 52]. As demonstrated in a recent review by Land et al. [55], a generalized prediction of temporal trends in environmental concentrations of short-chain PFAAs is currently not feasible due to limited monitoring data and insignificant time trends shown in most of the studies. Historical releases of short chain PFASs are hard to quantify [7]. Because the substances are not degradable, historical releases, i.e., as unintended by-products during the manufacturing of long chain PFASs contributed to the environmental stocks to a reasonable amount and impede the observation of significant trends. However, due to the phase-out of long-chain PFASs [18, 56], manufacturing and use of short-chain PFAAs and related substances are very likely to further increase in the near future. Thus, emissions of short-chain PFAAs will increase as well. Along with the expected increasing emissions, short-chain PFAAs will further enrich in the environment leading to increased background concentration levels, in the long-term especially in the aquatic systems [57].

The permanent exposure to short-chain PFAAs results in continuous and poorly reversible concentrations in organisms. There is a risk of adverse effects on humans and the environment, which will rise with increasing exposure

Considering that the exposure to short-chain PFAAs is unlikely to be stopped shortly, there will be increasing continuous and poorly reversible environmental background concentrations of short-chain PFAAs. Consequently, organisms and humans will be permanently exposed to short-chain PFAAs, resulting in continuous and poorly reversible internal concentrations. The poorly reversible internal concentrations in organisms are caused by the persistence of short-chain PFAAs and their continuous presence in the environment. Therefore, the organismal elimination efficiencies are of secondary relevance. This becomes more evident when considering that the half-lives of short-chain PFAAs in the environment exceed their half-lives in the organisms by far. Cousins et al. [41] addresses this approach in more detail, showing exemplary that the contamination of drinking

Table 1 Example monitoring data from Europe regarding PFBS, PFBA and PFHxA

Sampling	Short-chain PFAA and concentration[a]	Reference/sampling year
Tab water [ng/L]		
France, 8 locations	PFBS: 3.2 (32%);	[19]
	PFHxA: nd	Sampling year: 2014
Germany, 26 locations	PFBS: 2.7 (42%)	[21]
	PFHxA: 2 (23%)	
	PFBA 2 (19%)	
Spain, 84 locations	PFBA: 10 (52%)	[22]
	PFHxA: 4.7 (18%)	Sampling year: 2010–2011
	PFBS: 8.3 (35%)	
Surface water [ng/L]		
Spain, Ebro	PFBA: 35.2 (58%)	[23]
	PFHxA: 1.7 (8%)	Sampling year: 2010
	PFBS: nd	
Spain, Guadalquivir	PFBA: 214.3 (92%)	
	PFHxA: nd	
	PFBS: 10.1 (8%)	
Germany, Elbe	PFBA: 2.6 (100%)	[24]
	PFBS: 7.5 (100%)	Sampling year: 2015
	PFHxA: 1.5 (100%)	
Germany, Saale	PFBA: 0.5 (100%)	
	PFBS: 4.3 (100%)	
	PFHxA: 4 (100%)	
Snow [ng/L]		
European Alps	PFBA: 0.69	[25]
	PFHxA: 0.06	Sampling year: 2008
Sediments [ng/g dw]		
Baltic sea	PFBS: 0.00017 (75%)	[26]
	PFHxA: 0.115 (100%)	Sampling year: 2013–2014
Organisms [ng/g ww]		
Baltic sea		[26]
Zooplankton	PFBS/PFHxA: nd	Sampling year: 2013–2014
Herring	PFBS/PFHxA: nd	
Sprat	PFBS/PFHxA: nd	
Guillemot egg	PFBS: 0.0035 (100%)	
	PFHxA: 0.0026 (50%)	
Ingolstadt, Germany		[27]
Wild boar	PFHxA: 0.49 (66%)	Sampling year: 2011–2012
	PFBA: 0.73 (100%)	
	PFBS: 0.25 (53%)	
Svalbard, Norway		[20]
Reindeer	PFBA: 0.42 (56%)	
Ebro, Spain		[23]
Fish	PFBS: 4.9 (69%)	Sampling year: 2010
	PFBA: 0.6 (31%)	
	PFHxA: 268.4 (56%)	

[a] Mean values, including frequency detected

water resources with short-chain PFAAs leads to a poorly reversible exposure in humans, comparably to a contamination with long-chain PFAAs. Due to the high mobility of short-chain PFAAs and the missing suitable water treatment technologies for drinking water, short-chain PFAAs will remain in the water resources over time (this scenario proves true, see "Case example Rastatt"). This results in a permanent exposure via drinking water, independently of the elimination half-lives of short-chain PFAAs.

Nevertheless, elimination half-lives of short-chain PFAAs are non-negligible: Depending on the species, they range from a couple of hours to several days in some mammals [58–60], with longer half-lives in humans (e.g., 30 days for PFHxA [61]). The elimination half-lives are shorter compared to some long-chain homologues, but nevertheless of concern, as short-chain PFAAs will still remain in organisms with continuous exposure. Some short-chain PFAAs have considerable protein binding potentials [62, 63]. A high protein binding potential is of toxicokinetical relevance: the blood can easily distribute short-chain PFAAs within the body resulting in a potential to enrich particularly in blood rich tissues. Data from the exposure of mammals show that short-chain PFAAs can be widely distributed in the organism [64, 65].

Possible adverse effects, especially long-term effects, caused by a high protein binding potential are uncertain. In general, there is a high level of uncertainty, if the permanent exposure with low concentrations of short-chain PFAAs may cause adverse effects in organisms. There is insufficient data on the toxic properties of short-chain PFAAs [66], and therefore, sub-lethal long-term effects cannot be excluded. There might be unconsidered sensible organisms, certain development stages or effects on multiple generations, being not considered when assessing the toxicity of short-chain PFAAs. Mixture toxicity of different PFASs or the toxicity of PFASs in combination with natural and anthropogenic stressors is largely unknown [57].

The distribution of short-chain PFAAs in terrestrial systems and along food chains is unknown. Short-chain PFAAs are known to enrich in edible parts of plants

Short-chain PFAAs are known to enrich in plants and due to their high water solubility and low adsorption potential, especially in leaves and fruits [67–69]. This enrichment in the edible parts of plants is higher compared to long-chain PFAAs and might pose a risk regarding a distribution along the food chain, which has not yet been investigated. In contaminated soil, especially in former arable land, the accumulation in the edible parts of plants is of concern due to human exposure (exemplary shown in "Case example Rastatt"). Field studies do not allow drawing conclusions on distributions of short-chain PFAAs along the food chains. Especially, the accumulation in terrestrial organisms, as shown for long-chain PFAAs [70], cannot be excluded [71].

Case example Rastatt

In the surroundings of Rastatt (Baden-Wuerttemberg, Germany), 480 hectares of former arable land are contaminated with short-chain PFAAs and precursors. The pollution was detected in 2013 and has probably been caused by the longstanding application of compost mixed with sludge from paper production, contaminated with various precursors. Over time, the precursors contained in the soil degraded to short-chain PFAAs and were enriched in plants. Local authorities derived thresholds for short-chain PFAAs in food (in the µg/kg range) [72], based on guidance values for drinking water [73]. Pre-harvest monitoring showed that the concentration of short-chain PFAAs in some crops exceeded these thresholds, preventing the use as food. Crops enriching high amounts of short-chain PFASs are recommended not to be cultivated for consumption on these contaminated fields (e.g.,asparaguses, strawberries and other vegetables). Despite the recommendations for cultivation, threshold values are in parts exceeded to date. This might be due to a strong influence of insufficiently predictable abiotic factors, such as organic carbon content, on the enrichment of short-chain PFASs in plants [74]. Over time, the very mobile short-chain PFASs and precursors in the soil also wash out into the groundwater. Irrigating crops with contaminated water are causing further emissions to soil and uptake into plants. Two groundwater wells for drinking water production had to be closed [72].

For several years, the dimension of the contamination and the problems arising with the contamination of short-chain PFASs has not been recognized. Estimations addressing all adverse environmental effects and socio-economic costs resulting from the contamination are not available, but according to information given by the water work solely the cost for water treatment with charcoal filters amounts to several million Euros. Until now, no practicable solution for removing the short-chain PFASs from the soil or groundwater has been found. Effective solutions, such as a removal and replacement of the top soil or "pump and treat" methods, would be far too expensive. Furthermore, there are still high concentrations of short-chain PFASs and unknown precursors contained in the soil and there is no applicable solution for stopping them from reaching the groundwater. Research to find an appropriate solution is ongoing.

This Rastatt case clearly shows that once emitted to the environment, short-chain PFAAs cause irreversible contaminations, and thus causing high socio-economic costs and threats to man and environment. Besides Rastatt,

there is a large scale contamination of drinking water with short-chain PFASs in Uppsala known. The contamination in Sweden is mainly caused by the use of aqueous film forming fire-fighting foams at a military airport [33].

Strategy for regulation of short-chain PFASs under REACH

PFAAs themselves are not produced in high tonnages. Primarily manifold precursor substances degrading in the environment to PFAAs are responsible for their emission to the environment and subsequently to humans. Those precursor substances are defined by a similar length of the perfluorinated carbon chain compared to the short-chain PFASs, connected to a non-fluorinated moiety (see Fig. 1).

A regulation of every single precursor is impracticable due to the unknown but likely vast amount of precursors on the market. For an effective regulatory measure, it is mandatory to address both PFAAs and their precursor substances, considering also emissions from imported articles. These considerations have already been outlined by Vierke et al. [39] regarding the long-chain perfluoroalkyl carboxylic acid PFOA. Precursors registered under REACH are mainly used for manufacturing polymers according to industry. Those polymers (i.e., side-chain fluorinated polymers) contain unbound residues of PFASs precursors or the polymers may breakdown over time and release PFAS precursors [8]. Thus, polymers are included in such a regulation as well.

In short, as a first step identification as SVHC according to Article 57 of the REACH regulation needs to be considered. Such substances become included in the REACH candidate list. Article 57 of the REACH Regulation allows to include substances on the candidate list that (i) are classified as carcinogenic, mutagenic or toxic for reproduction (CMR) category 1A or 1B, (ii) have persistent, bioaccumulative and toxic (PBT) or (iii) very persistent and very bioaccumulative (vPvB) properties according to REACH (Annex XIII), or (iv) have an equivalent level of concern as CMR or PBT/vPvB substances. The inclusion of a substance in the candidate list results in obligations for the manufacturer to provide information to downstream users and to consumers (if > 0.1% proportion in articles). This regulatory measure alone is not sufficient to control the emissions of short-chain PFASs. But the inclusion into the candidate list is a strong signal itself since it contains all substances of very high concern identified within the EU. For substances on the candidate list REACH foresees authorisation as the regulatory measure. In such case, using the substance is only allowed if authorization was granted. However, an authorisation does apply only for the substance itself and does not include any precursor substances. Furthermore, the authorisation procedure does not include imported articles, probably contributing to the emissions of short-chain PFASs in Europe. Consequently, starting the authorisation procedure would not constitute an effective risk management option. A restriction (Article 67) can cover the placing of a substance on the market, the content of a substance in (imported) articles, the use of such a substance on its own or in a mixture and respective precursors. Thus, a general restriction can address all relevant emission routes and is considered the appropriate regulatory measure for short-chain PFASs under REACH. To decide if certain exemptions might be appropriate, further detailed information on uses and alternatives are necessary. Once in force, the restriction is valid for the European Economic Area (EEA), having a population of more than 500 million people.

The equivalent level of concern

With the current knowledge, short-chain PFASs seem not to fulfill the bioaccumulation or toxicity criteria of REACH Annex XIII. Due to the special properties of short-chain PFASs, they might not fulfill the "classical" properties of concern of SVHCs, being clearly defined within Article 57(d and e) of the REACH Regulation. However, given the properties of concern (see "Overview of concerns of short-chain PFAAs") and the already existing pollutions (see "Case example Rastatt"), there is an unequivocal need for regulation of short-chain PFASs. Within the REACH Regulation, it is possible to identify substances as SVHC that have an equivalent level of concern compared to CMR or PBT/vPvB substances, as defined in article 57(f) (see "Strategy for regulation of short-chain PFASs under REACH"). So far, the equivalent level of concern approach is applied for endocrine disrupting chemicals, sensitisers and specific target organ toxicity after repeated exposure only. However, in our opinion short-chain PFASs are also of equivalent level of concern compared to PBT/vPvB substances and can be identified as SVHC for the following reasons:

Article 1 of the REACH Regulation states that the provisions of the REACH Regulation are underpinned by the precautionary principle. The realization of the precautionary principle is apparent when looking at the vPvB criteria for the SVHC identification (Article 57(e)). Even though a substance does not cause any toxic effect, it can be identified as SVHC because it is due to its intrinsic properties expected to remain in the environment and to accumulate in organisms. The reasoning is that (i) the level of uncertainty in identifying long-term effects cannot be estimated with sufficient accuracy (vB) and (ii) consequences of an underestimation of adverse effects are not easily reversible by regulatory action (vP), i.e., the effect is occurring or is likely to occur at a certain point in time, and even if there is immediate regulatory

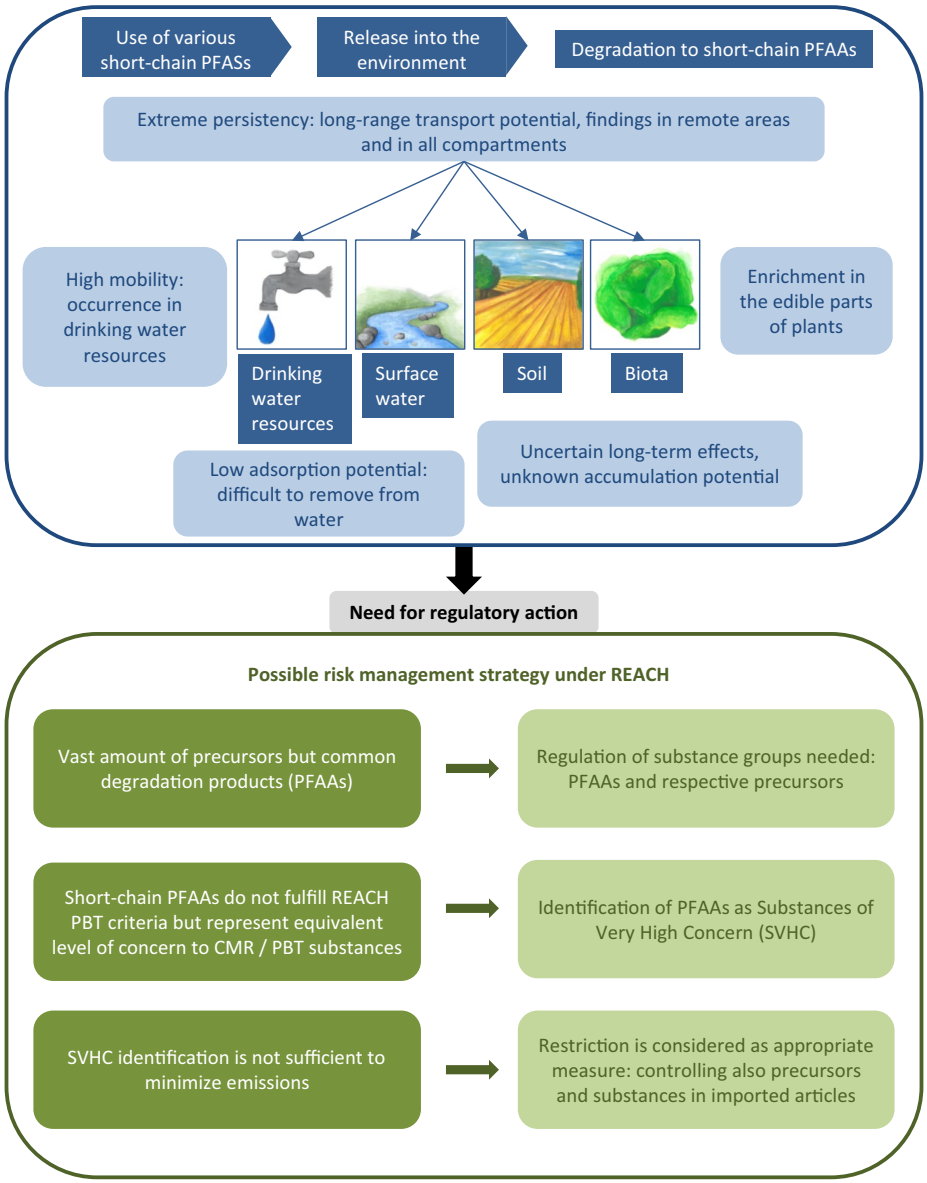


Fig. 2 Concerning properties of short-chain PFASs and a possible risk management strategy under REACH

action to prevent further emission, the adverse effects will continue. The extreme persistence and other intrinsic properties (e.g., low adsorption potential) of short-chain PFASs unquestionable fulfill the second concern. In practice, this is shown in the "case example Rastatt". The first issue, that long-term effects cannot be estimated with sufficient accuracy, is in case of vPvB substances met by the very high bioaccumulation potential. Short-chain PFASs do not fulfill the criteria according to Annex XIII of the REACH Regulation for being bioaccumulative. However, as they will not degrade in the environment, there is a permanent and irreversible exposure of organisms. With ongoing emission, the environmental concentrations of short-chain PFASs will most probably increase, due to the lack of degradation and the fact that emerging emissions come on top of already released amounts resulting in an accumulation in certain environmental compartments. There is a high uncertainty about the toxicity of short-chain PFASs, especially regarding long-term effects (see "Overview of concerns of short-chain PFAAs"). If emissions continue and environmental concentrations of short-chain PFASs exceed a certain limit, it seems very likely that adverse effects may occur. Even if the releases of short-chain PFASs will stop

immediately, the already emitted short-chain PFASs do irreversibly remain in the environment (see "Case example Rastatt"). These considerations and the additional concerns, such as enrichment in the edible parts of plants and the accumulation in water resources (see "Overview of concerns of short-chain PFAAs"), show that short-chain PFASs are of equivalent level of concern compared to PBT/vPvB substances.

Conclusion

Short-chain PFASs are increasingly used and are considered to have properties of very high concern according to Article 57(f) of the REACH Regulation: They are of equivalent level of concern to PBT or vPvB substances. The outlined concerns related to short-chain PFASs, the already existing pollution, i.e., locally restricted very high pollutions (e.g., Rastatt and Uppsala) and global pollutions due to historical emissions, and very likely further increasing concentrations in the environment and biota illustrate that a fast regulation is mandatory. In accordance with the regulation of long-chain PFASs, the most effective way constitutes an SVHC identification of the short-chain PFAAs followed by a restriction, allowing also the regulation of precursors. The SVHC identification is not a prerequisite but will be advantageous, as the concerns attributed to short-chain PFASs do not comply with the "classical" concerns considered in the REACH Regulation and need to be clearly defined. In addition to a regulation by authorities, voluntary measures by industry could contribute substantially in reducing the emissions of short-chain PFASs.

Methods

A literature review was conducted to obtain available information on short-chain PFASs. The concerns of short-chain PFASs and its equivalent level of concern with regard to the REACH Regulation were discussed and the concern was specified at a workshop in Berlin, organized by the German Environment Agency (UBA) in October 2016. Regulatory experts and scientists from different EEA Member States, the European Commission, the European Chemicals Agency, USA and Australia participated.

Abbreviations

CMR: carcinogenic, mutagenic or toxic for reproduction; EEA: European Economic Area; K_{OA}: octanol–air partition coefficient; K_{OC}: organic carbon–water partition coefficient; K_{OW}: octanol–water partition coefficient; PBT: persistent, bioaccumulative and toxic; PFAA: perfluoroalkyl acid; PFASs: per- and polyfluoroalkyl substances; PFBA: perfluorobutanoic acid; PFBS: perfluorobutane sulfonic acid; PFHxA: perfluorohexanoic acid; PFOA: perfluorooctanoic; PFOS: perfluorooctane sulfonic acid; pK_a: acid dissociation constant; POP: persistent organic pollutant; REACH: European Chemicals Regulation, EC No. 1907/2006, Registration, Evaluation and Authorization of Chemicals; SVHC: substance of very high concern; vPvB: very persistent and very bioaccumulative.

Authors' contributions

SB, ÉF, CS, LV and ABE contributed in equal parts to this publication. This paper does not necessarily reflect the opinion or the policies if the German Federal Environment Agency. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials

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EMERGING CONTAMINANTS (D CHIANG AND C WALECKA-HUTCHISON, SECTION EDITORS)

Sources, Fate, and Plant Uptake in Agricultural Systems of Per- and Polyfluoroalkyl Substances

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Abstract

Purpose of Review Per- and polyfluoroalkyl substances (PFAS) are a family of > 4700 recalcitrant compounds, many of which are ubiquitous in the environment. This review aims to (1) identify PFAS sources and fate processes relevant to agricultural systems and (2) expand on plant uptake mechanisms and plant responses to PFAS.

Recent Findings The number of PFAS being quantified in studies involving soil, water, and plants is increasing. Transformation of precursors that tend to stay in the rhizosphere can lead to long-term PFAS reservoir to plants. Some PFAS are readily taken up, particularly the shorter-chain PFAS, and can evoke metabolic responses and phytotoxic effects at high concentrations. PFAS translocation from roots to shoots occurs through both active and passive transport mechanisms. Both PFAS uptake and effects vary between and within species.

Summary As new PFAS emerge, it will be necessary to continue expanding the list of PFAS quantified in land-applied media and assessing their accumulation potential in plants. While controlled laboratory or greenhouse studies have merit, comprehensive field studies are needed to provide clarity on PFAS fate and their relative risk in agricultural systems. Field studies should include identifying site-specific PFAS sources, quantifying a broader suite of PFAS and identifying potential precursors, evaluating plant uptake of replacement PFAS, reporting of soil properties and climatic conditions, and assessing risk of impacts to source and irrigation waters. This information can be utilized to inform future studies towards evaluating and mitigating risks to our food chain associated with PFAS in agricultural systems.

Keywords PFAS · PFOS · PFOA · Soil amendments · Phytotoxicity · Crops · Vegetables

Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a widely utilized chemical family [1–3] now referred to as forever chemicals due to their high thermal and chemical stability as well as minimal biodegradability [4]. The perfluoroalkyl chain length (C_nF_{2n+1}–), the functional head group (e.g., carboxylic acid, sulfonate, alcohol, phosphate, amino, or other groups), which may be attached to a nonfluorinated hydrocarbon entity, and structural differences in the fluoroalkyl chain itself (e.g., branching, ether moiety) govern their behavior, subclassification, and nomenclature [5]. Some PFAS are highly bioaccumulative and have been reported in blood serum and breast milk of humans throughout the globe [6–8] and have been associated with adverse health effects [9]. Two classes within the PFAS family that have received the most attention are the perfluoroalkyl sulfonic acids (PFSAs) and the perfluoroalkyl carboxylic acids (PFCAs) [10•] of which perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), respectively, are the most researched to date. Due to their highly bioaccumulative nature, PFOS and PFOA have been voluntarily phased out and are on the Stockholm Convention persistent organic pollutant lists Annex B (restricted) and Annex A (eliminated), and perfluorohexane sulfonic acid (PFHxS) is under review [11]. A range of less studied and often more mobile PFAS that are substitutes for PFOS and PFOA [12] have been found to be equally persistent and often with similar adverse effects, albeit often at higher concentrations [9], thus leading to additional management and regulatory challenges.

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The primary PFAS exposure routes researched to date are drinking water, meat, fish, milk, food packaged in PFAS-containing materials, and indoor dust inhalation [13–16]. More recently, research has included evaluating PFAS exposure from commonly consumed agricultural products (grains, cereals, vegetables, fruits); therefore, it is crucial to understand PFAS sources to plants and the processes controlling how much of each PFAS is taken up by various plant types. Sources of PFAS to agricultural field crops consist of atmospheric deposition via precipitation or particle-bound PFAS, and absorption from the gaseous phase [17, 18], irrigation with contaminated well water or treated wastewater effluent [19–23], pesticides [24•, 25], aqueous film-forming foams (AFFFs) used to extinguish fires [26], and land-applied sewage sludge or biosolids [27•, 28–32, 33•], as well as industrial or municipal compost [34, 35]. Likewise, food grown in hydroponic and greenhouse systems can be impacted by contaminated water as well as other sources. Relative PFAS contributions from different sources will vary depending on location-specific activities and facilities. For example, PFAS contributions from atmospheric deposition have been especially concerning for crops grown near fluorochemical manufacturing facilities [36, 37]. AFFFs are typically the major PFAS source of highly contaminated water near fire training areas; however, impacts to agriculture are generally limited to irrigation with AFFF-contaminated water [26] which could significantly increase exposure risks [38]. Much less is known about the relative PFAS contribution to crops from land-applied biosolids and composts, which serve as both a valuable resource for improving crop yields and a waste management strategy. Also, factors and mechanisms controlling PFAS uptake by plants are not well understood. A critical understanding of these sources and mechanisms is necessary to determine the associated risks, trade-offs, and need for regulatory action [39–41].

Aim and Scope

This review will address PFAS in agricultural systems with an emphasis on land application scenarios, PFAS reservoirs in the rhizosphere, soil–plant transfer, and plant health. A recent review by Ghisi et al. [42•] summarized research on PFAS uptake and occurrence in grains, vegetables, and fruit prior to 2018 with an emphasis on comparing bioaccumulation trends between plants and impacts of environmental factors with a primary focus on C4 and C8 PFCAs and PFSAs. Studies after 2018 have addressed an expanded list of PFAS and began to address precursor contributions to plant uptake. Precursors are PFAS that can degrade to PFCAs or PFSAs, which are the terminal metabolites and collectively referred to as perfluoroalkyl acids (PFAAs). Precursors are often less mobile than PFAAs, thus they can serve as a PFAA reservoir in the rhizosphere. The previous review did not include several field studies that provide valuable information on soil–plant transfer of PFAS under field conditions. In addition, insight into uptake mechanisms and effects to plant health were not specifically addressed. Therefore, this review expands upon the work by Ghisi et al. [42•] accordingly. In addition, hydroponic, pot, and field studies will be compared and contextualized to inform future studies. Recent studies on uptake of PFAS in different agricultural plants are synthesized and discussed in light of previously hypothesized uptake mechanisms and trends. Furthermore, studies on plant responses to PFAS contamination are discussed. Immediate data gaps are highlighted to guide future plant uptake studies, clarify potential PFAS sources in agricultural systems, and better inform relative risk of PFAS exposure through our food chain.

The Expanding List of PFAS

At least 4700 PFAS have been used in industrial and commercial processes and thus potentially released to the environment [3, 43]. PFAS include anionic, cationic, zwitterionic, and neutral compound groups with a range of functional groups (e.g., carboxylic acid, sulfonic acid, ether sulfonate, sulfonamide, sulfonamido acetic acid, phosphate diester, acrylate, amido ammonium salt, amido betaine, and others) [44, 45]. In addition, for a given PFAS, there can be multiple isomers depending on the manufacturing process, e.g., PFOS produced from an electrochemical fluorination process yields multiple branched isomers in addition to the linear isomer [5]. Initial PFAS occurrence studies targeted only PFOS and/or PFOA, and without isomer delineation. Research involving additional PFAS has increased as awareness of the numbers of PFAS in the environment, analytical method development, and analytical standard availability have increased. Table 1 provides a classification and acronym summary for the PFAS that have been included in the plant uptake studies reviewed. PFAS in these studies were quantified using liquid chromatography (LC) paired with mass spectrometry (MS), tandem mass spectrometry (MS/MS), high-resolution mass spectrometry (HRMS), or quadrupole time of flight MS (QToF-MS) [46, 47]. Targeted quantification is limited to availability of standards, which currently includes approximately 60 PFAS. Suspect and nontarget screening with advanced MS instrumentation (e.g., QToF-MS) may be used to identify other PFAS including precursors and intermediates in the pathways to PFAAs. Precursor transformation to PFAAs typically involves multiple transformation steps with different degradation rates and some quite stable intermediates. Degradation rates, metabolites, and metabolite yields vary with each PFAS class as well as environmental factors commonly known to affect microbial degradation [48]. For example, aerobic half-lives of fluorotelomer alcohols are < 1 week with yields to PFOA as high as 40% whereas aerobic soil

Table 1 PFAS included in analytical methods used in plant uptake studies along with acronyms and chemical formulas

Class	PFAS	Acronym	Formula
Carboxylic Acid (PFCA)	Trifluoroacetic acid	TFA	CF_3COOH
	Perfluoropropanoic acid	PFPrA	CF_3CF_2COOH
	Perfluoro-butanoic acid	PFBA	$CF_3(CF_2)_2COOH$
	Perfluoropentanoic acid	PFPeA	$CF_3(CF_2)_3COOH$
	Perfluorohexanoic acid	PFHxA	$CF_3(CF_2)_4COOH$
	Perfluoroheptanoic acid	PFHpA	$CF_3(CF_2)_5COOH$
	Perfluorooctanoic acid	PFOA	$CF_3(CF_2)_6COOH$
	Perfluorononanoic acid	PFNA	$CF_3(CF_2)_7COOH$
	Perfluorodecanoic acid	PFDA	$CF_3(CF_2)_8COOH$
	Perfluoroundecanoic acid	PFUnDA	$CF_3(CF_2)_9COOH$
	Perfluorododecanoic acid	PFDoA	$CF_3(CF_2)_{10}COOH$
	Perfluorotridecanoic acid	PFTrDA	$CF_3(CF_2)_{11}COOH$
	Perfluorotetradecanoic acid	PFTeDA	$CF_3(CF_2)_{12}COOH$
	Perfluorohexadecanoic acid	PFHxDA	$CF_3(CF_2)_{14}COOH$
	Perfluorooctadecanoic acid	PFODA	$CF_3(CF_2)_{16}COOH$
Sulfonic Acid (PFSA)	Perfluoroethane sulfonate	PFEtS	$CF_3CF_2SO_3$
	Perfluoropropane sulfonate	PFPrS	$CF_3(CF_2)_2SO_3$
	Perfluorobutanesulfonate	PFBS	$CF_3(CF_2)_3SO_3$
	Perfluoropentanesulfonate	PFPeS	$CF_3(CF_2)_4SO_3$
	Perfluorohexanesulfonate	PFHxS	$CF_3(CF_2)_5SO_3$
	Perfluoroheptanesulfonate	PFHpS	$CF_3(CF_2)_6SO_3$
	Perfluorooctanesulfonate	PFOS	$CF_3(CF_2)_7SO_3$
	Perfluorodecanesulfonate	PFUdA	$CF_3(CF_2)_9SO_3$
Perfluoroalkane Sulfonamide (FASA)	Perfluorooctane sulfonamide	FOSA, PFOSA	$CF_3(CF_2)_7SO_2NH_2$
	N-methylperfluorooctane sulfonamide	N-MeFOSA	$CF_3(CF_2)_7SO_2NHCH_3$
	N-ethylperfluorooctane sulfonamide	N-EtFOSA	$CF_3(CF_2)_7SO_2NHCH_2CH_3$
Perfluoroalkane Sulfonamido Ethanol (FASE)	N-Methylperfluorooctanesulfonamidoethanol	N-MeFOSE	$CF_3(CF_2)_7SO_2N(CH_3)(CH_2CH_2OH)$
	N-ethylperfluorooctanesulfonamidoethanol	N-EtFOSE	$CF_3(CF_2)_7SO_2N(CH_2CH_3)(CH_2CH_2OH$
Chlorinated Polyfluoroalkyl Ether Sulfonate (Cl-PFAES)	6:2 chlorinated polyfluoroalkyl ether sulfonate	6:2 Cl-PFAES	$Cl(CF_2)_6O(CF_2)_2SO_3$
	8:2 chlorinated polyfluoroalkyl ether sulfonate	8:2 Cl-PFAES	$Cl(CF_2)_8O(CF_2)_2SO_3$
Perfluoroalkane Sulfonamido Acetic Acid (FASAA)	N-methyl perfluorooctane sulfonamido acetic acid	N-MeFOSAA	$CF_3(CF_2)_7SO_2\ N(CH_2)(CH_2CO_2)$
	N-ethyl perfluorooctane sulfonamido acetic acid	N-EtFOSAA	$CF_3(CF_2)_7SO_2\ N(CH_2CH_3)(CH_2CO_2)$
Fluorotelomer Phosphate Diester (DiPAP)	6:2 fluorotelomer phosphate diester	6:2 DiPAP	$[CF_3(CF_2)_5(CH_2)_2\ O]_2PO_2$
	8:2 fluorotelomer phosphate diester	8:2 DiPAP	$[CF_3(CF_2)_7(CH_2)_2\ O]_2PO_2$
	10:2 fluorotelomer phosphate diester	10:2 DiPAP	$[CF_3(CF_2)_9(CH_2)_2\ O]_2PO_2$

Table 1 (continued)

Class	PFAS	Acronym	Formula
Fluorotelomer Sulfonic Acid (FTSA)	6:2 fluorotelomer sulfonic acid	6:2 FTSA	$CF_3(CF_2)_5(CH_2)_2SO_3$
Fluorotelomer Carboxylate (FTCA)	3:3 fluorotelomer carboxylic acid	3:3 FTCA	$CF_3(CF_2)_2CH_2CH_2COOH$
	5:3 fluorotelomer carboxylic acid	5:3 FTCA	$CF_3(CF_2)_4CH_2CH_2COOH$
	7:3 fluorotelomer carboxylic acid	7:3 FTCA	$CF_3(CF_2)_6CH_2CH_2COOH$
	6:2 fluorotelomer carboxylic acid	6:2 FTCA	$CF_3(CF_2)_5CH_2COOH$
	8:2 fluorotelomer carboxylic acid	8:2 FTCA	$CF_3(CF_2)_7CH_2COOH$
	6:2 unsaturated fluorotelomer carboxylate	6:2 FTUCA	$CF_3(CF_2)_4CF{=}CHCOOH$
	8:2 unsaturated fluorotelomer carboxylate	8:2 FTUCA	$CF_3(CF_2)_6CF{=}CHCOOH$
Fluorotelomer Alcohol (FTOH)	6:2 fluorotelomer alcohol	6:2 FTOH	$CF_3(CF_2)_5(CH_2)_2OH$
	8:2 fluorotelomer alcohol	8:2 FTOH	$CF_3(CF_2)_7(CH_2)_2OH$
	10:2 fluorotelomer alcohol	10:2 FTOH	$CF_3(CF_2)_6(CH_2)_2OH$

degradation of fluorotelomer sulfonates, which is both a precursor and an intermediate of some larger S-containing PFAS, is much slower with desulfonation being the rate-limiting step [49].

Other approaches for estimating the contribution of unknown PFAS loads include conducting a fluorine mole balance using bulk organofluorine measurements or chemical assays such as the total oxidizable precursor (TOP) assay, particle-induced gamma-ray emission (PIGE) method, and adsorbable organic fluorine (AOF) or extractible organic fluorine (EOF) paired with combustion ion chromatography (CIC) methods [50]. Understanding the contribution of the unknown PFAS is helpful when making cross-study comparisons between ∑PFAS, ∑PFSAs, and ∑PFCAs in targeted studies, due to variations between media and precursor degradation in temporal studies. For example, the PFOS precursor sulfluramid (active ingredient EtFOSA), which is a pesticide used in the region to control leaf-cutting ants, was proposed as the most likely source of measured PFOS in Brazilian soils (0.020–3.77 ng/g) [24•]. In a carrot uptake study using soil fortified with EtFOSA, temporal generation of FOSAA and FOSA (intermediates to PFOS) and PFOS with yields up to 34% was attributed to EtFOSA degradation [25]. Likewise, in a wheat uptake study using FOSA-fortified soil, degradation to PFOS was observed in both the soil and the earthworms [51]. A small subset of these now known precursors is starting to be routinely quantified; however, currently, there are still many known precursors that are often not quantified. In addition, there are likely still many unknown and difficult to quantify precursors that may be a significant fraction of the total PFAS present and could serve as a continual source of PFAAs depending on degradation potential and degradation rates. For example, a recent study looking at several Canadian biosolids found two side-chain fluorinated polymer surfactants used in consumer products at higher concentrations than the total for targeted PFAAs [33•]. Therefore, although the list of PFAS typically quantified is likely to expand rapidly over the next few years, PFAS occurrence and potential PFAA reservoir are likely underestimated, especially in, but not limited to, earlier studies.

PFAS Sources and Presence in Soils and Growing Media

To provide a foundation to discuss PFAS availability to plants in different growing media, typical PFAS types including precursors and concentration ranges are briefly detailed in this section. PFAS have become so ubiquitous in the environment that finding pristine soils is rare. A recent review by Vedagiri et al. [52] of soils in North America with no known PFAS

point sources found background levels of PFOS and PFOA ranged from 0.018 to 2.55 ng/g ($n = 38$ studies) and 0.059 to 1.84 ng/g ($n = 40$), respectively. A global survey of 32 PFAS in soils taken from 62 locations with limited to no anthropogenic impact revealed PFAS presence in every sample; long-range transport was identified as the source [53]. Of the data reviewed, 33 samples from North America only reported PFOS and PFOA values. Globally, ∑PFCAs (C6–C14) ranged from 0.03 to 14.3 ng/g, and ∑PFSAs (C6–C10) ranged from < LOD to 3.27 ng/g. Other PFAS quantified are intermediates and precursors in the PFAA degradation pathway including a series of ten FTUCAs and ten FTCAs, which ranged from < LOD to 0.106 ng/g and < LOD to 0.048 ng/g in soils, respectfully. Comparison across the globe indicated that the northern hemisphere (especially Asia and North America) had higher PFAS concentrations than the southern hemisphere, which is consistent with results from previous atmospheric distribution studies and oceanic studies [53].

Biosolids and irrigation waters are the most prominently studied sources of PFAS in agricultural soils. PFAS are found in multiple water resources around the world [52], which when utilized as an irrigation source can lead to higher PFAS loads in soils then global background concentrations. Irrigation with well water, treated wastewater effluent, and surface water is essential to agriculture in many regions, and thus is a source of PFAS to plants that is difficult to avoid. Of 13 PFAS tested in agricultural soils from a Ugandan wetland irrigated with surface water receiving effluent discharged by wastewater treatment plants (WWTPs), PFOS was the most abundant (36–50% of ∑PFAS, 0.6–3.0 ng/g dw) > PFOA (6.2–15%, 0.48–0.91 ng/g dw) > PFHxA (4.7–18% dw, 0.2–0.5 ng/g dw) [23]. In a South Korean rice paddy irrigated with surface water impacted by effluent from WWTP receiving textile industry waste, the soil contained ∑PFAS ranging from 0.12 to 13.9 ng/g dw [54]. Zhang et al. [55] reported ∑PFAAs in irrigated agricultural fields in China ranging from 0.29 to 4.28 ng/g (mean 1.62 ng/g) with PFOA (39% of ∑PFAAs) > PFDA (16%) > PFBA (9%) > PFHxA (7%) = PFNA (7%). In home gardens in the USA irrigated with landfill leachate-contaminated groundwater, several PFAAs, including PFOA (0.11–3.0 ng/g), PFOS (0.57–12.0 ng/g), PFBA (0.04–13.0 ng/g), PFPeA (ND—0.57 ng/g), PFHxS (ND—0.24 ng/g), and PFHxA (ND—0.66 ng/g), were detected in over 70% of the soil samples from 20 home gardens [22•]. Comparatively lower concentrations were found in 3 irrigated gardens outside the contaminated zone: PFOS (0.93–2.1 ng/g), PFOA (0.29–0.54 ng/g), and PFBA (0.073–0.49 ng/g).

Waste-derived soil amendments and fertilizers, including biosolids and composts made from biodegradable solid wastes, are frequently land-applied as an organic matter source that improves soil structure and water-holding capacity as well as a slow-release source of nitrogen and other micro- and macronutrients [56–58]. Concerns that these waste-derived soil amendments are significant sources of PFAS to the environment have been increasing over the past decade [27•, 30, 33, 35, 59, 60]. Biosolids, which are prepared from the sludge produced in the wastewater treatment process, inherently contain higher concentrations of the more sorptive longer perfluoroalkyl chains and larger precursors than the corresponding wastewater effluent. Longer-chain PFAS refer to those that have six or more perfluoroalkyl carbons. Degradation of these precursors throughout the sludge treatment process and after land application can lead to increased concentrations of the shorter-chain PFAAs [61]. PFAS loads to soil from biosolid application depend on the PFAS sources to WWTPs, the PFAS concentrations in the biosolids, and biosolid application rates [33•, 62, 63]. Furthermore, given the persistence of PFAS, multiple biosolids applications may result in higher PFAS concentrations [63, 64]. Sepulvado et al. [64] investigated PFAS at a site in Illinois where biosolids were applied over a 3-year period. Various loading rates and soil types were utilized, along with 6 different biosolids that contained a mean ∑PFAS concentration of 433 ng/g. PFOS (80–219 ng/g), MeFOSAA (63–143 ng/g), EtFOSAA (42–72 ng/g), and PFOA(8–68 ng/g) were detected most frequently in biosolid samples [64]. PFAS leaching at the site increased with decreasing carbon chain length, thus greater leaching of short-chain PFAS was observed [64]. While Sepulvado et al. [64] did include known PFAA precursors MeFOSAA and EtFOSAA in their study, other precursors yet to be identified may have been present. For example, in soils from a biosolid-amended field in Ontario, Chu and Letcher [30] found, for the first time, two side-chain fluorinated polymer surfactants (S1 and its shorter-chain replacement S2) from Scotchgard™ fabric protectors totaling ~240 ng/g dw, which was one hundred times higher than the total sum of 22 other more typically targeted PFAS [30]. Later, they found these same PFAS in biosolids from numerous wastewater treatment plants in Canada [33•]. While studies have yet to be conducted to quantify the degradation of these larger PFAS, PFAS used in textiles and leather for stain and water resistance may be a long-term source in domestic wastewater with potential to generate PFAAs.

Most commercially available waste-derived products sold in local or major store chains, which are typically purchased for use in urban and sub-urban gardens, golf courses, and public and homeowner lawns, have been found to contain PFAS. Kim Lazcano et al. [59] found 9.0–181 ng/g of total PFAAs in commercially available municipal biosolid-based products. PFAS are also present in non-biosolid urban waste-derived composts made from compostable paper products, food wastes, and tree and grass clippings. Total PFAAs in organic waste composts ranged from 31 to 75 ng/g for those containing food packaging with PFAS concentrations being lower in composts of only food and yard wastes (≤ 18.89 ng/g) [35, 59]. All these biosolid and non-biosolid waste-derived

composts contained PFOA and PFOS even though phase out was several years earlier than when these materials were produced. Several PFAS precursors were also detected with the most common being the 6:2 diPAP and 6:2 FTS [35, 59]. Likewise, total PFAAs up to 80 ng/g dw were found in biowaste from biogas production [31]. Overall shorter-chain PFAAs were higher in municipal solid waste- and biowaste-derived amendments compared to biosolid-based products [31, 35, 59]. Other waste-derived materials used as soil amendments that have not been studied for PFAS occurrence include paper mill wastes [65] which are expected to contain PFAS associated with PFAS-based paper coatings. Other PFAS sources applied to agricultural soils include PFAS-based pesticides, e.g., sulfluramid as exemplified already, or pesticides that may contain PFAS in their formulations as an ingredient in the surfactant carrier of which little is known.

PFAS production or use in manufacturing can lead to PFAS additions to agricultural soils through atmospheric deposition and/or contaminating water used for irrigation. Soil samples in agricultural fields located in five cities near fluorochemical manufacturing sites were commonly found to contain PFAS with detection frequency of PFBA (18.2%) > PFOA (31.8%), > PFDA (11.4%) > PFNA(12.6%) [66]. Liu et al. [36] reported total PFAS concentrations in agricultural soils of 79.9 to 200 ng/g and 2.09 to 3.75 ng/g within 0.3 km and 10 km, respectively, of a fluorochemical plant. PFOA made up the greatest portion (83.4%, up to 181 ng/g) of the total quantified with the remainder being primarily the shorter-chain PFCAs [36].

Use of AFFFs has led to release of a wide range of both PFAS types and concentrations to the environment. For example, in Australia, 60 different PFAS were detected in AFFF-impacted soil, including novel PFAS identified with nontarget techniques [26]. Several PFSAs, PFCAs, chlorinated perfluoroalkyl sulfonate (Cl-PFSAs), ketone perfluoroalkyl sulfonates, FASA, perfluoroalkyl sulfinates, perfluoroalkyl sulfonamidoethanols, fluorotelomer sulfonates, and perfluoroalkyl sulfoamido amines as well as one fluorotelomer thioamido sulfonate were detected. This exemplifies the need to include nontarget screening in future studies, particularly at, but not limited to, AFFF-impacted sites. High total PFAS concentrations are often observed at fire training sites, e.g., Dauchy et al. [67] reported up to 710,126 ng/g in surface soils and 300 to 8300 ng/L in groundwater.

PFAS Sorption and Mobility Characteristics

PFAS interactions with soil moderate PFAS mobility and plant availability, thus the long-term dynamics of PFAS in agricultural systems. Within a class of PFAS (e.g., PFCAs, PFSAs), PFAS sorption to soils increases with increasing perfluoroalkyl chain length [68]; therefore, leaching and bioavailability increase with decreasing chain length [64, 69]. For a given chain length, sorption tends to be higher for PFSAs compared to PFCAs [68]. Cationic and some zwitterionic PFAS tend to have a high affinity to agricultural soils, since healthy soils typically contain a significant cation exchange capacity [45, 70]. Although soil organic carbon (OC) generally increases sorption of organic contaminants, in a review by Li et al. [60], no consistent trend was apparent between OC and PFAS sorption by soils across the globe. Although parameters that may affect sorption were not provided in all papers, Li et al. [60] were able to evaluate trends between sorption, pH, and cation concentrations. They found pH to be significantly correlated to sorption for only EtFOSAA ($n = 10$), MeFOSAA ($n = 10$), and PFDS ($n = 10$), while a general trend of increasing PFAA sorption with increasing cation concentration and overall salinity was evident [60]. Correlations to other soil properties such as exchange capacities were constrained because property information was most often not reported [60]. Using PFAA sorption data obtained for a single soil and a single concentration but with different solution pH and cation presence (Al, Ca, and Na), Campos Pereira et al. [68] generally observed inverse correlations between OC-normalized sorption coefficients and pH. Both PFAAs and acid functional groups in soil organic matter (SOM) become more anionic with increasing pH, thus lower sorption with higher pH may be expected for anionic PFAAs. Cation effects were more varied and complicated since their addition can invoke pH changes as well. Overall, the authors attributed the effects observed to changes in the net charge of organic matter, which can be impacted by pH as well as cation charge and concentration. They also hypothesized that longer-chain PFAAs preferentially sorb to the humin SOM fraction whereas sorption of the shorter chain was more to humic and fulvic acid domains [68]. Although data were limited, results indicated that different OM sources (e.g., OM arising from different crop and management strategies including land-applied waste-derived amendments) may alter PFAS retention, thus mobility and plant uptake potential. Factors not considered by Campos Pereira et al. [68] include nonlinear sorption behavior [71] and the effect of cation charge and concentration on PFAA clustering [72].

Inorganic anions can also impact PFAA sorption. Addition of phosphate decreased sorption of PFOS due to site-specific competition with the greatest impact being in soils with low OM content and high ferric oxide content [71]. Given the importance of phosphorus as a nutrient in agricultural systems, further studies on the effect of phosphorus speciation and concentration on sorption of additional PFAS are warranted. Lastly, other sorption mechanisms unique to PFAS as surfactants include the potential for enhanced retention at the air–water interface in the vadose zone [73, 74] (the unsaturated zone of soil above the water table including the root zone).

In unsaturated soils, air–water partitioning of PFOS [74] and PFOA [73] at higher concentrations typical of AFFF-impacted sites accounted for 32% and up to 75% of the retention by soil, respectively. This indicates that rain events that lead to saturation may temporarily mobilize sorbed PFAS. The role of interfacial tension at PFAS concentrations that may be released from typical waste-derived soil amendments versus AFFFs is yet to be determined.

Uptake into Agricultural Plants

The plant uptake studies reviewed include hydroponic studies ($n = 17$), pot studies ($n = 19$), and field studies ($n = 14$) (Table S1). Table 2 provides a summary of the plant species studied, reported uptake and comparisons between study types for the most commonly studied PFAAs, and the range in number of PFAS that have been included in at least one study for the given species organized by classification. A total of 63 field crops and produce types have been studied with the most studied reported in Table 2. Grains, leaf vegetables, and root vegetables were the most studied plants, with sweet fruits being the least studied. Generally, vegetables and vegetative plant components had higher PFAS concentrations than grains and fruits. In home gardens, floret vegetables had higher concentrations of PFAS than other plant categories [22]. Studies indicate that long-chain PFAAs will be less susceptible to leaching and less likely to transfer from soils to plants or be translocated compared to the shorter-chain replacements which are more water soluble [12, 35, 75•]. Likewise, precursors can serve as a reservoir of smaller more mobile and bioavailable PFAS (intermediate metabolites and subsequent terminal PFAAs) [51]. The source strength of the precursor reservoir will depend on degradation rates and PFAA yield potential [48], which has not been determined for many precursors especially those more recently identified.

Synthesizing data from plant uptake studies can be challenging due to reported differences between plant species, within plant species (different cultivars), and within the different plant components (root, shoot, leaves, fruit) [42•, 82, 92•], as well if data are reported on a wet or dry weight basis. To compare between treatments and different systems, several ratios have been utilized including the root concentration factor (RCF, ratio of root to soil concentration), translocation factor (TF, ratio of shoot to root concentration) or sometimes called the foliage to root concentration ratios (FRCFs), shoot concentration factor (SCF, ratio of shoot to the growing media), and bioconcentration factor (BCF, ratio of the plant to growing media). In addition, a transpiration stream concentration factor (TSCF) can be used to describe translocation of PFAS via the transpiration stream; however, TSCF is not highly reported and is better suited to hydroponic studies; plants grown in soil require a porewater analysis to calculate TSCF [102•].

In studies using different ratios of PFAS between compartments in various plant systems, the PFAS characteristic appears to be the single most consistent factor affecting TFs and RCFs [20, 36, 62, 75•, 74–76, 77•, 79–81, 102•, 103, 104], which allots some insight into uptake mechanism. RCFs generally increased with increasing chain length and were greater for PFSAs compared to PFCAs of similar chain length [76, 80, 102•, 104], whereas TFs generally increased with decreasing chain length [20, 36, 62, 75•, 76, 79, 80]. However, there are exceptions to these general trends attributed to plant-specific mechanisms to be discussed in the mechanism section [91, 105•]. For a given PFAS, there are also notable trends with PFAS concentrations in the growing media. Current trends described in the literature indicate that root uptake concentrations increase with increasing PFAS concentrations [82, 91, 96]. This leads to relatively constant RCF values for given PFAS unless sorption to tissues reaches a maximum (e.g., nonlinear sorption to tissues) in which case the RCFs may decrease [91]. Across many species, short-chain PFAAs readily uptake and translocate throughout the plants [36, 42•, 75•, 79, 104], thus they tend to have higher TFs than longer chain. Short-chain PFAAs translocated to edible portions of crops more often than long-chain PFAAs [66], partially because short-chain PFAS sorb less to soils [106] and thus are more bioavailable [22•, 104, 107]. Also, it is plausible that with smaller size PFAS, plant root barriers may have a reduced impact on restricting their translocation [75•] as will be discussed in regard to plant uptake mechanisms.

Study type and design will affect PFAS bioavailability, the contact period during which the plant can uptake PFAS and/or PFAS effects on the plant. In hydroponic systems, overall PFAS availability is high compared to soil since it is not moderated by sorption; however, the root surface area where uptake occurs can be reduced in a hydroponic system. For example, red chicory root development in hydroponic systems was reduced; thus, uptake surface area decreased compared to chicory grown in soil [102•]. Most studies, particularly in pot and hydroponic studies, invoke PFAS treatments to seedlings (germination occurs in a different environment); thus, potential effects on germination and early growth are missed. Field studies often include impacts on germination since seeds are planted rather than seedlings and have additional variables that can impact PFAS availability for plant uptake such as potential for compounds to leach out of the root zone and climate variability. Also in most pot studies, leaching is minimized or prevented; thus, short-chain PFAS remain in the root zone unlike what is likely to occur in the field. For example, decreases were reported in short-chain PFAS concentrations in the soil profile throughout a growing season due to leaching [64, 106], whereas in a pot study short-chain PFAS became enriched in the bottom layers of the pot compared to the longer-chain PFAS and remained accessible for

Table 2 Comparison between three study types (A = hydroponic, B = pot studies, C = field studies) conducted on agricultural plants for PFBA (C4), PFHxA (C6), PFOA (C8), PFBS (C4), PFHxS (C6), and PFOS (C8) with parenthetical indicating total carbon chain length

Plant	Study type (# of studies)			Results										References
	A	B	C	PFAS class (range studied within the class for a given study)		Concentration ranges (ng/g dw)			RCF (range)		TF (range)			Hydroponic[a], pot[b], field[c]
						A	B	C	B	C	A	B	C	
Wheat	5	4	2	PFCA (1–9)	PFBA	200–1400	3170–406,080	1–1100	18–19	2.7–43.91	0.7–2.5	1.2–2.3	0.6–1.4	[20, 75–78][a]
					PFHxA	500–2000	810–8060	0.3–135	0.2–6.8	2.8–4.3	–	1.1–1.9	0.3–1.0	[79–82][b]
				PFSA (0–3)	PFOA	100–10,800	30–341,000	1–809	0.05–2	1.3–4.9	0.02–0.3	0.1–1.1	0.2–0.5	[36, 62] [c]
					PFBS	–	310–15,280	< LOQ–60	0.4–1.6	NA- 1.8	–	0.1–1.3	NA–0.4	
				Cl-PFAES (0–2)	PFHxS	–	150–7240	< LOQ–68	0.1–2	NA- 2.8	–	0.2–1.2	NA–0.2	
					PFOS	500–28,600	100–76,900	0.2–12,500	0.02–1.4	0.8–6	0.018	0.1–1	0.2–1	
Ryegrass		3		PFCA (1)	PFBA	–	–	–	–	–	–	–	–	[82–84] [b]
				PFSA (1)	PFHxA	–	–	–	–	–	–	–	–	
				FASA (0–2)	PFOA	–	1–100,300	–	2.35	–	–	0.6	–	
					PFBS	–	–	–	–	–	–	–	–	
				FASAA (0–1)	PFHxS	–	–	–	–	–	–	–	–	
					PFOS	–	1–42,000	–	1.4–1.5	–	–	0.1–2.1	–	
Maize		5	5	PFCA (0–13)	PFBA	–	30–35,200	< LOQ–1449	–	11–25.5	–	–	0.7–1.3	[28, 82–85] [a]
					PFHxA	–	30–2800	< LOQ–116	–	1.9–11.3	–	–	0.6–0.7	[22, 23, 36, 63, 86][c]
				PFSA (1–4)	PFOA	–	< LOQ–640	< LOQ–2478	–	1.1–2.4	–	–	0.1–0.3	
					PFBS	–	2–1800	< LOQ–100	5	–	–	–	–	
				FASA (0–2)	PFHxS	–	< LOQ–7980	< LOQ–0.05	2.6	–	–	–	–	
					PFOS	–	< LOQ–23100	< LOQ–0.2	8.8	–	–	–	–	
				FASE (0–2)										
				FASAA (0–2)										
				FTSA (0–1)										
				FTCA (0–7)										
				FTOH (0–3)										
				DiPAP (0–3)										
				Cl-PFESA (0–2)										
Rice		1	1	PFCA (10–13)	PFBA	–	ND	0.01–2.4	–	–	–	2.2–60	–	[19] [b]
					PFHxA	–	ND	0.02–1	–	–	–	4.3–6.2	–	[54][c]
				PFSA (4–5)	PFOA	–	ND–1.73	< LOQ − 1.9	–	–	–	0.1–1.6	–	
					PFBS	–	ND	< LOQ–0.03	–	–	–		–	
				FASA (0–2)	PFHxS	–	ND	< LOQ–3.8	–	–	–	0.1–0.5	–	
					PFOS	–	ND	< LOQ–55.5	–	–	–	0.1–0.2	–	
				FASAA (0–1)										

Table 2 (continued)

Plant	Study type (# of studies)			Results									References
	A	B	C	PFAS class (range studied within the class for a given study)		Concentration ranges (ng/g dw)			RCF (range)		TF (range)			Hydroponic[a], pot[b], field[c]
						A	B	C	B	C	A	B	C	
Soybean	1	2	1	PFCA	PFBA		–	223–2378	–	69.5	–	–	0.7	[87][a]
				(0–9)	PFHxA		–	5.5–212	–	6.4	–	–	0.6	[83, 84] [b]
				PFSA	PFOA	ND	120–1340	0.3–3967	–	1.7	–	0.1	0.002	[36] [c]
				(0–3)	PFBS	0.02–0.15	–	< LOQ	–	–	0.1	–	–	
				FASA	PFHxS	0.02–0.2	–	< LOQ	–	–	0.1	–	–	
				(0–2)	PFOS	0.3–15	20–720	0.12.3	2.3–4.7	5.6	0.02	0.1–1.2	0.8	
				FASAA (0–2)										
Alfalfa		3	1	PFCA	PFBA	–	–	ND	–	–	–	–	–	[83, 84, 88] [b]
				(0–11)	PFHxA	–	–	ND	–	–	–	–	–	[89] [c]
				PFSA	PFOA	–	1311.5–4310.3	ND	10.3	–	–	0.304	–	
				(1–4)	PFBS	–	–	ND	–	–	–	–	–	
				FASA	PFHxS	–	–	ND	–	–	–	–	–	
				(0–3)	PFOS	–	10–481.4	ND	2.3–3.12	–	–	0.131–1.1	–	
				FASAA (0–2)										
Lettuce	3	8	3	PFCA	PFBA	< LOQ–84	< LOQ–25,100	< LOQ–2365	–	–	2.7	–	–	[21, 90, 91] [a]
				(1–11)	PFHxA	< LOQ–14.4	< LOQ–9460	< LOQ–72	–	–	0.7	–	–	[34, 63, 83, 84, 88, 92–94][b]
				PFSA	PFOA	0.02–135	< LOQ–2523	< LOQ–1038	–	6	0.3	0.2	–	[22, 36, 63] [c]
				(0–5)	PFBS	< LOQ–17	< LOQ–3670	< LOQ–1.6	–	–	0.3	–	–	
				FASA	PFHxS	< LOQ–30	< LOQ–1250	< LOQ–0.5	–	–	0.2	0.1–1.6	–	
				(0–2)	PFOS	< OQ–205	< LOQ–279	< LOQ–3.5	0.2–14.6	3.8–3.9	0.1	0.02–0.4	–	
				FASAA (0–2)										
				DiPAP (0–1)										
Spinach		1	4	PFCA	PFBA	–	ND	ND–6.7	–	–	–	–	–	[28] [b]
				(9–13)	PFHxA	–	ND	ND–1.2	–	–	–	–	–	[22, 55, 66, 95] [c]
				PFSA	PFOA	–	ND–2.4	ND–6.7	–	–	–	–	–	
				(2–8)	PFBS	–	ND	ND–1.7	–	–	–	–	–	
				FASA	PFHxS	–	–	ND–0.1	–	–	–	–	–	
				(0–3)	PFOS	–	1–1.6	ND–0.1	–	–	–	–	–	
				FASAA (0–2)										
				FTCA (0–1)										
Cabbage	1		2	PFCA	PFBA	< LOQ–10.9	–	2.5–17.8	–	–	1.5	–	–	[96] [a]
				(9–11)	PFHxA	0.1–14.4	–	0.2–1.4	–	–	0.6	–	–	[22, 55] [c]
				PFSA (3)	PFOA	0.1–10.9	–	1.3–4.0	–	–	0.4	–	–	
					PFBS	0.2–31.5	–	ND–0.1	–	–	0.7	–	–	
					PFHxS	0.1–31.2	–	ND–0.1	–	–	0.4	–	–	

Table 2 (continued)

Plant	Study type (# of studies)			Results									References
	A	B	C	PFAS class (range studied within the class for a given study)		Concentration ranges (ng/g dw)			RCF (range)		TF (range)			Hydroponic[a], pot[b], field[c]
						A	B	C	B	C	A	B	C	
					PFOS	0.1–90.1	–	ND–0.08	–	–	0.2	–	–	
Celery		1	2	PFCA (7–9)	PFBA	–	< LOQ–80.8	433.2–517.8	17.3	133.5	–	1.4	0.8	[97] [b]
					PFHxA	–	7.2–137.1	18.4–19.9	4.8	16.2	–	1.3	1.1	[22, 36] [c]
				PFSA (3–5)	PFOA	–	2–111.3	75.4–218.2	1.4	2.7	–	0.3	0.3	
					PFBS	–	4.5–122.6	0.05–0.07	2.5	–	–	0.5	0.7	
					PFHxS	–	0.4–3.9	0.05–0.09	5	–	–	0.5	0.6	
					PFOS	–	17.2–209.8	0.07–0.11	4.2	1.8	–	0.2	0.6	
Cucumber		3	5	PFCA (1–13)	PFBA	–	17–63	0.1–13.6	–	–	–	–	–	[88, 98, 99] [b]
					PFHxA	–	ND–0.3	ND–1.4	–	–	–	–	–	[22, 37, 55, 66, 95] [c]
				PFSA (1–8)	PFOA	–	0.5–797	0.005–1.4	–	–	–	–	–	
					PFBS	–	3.8–15	ND–0.06	–	–	–	–	–	
				FASA (0–3)	PFHxS	–	0.2–0.3	ND–0.004	–	–	–	–	–	
					PFOS	–	ND–119	ND–0.06	–	–	–	–	–	
				FASAA (0–2)										
				FTCA (0–1)										
Zucchini	1		2	PFCA (9–13)	PFBA	< LOQ–2.6	–	1.5–2	–	–	0.6	–	–	[96] [a]
					PFHxA	< LOQ–9.6	–	0.03–0.1	–	–	1	–	–	[55, 95] [c]
				PFSA (3–5)	PFOA	< LOQ–28.9	–	ND–0.64	–	–	0.4	–	–	
					PFBS	< LOQ–19.0	–	ND	–	–	0.1	–	–	
				FASA (0–3)	PFHxS	< LOQ–19.8	–	ND	–	–	0.2	–	–	
					PFOS	< LOQ–81	–	ND	–	–	0.1	–	–	
				FASAA (0–2)										
				FTCA (0–1)										
Pumpkin	2		2	PFCA (2–13)	PFBA	< LOQ–0.6	–	< LOQ–638.1	–	–	0.6	–	–	[87, 100] [a]
					PFHxA	< LOQ–0.2	–	< LOQ–11.7	–	–	0.5	–	–	[36, 66] [c]
				PFSA (3–8)	PFOA	< LOQ	–	0.05–15.1	–	–	0.2	–	–	
					PFBS	< LOQ–0.05	–	< LOQ	–	–	0.4–0.5	–	–	
				FASA (0-1)	PFHxS	< LOQ–0.2	–	< LOQ	–	–	0.2–0.4	–	–	
				FTSA (0-1)	PFOS	< LOQ–15	–	< LOQ–0.09	–	–	0.2–0.3	–	–	
Pepper			5	PFCA (5–13)	PFBA	–	–	0.1–946.5	–	–	–	–	–	[22, 36, 37, 55, 95] [c]
					PFHxA	–	–	0.2–74.4	–	–	–	–	–	
				PFSA (3–5)	PFOA	–	–	0.007–39.3	–	–	–	–	–	
					PFBS	–	–	ND–0.2	–	–	–	–	–	
				FASA (0–3)	PFHxS	–	–	ND–0.005	–	–	–	–	–	
					PFOS	–	–	ND–0.2	–	–	–	–	–	
				FASAA (0–3)										

Table 2 (continued)

Plant	Study type (# of studies)			Results										References
	A	B	C	PFAS class (range studied within the class for a given study)		Concentration ranges (ng/g dw)			RCF (range)		TF (range)			Hydroponic[a], pot[b], field[c]
						A	B	C	B	C	A	B	C	
Eggplant			5	FTCA (1) PFCA (9–13) PFSA (3–8) FASA (0–3) FASAA (0–2) FTCA (1)	PFBA PFHxA PFOA PFBS PFHxS PFOS	–	–	0.5–4.5 ND–0.4 0.2–0.8 ND ND–0.001 ND	–	–	–	–	–	[22, 37, 55, 66, 95] [c]
Tomato	1	6	6	PFCA (9–13) PFSA (3–8) FASA (0–3) FASAA (0–2) FTCA (0–1)	PFBA PFHxA PFOA PFBS PFHxS PFOS	< LOQ–48 < LOQ–39.3 < LOQ–82.1 < LOQ–78.7 < LOQ–84.4 < LOQ–490	ND–121.9 ND–102.8 ND–190.2 ND–177.1 ND–7.7 ND–225.1	< LOQ–3.3 ND–1.4 ND–0.5 ND–0.3 ND–0.004 ND–0.2	5 1–1.4 1–4.4 0.7 1.8 0.2–4.5	– – – – – –	2.1 1.8 1.3 0.5 0.4 0.1	5.2–15.35 1.77–6.2 0.5–2.5 5.1 1.8 0.5–4.5	– – – – – –	[96][a] [28, 63, 88, 94, 97, 99] [b] [22, 37, 55, 63, 66, 95] [c]
Strawberry		2	2	PFCA (2–13) PFSA (2–4) FASA (0–2) FASAA (0–3) FASE (0–2) FTSA (0–1)	PFBA PFHxA PFOA PFBS PFHxS PFOS	–	< LOQ–11,200 < LOQ–1380 < LOQ–302 < LOQ–373 < LOQ–150 < LOQ–132	< LOQ < LOQ < LOQ < LOQ < LOQ–0.14 < LOQ	–	–	–	–	–	[88, 93] [b] [22, 101] [c‡]
Radish		4	3	PFCA (7–9) PFSA (3–5)	PFBA PFHxA PFOA PFBS PFHxS PFOS	–	< LOQ–13.7 7.3–44.5 8.1–2227 23.9–164.2 2.8–10.3 17–1250.3	1–1167.5 0.1–103.3 0.08–1879.8 < LOQ–0.5 ND–0.1 ND–1.8	2.9 1.2 0.8–3.0 1.3 2 0.7–2.6	10.8–15.2 3.1–14.2 0.7–1.4 NA NA NA–0.9	–	9.5 4.3 1.8–15.9 3.8 2.9 1.2–6.6	2.1–13.9 2.2–4.9 9.4–19.7 NA NA 0.6–30.8	[83, 84, 88, 97][b] [22, 36, 55] [c]
Carrot		4	4	PFCA (1–13) PFSA	PFBA PFHxA PFOA	–	36–130 3.1–144 ND–3567	0.02–865.8 ND–32.4 0.005–138.6	4.74 0.86 0.5–0.6	7.6–38.9 1.6–4.2 0.3–0.6	–	13.7 9.6–15.8 2.8–9.6	2.2–3.1 3.2–4.3 2.7–4.0	[25, 34, 94, 98][b] [22, 36, 55, 95] [c]

Table 2 (continued)

Plant	Study type (# of studies)			Results									References
	A	B	C	PFAS class (range studied within the class for a given study)		Concentration ranges (ng/g dw)			RCF (range)		TF (range)			Hydroponic[a], pot[b], field[c]
						A	B	C	B	C	A	B	C	
				(1–5) PFCA (1–13) PFSA (0–3) FASAA (0–2) FTCA (0–2) DiPAP (0–1)	PFBS PFHxS PFOS	– – –	– – 0.5–782	ND–1.0 ND–0.07 ND–1.73	– – 0.1–1.3	NA–3 NA–0.07 NA	– – –	– – –	NA–10.9 NA–1.4 NA–2.2	
Potato		2	2	PFCA (1–13) PFSA (1–5) FASA (0–3) FASAA (0–2) FTCA (0–1)	PFBA PFHxA PFOA PFBS PFHxS PFOS	– – – – – –	– – ND–234 – – ND–590	0.8[d] 0.006 [d] 0.01 [d] ND [d] 0.0008 [d] ND [d]	– – – – – –	– – – – – –	– – – – – –	– – – – – –	– – – – – –	[82, 98] [b] [22, 95] [c]

Additional PFAS classes studied for each plant type are reported PFAS class column. Plant species with only one study, or one study and studies by Bao et al. [37] or Scher et al. [22] which reported collective values by plant types are not listed. Spiked and biosolid amended pot studies are combined in category B. The PFAS class column indicates additional PFAS studied in reported plants; however, sufficient data were not available for comparisons across study types and within a given species for these additional PFAS

Variables reported include concentration ranges, root concentration factors (RCF), and translocation factors (TF)

< *LOQ* below method limit of quantitation, *ND* not detected, *NA* not applicable, *d* value estimate

plant uptake [104]. Thus, study design must be considered when interpreting plant uptake magnitudes and mechanisms.

Field studies on plant uptake of PFAS and the number of different PFAS analyzed have increased in recent years; eleven field studies are summarized here that were not previously reviewed [42•]. Two field studies noted a correlation between the level of short-chain PFAS taken up by crops and the volume of PFAS-contaminated irrigation water used [22•, 55]. For example, 60% of the variability in PFBA concentrations in home garden–grown produce was accounted for by differences in the volume of PFAS-contaminated water used to irrigate the gardens [22•]. For a variety of lab and greenhouse designed studies, PFCAs have been shown to translocate from plant roots to shoots more readily than PFSAs. However, field-scale translocation and soil–root transfer data are sparse; sampling rarely includes harvest of non-edible crop components. In cases where soil–root transfer was evaluated, PFAS contributions from atmospheric deposition confounded accurate TF and BCF comparisons, especially in plants grown near fluorochemical manufacturing. For example, field-grown lettuce at a site 0.3 km from fluorochemical manufacturing had up to 2370 ng/g PFBA and 1040 ng/g PFOA in lettuce and only 5 ng/g PFBA and 90 ng/g PFOA in soil [36], whereas lower concentrations in lettuce (no more than 270 ng/g PFBA and 200 ng/g PFOA) were observed in pot studies grown at similar soil PFAS concentrations (6 ng/g PFBA and 80 ng/g PFOA in soil at the time of harvest) [63]. Though costly, future field study designs should target inclusion of data that will enable estimations of BCFs and TFs to different plant domains to better ascertain uptake mechanisms and predict risks associated with accumulation in both human and animal edible components.

Studies that include additional PFAS classes as well as precursor and precursor degradation intermediates in plant studies are limited. A single study that included Cl-PFAESs found that the TF in wheat of 6:2 Cl-PFAES (a PFOS replacement) was similar to that of PFOS, while 8:2 Cl-PFAES had a lower TF, indicating that chain length effects occur within other PFAS classes similar to those observed for PFCAs and PFSAs [77•]. A single study addressed uptake of ultra-short-chain PFCAs (C2 and C3) [75•]. This study was with hydroponically cultivated wheat in which they found high uptake of C2 and C3 PFCAs into the roots and shoots due to multiple uptake mechanisms [75•]. As previously noted, EtFOSA-fortified soils produced a series of degradation products (FOSAA, FOSA, and PFOS) which increased when growing carrots [25]. Both the intermediate FOSA and terminal metabolite PFOS were found on the carrot peel as well as transported into the leaves along with small amounts into the carrot core whereas the precursor EtFOSA remained in the soil with only small amounts found on the peel [25]. Zhao et al. [108] exposed hydroponically cultivated wheat, soybean, and pumpkin to EtFOSA (1 mmol/mL) and proposed in vivo transformation of EtFOSA to FOSAA, FOSA, and PFOS in solution by microbes and further metabolic degradation in plant tissue to PFOS, PFHxS, and PFBS. Impurities in the EtFOSA standard lead to initial PFOS concentrations in the incubation solution; however, PFOS concentrations significantly increased in the presence of plant roots and associated microbes [108]. Similar results were observed for wheat with FOSA-fortified soils [51] and hydroponically grown soybeans and pumpkin [87] except that additional shorter-chain PFSAs (PFHxS and PFBS) were observed, particularly in the roots with some in the shoots, albeit at much lower concentrations than PFOS. PFOS is a known microbial degradation product of FOSA while PFBS and PFHxS are not [34]. The authors attributed the formation of short-chain PFSAs to a unique metabolic pathway. However, there are several noteworthy points to consider. First, the FOSA used was a technical grade (90–92% purity) with 8 mol% PFOS. Analysis targeted only FOSA, PFOS, and shorter-chain PFSAs and PFCAs; therefore, other impurities would have been missed such as shorter perfluoroalkyl chain sulfonamides, which would lead to PFSA degradation products of the corresponding chain length. In addition, in the case of wheat grown in both systems, higher levels of these short chains were found when grown in soils where microbial degradation would be higher [51]. Also in the hydroponic systems for soybean and pumpkin, small amounts of both PFBS and PFHxS were found in the plant controls (no FOSA added) [87]. Lastly, in order to form PFBS and PFHxS from FOSA, cleavage to produce a shorter fluorinated alkyl chain with reattachment of either a fluorine atom (if C-C cleavage occurred) or a sulfonate group (if C-S cleavage occurred) would have had to happen, which seems thermodynamically unlikely. Therefore, although the authors propose that production of PFBS and PFHxS from FOSA indicates a unique plant-mediated metabolism, it is much more plausible that these results are due to impurities in the technical FOSA used, for which additional support using oxidative stress measures was provided [87]. Enhanced degradation in the presence of plants and formation of additional metabolites relative to what is known to occur in microbially active soils have also been shown for 6:2 FTSA [87] and 8:2 diPAP [34]. Carrots enhanced 8:2 diPAP degradation and yielded additional PFCAs compared to what occurred in soil-only controls as well as what was observed with lettuce [34]. Whereas acid metabolites translocated, 8:2 diPAP remained primarily in plant portions in contact with the soil (e.g., carrot, lettuce heart) [34]. Therefore, plant-mediated degradation of 8:2 diPAP was likely due to carrot exudates rather than degradation within the plant. In 6:2 FTSA exposure to hydroponically grown pumpkin, series of PFCAs (C2–C7) were produced with the C2 and C3 acids not present in root exudates controls; therefore, the authors concluded some 6:2 FTSA biotransformation was occurring within the plant. Such complexities can complicate interpretation of PFAS-specific uptake.

Plant Uptake Mechanisms

Plant mechanisms involved in chemical uptake are plant-specific, but must first involve initial transfer to the root and adsorption to apoplastic plant tissue followed by translocation through the xylem in the central vasculature to the shoot and remainder of the plant. It is widely accepted that the Casparian strip, which is located in the root endodermis and made up of lignified structures that regulate water and mineral uptake by the roots, also serves to constrain translocation of contaminants from roots to the central vasculature, thus the rest of the plant [109]. The Casparian strip prevents passive transport of compounds across the endodermis, by sealing the nonliving spaces between cells and cell membranes (apoplast) [110]. The suberin lamella is an additional selective barrier that is formed in some plants by covering the endodermal cells with the hydrophobic polymer suberin [109].

Trends discussed in PFAS plant uptake studies are consistent with this hypothesis that the Casparian strip constrains translocation of long-chain PFCAs, PFSAs, FOSAs, and Cl-PFAESs, thus resulting in TF < 1 for these PFAS. Felizeter et al. [91] hypothesized that transfer of long-chain PFAS was inhibited by the Casparian strip while the more soluble shorter chains were transported with water into the foliage by comparing RCF, FRCF, and TSCF values for C4-C14 PFCAs and C4-C8 PFSAs in hydroponic studies with lettuce and in light of sorption to root isotherms. They showed that both RCFs and TSCFs had U-shaped curves with the minimum occurring with C7 PFCA while FRCFs consistently decreased with increasing chain length. They also showed that sorption to root isotherms were only linear for C4-C6 PFCAs and PFBS while all longer-chain PFAS exhibited nonlinear isotherms. Findings from hydroponic studies may not transfer well to studies with soils due to the strong chain-length–dependent interactions of PFAS with soils, thus affecting RCFs and subsequent translocation. Müller et al. [105•] further investigated this U-shaped curve phenomenon by measuring uptake, depuration, and translocation kinetics for C4–C10 PFAAs in hydroponically cultivated *Arabidopsis thaliana* in which they evaluated uptake kinetics to root and shoot independently. They also evaluated sorption to dead roots which they used to calculate sorption normalized concentration factors (SNCFs) to better differentiate between physical adsorption and active uptake. They observed preferential uptake of PFBA followed by slow and incomplete depuration. Thus, they proposed a 2-compartment uptake process occurs in which PFBA uptake by the root symplast is reversible whereas uptake by one or more compartments is not reversible, which may involve the central vasculature and/or organelles and be influenced by active transport from the roots [105•]. Other hydroponic studies with wheat also saw enhanced translocation of shorter-chain PFBA compared to the longer-chain PFAAs [75•, 78]. Different transport inhibitors were used to elucidate active transport mechanisms in hydroponically grown wheat exposed to C2–C8 PFAAs [75•] and in an Asian wetland plant (*Alisma orientale*) exposed to PFOA and PFOS [111]. Both studies observed Michaelis-Menten type uptake behavior and when coupled to the effects of inhibitors concluded that PFAA uptake is an energy-dependent active uptake process mediated by carrier proteins. Depending on the specific PFAA and plant species, transport of these carriers could involve anion channels and/or aquaporin channels [75•, 111]. For chicory grown hydroponically, Gredelj et al. [102•] did not observe a pronounced U-shape trend in PFAA (C4–C10) uptake behavior, which was attributed to using higher PFAA exposure concentrations than comparable studies [91, 105•]. Gredelj et al. [102•, 104] also exemplified that chain-length–dependent uptake patterns observed hydroponically may not compare directly to soils grown in soils due to PFAS-soil interactions.

Several studies indicate that root proteins and lipids may influence uptake and bioaccumulation of PFAS in plant tissues [76, 83, 84, 108, 111]. Wen et al. [83, 84] found positive correlations between PFOS and PFOA RCFs and root protein content [83] as well as between TFs and shoot to root protein ratios [84] across seven plant species (alfalfa, lettuce, maize, mung bean, radish, ryegrass, and soybean). Likewise for the same plants, Wen et al. [83] found that although root protein content could account for 55% of the variations in N-EtFOSAA plant concentrations, when combined with lipid content, 85% of the variation across species was predicted. This was in contrast to PFOS and PFOA in which RCFs were negatively correlated to lipid content. In hydroponic studies, H. Zhao et al. [76] attributed increasing root accumulation with increasing PFCA chain length to sorption to root lipids or membrane proteins resulting in lower translocation of the longer-chain PFCAs (e.g., PFDoA) compared to the shorter-chain PFCAs. Zhao et al. [108] found that RCFs for N-EtFOSA increased with increasing root lipid content of hydroponically grown pumpkin, wheat, and soybean. Wang et al. [111] demonstrated that PFOS and PFOA partitioned differently into the subcellular plant components of the hydroponically grown wetland plant *Alisma orientale*, with PFOA residing primarily in the water-soluble fractions of stems, roots, and leaves and PFOS residing primarily in cell walls of roots and leaves and the water-soluble fraction of stems. PFOA and PFOS increased in the cell walls (anionic) and organelles (15–30% lipid) of roots, stems, and leaves with time, and reached an approximate equilibrium after 8 days of exposure [111]. When plants were transplanted into new PFAS-free culture solutions, approximately 80% of PFAS originally taken up was released [111]. These results exemplify that PFAS properties impact uptake to various plant components as well as differences in the subcellular distribution within a plant component.

Contaminants other than PFAS can invoke responses by the Casparian strip and suberin lamellae. For example, maize

roots responded to Cd exposure by developing suberin lamella, which along with the Casparian strip can inhibit the translocation of Cd and other contaminants to the xylem and the remainder of the plant [112]. Co-contamination of PFOS or PFOA with Cd decreased the bioaccumulation of these PFAAs in both wheat and rapeseed; however, the PFAA TFs decreased in wheat only and increased in rapeseed. Interestingly, both the bioaccumulation and TFs of Cd were increased in both plant types in the presence of these PFAAs [81]. Although the authors hypothesized that the cause of co-contamination effects was due to impacts on sorption to soil, thus soil solution concentrations, this is not well supported given the inconsistent data trends. It is more likely that Cd invoked changes in the plant. Wang et al. [113] observed an increased presence of suberin lamella or inactivation of aquaporin channels in response to Cd, which may also decrease PFAS translocation [81]. Additionally, potential PFAS-induced damage to the barriers in root structure at high concentrations (200 mg/L) [78] may allow for increased uptake. Therefore, future studies should consider plant properties that may impact PFAS uptake in addition to sorption dynamics.

Identifying and differentiating PFAS source contributions especially in field studies can be difficult as previously noted. PFAS in irrigation water are readily bioavailable for plant uptake, as demonstrated by Gredelj et al. [104] who showed chicory irrigated with PFAA-containing water having an increased uptake of long-chain PFAAs into the edible heads whereas PFAA soil concentration had a stronger impact on PFAA root concentrations. Seo et al. [114] attributed higher concentrations in plants than expected from soil transfer alone to atmospheric deposition [36]. Seo et al. [114] showed that PFCAs, neutral PFAS, and PFBS commonly partition to the gas phase, while PFOS tends to partition onto airborne particles. Gaseous uptake by tree bark from multiple species in China was identified as the main uptake mechanism for short-chain PFAS, which associated well with high lipid content [115]. In contrast, the presence of long-chain PFAS was attributed to airborne particles being trapped in bark fissures given the lower concentrations in the smooth bark species [115]. The influence of particles and surface texture on PFAS concentrations may also be responsible for higher PFAS concentrations in potato peel than flesh [42•]. For example, recent work showed the presence of PFAS-containing soil mineral derived micron-sized particles on the surface of potatoes even after washing [95]. Therefore, while field studies are critical to bounding PFAS occurrence levels in plants, the multiple variables and variations that exist in field-scale studies confound data interpretation targeted at understanding uptake mechanisms.

Metabolic Responses and Phytotoxicity

PFAS presence and uptake can elicit a metabolic response in plants [21, 75•, 100, 116] which may include chemical modification, conjugation, and compartmentation. Superoxide dismutase (SOD), peroxidase (POD), catalase (CAT), glutathione (GSH), glutathione-S-transferase (GST), cytochromes P450 (CYP450), and malondialdehyde (MDA) are enzymes and metabolites that collectively serve as a defense against damage from superoxide radicals and reactive oxygen species (ROS) by preventing their formation or destroying those formed. PFAS exposure induces plant responses including enzymatic activity [78, 81, 87, 100, 103, 116] and metabolite production [21, 90] that may play a role in reducing phytotoxic impacts of PFAS within plants and/or promote in vivo degradation [87, 100].

Metabolic and phytotoxic responses were reported in crops and produce. Co-exposure of PFOS and PFOA caused several inorganic plant elements (Na, Mg, Cu, Fe, Ca, Mo, and K) to decrease in lettuce leaves while Zn increased, which may be due to ROS-induced ion channel leakage [21]. Also in lettuce, PFOS and PFOA altered amino acid metabolites, dipeptides, fatty acids, lipids, phytol, purine nucleosides, phenolic antioxidants, and flavonoids, as a result of stress responses to DNA injury, photosynthesis inhibition, and impact to energy metabolism [90]. PFAS exposure significantly increased chlorophyll, MDA, and POD, but slightly decreased SOD in rapeseed [81]. Co-contamination with Cd led to PFAS stress responses including decreased urease activity, POD activity, and biomass in rapeseed. In wheat, chlorophyll and MDA inhibition occurred [81]. Also, wheat shoot and root biomass decreased at higher PFAA exposure concentrations (2000 ng/g) while root biomass increased at lower exposure concentrations (200 ng/g) [79]. Additionally in wheat, exposures of PFOS at higher concentrations (100–200,000 μg/L) invoked changes in chlorophyll, protein synthesis, growth, SOD, and POD [78]. Chlorophyll *a* and chlorophyll *b* increased with exposure to long-chain PFAAs while exposure to short-chain PFAAs led to decreases in chlorophyll *a* [79]. Pumpkin and soybean exposure to FOSA increased SOD (soybean 19.2–30.8%, pumpkin 39.2–92.8%) and POD (soybean 19.2–20.7%, pumpkin 21.1–37.6%), likely in response to increased production of ROS [87]. GST and CYP450 also increased with FOSA exposure. Both enzymes are known to play a role in detoxification of contaminants, and thus may have also played a role in plant-mediated FOSA degradation [87]. CYP450 activity increased in pumpkin exposed to 6:2 FTSA and when CYP450 activity was reduced by addition of a CYP450 oxidation inhibitor (1-aminobenzotriazole), PFCA metabolites from 6:2 FTSA degradation decreased, supporting plant-mediated biotransformation [100]. Thus, metabolic responses may lead to some oxidative degradation of PFAS, which will be plant and PFAS dependent. However, stress

responses at the field-scale when irrigating fields or land applying waste-derived fertilizers have not been reported or observed. This is likely due to environmental concentrations typically being lower than those used in lab-based studies, the positive attributes of the amendments to the plants, and their ability to compensate for chemical-induced stress.

Conclusions and Data Gaps

The PFAS list previously considered to be of interest in soil-plant transfer studies has expanded from select PFAAs (mainly PFOS, PFOA, PFBA, and PFBS) to include PFAS precursors, additional PFAAs, and additional PFAS classes (FASAs, Cl-PFAESs, FASAAs, diPAPs, FTSAs, and FTCAs). Of the PFAS discussed, side-chain fluorinated polymer surfactants, diPAPs, FASAAs, and FTSAs, were identified in waste-derived fertilizers or fields treated with waste-derived fertilizers. Cl-PFAESs should also be considered, especially in China [12, 77]. Future field studies on plant accumulation would benefit from including either nontarget PFAS screening and/or utilizing non-specific tests to better evaluate the level of precursors present that may serve as a PFAA reservoir. Degradation rates and pathways (intermediates on the way to PFAAs) in agriculturally relevant soils and conditions are lacking for many precursors and those for recently identified are completely unknown [30, 33•]. Such studies are needed to elucidate the true potential for these precursors to contribute to PFAS intermediates and PFAAs becoming available in the root zone for uptake during the life of the plant. Field studies should also expand upon the number of PFAS quantified as increasingly more standards are becoming available. Future studies on PFAS in agricultural soils in both greenhouse and field studies should include sufficient details on soil and soil amendment properties that can influence PFAS mobility, and thus plant availability [60].

Land application of PFAS-containing media results in plant uptake of short-chain PFAS into plant components that are consumed by humans, utilized as fodder, or land-applied. Long-chain compounds typically sorb to or are taken up into plant roots and largely remain in the roots while short-chain compounds have a higher propensity to translocate into plant shoots. Uptake varied between species and within species and was associated with different plant properties including root lipids and proteins. However, more research is needed to make further inferences on the effects of plant characteristics on uptake. Uptake was shown to be an active carrier protein-mediated process in wheat, which contrasts with frequently cited passive transport processes that are constrained by the Casparian strip. Plant uptake depends on how long PFAS reside in the root zone and on PFAS concentrations. Therefore, the use of high concentrations and growing conditions that minimize leaching could explain why plants grown in pot studies generally have higher concentrations of short-chain PFAS than have been observed in field studies. However, when plants are grown in fields close to fluorochemical manufacturing plants, higher concentrations than predicted from PFAS concentrations in soils may be observed due to atmospheric deposition or irrigation with PFAS-contaminated water. Likewise, comparisons made between hydroponic and soil-based studies must take into consideration the impacts of soil-based sorption, air–water interface sorption variability, porewater available compounds in soil, and morphological growth differences (root structure and surface area). Lastly, in some cases, plant enzymes were found to enhance degradation rates of precursors and increase the yields of the more bioavailable PFAAs.

Knowledge on mechanisms of soil–plant transfer, phytotoxicity, and PFAS metabolism in plants is growing and can inform future decision-making regarding cultivation on PFAS-laden soils. Similar to how lower PFAS levels are found in agricultural fields than pot studies, phytotoxic effects were observed at exposure concentrations that are generally considerably much higher than those observed in field studies. Risk of PFAS exposure from plant uptake is multifaceted [38] and encompasses not only plants that are directly consumed, but also through the food web (e.g., bioaccumulation in livestock feeding on PFAS contaminated water, forage, and feed) [117]. Field studies that demonstrate plant uptake, fate of PFAS, and risks associated with land-applied media containing PFAS are needed to inform farmers, landowners, and policymakers on how farming practices will impact the food supply chain.

Future studies should aim to:

- Investigate paper mill waste, industrial byproducts, recycled water, and pesticides as potential sources of PFAS in agricultural systems and their impact on source water in agricultural operations
- Conduct additional field studies, particularly those involving land application of typical waste-derived fertilizers or treated effluent
- Include a larger suite of PFAS for quantification consistent with current knowledge as well as analytical approaches that identify allow insight into additional PFAS including precursors that may serve as a long-term release reservoir of more mobile PFAS
- Investigate soil–plant transfer of replacements compounds, e.g., GenX, ADONA, and others as they become known
- Include more realistic PFAS concentrations in studies designed to improve our understanding of plant-specific uptake mechanisms and plant responses to PFAS exposure
- Include studies that improve our ability to quantify the role of plant enzymes on enhanced precursor degradation in the rhizosphere and within the plant

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Compliance with Ethical Standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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- •• Of major importance

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Critical Review

Per- and Polyfluoroalkyl Substance Toxicity and Human Health Review: Current State of Knowledge and Strategies for Informing Future Research

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Abstract: Reports of environmental and human health impacts of per- and polyfluoroalkyl substances (PFAS) have greatly increased in the peer-reviewed literature. The goals of the present review are to assess the state of the science regarding toxicological effects of PFAS and to develop strategies for advancing knowledge on the health effects of this large family of chemicals. Currently, much of the toxicity data available for PFAS are for a handful of chemicals, primarily legacy PFAS such as perfluorooctanoic acid and perfluorooctane sulfonate. Epidemiological studies have revealed associations between exposure to specific PFAS and a variety of health effects, including altered immune and thyroid function, liver disease, lipid and insulin dysregulation, kidney disease, adverse reproductive and developmental outcomes, and cancer. Concordance with experimental animal data exists for many of these effects. However, information on modes of action and adverse outcome pathways must be expanded, and profound differences in PFAS toxicokinetic properties must be considered in understanding differences in responses between the sexes and among species and life stages. With many health effects noted for a relatively few example compounds and hundreds of other PFAS in commerce lacking toxicity data, more contemporary and high-throughput approaches such as read-across, molecular dynamics, and protein modeling are proposed to accelerate the development of toxicity information on emerging and legacy PFAS, individually and as mixtures. In addition, an appropriate degree of precaution, given what is already known from the PFAS examples noted, may be needed to protect human health. *Environ Toxicol Chem* 2021;40:606–630. © 2020 SETAC

Keywords: Per- and polyfluoroalkyl substances; Perfluorooctane sulfonate; Perfluorooctanoic acid; Persistent compounds; Contaminants of emerging concern

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are ubiquitous in environmental media because of their prolific use in a variety of industrial and consumer products and processes (Jian et al. 2018; Sunderland et al. 2019). Widespread human exposure to PFAS in water, food, and air coupled with the lengthy environmental persistence and biological half-lives of some PFAS have led to measurable PFAS in the blood of nearly the entire population in developed countries, with health effects reported globally (Kato et al. 2011; Khalil et al. 2016; Stubleski et al. 2016; Jian et al. 2018). Information needed to evaluate the potential risk of harm from PFAS includes the types of adverse health effects that might occur at environmentally relevant exposures, especially in sensitive life stages. Information is also needed regarding the mode(s) of action for

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PFAS toxicity, PFAS toxicokinetics in both humans and laboratory animal models, and dose–response relationships. Risk estimates can be used to inform public health exposure limits that will determine the need for exposure mitigation and environmental cleanup.

There are several challenges in obtaining the information needed to assess human health risk from the large number of PFAS with a wide range of structures and chemical properties (Buck et al. 2011; Wang Z et al. 2017; Organisation for Economic Co-operation Development 2018). Data on the identity, composition, and quantity of PFAS used in products and processes are often treated as confidential business information, hampering efforts to estimate exposure sources and routes. The Organisation for Economic Co-operation and Development's (OECD's) chemical inventory reports over 4000 substances that contain at least one perfluoroalkyl (–CnF2n–) moiety (Organisation for Economic Co-operation Development 2018), and the US Environmental Protection Agency (USEPA) has a curated list of over 8000 PFAS included, based on structure (US Environmental Protection Agency 2018) from the CompTox Chemicals Dashboard (Williams et al. 2017). The USEPA estimates that more than 600 PFAS are currently in commercial use (US Environmental Protection Agency 2019). Experimental studies of PFAS have been limited by funding and the availability of analytical standards, confounded by the prevalence of background contamination in laboratory materials, and challenged by physicochemical properties such as high surface activity that can interfere with and complicate measurements. Consequently, sufficient information to conduct quantitative risk assessment is currently available for only a relative few PFAS (Post 2020). Further, although typical human exposures involve various combinations of PFAS (Centers for Disease Control and Prevention 2017), only a few efforts address interactions of PFAS mixtures; and a well-founded, scientific basis on which to evaluate their combined toxic potential does not yet exist (Carr et al. 2013; Wolf et al. 2014; Zhou et al. 2017; Hoover et al. 2019; US Environmental Protection Agency 2020).

The Society of Environmental Toxicology and Chemistry (SETAC) North America held the focused topic meeting and workshop "Environmental Risk Assessment of PFAS" on 12 to 15 August 2019, covering a wide range of topics related to the characterization of health risks posed by PFAS. The overarching purpose of the meeting was to begin a scientific discussion on how best to approach studying, grouping, and regulating the large number of PFAS to which people and other species are potentially exposed (for charge questions and other details, see Johnson et al. 2020). We refer to these PFAS as "legacy" (those perfluoroalkyl acids for which there are accumulating health data but that may be phased out or decreased in use) and "emerging" (those which are being used as replacements, often with minimal health effects data). The objectives of the Human Health Toxicity section were to provide an assessment of the state of the science in understanding toxicological effects of PFAS and to explore and discuss strategies for advancing knowledge on the toxicity of individual and groups of PFAS.

CURRENT KNOWLEDGE OF PFAS TOXICITY IN HUMANS

Like other chemicals, PFAS are potentially capable of producing a wide range of adverse health effects depending on the circumstances of exposure (magnitude, duration, and route of exposures, etc.) and factors associated with the individuals exposed (e.g., age, sex, ethnicity, health status, and genetic predisposition). Aspects to consider when establishing the health effects of greatest concern are 1) effects for which evidence is the strongest (strength of evidence can come from consistency of effect across studies, strength of effect associations in epidemiological studies, and species concordance, as examples), and 2) effects for which potential impact is greatest (factors contributing to impact can include severity of effect, functional impairment, persistence, and specific age groups that are susceptible, as examples). Brief summaries of candidate PFAS health effects from human and experimental reports are provided in this section (Figure 1).

Immune function

Epidemiological studies have explored relationships between PFAS exposure and laboratory biomarkers of immunomodulation, such as vaccine responses. A doubling of perfluorooctane sulfonate (PFOS) in maternal serum was associated with a 39% ($p < 0.001$) reduction in diphtheria antibody concentration in children (age 5 yr), with increased odds of falling below clinically protective values against diphtheria and tetanus at age 7 yr. The authors noted that a "2-fold greater concentration of major PFCs [perfluorinated compounds] in child serum was associated with a difference of −49% (95% CI, −67% to −23%) in the overall antibody concentration" (Grandjean et al. 2012). Decreased immunological response persisted at age 13 yr (Grandjean et al. 2017). Adverse associations were also noted for responses to rubella, mumps, and *Hemophilus* influenza vaccinations in children and to vaccinations in adults (Granum et al. 2013; Looker et al. 2014; Stein et al. 2016; Abraham et al. 2020). In a single study, modest down-regulation of C-reactive protein response, a marker of human systemic inflammation, was also reported to be associated with perfluorooctanoic acid (PFOA) blood levels (Genser et al. 2015).

Disease outcomes linked with immunosuppression such as clinician-recorded diagnoses of childhood infections have also been associated with prenatal exposures to PFOS and perfluorohexane sulfonate (PFHxS) (Goudarzi et al. 2017). A pregnancy cohort study prospectively detected increased risk of airway and throat infections and diarrhea in children through age 10 yr, correlated with cord-blood PFAS measurements (Impinen et al. 2018, 2019). A recent review concluded that exposure to PFAS in infancy and childhood resulted in an immunosuppressive effect characterized by an increased incidence of atopic dermatitis and lower respiratory tract infections (Kvalem et al. 2020). Some of the immunological effects were sex-specific, but the authors cautioned that there were inconsistencies across studies (Kvalem et al. 2020).

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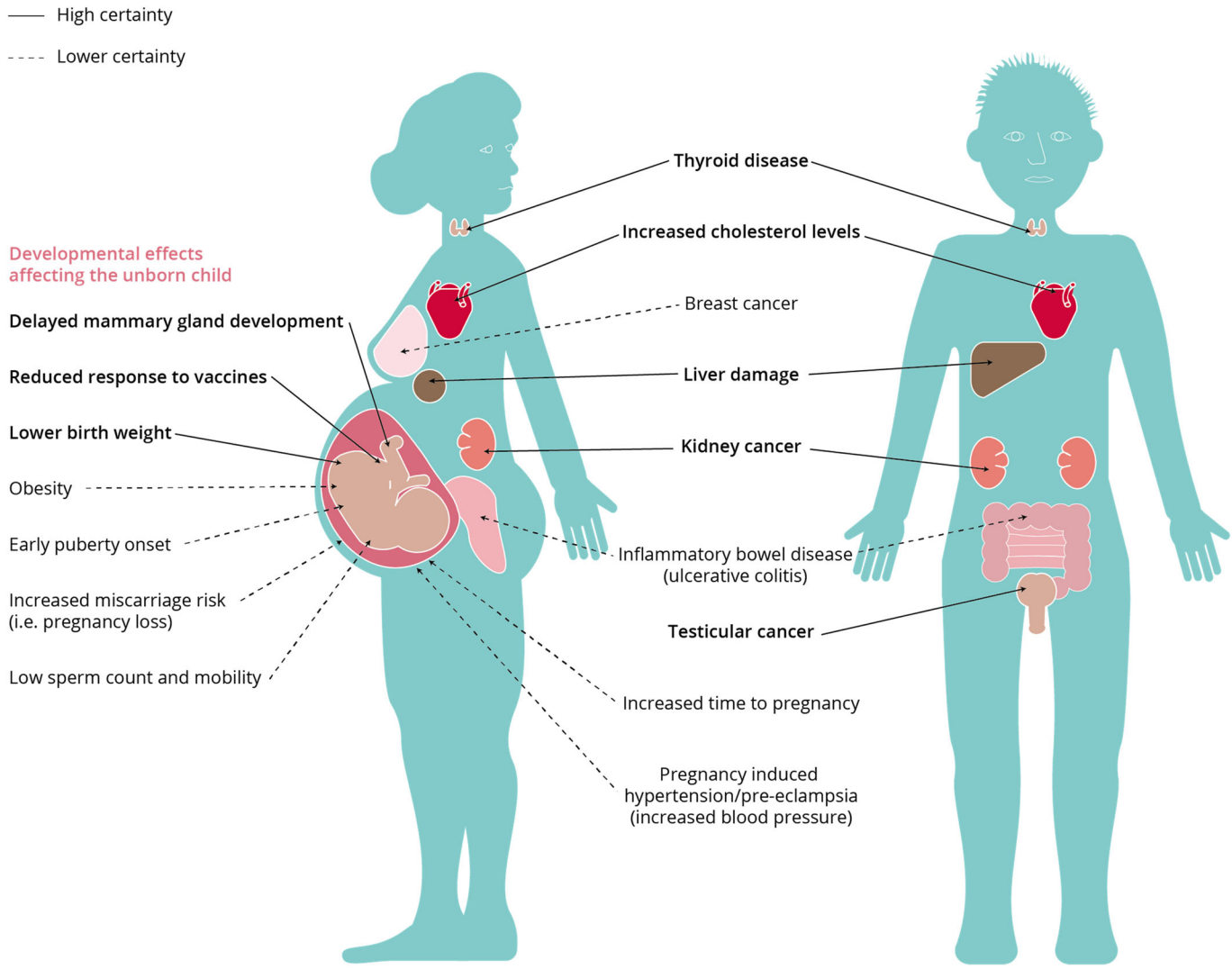


FIGURE 1: Effects of per- and polyfluoroalkyl substances on human health. Used with permission from European Environment Agency (2019). Original sources for this figure: National Toxicology Program (2016), C8 Science Panel (2012), IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (2017), Barry et al. (2013), Fenton et al. (2009), and White et al. (2011b).

Overall, available data provide strong evidence that PFAS exposure can suppress the human immune response.

Population studies of immune hyperreactive diseases have resulted in mixed findings. Studies on childhood allergy and asthma outcomes have shown no association with PFAS (Impinen et al. 2018, 2019), whereas others have found substantial effects, including provocative evidence that subgroups of individuals not adequately immunized may be at an increased risk for disease a priori (Qin et al. 2017; Timmermann et al. 2017a). For example, a case–control study of Taiwanese children compared the first and fourth quartiles of serum measurements for 11 PFAS with asthma and other immune markers and reported confidence intervals well above 1.0 for PFOA and others (Qin et al. 2017). However, review articles concerning PFAS and childhood allergy and asthma offer nuanced, age- and sex-specific interpretations and advise against firm conclusions (Kvalem et al. 2020).

Chronic autoimmune outcomes, including thyroid disease (see section *Thyroid function*) and inflammatory bowel disease (IBD), have also been considered. A study in contaminated communities ($n = 32\,254$) detected an association between both prevalence and incidence of ulcerative colitis (UC) and PFOA exposure (linear trend $p = 0.0001$ [Steenland et al. 2013]). A worker study ($n = 3713$) found a higher prevalence ($p = 0.01$) and incidence ($p < 0.05$) of UC with increasing log PFOA serum concentrations (Steenland et al. 2015). A case–control study of children and young adults from a background exposure community in Atlanta, Georgia, USA, also found higher serum PFOA levels in patients with UC (Steenland et al. 2018b). In contrast to PFOA-related associations in US populations, a study of a contaminated community in Sweden ($n = 63\,074$) did not show a consistent association of IBD with any PFAS exposure (Xu et al. 2020b).

Recent, thorough reviews (National Toxicology Program 2016; DeWitt et al. 2019; Pachkowski et al. 2019) emphasize some key concepts: 1) there is concordance between animal studies and human epidemiological observations that PFAS modify the immune response, and 2) there are noted

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complexities in assuming dose–response continuums, including possible differences in life-stage vulnerability. Authors of these reviews note uncertainty about which outcome will be of most importance but agree that immunotoxicity should be included among sensitive human PFAS toxicity endpoints.

Thyroid function

The C8 Science Panelists concluded that there is a "probable link" of PFOA exposure to thyroid disease, with sex-specific outcomes in women (for hyperthyroid disease) versus men (hypothyroid disease) (C8 Science Panel 2012). Subsequent reviews drew attention to hypothyroid outcomes in women and children and to the possibility that populations with a priori circulating antithyroid peroxidase antibodies may be at additional risk (Coperchini et al. 2017). A broad childhood disease review noted "some evidence" that PFAS cause childhood hypothyroidism and characterized the number of studies as "limited" for childhood disease conclusions (Rappazzo et al. 2017). A meta-analysis of 12 child and adult studies that excluded populations with higher exposures noted that PFAS exposure is negatively associated with serum total thyroxine levels and that "PFAS could induce thyroid dysfunction and disease" (Lee and Choi 2017).

Human thyroid disease is mostly the result of an autoimmune response and is 5 to 10 times more prevalent in women than men (Tadic et al. 2018). Concerning PFAS and clinically diagnosed outcomes, women in the highest quartile of PFOA exposure (>5.7 ng/mL) reported clinical hypothyroid disease (odds ratio 2.2, 95% confidence interval [CI] 1.4–3.7) over 3 cycles of National Health and Nutrition Examination Survey (NHANES) data (1999–2006, $n = 3974$ adults), with similar findings in men (Melzer et al. 2010). The C8 Science Panel studies (median serum PFOA 26.1 ng/mL) found thyroid disease hazard ratios of 1.00, 1.24, 1.27, 1.36, and 1.37 across cumulative exposure quintiles in women (log-linear trend $p = 0.03$ [Winquist and Steenland 2014b]), with parallel hypothyroid findings in children aged 1 to 17 yr (Lopez-Espinosa et al. 2012). The Ronneby, Sweden, population experienced excess risk of thyroid disease in a discrete time period (1984–2005) among women (hazard ratio 1.29, 95% CI 1.05–1.57) that did not persist over time despite higher cumulative PFAS exposure (Andersson et al. 2019). The authors did not link exposure to hypothyroid outcome, noting a nonmonotonic dose–response relationship (Andersson et al. 2019).

Human population studies augment experimental data that PFAS interact with thyroid hormone binding proteins (Berg et al. 2015; Ren et al. 2016; Zhang J et al. 2016), one of several mechanisms by which PFAS can perturb feedback relationships between free thyroid hormone and the hypothalamic–pituitary–thyroid axis. Exposures to PFAS also interfere with thyroid peroxidase (TPO) enzyme activity in vitro (Song et al. 2012). Several PFAS studies have pursued this putative mechanism, finding that maternal and neonatal thyroid hormone outcomes were more readily detected in those with a priori abnormally high circulating anti-TPO antibodies (Webster et al. 2014, 2016). One case–control study investigated congenital hypothyroidism, a rare condition. Serum concentrations of PFOA (5.40 vs 2.12 ng/mL; $p < 0.01$), perfluorononanoic acid (PFNA; 1.93 vs 0.63 ng/mL; $p < 0.001$), perfluorodecanoic acid (PFDA; 0.52 vs 0.30 ng/mL; $p < 0.005$), and perfluoroundecanoic acid (0.98 vs 0.44 ng/mL; $p < 0.005$) were higher in the diagnosed newborns; and levels of several PFAS, including PFOA and PFHxS, were correlated with thyroid autoantibodies (Kim et al. 2016).

Thyroid disease is not the only concern. Clinicians are concerned about subclinically elevated thyroid-stimulating hormone (TSH) in early pregnancy because it may be associated with several possible adverse maternal and fetal outcomes (Forhead and Fowden 2014). This general concern has prompted numerous PFAS-exposure evaluations of corresponding TSH in maternal serum, cord blood, and newborns. A review of maternal and child biomarkers with PFAS exposure noted that higher TSH has been reported in 4 second-trimester studies (Ballesteros et al. 2017), but there are also conflicting findings. Studies measuring PFAS in the first trimester have also found associations between PFAS exposure and altered TSH levels in newborns, including nonmonotonic patterns of dose response that mirror the marked alterations of thyroid hormone levels during pregnancy (Inoue et al. 2019).

From the available studies, PFAS definitively alter human thyroid hormones and potentially contribute to thyroid autoimmunity but do not so far appear to be a cause of thyroid cancer (Barry et al. 2013; Vieira et al. 2013). Also, thyroid cancer is usually survived; thus, morbidity rather than mortality studies are useful.

Liver disease and cancer

The liver is a primary target organ for long-chain PFAS storage, and accompanying experimental evidence of toxicity includes hepatocyte fat infiltration, specific P450 (CYP) pathway induction, apoptosis, hepatocellular adenomas and carcinomas, and disrupted fatty acid trafficking that can be peroxisome proliferator–activated receptor alpha (PPARα)–dependent or –independent and present across species (Maestri et al. 2006; Cui et al. 2009; Wan et al. 2012; Huang et al. 2013; Perez et al. 2013; Filgo et al. 2015; Xu et al. 2016, 2020a; Yao et al. 2016; Zhang L et al. 2016b; Hui et al. 2017; Li et al. 2017a; Guillette et al. 2020; National Toxicology Program 2020a).

Population studies demonstrate significant associations of long-chain PFAS (>6 fluorinated carbons) exposure to higher liver enzymes, such as alanine aminotransferase in adults and adolescents (Sakr et al. 2007a; Gallo et al. 2012; Yamaguchi et al. 2013; Gleason et al. 2015; Attanasio 2019; Nian et al. 2019), including in longitudinal studies (Sakr et al. 2007b; Darrow et al. 2016). Following low-dose exposures, these associations may be more evident in obese participants (Lin et al. 2010; Gallo et al. 2012; Jain and Ducatman 2019e).

Based on experimental data (Martin et al. 2007; Wan et al. 2012; Wang et al. 2013; Das et al. 2017), nonalcoholic

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fatty liver disease (NAFLD) has been investigated as a clinical outcome of PFAS exposure mediating consistent population PFAS-altered liver enzyme findings. Studies with NAFLD cytokeratin C18 biomarkers have provided supportive evidence for PFAS inducing steatosis (Bassler et al. 2019). Metabolomic studies have been directed at potentially explanatory human glycerophosphocholine and fatty acid profiles (Kingsley et al. 2019; Salihovic et al. 2019; Wahlang et al. 2019). Processes which favor steatosis promote advanced liver disease including liver cancer in humans (Massoud and Charlton 2018; National Toxicology Program 2020a). Associations of PFAS with advanced human liver disease and liver cancer are technically hard to study for reasons including (and not limited to) lethality, selection of comparison populations, and alterations of excretion mechanics associated with disease states. In a clinic-based study, mostly obese (85%) children aged 7 to 19 yr with biopsy-proven NAFLD had more advanced disease associated with PFOS and PFHxS exposure as well as associations with lipid and amino acid pathways linked to NAFLD pathogenesis (Jin et al. 2020). However, an adult study reported that serum PFHxS was inversely associated with hepatic lobular inflammation in morbidly obese bariatric surgery patients (Rantakokko et al. 2015). A study of heavily exposed workers ($n = 462$, geometric mean serum PFOA of 4048 ng/mL) detected significantly increased incident mortality for cirrhosis (relative risk = 3.87, 95% CI 1.18–12.7) and liver cancer (relative risk = 6.69, 95% CI 1.71–26.2) compared to a regional population (Girardi and Merler 2019), whereas no PFAS association to cancer or advanced liver disease was reported in a 3M worker cohort or in the C8 Health study population (Lundin et al. 2009; Barry et al. 2013; Vieira et al. 2013).

Emerging animal toxicology and histology and human population data provide mechanistic clues that PFAS disrupt hepatic metabolism, leading to increased bile acid reuptake and lipid accumulation in liver (Salihovic et al. 2020; Schlezinger et al. 2020). A review of NAFLD and toxicant exposure concluded that PFAS are associated with early steatosis ("fatty liver"), the preclinical stage of NAFLD (Armstrong and Guo 2019).

Lipid and insulin dysregulation

Cross-sectional and longitudinal investigations indicate that PFAS increase serum total and low-density lipoprotein cholesterol in adults and children (Steenland et al. 2009; Frisbee et al. 2010; Nelson et al. 2010; Eriksen et al. 2013; Fisher et al. 2013; Fitz-Simon et al. 2013; Geiger et al. 2013; Fu et al. 2014; Starling et al. 2014; Winquist and Steenland 2014a; Skuladottir et al. 2015; Zeng et al. 2015; Koshy et al. 2017; Convertino et al. 2018; He et al. 2018; Seo et al. 2018; Dong et al. 2019; Lin et al. 2019; Li et al. 2020; Liu G et al. 2020), including clinically defined high cholesterol (Steenland et al. 2009; Winquist and Steenland 2014a; Lin et al. 2019). Studies of large populations, featuring wide exposure ranges, demonstrate that serum lipids rapidly increase beginning at background (1–10 ng/mL) serum concentration and then are followed by attenuating ("plateaued") cholesterol measurements as (log-transformed) exposures to long-chain PFAS increase (Steenland et al. 2009; Frisbee et al. 2010; Li et al. 2020). These findings suggest partially saturable mechanisms; thus, the cholesterol dose response at pharmacologic or acutely toxic doses should be viewed with caution; associations can be missed or may be misleading when an environmental range of exposure is absent. At background exposure levels, residual associations may be more detectable in obese participants (Timmermann et al. 2014; Jain and Ducatman 2019d), a finding congruent with experimental PFAS outcomes in rodents fed "Western" or high-fat diets (Tan et al. 2013; Quist et al. 2015; Rebholz et al. 2016). Human gene expression pathways provide support for an interaction of obesity and PFAS exposures and suggest possible sex differences (Fletcher et al. 2013). A pharmacokinetic model predicts that approximately half of the PFOS-exposed population would experience a >20% rise in serum cholesterol (Chou and Lin 2020). Risk-assessment implications for low-PFAS dose increases in cholesterol have been noted (New Jersey Drinking Water Quality Institute Health Effects Subcommittee 2017; Li et al. 2020), and a review of population and toxicity data concluded that dyslipidemia is the strongest metabolic outcome of PFAS exposure (Sunderland et al. 2019).

Human PFAS lipid findings may be related to experimental findings of induced adipogenesis, impaired bile acid metabolism/synthesis, strongly decreased CYP7A1 enzyme activity, altered fatty acid transport, and intracellular lipid accumulation with steatosis, including in PPAR-α-null or PPAR-α-humanized animals (Guruge et al. 2006; Lau et al. 2007; Bijland et al. 2011; Bjork et al. 2011; Wang et al. 2014; Filgo et al. 2015; Das et al. 2017; Salihovic et al. 2019; Zhang et al. 2019; Behr et al. 2020a; Liu S et al. 2020b; Schlezinger et al. 2020). Independent of PFAS exposure, similar alterations in metabolic pathways have been related to disrupted fatty acid beta-oxidation and increased free cholesterol in toxicology studies (Perla et al. 2017).

Cross-sectional studies of diabetes outcomes can be misleading for reasons discussed in the renal section (see section *Kidney disease, uric acid, and kidney cancer*). Emerging longitudinal and diabetes clinical trial data indicate that PFAS may increase human insulin resistance, associated with dysregulated lipogenesis activity (Alderete et al. 2019; Lin et al. 2019). Longitudinal studies of clinically diagnosed diabetes patients have sometimes associated PFAS exposures with diabetes (Sun et al. 2018) or with small changes in glycemic markers (Cardenas et al. 2017); however, diabetes associations to date are not consistent (Karnes et al. 2014; Cardenas et al. 2017; Donat-Vargas et al. 2019). Future studies should consider whether PFAS may instigate autoimmune diabetic outcomes in humans, as shown in experimental studies (Bodin et al. 2016). Experimental data reveal that PFAS activate G protein–coupled receptor 40, a free fatty acid–regulated membrane receptor on islet ß cells, stimulating insulin secretion (Qin et al. 2020; Zhang L et al. 2020).

Kidney disease, uric acid, and kidney cancer

Extended human half-lives of long-chain PFAS are attributed to active renal tubular reabsorption. Of concern, legacy PFAS

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such as PFOA and PFOS are concentrated in renal tissues, and histopathologic, molecular, oxidative stress, and epigenetic studies provide evidence of potential nephrotoxicity (Wen et al. 2016; Stanifer et al. 2018; Sakuma et al. 2019; Rashid et al. 2020). In addition, the strong influence of kidney reabsorption on the extended half-lives of long-chain PFAS is consistent with both human protein binding and experimental PFAS excretion data.

Human studies have associated legacy PFAS exposure to diminished glomerular filtration and/or defined chronic kidney disease in adults and children (Shankar et al. 2011; Watkins et al. 2013; Kataria et al. 2015; Blake et al. 2018). However, this outcome may be due to reverse causation (Watkins et al. 2013; Dhingra et al. 2017). Some reviews of the available epidemiologic and toxicologic evidence suggest causative links between PFAS and diminished kidney function and chronic kidney disease (Stanifer et al. 2018; Ferrari et al. 2019); these authors also note several knowledge gaps and uncertainty about which proposed mechanisms of action are most important. A propensity score approach to NHANES data (Jain and Ducatman 2019c; Zhao et al. 2020) and a study with repeated PFAS and health measures over an 18-yr period (Blake et al. 2018) recently concluded that PFAS exposure likely causes diminished renal glomerular filtration.

Uric acid, a biomarker of increased risk for renal disease (Obermayr et al. 2008), is also consistently associated with PFAS exposure in adults and children (Steenland et al. 2010; Geiger et al. 2013; Gleason et al. 2015; Kataria et al. 2015; Qin et al. 2016; Zeng et al. 2019), including a visible dose–response curve that begins at or near historic background levels in human populations (Steenland et al. 2010; Zeng et al. 2019). Serum PFAS concentrations exhibit an inverted U-shaped pattern related to glomerular filtration, initially exhibiting a modest accumulation as glomerular filtration begins to decrease and then decreasing in advancing renal disease, likely due to failure of normal strong reabsorption mechanisms in moderate to severe kidney disease (Jain and Ducatman 2019c). This finding is more dramatic across stages of glomerular filtration when there is also albuminuria (Jain and Ducatman 2019b). Studies suggest that the association of PFAS to uric acid is not due to reverse causation and is underestimated because the failing kidney excretes long-chain PFAS but retains uric acid. An implication is that population outcomes that occur in the presence of either albuminuria or moderate to severe renal disease such as hypertension (Jain 2020) increasing presence of and uric acid (a biomarker of renal disease; Jain and Ducatman 2019a; Zeng et al. 2019) can be underestimated in cross-sectional studies; in other words, the link between these health outcomes and PFAS exposure is obscured in these studies because of enhanced PFAS excretion patterns in the presence of either albuminuria or moderate to severe kidney disease. Furthermore, the strong influence of renal reabsorption on the long half-lives of long chain PFAS is consistent with both human protein binding of PFAS and experimental PFAS excretion rates in high-dose rodent studies (Cheng and Ng 2017).

Kidney cancer diagnoses have been increasing since 1975, a finding that is partially independent of improved detection, with 5-yr cancer-specific survival of approximately 80% (Gandaglia et al. 2014). The C8 Health studies noted longitudinal ($n = 32\,254$) increases of kidney cancer (hazard ratio = 1.10, 95% CI 0.98–1.24) and kidney cancer mortality (Steenland and Woskie 2012; Barry et al. 2013; Vieira et al. 2013). A review of 6 published studies found long-chain PFAS exposure associated with kidney cancer or kidney cancer mortality, with risks ranging from 1.07 to 12.8 (Stanifer et al. 2018). Subsequent preliminary data from the heavily exposed Veneto, Italy, population also suggest a significant increase in kidney cancer mortality with PFAS exposure (Mastrantonio et al. 2018). Evidence is accumulating for PFAS as a cause of chronic disease and kidney cancer. Study designs must consider the peculiar PFAS excretion mechanics involved in and associated with kidney disease.

Reproductive and developmental outcomes

Exposure to PFOA impairs human sperm motility and sperm penetration into viscous media (Sabovic et al. 2020; Yuan et al. 2020) and is longitudinally associated with lower sperm concentration and count and higher adjusted levels of luteinizing and follicle-stimulating hormones in young men (Joensen et al. 2009; Vested et al. 2013; Song et al. 2018). Serum concentrations of PFAS are also cross-sectionally associated with deleterious markers of semen quality (Louis et al. 2015; Pan et al. 2019).

Legacy and emerging PFAS have been found in follicular fluid (Kang et al. 2020). They appear to alter endometrial regulation such as progesterone activity in young women (Di Nisio et al. 2020b) and possibly menstrual cycle length (Lum et al. 2017). Associations with menarche and menopause may be substantially due to reverse causation because menstruation is a route by which women eliminate PFAS (Dhingra et al. 2017), partially explaining why men have higher PFAS levels than women in the same communities. Women on birth control and who do not menstruate or with poor cyclicity because of age, activity level, or disease may have elevated PFAS levels in comparison with menstruating women. Exposure to PFAS has been associated with endometriosis in the United States and in China (Louis et al. 2012; Campbell et al. 2016; Wang B et al. 2017a), but the specific PFAS associated with this effect vary among studies.

Time-to-pregnancy (fecundity) studies provide indirect evidence of changes in fertility. Methodologic considerations include maternal and paternal age, parity (which in turn affects serum PFAS), and health status. Among 1240 women in the Danish National Birth Cohort, PFOS exposure was associated with decreased fecundity (median serum PFOS 35.5 ng/mL; Fei et al. 2009). Reverse causation may explain this finding because it is duplicated in parous, but not among nonparous, women (Whitworth et al. 2012; Bach et al. 2015). Prospective odds of actual infertility in the Maternal–Infant Research on Environmental Chemicals cohort ($n = 1743$) at low-dose exposures were associated with PFOA (geometric mean 1.66 ng/mL; odds ratio = 1.31, 95% CI 1.11–1.53) and PFHxS

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(odds ratio = 1.27, 95% CI 1.09–1.48; Velez et al. 2015). The reported fertility rate improved following water filtration in a PFAS-contaminated community (incidence rate ratio 0.73, 95% CI 0.69–0.77 prior to filtration) along with measures of birth weight (Waterfield et al. 2020).

Per- and polyfluoroalkyl substances reliably move across the placenta and enter breast milk (Gyllenhammar et al. 2018; VanNoy et al. 2018); serum PFAS levels in young children generally exceed maternal serum concentrations (Fromme et al. 2010; Papadopoulou et al. 2016; Eryasa et al. 2019). Population studies provide evidence that breastfeeding duration and milk quantity are adversely affected by PFAS exposure (Romano et al. 2016; Timmermann et al. 2017b; Rosen et al. 2018).

A systematic review reported that PFOA exposure was associated with a small decrease in infant birth weight; the meta-analysis estimated that a 1-ng/mL increase in PFOA was associated with an approximately 19-g reduction (95% CI −29.8 to −7.9 g) in birth weight (Lam et al. 2014). The authors noted similarities in experimental studies (Johnson et al. 2014; Koustas et al. 2014) and concluded that there was "sufficient" human and corroborative toxicology evidence of a detrimental effect of PFOA on birth weight (Johnson et al. 2014; Koustas et al. 2014; Lam et al. 2014). However, another meta-subpopulation analysis, focused on early pregnancy or the time shortly before conception, detected only a small and nonsignificant association, which was less subject to bias (Steenland et al. 2018a). Different approaches to the possible confounding role of shifting glomerular filtration rates in pregnancy can affect interpretations; evidence suggests this consideration can, at most, only partially explain associations of PFAS exposure to decreased birth weight (Interstate Technology and Regulatory Council 2020; Wikstrom et al. 2020). A recent review of mostly prospective cohort studies ($n = 24$ studies) noted PFAS associated with altered fetal and postnatal growth measures, such as lower birth weight. Many ($n = 22$) of the relevant studies suggest developmental and childhood immunomodulatory effects, whereas 21 studies concerning neurodevelopment were inconclusive (Liew et al. 2018). The authors of the review noted methodologic challenges of developmental and newborn epidemiology, including consideration of critical exposure windows for developmental effects, the effects of breastfeeding and parity on maternal PFAS levels, and the variety of possible mechanistic explanations for growth outcomes, such as disruption of glucocorticoid and thyroid hormone metabolism in utero (Liew et al. 2018). Recent Faroe Island studies report that prenatal PFAS effects on thyroid hormone status do not support a causal relationship (Xiao et al. 2020).

Review articles suggest that prenatal exposure to PFOA may increase risk of subsequent childhood adiposity, noting that steroid hormones, retinoid X receptor, and other pathways may be contributing to this effect (Halldorsson et al. 2012; Hall and Greco 2019). Prospective evidence supports this relationship in adults with a high risk of diabetes (Cardenas et al. 2017). However, some well-performed community studies do not support this outcome in adults or children (Barry et al. 2014; Martinsson et al. 2020).

Based on several preliminary findings, supported by longitudinal follow-up studies (Stein et al. 2009; Savitz et al. 2012; Darrow et al. 2013; Avanasi et al. 2016a, 2016b), the C8 Science Panel concluded that PFOA is probably linked to pregnancy-induced hypertension or preeclampsia. Population-level evidence implicating additional PFAS having this effect has included studies with longitudinal designs (Huang et al. 2019; Wikstrom et al. 2019; Borghese et al. 2020). Experimental support includes PFAS effects on human trophoblast migration in vitro (Szilagyi et al. 2020) and recent evidence of PFOA and GenX (or hexafluoropropylene oxide dimer acid) effects on mouse placenta, as well as excessive gestational weight gain (Blake et al. 2020). However, a recent longitudinal study did not find an association of PFAS with pregnancy-associated hypertension (Huo et al. 2020).

The possibility that circulating PFAS may reduce bone mineral density has been investigated. Cross-sectional and practical trial associations have been found in adults (Lin et al. 2014; Hu et al. 2019; Di Nisio et al. 2020a), and there is emerging longitudinal evidence from a mother and child pair study indicating that children may also be affected (Cluett et al. 2019).

Testicular cancer diagnoses are increasing steadily, a trend unrelated to improved detection (Cheng et al. 2018; Park et al. 2018). Most patients diagnosed (>90%) will be cured and die of other causes; mortality studies therefore provide little help in understanding disease risk factors. The C8 Science Panel detected longitudinal evidence for increased testicular cancer risk (1.35, 95% CI 1.00–1.79) for cumulative PFOA exposure (Barry et al. 2013). There are ample supportive data of testicular damage following PFAS exposure, including strong evidence of endocrine disruption; but the cell-specific associations are different in humans (germ cell) than the outcomes in rodents (stromal).

Per- and polyfluoroalkyl substances have deleterious effects on conception, pregnancy, and infant development. The underlying birth weight data are mostly supportive, although the subsequent growth and adiposity literature is mixed. The most sensitive reproductive and developmental outcomes are a topic of ongoing discussion.

Outcomes replicated across populations, such as perfluorocarboxylate (PFCA) and perfluorosulfonate (PFSA) exposures associated with down-regulation of immune response; increases in cholesterol, liver enzymes, and uric acid; alterations in thyroid hormone binding proteins; growth deficits; and effects on breast milk and lactation, indicate priority areas for understanding mechanisms and health implications.

CURRENT KNOWLEDGE OF PFAS TOXICITY IN EXPERIMENTAL MODELS

Animal studies have focused most intensely on PFOA and PFOS, using laboratory rodents and, more recently, zebrafish as models. Perfluoroalkyl acids of varied carbon-chain lengths as well as a few replacement chemicals with ether linkages in the carbon backbone (such as GenX and 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid], or ADONA) have also

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been examined, with outcome profiles thus far generally consistent with legacy chemicals. The varying extent of responses is likely related to toxicokinetic disposition (excretion or half-life) and relative potency and affinity of the individual chemical for binding to receptor proteins. Some PFAS (i.e., PFHxS, PFOA, and PFNA) have longer half-lives in mice than rats and typically much longer half-lives in humans (Table 1). These differences in elimination kinetics complicate the cross-species evaluation of toxicity. In addition, some PFAS (such as PFOA and PFNA) exhibit a profound sex difference in the rate of chemical elimination and bioaccumulation in the rat: females eliminate them much faster than males (Table 1). Sex differences in half-lives, although important, are much smaller in humans and have a different explanation. The mouse also typically has more limited sex-based PFAS elimination differences, making this species more amenable for extrapolation to humans, especially for mechanistic and toxicity evaluations.

In general, human health effects associated with PFOA and PFOS exposure (described in section *Current Knowledge of PFAS Toxicity in Humans*) have also been reported in animal models: hepatic/lipid metabolic toxicity, developmental toxicity, immune suppression, tumor induction, endocrine disruption, and obesity. These findings are often derived from well-controlled laboratory experiments in more than one species using wide dose ranges that are often orders of magnitude higher than typical human exposure, to account for differences in half-life across species. Some of the phenotypic findings are supported by in vitro mechanistic investigation and/or molecular queries on target tissues. Our understanding of the toxicologic properties of PFAS other than PFOA and PFOS is notably less advanced and, in the case of emerging replacements and by-products, completely unexplored.

Hepatic and metabolic toxicity

In rodent studies, dose-dependent increases in liver weight, in hepatocellular hypertrophy associated with vacuole formation, and with or without increased peroxisome proliferation have been observed with a significant body burden of PFAS, especially for the most persistent and potent long-chain homologs. Hepatocyte proliferation, necrosis, and apoptosis are outcomes occurring at relatively low doses. This is also true for a new replacement chemical, GenX, which altered liver histopathology and function and increased apoptosis in mice and fish (Blake et al. 2020; Guillette et al. 2020). Correspondingly, transcriptional activation of mouse and, to a lesser extent, human PPARα-related genes in liver was detected in adult-exposed models; activation of other nuclear receptors such as PPARγ, constitutive androstane receptor (CAR), and pregnane X-receptor (PXR) has also been reported. These nuclear receptors, metabolic sensors that regulate lipid and glucose metabolism and transport and inflammation, tend to be more responsive in tissues of rodents than in humans (Wolf et al. 2012; Rosen et al. 2017). Recent work using developmental models reports that

TABLE 1: Per- and polyfluoroalkyl substances serum half-life estimates in rat, mouse, monkey, and humans

	PFBS (C4)		PFHxS (C6)		PFOS (C8)		PFBA (C4)		PFHxA (C6)		PFHpA (C7)		PFOA (C8)		PFNA (C9)		PFDA (C10)		F-53B		GenX	
	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M	F	M
Rat	0.6–4.0 h	2.1–4.5 h	1.8 d	6.8 d	62–71 d	38–41 d	1.0–1.8 h	6–9 h	0.4–0.6 h	1.0–1.7 h	1.2 h	2.4 h	2–4 h	4–6 d	1.4–6.4 d	31–55 d	59–75 d	40–80 d			8 h	3 h
Mouse	4.5 h	5.8 h	25–2 d	28–3 d	31–3 d	36–4 d	3 h	12 h	~1.2 h	~1.6 h			16 d	22 d	26–6 d	34–6 d					18 h	20 h
Cynomolgus Monkey	3.5 d	4.0 d	87 d	141 d	110 d	132 d	1.7 d		2.4 h	5.3 h			30 d	21 d								
Human	28 d		5.3–8.5 yr		3.4–5.0 yr		3 d		32 d		1.2–2.5 yr		2.1–3.8 yr		2.5–4.3 yr		15.3 yr					

GenX = hexafluoropropylene oxide dimer acid; PFBA = perfluorobutanoic acid; PFBS = perfluorobutanesulfonic acid; PFDA = perfluorodecanoic acid; PFHpA = perfluoroheptanoic acid; PFHxA = perfluorohexanoic acid; PFHxS = perfluorohexane sulfonate; PFNA = perfluorononanoic acid; PFOA = perfluorooctanoic acid; PFOS = perfluorooctane sulfonate.

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mitochondrial dysfunction is associated with hepatocellular hypertrophy in young adult mice (Quist et al., 2015) and that other fatty acid metabolism pathways are activated (Jones et al. 2003; Shabalina et al. 2016). Steatosis is also a common feature of PFAS chronic exposure in rodents. Exposure in rodent models typically decreases serum cholesterol, whereas elevations of circulating cholesterol levels have been reported in humans. The mode of action concerning serum cholesterol is debatable. For example, PFOA exposure increased liver weight, increased liver enzymes, and led to persistent histopathological changes (particularly damage to the bile duct) in livers of wild-type and PPARα-null rodent strains (reviewed in Division of Science and Research, New Jersey Department of Environmental Protection 2019). Many of these effects are reversible on cessation of PFAS exposure, and this observation has been interpreted by some as evidence of "adaptive" responses to exposure. However, this reversibility is irrelevant to ongoing environmental PFAS exposure (for instance, from drinking water) because exposure will persist until contamination is remediated. In summary, there is a strong confluence of animal toxicology and histology and human population data that PFAS disrupt hepatic metabolism and lead to lipid accumulation in liver, although the mechanism(s) is unclear. Effects on bile acid metabolism, mitochondrial perturbation, and cholestatic mechanisms deserve further investigation at human-relevant exposures.

Reproductive and developmental toxicity

Only a few reproductive toxicity studies of males and females are available, primarily focusing on long-chain PFAS. Profound developmental toxicity has been described following gestational and lactational exposure to PFOS, PFOA, and PFNA in mice (Thibodeaux et al. 2003; Lau et al. 2006; Das et al. 2015) and in mice and rats gestationally exposed to GenX (Conley et al. 2019; Blake et al. 2020). Neonatal morbidity and mortality were seen with exposure to high doses of legacy PFAS; growth deficits and developmental delays were noted in offspring exposed to lower doses. Evidence of lactation impairment was seen in mice at doses of 5 mg PFOA/kg body weight (White et al. 2007), leading to increased offspring mortality (Lau et al. 2006); recent studies have indicated a role of placental dysfunction in these adverse developmental outcomes (Blake et al. 2020). Deficits of mammary gland development were also observed in mice exposed to PFOA (doses of 1 mg/kg body wt and lower) during gestation, which persisted into adulthood, although these exposure levels did not alter body weight, lactational function, or neonatal growth of offspring (F1 or F2 mice; Macon et al. 2011; White et al. 2011b; Tucker et al. 2015). Systematic reviews support a relationship between in utero exposure to PFOA and PFOS and reduced fetal growth in animals and humans, and the relationship between PFOA and reduced fetal growth in mice was recently validated (Koustas et al. 2014; Blake et al. 2020). Also, PFAS are reported to have reproductive effects such as ovulation failure in mice (Zhang Y et al. 2020).

Immunotoxicity

A few long-chain PFAS (PFOS, PFOA, PFNA, and PFDA) have been shown to alter immune status in rodents and nonhuman primates. Effects are predominantly immunosuppressive and include reductions in thymus and spleen weights and associated immune cell populations, in numbers of circulating immune cells, in certain aspects of innate immunity (i.e., natural killer cell cytotoxicity), in infectious disease resistance, and in antibodies produced in response to an antigen (i.e., analogous to the vaccine response in humans). In their 2018 draft *Toxicological Profile for Perfluoroalkyls*, the US Agency for Toxic Substances and Disease Registry (ATSDR) noted changes to the aforementioned immune parameters observed in experimental rodents exposed to PFOA, PFOS, PFNA, PFHxS, PFDA, perfluorobutanesulfonic acid (PFBS), or perfluorobutanoic acid (PFBA; Agency for Toxic Substances and Disease Registry 2018). The US National Toxicology Program conducted a systematic review of the immunotoxicological literature for PFOA and PFOS and concluded that PFOA and PFOS were presumed to be immune hazards to humans based on a high level of evidence for suppression of antibody responses in experimental animals and a moderate level of evidence for suppression of antibody responses in humans (National Toxicology Program 2016). The ATSDR (Agency for Toxic Substances and Disease Registry 2018) also included a decreased antibody response to vaccines (PFOA, PFOS, PFHxS, and PFDA) and increased risk of asthma diagnosis (PFOA) among the list of adverse health effects in PFAS-exposed humans. Reduction in the antibody response to a vaccine, an adaptive immune function, is a well-accepted measure of immunotoxicity, is consistent with the mode of action for the effects of fatty acids on immune system function (Fritsche 2006), and is compelling evidence that the immune system is a sensitive target of PFAS.

Tumor induction

Per- and polyfluoroalkyl substances are not known to be directly mutagenic; PFOA, PFOS, and other tested PFAS show little or no evidence for induction of gene mutation, clastogenicity, or aneuploidy in vitro or in vivo by a direct mode of action (see EFSA Panel on Contaminants in the Food Chain [2020] for details). There is evidence that PFAS can induce DNA damage, such as strand breaks, and other genotoxic effects, secondary to oxidative stress (EFSA Panel on Contaminants in the Food Chain 2020). This occurs at concentrations or doses that are high relative to human environmental exposures to PFAS, and the mechanism is such that their dose–response will be sublinear. Hence, PFAS are unlikely to be of mutagenic concern in exposed populations.

In adult-exposed rodents and fish, PFOA and PFOS have been shown to induce tumors. Liver adenomas, pancreatic acinar cell tumors, and testicular Leydig cell adenomas have been detected in rats treated chronically with PFOA (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans 2017) as well as its replacement, GenX (Caverly Rae et al. 2015). Following

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gestational and chronic exposure to PFOA, 58% of male rats demonstrated pancreatic tumors at the lowest dose administered (National Toxicology Program 2020b). This finding has spurred Minnesota and California policymakers to consider cancer as an endpoint in risk assessment, whereas the European Food Safety Authority (EFSA Panel on Contaminants in the Food Chain 2020) has the opinion that there is not adequate evidence for a link between exposure to PFAS and cancer risk in humans. This "tumor triad" profile has been associated with the PPARα-mediated molecular signaling pathway in rats exposed to high doses of PFAS. Consequently, liver tumors involving this mode of action are not considered relevant to humans at equivalent PFAS exposures (Post et al. 2017). The human relevance of PPARα-mediated pancreatic tumors in rodents remains to be determined. Liver lesions evident in PPARα-null mice exposed to PFOA during pregnancy and lactation (Filgo et al. 2015) suggest a non-PPARα-mediated liver response. Induction of liver tumors mediated by estrogen receptor (ER) activation has also been reported in fish (Tilton et al. 2008), and several non-PPARα-mediated hypotheses, including increased reactive oxygen species formation, oxidative stress, and mitochondrial dysfunction; decreased tumor cell surveillance by the immune system; and diminished gap junction cellular communication, are documented (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans 2017; New Jersey Drinking Water Quality Institute Health Effects Subcommittee 2017).

Endocrine disruption

The primary evidence for the endocrine-disrupting potential of PFAS involves induction of hypothyroxinemia and reduction of serum testosterone in rats. An early review of PFAS endocrine-disrupting properties in humans concluded that the "thyroid may be one axis significantly affected by PFOA exposure while the animal toxicology literature is less certain due to technical issues" (White et al. 2011a).

The effects of PFAS on thyroid hormone status detected in animal studies differ from classical hypothyroidism, in that reduction of circulating total thyroxine is not accompanied by a compensatory increase of TSH. A possible mechanism for these effects may be related to the propensity of protein binding of legacy PFAS, which could lead to displaced total thyroxine binding to its carrier proteins (transthyretin and thyroxine-binding globulin). Human population studies augment animal data showing that PFAS interact with thyroid hormone binding proteins (Berg et al. 2015; Ren et al. 2016; Zhang J et al. 2016a), one of several mechanisms by which PFAS can perturb feedback relationships between free thyroid hormone available to cells (free total thyroxine) and the hypothalamic–pituitary axis. Some estrogenic effects of PFAS have also been illustrated by in vitro studies, although there is no evidence of direct transactivation of estrogen, androgen, or glucocorticoid receptors (Behr et al. 2018, 2020b).

The evidence for PFAS affecting ER signaling in humans and animals is mixed. Although studies have identified some PFAS as being without estrogenic activity (Behr et al. 2018; Borghoff et al. 2018; Gogola et al. 2019), others suggest an ability of PFAS to modulate or even activate ER-mediated effects (Benninghoff et al. 2010; Kjeldsen and Bonefeld-Jørgensen 2013; Wang et al. 2018; Bjerregaard-Olesen et al. 2019; Qiu et al. 2020), with some effects only observed in aquatic organisms (Wei et al. 2009; Chen et al. 2016, 2018). Microarray analyses of human primary hepatocytes confirmed that PFOA activated the ER pathway (Buhrke et al. 2015).

Neurotoxicity

Potential adverse effects of PFAS on the nervous system and functions have not been widely investigated. A few studies reported neurotoxicity of PFOS, PFHxS, and PFOA in cell culture systems (Slotkin et al. 2008), as well as altered behavioral responses (Goulding et al. 2017) and deficits in learning and memory ability in rodents (Viberg et al. 2013). In contrast, no significant developmental neurotoxic effects were seen from prenatal exposure to PFOS in USEPA guideline–based studies with rats (Butenhoff et al. 2009).

Obesity

Numerous cell-based assays in human and mouse preadipocytes and animal studies with and without high-fat diets have consistently shown that some PFAS have the potential to increase lipid production by adipocytes and fat pads (van Esterik et al. 2016). Exposure of pregnant mice to low doses of PFOA produced obesity in young adult female offspring (Hines et al. 2009; van Esterik et al. 2016), a finding that was recapitulated in Danish women exposed in utero to PFOA (Halldorsson et al. 2012). Both PFOA and GenX increased weight gain of pregnant mice (Blake et al. 2020), an effect also seen in women during pregnancy (Ashley-Martin et al. 2016), although discordant results have been reported in other studies (Barry et al. 2014; Ngo et al. 2014). These apparently disparate findings in experimental models may be associated with differences among mouse strains examined, exposure periods, statistical methodology, and/or the rodent diets used.

There are specific differences in human and rodent health outcomes that deserve further investigation: 1) cholesterol metabolism, 2) thyroid effects, 3) mode of action for liver effects (different or same), and 4) kidney transporter or other mode of action leading to large differences in half-life. However, species concordance in the 6 human health effects discussed in the present review supports a weight of evidence for these effect for the handful of extensively studied PFAS.

Human health advisory and guidance values for a few PFAS have been issued to date by the USEPA, the ATSDR, several individual state environmental agencies or health departments, as well as regulatory agencies in Canada and Europe that are largely (but not exclusively) based on toxicological findings in animal models. However, risk-assessment scientists have not reached consensus in selecting a singular apical endpoint as the basis for a point of departure for assessments. Three

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toxicological features of PFAS that have been commonly highlighted, based on their sensitivity (low dose effect), strength of evidence (robust corroborating studies with mechanistic support for human relevance), and corresponding findings noted in epidemiological investigation, are hepatotoxicity (and alterations in lipid metabolism), developmental toxicity, and immunotoxicity. It should be noted that apical endpoints that drive risk assessments often differ among individual PFAS, perhaps highlighting the complexity of these chemicals and the family of PFAS, in general.

IMPORTANCE OF TOXICOKINETICS IN UNDERSTANDING PFAS TOXICITY

Species and sex differences

Few of the substantial number of structurally diverse PFAS have been tested for toxicological effects. Some available toxicological information has come from studies in animals, where marked species and (in rat) sex differences in half-life for some PFAS (Table 1) have been observed and the relevance to humans is uncertain. These differences are due to toxicokinetic and toxicodynamic factors. There are also differences in mean PFAS serum levels between men and women in the same communities. Children may have elevated serum levels compared to parents, even with the same exposures (Emmett et al. 2006; Daly et al. 2018; Graber et al. 2019), for reasons relating to transplacental transfer, breastfeeding, and body mass (Emmett et al. 2006; Daly et al. 2018; Graber et al. 2019; Blake et al. 2020). Transplacental transfer of PFAS confers a substantial burden to the newborn infant. Because the infant has a smaller overall mass and blood volume, PFAS are concentrated, increasing PFAS per volume (Koponen et al. 2018). In addition, transfer of PFAS is common through lactation, and the longer a child breastfeeds, the higher the body burden (Gyllenhammar et al. 2018; VanNoy et al. 2018).

Effects of comorbidity on PFAS toxicokinetics

Factors affecting renal function can influence PFAS toxicokinetics. As discussed, opposing types of causation should be considered. Human toxicokinetics appear to vary bidirectionally with changing renal function, leading to nonmonotonic dose–response relationships and, depending on the study goal, possibly to errors in estimating disease associations. As progress is made in the field of PFAS toxicokinetics, new chemistries may have different clearance factors and nuances that vary by PFAS group or structures, and that will need to be investigated to accurately model half-lives in different exposure subgroups.

Sources of information on toxicokinetics in humans: strengths and limitations of studies

Some PFAS half-life data in humans were obtained from retired industry workers, particularly those who worked with PFOS, PFOA, and PFHxS (Olsen et al. 2007). Since then, these estimates have been modified slightly or confirmed with longitudinal data and modeling from contaminated communities once uncontaminated water options were provided (Bartell et al. 2010; Li et al. 2018). Other contemporary PFAS estimates are derived from biomonitoring studies of production workers, blood donors, study participants, and/or occupationally exposed cohorts (Olsen et al. 2009, 2017; Russell et al. 2013; Zhang et al. 2013). Some caution must be taken in using these data because variables affecting PFAS clearance may not be taken into consideration (age, sex, menstruation, disease, and medication status) and may contribute to confounding.

The challenge in determining a reliable human half-life in these types of studies is that exposure does not end with a clean water source, retirement, or a change of job and that continued exposures vary over potential depuration periods. Model components may also vary in subclasses. Children (small blood volumes and a large fraction of exposures comes from drinking), pregnant women (large increase in blood volume and water intake), parous women (transfer to fetus and breast milk), and athletes (water intake elevated) are examples of subpopulations with expected variation in half-life compared to adult men (Post et al. 2017). There will be more human estimates of PFAS forthcoming that involve variations in half-life (Post et al. 2017). Realistic computational modeling can help, so long as it clearly characterizes exposures and applicable populations. The continued goal should be to provide predictive values for those PFAS lacking actual measurements, based on chemical structures and trusted physiological parameters.

Physiologically based pharmacokinetic/toxicokinetic modeling in different-aged populations

In the blood and other tissues, PFAS toxicokinetics are influenced by their interactions with proteins (Andersen et al. 2006; Katakura et al. 2007; Nakagawa et al. 2008; Weaver et al. 2009; Figure 2). Certain toxicokinetic features are saturable, and thus dosing in toxicokinetic studies is of profound importance. Studies of renal reabsorption mechanisms in mammals show that reduced activity of transporters such as organic anion transporting polypeptide 1a1, through inactivation (e.g., genetic manipulation, castration, treatment with estrogen) or by saturation at increasing doses, leads to substantial reductions in half-lives of PFOA and PFOS (Andersen et al. 2006; Nakagawa et al. 2008; Weaver et al. 2009; Yang et al. 2009).

These protein-associated toxicokinetic processes were recently incorporated into a model for PFOA in the male Sprague-Dawley rat (Cheng and Ng 2017), which provides a useful platform to explore how changes in protein interactions might affect estimates of PFAS half-life (Figure 3). At high doses, it is typical to see clear biphasic behavior with rapid initial clearance, during which the serum half-life appears to be shorter especially at high enough doses that processes such as renal reabsorption are saturated, followed by a much longer tail

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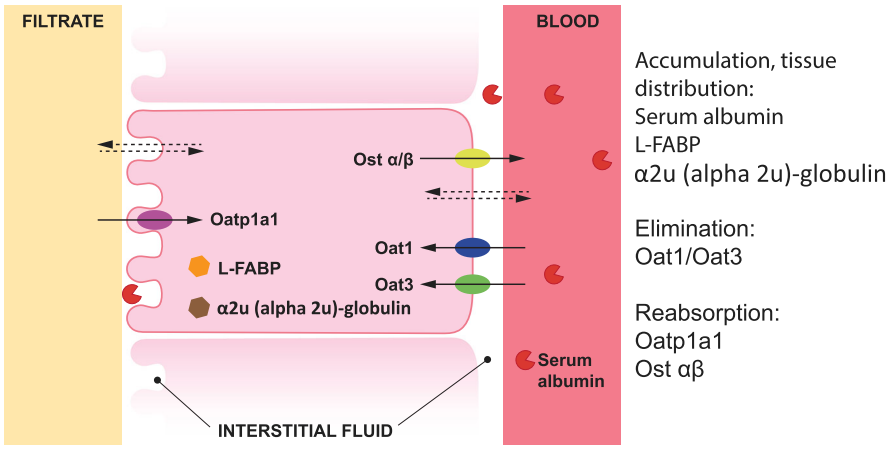


FIGURE 2: Example of proteins that are known to influence per- and polyfluoroalkyl substance toxicokinetics through binding (which affects tissue distribution and accumulation) and facilitation of membrane transport (which affects clearance and reabsorption). Illustrated for kidney and blood. L-FABP = liver fatty acid binding protein; Oat1 = organic anion transporting 1; Oatp1a1 = organic anion transporting polypeptide 1a1; Ost = organic solute transporter.

(Figure 3A). In a similar fashion, the magnitude of internal dose and rate of serum clearance can be profoundly influenced by proteins known to bind PFAS, such as serum albumin (Figure 3B). Increasing and decreasing the extent of reabsorption in the kidney increases and decreases the serum half-life, respectively (Figure 3C). Finally, the effect of saturating reabsorption is magnified when the half-life is longer because of increased serum binding (Figure 3D). In this case, taking an initial slope to calculate the serum half-life at high doses would lead to a profound underestimation.

Differences in protein expression, circulating levels, and even protein type across populations, sex, and species could lead to important species and sex differences in PFAS biological half-lives (Han et al. 2012); such differences should be

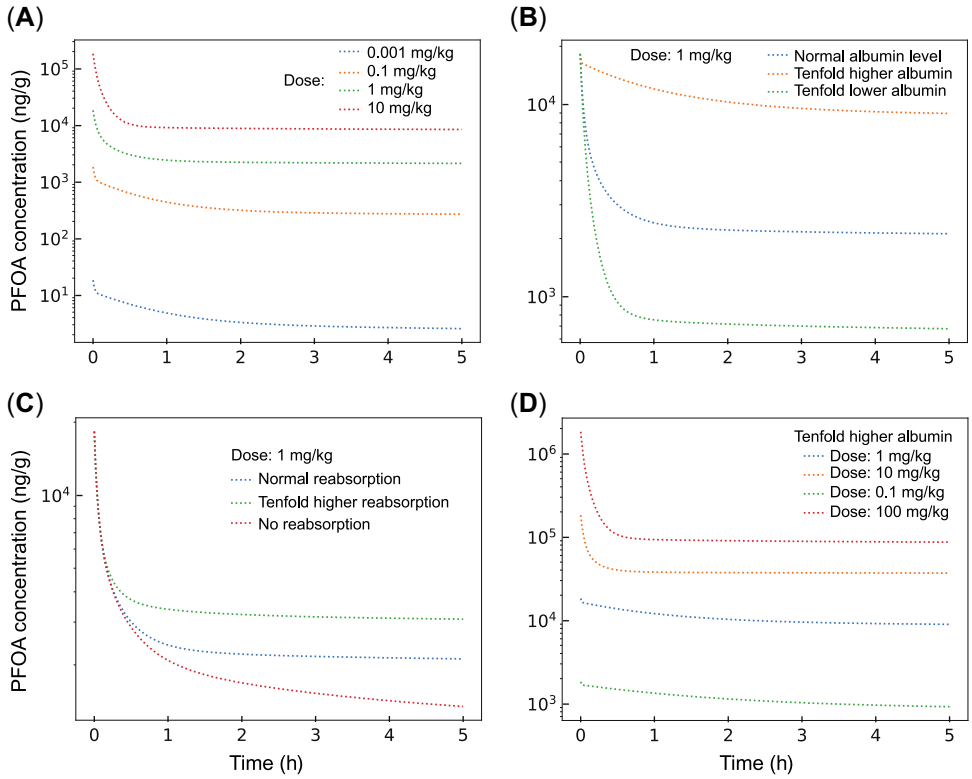


FIGURE 3: Simulations based on Cheng and Ng (2017), perfluorooctanoic acid (PFOA) toxicokinetic model for Sprague-Dawley rats. (**A**) Effect of dose on initial half-life. (**B**) Effect of higher and lower levels of serum albumin, which binds to PFOA, on serum clearance dynamics. (**C**) Effect of extent of reabsorption in kidney on serum half-life, based on organic anion transporting polypeptide 1a1 activity. (**D**) Effect of dose on elimination kinetics when half-life is longer because of higher albumin binding. Oat1 = organic anion transporting 1; Oat3 = organic anion transporting 3; Ost = organic solute transporter.

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investigated and taken into account in the extrapolation to human equivalent doses. Because expression of proteins may change at different life stages, clearance factors and toxicokinetics may also change.

Given the large number of species-, sex-, and age-specific differences that have been observed, coupled with the lack of data for many PFAS, the parameterization of complex physiologically based toxicokinetic models remains a persistent challenge. Therefore, lower-resolution models (e.g., one-compartment or few-compartment models) may be more appropriate for species and settings where insufficient data are available for reasonably accurate parameterization. Alternatively, in silico and in vitro methods are under development that could aid in parameterization in the absence of in vivo data, as discussed in the section *New approaches for developing PFAS toxicity information*.

SO MANY PFAS, SO LITTLE TIME: ACCELERATING THE PACE OF DISCOVERY

Importance of determining mode of action and adverse outcome pathways

Information on modes of action and/or adverse outcome pathways (AOPs) is invaluable in 1) establishing human relevance of experimental evidence, 2) assessing causality in epidemiological studies, 3) applying "read-across" to PFAS for which there is little toxicological information, 4) assessing risks from mixtures, 5) guiding development and interpretation of new approach methodologies, 6) informing the development of biomarkers in epidemiologic investigation, and 7) identifying potentially vulnerable subpopulations and life stage–specific effects (Meek et al. 2014; LaLone et al. 2017). Verified modes of action and AOPs can inform risk assessment based on intermediate effects and enable development of new methodology-based approaches to assess PFAS safety (Meek et al. 2014).

Postulated modes of action/AOPs for PFAS

Mechanistic studies have been performed on only a few PFAS. These have been shown to activate a range of putative molecular initiating targets, among which are the nuclear receptors PPARα, PPARγ, PPARβ/δ, CAR, PXR, liver X receptor α, and ERα (Bijland et al. 2011; Bjork et al. 2011; Rosen et al. 2017; Li et al. 2019). However, modes of action verified by agreed procedures (World Health Organization 2020) have been established for few reported effects of PFAS, and those that have been interrogated involve activation of PPARα and, at higher doses, CAR as molecular initiating events (Klaunig et al. 2012; Rosen et al. 2017). Several AOPs involving these molecular targets are in various stages of development (Organisation for Economic Co-operation Development 2020), but few have been endorsed by the OECD following its agreed procedures (Organisation for Economic Co-operation Development 2017). Demonstration of receptor activation alone is insufficient to establish involvement of a mode of action or AOP in an observed effect, for which an overall weight-of-evidence approach is necessary (World Health Organization 2020).

Andersen et al. (2007) provide a useful, albeit dated, review of possible PFAS modes of action. Established modes of action are restricted largely to the liver and include species-specific hepatic hyperplasia and liver tumors (Butenhoff et al. 2012; Elcombe et al. 2012; Corton et al. 2018). Available studies on PFBS, PFHxS, perfluorohexanoic acid, PFNA and PFDA suggest that they share molecular targets with similar consequences, albeit with differences in potency, in part due to differences in their excretion and protein-interaction kinetics (Zeilmaker et al. 2018). However, studies in vitro have established intrinsic differences in potency among PFAS analogues. Potency in activating PPARα showed some relationship with PFAS chain length (Wolf et al. 2008). A mode of action or AOP provides a causal chain of key events between chemical exposure and outcome. The established modes of action for PFOS and PFOA provide a causal explanation for development of liver tumors observed in rodents on exposure to these compounds, through activation of PPARα, and the possible relevance to humans. However, this does not mean that other effects of PFAS are due to activation of PPARα or that other pathways might not lead to liver tumors in humans, such as secondary to the primary effect of steatosis.

Until recently, there has been little study of modes of action/AOPs for effects of PFAS other than hepatic outcomes in rodents, particularly for critical effects, such as immunosuppression and developmental toxicity, and from PFAS other than PFOS and PFOA (EFSA Panel on Contaminants in the Food Chain 2020; Temkin et al. 2020). The ability of various PFAS to interact with and modify lipid metabolism is, however, an intriguing hypothesis (Xu et al. 1999; Jones et al. 2003; Andersen et al. 2007; Tan et al. 2013; Pouwer et al. 2019). Other putative molecular initiating/key events for PFAS, in addition to nuclear receptor activation, include gap junctional inhibition to disrupt cell–cell communication, mitochondrial dysfunction, interference of protein binding, partitioning into lipid bilayers, oxidative stress, altered calcium homeostasis, and inappropriate activation of molecular signals controlling cell functions. Many of these effects are consistent with a nonspecific action of PFAS on the cellular lipid membrane (Spector and Yorek 1985; Bourre et al. 1989; Dodes Traian et al. 2012; Casares et al. 2019). However, these alternative events lack robust evidence to support a specific pathophysiological role in the multifaceted effects of PFAS. A better characterization of the modes of action/AOPs for PFAS toxicities remains an important area of future investigation, necessary to improve our understanding of PFAS impacts on human health.

At present, there is insufficient evidence to determine which of, and to what extent, these molecular interactions play a pathophysiological role in observed adverse outcomes of PFAS (Michigan PFAS Science Advisory Panel 2018). Hence, there is a need to integrate such mechanistic information into a weight-of-evidence framework, first by establishing the mode of action or AOP linking a proposed chain of key events to an adverse outcome and then by demonstrating that at human exposure levels of PFAS the established AOP or mode of action is causal in the adverse outcome observed. The substantial advantage

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offered by such an approach is the ability to read across from representative members of appropriate PFAS groupings, based on quantitative information from new approach methodologies and exposure estimates. Hence, better characterization of the modes of action/AOPs for PFAS toxicities remains a critical area of future investigation and will allow us to understand which adversely PFAS-modified pathways must be interrogated prior to new chemicals joining this class. Predicting PFAS activity in the body should be the goal prior to approving novel PFAS for use.

New approaches for developing PFAS toxicity information

When it comes to determining which PFAS should be prioritized for further testing, there are too many chemicals, even in one subclass, for traditional approaches. Numerous creative and high-throughput methodologies are being developed and tested to provide valuable data on PFAS with no toxicity data.

Collaborative approaches. Problem formulation and approach must be guided by available equipment, funds, and technical staff, and important principles: 1) What biological activity and toxicology information can be generated in a *responsive time frame*? 2) Can this information be used to make public health decisions? 3) What are appropriate tools to bring to this problem (platforms, species/sex of cells used, metabolic competency of the model system, and data analysis)? 4) How do we organize, and what are the best mechanisms to report useful biological activity/toxicological information?

Developing "how" to evaluate potential health effects of new PFAS requires some thought to PFAS heterogeneity. Although subclass names have been suggested by several investigators (Buck et al. 2011; Wang Z et al. 2017; Sha et al. 2019), there is still disagreement on those groupings. In addition, half-lives and biological persistence are not predictable based on structure, and exposure routes may be complex. Given that traditional approaches to generate toxicity information are resource-intensive, new approach methodologies, which may include in vitro high-throughput toxicity screening and toxicokinetic testing, will be needed to inform further (in vivo) testing of PFAS.

One example of how agencies/institutes are collaborating to prioritize a list of PFAS needing further study is the REACT Program (Responsive Evaluation and Assessment of Chemical Toxicity). Scientists from the USEPA and the National Institute of Environmental Health Sciences (NIEHS) National Toxicology Program have joined forces to determine if read-across approaches would work. Essentially, they will use existing data for a data-rich substance (the source, e.g., PFOA or PFOS) as an anchor for a data-poor substance (the target, a novel PFAS), which is considered similar enough to the source substance to use the same data as a basis for the safety assessment. For example, the US National Toxicology Program 28-d PFAS or chronic PFOA data set (National Toxicology Program 2020c) could be used as an anchor. The goal is to group PFAS by biological activities and then use in vitro to in vivo extrapolation data and models to estimate oral equivalent exposures for PFAS. For example, multiple biological endpoints (Table 2) were chosen to generate data on 150 PFAS (Patlewicz et al. 2019), representing several structural subclasses for use in read-across.

Selecting assays shown in Table 2 based on PFOA and PFOS health effects covers a broad range of biology. However, because of the structural diversity of PFAS, biological activity of subclasses of PFAS may be missed; but this can be addressed in 2 ways. First, using transcriptomics as a screen, similar and unique pathways altered by different PFAS can be identified. Second, structure–activity relationships may predict potentially missing biological activities. As an example, Leadscope model predictions conducted at the NIEHS predicted biology that was covered in assays already chosen for evaluation, which increased confidence in the approaches chosen. Because model predictions are only as robust as data sets from which they are generated, these outputs should be used to identify assays for screening efforts and not as synonymous with toxicities induced by PFAS. Ultimately, the REACT program aims to prioritize PFAS for additional targeted testing and follow-up with in vivo studies as needed.

Molecular dynamics and protein interactions. Advances in computational tools, many developed for drug discovery, allow environmental and public health researchers to better anticipate some impacts of emerging contaminants even in the absence of substantial experimental data (Rabinowitz et al. 2008). For example, molecular docking and molecular dynamics to predict strengths of interactions between biomolecules and

TABLE 2: Fit-for purpose assays proposed in the REACT program

Endpoint of interest	Assay proposed
High-throughput transcriptomics	Metabolically competent human liver cells/MCF-7 (Tempo-Seq®)
Hepatotoxicity	2D HepaRG® cells
Developmental toxicity	Zebrafish embryo assay
Developmental neurotoxicity	Multielectrode array in neonatal cortical cells and neurite outgrowth
Immunotoxicity	Cytokine alterations in human vascular endothelial cells (BioSeek®)
Hepatic clearance	Metabolic clearance in 50 donor-pooled hepatocyte suspensions
Plasma protein binding	Serum protein binding assay using human serum
Enterohepatic recirculation	Qualyst B-CLEAR® hepatocyte transporter assay
In vitro disposition	In vitro disposition in cell lines under study

REACT = Responsive Evaluation and Assessment of Chemical Toxicity.

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contaminants can be an in vitro screening tool for assessing legacy and emerging PFAS for bioaccumulation potential, to identify potential sites of toxic action (Salvalaglio et al. 2010; Ng and Hungerbuehler 2015; Cheng and Ng 2018; Li et al. 2019) and to gain insights into toxic mechanisms (Sheng et al. 2018). Relatively strong binding with particular proteins (e.g., serum albumin, liver fatty acid binding protein) has already proven useful in correlating PFAS structure with potential for bioaccumulation (Ng and Hungerbühler 2014; Cheng and Ng 2017). Tools including molecular docking and molecular dynamics can correlate relative binding affinities of emerging PFAS with these target proteins and subsequently compare with affinities of legacy chemicals with known bioaccumulation potentials, thus providing a first-tier rapid screening mechanism (Luebker et al. 2002; Cheng and Ng 2018).

The use of fluorinated substances in pharmaceutical products has led to an unexpected data source for discovery of structural features in PFAS associated with various types of bioactivity. These data were recently used to train machine learning models to predict potential bioactivity for thousands of untested PFAS (Cheng and Ng 2019). Classification approaches such as these serve as preliminary screening tools for identifying PFAS as a first step in a tiered assessment when detailed mechanistic information is not available.

Addressing mixtures. Based on their potential for complex exposure patterns, PFAS are a mixtures issue. Communities with water-monitoring programs reporting PFAS concentrations demonstrated that they are exposed to mixtures of PFAS. This mixture may be from one or more point sources releasing multiple PFAS and/or PFAS by-products into the air and water, such as a Chemours plant in North Carolina, and suggest that exposures may be substantial (McCord and Strynar 2019). However, numerous other PFAS sources are known to impact community exposure to PFAS mixtures, such as landfill leachate, biosolids recycling, and aqueous film–forming foam contamination of drinking water sources, among others (Sunderland et al. 2019; Solo-Gabriele et al. 2020). Aqueous film–forming foam and other mixtures evident in drinking water, food packaging, health and beauty products, and food-based sources are often poorly characterized (Sunderland et al. 2019; Susmann et al. 2019).

Discussions on whether PFAS may be addressed using a relative potency framework or toxic equivalency factor approach are ongoing. Substances could be grouped by bioaccumulation and persistence (toxicokinetics), function (biology), molecular initiating events, with potency factors derived from several assays, or subclass (structural similarity).

SPECIAL CONSIDERATIONS IN FUTURE STUDY DESIGNS

Future epidemiological studies

Future human studies need to characterize immune outcomes including (and not limited to) immune effects from exposure in early pregnancy and possible roles of PFAS in initiating allergic and autoimmune processes, conditions for which a dose response is hard to predict. Interactions of immune pathways with liver and lipid toxicity deserve additional consideration.

Liver and lipid studies have reasonably characterized associations between PFAS and effects and should now address why and what to do about it. Characterization of possible a priori susceptibility, such as in the obese, is important. Human and animal lipid data suggest that future experimental studies should focus on mitochondrial toxicity, alterations in bile acid metabolism, cholestasis, and resultant steatosis. These outcomes are already known to be associated with altered serum lipids, liver enzymes, and uric acid in the human population regardless of PFAS (Cohen and Fisher 2013; Sattar et al. 2014; Arguello et al. 2015; Jensen et al. 2018).

Studies of human kidney markers related to PFAS exposures illustrate the importance of understanding physiology to inform study design choices and reasonable interpretations. These substances have complex excretion mechanics that vary with dose, state of the healthy or progressively diseased kidney, as well as a potentially additional causative effect on kidney disease outcome(s). Appropriate definition of biological and mechanistic targets and more precise investigation of PFAS subclasses will better inform study designs and research questions. For example, consistent reports of disrupted cholesterol metabolism should prompt mechanistic studies evaluating effects on steroid hormones that may influence cancer, fecundity, lactation, and developmental signals seen in human population data. More attention could be given to effects of PFAS on the hypothalamic–pituitary–gonadal axis and then reconsidered based on life stages.

The history of long-chain PFAS studies indicates that collaborative team approaches featuring clinical, epidemiologic, computational modeling, and laboratory toxicological expertise are needed. Future population designs and more sensitive analytical methodologies should address replacement chemicals, typically found as mixtures; study designs must account for shorter PFAS half-lives and unpredictable PFAS detection in exposed individuals/communities. Innovative use of biomarkers in specifically designated risk subpopulations (obesity, immune) will likely be important.

Sex differences, nonmonotonic dose responses, sensitive subpopulations

Although serum-level differences exist between men and women similarly exposed to individual PFAS, sex-dependent differences in half-life have not been reported in human populations for short-chain (PFBS, PFBA) or long-chain perfluoroalkyl acids thus far (Li et al. 2017b). Perhaps the half-life differences between the sexes is similar to interindividual variability and cannot be detected above background, or studies deriving data sets used to model half-lives were not designed to detect sex differences (convenience sampling or workers were mostly male, etc.). However, sex-specific elimination half-lives are defined (Table 1) for some PFAS in rodent models.

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In addition, developmental exposure studies in experimental models have consistently shown effects at lower doses than adult-only exposures and should be given priority in testing replacement chemicals. In vitro and alternative models that capture developmental susceptibility are encouraged. In summary, care should be taken in testing replacement PFAS in rodent or alternative (cell-based or zebrafish, for example) models to consider 1) the possibilities of sex-based differences in elimination half-lives, 2) dose range used (to include human relevant exposures), 3) life stage represented in the model system, and 4) variability of the response to enable the use of data generated for risk assessment.

Future experimental model studies

Experimental rodent studies have been essential in confirming PFAS health effects (liver and thyroid disease, lipid homeostasis), even when effects were not identical to those in humans; in some cases, novel targets (mammary and immune changes) were identified in animals. Future animal, cell-based, and high-throughput toxicity screening should enhance transparency in reporting to include blinded dose allocation, reporting of all data, adherence to Animal Research Reporting In Vivo Experiments (ARRIVE) guidelines (Kilkenny et al. 2010), and dose ranges that approach human relevance (adjusted to reflect the differences in elimination between species and potentially chronic exposures) so that they suitably inform systematic reviews that may be used in chemical regulation.

Model selection for health effects evaluation is critical. An appropriate model should be sensitive, be susceptible to the outcome(s) of interest (obesity, immune), and produce outcomes that will inform human health effects. Alternative research models, such as transgenic mice, zebrafish, developmental models for most affected target tissues, and diet-challenged designs in susceptible rodent strains, will strengthen our knowledge of PFAS-related health effects. Validation of fish neurobehavior models to inform mammalian, including human, developmental responses is needed.

Finally, advanced human cell-based platforms—that have been validated for relevant outcomes in humans—will facilitate concurrent screening of larger numbers of PFAS, but bioavailability of PFAS in the culture system needs to be understood because binding to media proteins or labware, the instability of some PFAS in some vehicles, and altered metabolism may exist in some cases (Gaballah et al. 2020; Liberatore et al. 2020).

Future alternative approaches

One way to determine the toxicity of the large number of PFAS compounds currently used in commerce is to develop quantitative structure–activity relationships (QSAR). Such QSAR attempt to define relationships between a PFAS compound structure with a specific biological activity or response that identifies or is a biomarker for toxicity. Few data are available for receptor binding of PFAS, mainly limited to a few PFCAs and PFSAs; and even between carboxylates and sulfonates of similar chain length substantial differences have been observed (Cheng and Ng 2017, 2018). If there are substantial differences between perfluoroalkyl carboxylic and sulfonic acids, which differ only in their acid head group, construction of successful QSAR for the large and diverse class of all PFAS will be particularly challenging. Several QSAR may be developed, each predictive of toxicity of a distinct class or subclass of PFAS, based on a unique functional moiety or other feature. Although this brings additional challenges in finding sufficient data for QSAR training and validation, big data approaches, such as the recently developed machine learning models to predict PFAS bioactivity (Cheng and Ng 2019), show promise for advancing these computational approaches at the screening level.

For example, it may be determined by affinity for receptor-specific binding and nonspecific interactions with cellular membranes that the specific toxic effect exhibits a multiphasic dose response reflecting 2 potential modes of action. In addition, the critical effect may change with levels of PFAS exposure. Add to this that people are typically exposed to PFAS mixtures, each of which may have a different affinity for a binding site and ability to impact cellular membrane fluidity, and the potential to predict PFAS toxicity becomes extremely complicated. In the foreseeable future, we may be limited to assessing PFAS toxicity using high-throughput assays designed to inform regulators as to the relative toxicity of PFAS mixtures or compounds. Such approaches are suited to the use of artificial intelligence (i.e., machine learning approaches) that integrate data from multiple sources to identify bioaccumulation potential, relevant pathways triggered, protein binding affinities, and modes of action involved in the development of individual and mixture toxicity of PFAS.

The utility of any future approach to determining PFAS toxicity must consider tissue-specific modes of action. Such an approach may rely on molecular interactions with specific binding sites on enzymes/storage/transport proteins or the nonspecific ability to alter cell membrane fluidity by which membrane-bound protein activities are altered within a particular organ/system. Regardless of the mode of action, model, and/or simulation, the predictive result should be biologically plausible and represent dose–effect responses across species.

CONCLUSION

Future research on the health effects of replacement PFAS and mechanistic studies on legacy PFAS must apply "lessons learned" such as those highlighted in the present review. There are only a handful of PFAS with enough health effects data for use in decision-making, as evidenced by state-led standard setting. There are numerous health effects reported for those PFAS tested, which sets this family of chemicals apart from many others and elevates the need for precautionary action. With hundreds of PFAS lacking health effects data, translational research teams using innovative methodologies and carefully designed studies will be critical to our state of knowledge on

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PFAS-related health effects and our enhanced strategies for informing risk assessment of this large family of chemicals.

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Water Resources Research

RESEARCH ARTICLE
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Quantification of Emission Potential of Landfill Waste Bodies Using a Stochastic Leaching Framework

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Key Points:

- Landfill emission potential, the amount of mass that can leach from a waste body, can be quantified by modeling the water and mass balance
- Stochastic travel time based on life expectancy distributions allows for quantification of the emission potential of conservative species
- Emission is driven by net precipitation and long-term precipitation scenarios allow for estimation of future emission dynamics

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Sanitary engineered landfills require extensive aftercare to safeguard human health and the environment. This involves monitoring emissions like leachate and gas, maintaining cover layers, and managing leachate and gas collection systems. Researchers have explored methods to conclude or extend aftercare. Quantifying emission potential, a key concept integrating various processes influencing emissions, is essential for managing and predicting landfill impacts. In this study we developed a stochastic travel time model based on water life expectancies. The model is used to predict leachate production rates and leachate chloride concentrations from landfill waste bodies. Unknown parameters are quantified by matching model output to measured time series using Bayesian inference. Once parameter distributions have been obtained, we are able to describe the measured long-term leachate dynamics. By analyzing the parameters and evolution of model states, we obtain a deeper understanding of the water and mass balance of the waste bodies. We demonstrate that the model can be used to quantify the chloride emission potential and the estimated values of total chloride mass match data quantified by sampling from the waste body. The results confirm that emissions with leachate are dominated by preferential flow infiltrating from the cover layer. Similar results have been obtained by applying the model to datasets from four different waste bodies, demonstrating that the approach is generally applicable for conservative solutes. Understanding of the water balance of the landfill together with conservative solute leaching is a necessary first step for further evaluating emission of reactive species.

Plain Language Summary Landfills have historically been the primary waste disposal method in Europe, leading to numerous legacy sites requiring extensive aftercare to safeguard human health and the environment. Long-term aftercare of sanitary engineered landfills requires insight in the risk associated with possible emission of contaminants from the landfill waste body. In this research we developed an approach where data measured at the landfill sites are combined with a model in order to quantify the amount of mass that will emit from the waste body over a certain period of time. This is important information for landfill operators and responsible authorities in order to develop approaches for landfill aftercare. Especially because after-care is expected to last for a very long time (up to several centuries).

1. Introduction

Landfills have long been the primary method of waste disposal in Europe, resulting in a large number of legacy landfills that require aftercare to protect human health and the environment. Aftercare typically involves monitoring emissions such as leachate and gas, as well as maintaining the cover layer and collection systems. The European Landfill Directive (EC, 1999) mandates a minimum 30-year aftercare period, but regulatory authorities may choose to shorten or extend this period based on a range of factors. To aid in decision-making, several authors have reviewed different approaches to ending or prolonging landfill aftercare (Barlaz et al., 2002; Laner et al., 2011). Several authors (Butt et al., 2008; Laner et al., 2012) have advocated for using risk-based assessments to evaluate the potential for harm. By exploring these and other solutions, we can work toward reducing the environmental impact of legacy landfills while ensuring the continued protection of public health.

In many cases the aftercare of sanitary engineered landfills consists of post-closure monitoring of emissions (e.g., leachate and gas) and maintenance of the cover layer and leachate and collection systems. Laner et al. (2012) postulate that post-closure care can end once a landfill no longer poses a threat to human health and the environment. Quantitative predictions of future emissions are important in order to assess future threat. Barlaz et al. (2002) advocate the use of technical criteria based on measured time-series of leachate composition, and leachate and gas production rates. One such technical criterion is the presence of barrier systems which require

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maintenance during the aftercare period. Laner et al. (2011) address the importance of assessing the remaining substance release potentials. The assessment should be site specific and take into account the deposited waste and the relevant boundary conditions that influence the flow of water through the landfill including the performance of the barrier systems. They propose a continuous emission model assuming that the status quo persists (after installation of a cover layer) based on a first order decay rate as proposed by Belevi and baccini (1989). Although Laner et al. (2011) give suggestions how to quantify the remaining substance source term, no experimental data are provided.

A research program aiming to achieve a significant reduction in emissions from Municipal Solid Waste landfills is currently being carried out in the Netherlands (Kattenberg et al., 2013). More information on this program can be found at the website of the research program (Stichting Duurzaam Storten, 2022a, 2022b). In this program different approaches to stabilize waste bodies by irrigation, recirculation and discharge of leachate and aeration of the waste body are being tested. The approaches are tested at full-scale at three different landfills. In order to assess the success of the stabilization measures, site specific Environmental Protection Criteria have been derived (Brand et al., 2016; Dijkstra et al., 2018). These criteria are defined to be the maximum allowable concentration of contaminant in the drainage system below the waste body, which will not lead to a concentration in the groundwater 20 m downstream of the landfill which damages human health or the ecosystem. The underlying modeling approach assumes that source term for all compounds in the drainage system remain constant over the complete evaluation period of 500 years.

In all the papers cited above, there is a common agreement that it is important to have a quantitative understanding of the source term controlling emissions of the contaminants present in the waste body. In this paper we would like to propose some definitions in order to clarify different approaches to quantify the source term.

The total mass of different compounds can be measured in the laboratory from samples taken from the field using destructive analytical techniques. Because contaminants can be bound in solids, total mass can lead to a significant overestimation of leachable mass. Leachable mass can be quantified in the laboratory using different types of leaching methods (Kosson et al., 2002; van der Sloot et al., 2017). However, characterization of heterogeneous landfill waste bodies using sampling and laboratory analysis requires a large amount of samples because of the inherent uncertainty caused by spatial variability (Sormunen et al., 2008a, 2008b). In addition to the spatial variability it is also important to realize that waste bodies most likely contain zones or pockets which isolate volumes of waste from mobile water, such as waste stored in a closed plastic bag. The presence of dead zones implies that not all contamination present in the waste body will be released from the waste body. Consequently, laboratory techniques to assess the source term of contaminants may overestimate the amounts that can be released under field conditions.

In this paper we introduce the term emission potential in order to describe the amount of mass that can be released from the waste body. The emission potential is the result of all processes involved in causing emissions of compounds from waste bodies. It is related to the multi-physical coupling between fluid flow, solute transport, bio geochemical transformations, waste body settlements and many more. The emission potential is the source term in a modeling framework that is able to describe the leachate flux and leachate concentration as a function of time. For conservative solutes we hypothesize that the emission potential can be quantified by fitting models to measured time series. Finally, using these models allows us to quantify the emission from the waste body under different scenarios, for example, over a time period of 500 years. Understanding the water balance and mass balance behavior of conservative solutes is a necessary first step for evaluating the emissions of reactive compounds.

Fellner and Brunner (2010) give an overview of modeling approaches available in the literature for quantifying leachate production. They show that preferential flow is a dominant process in waste bodies and needs to be incorporated in models in order to describe landfill leachate production dynamics (Fellner & Brunner, 2010; Uguccioni & Zeiss, 1997). In order to describe the heterogeneous flow and transport through waste bodies, several Lagrangian based travel time models have been developed (Malmström et al., 2004; Rosqvist & Destouni, 2000; Zacharof & Butler, 2004a, 2004b). Lagrangian modeling of water flow and solute transport in catchment systems has seen significant progress since then (Benettin & Bertuzzo, 2018; Benettin et al., 2015; Benettin et al., 2015, 2015, 2017; Harman, 2015; Harman, 2015, 2015; Hrachowitz et al., 2016; Rinaldo et al., 2015). The advantage of these Lagrangian approaches is that is allows for describing water flow and solute transport in large scale systems where heterogeneity is captured through probability distributions.

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Given the large heterogeneity present in landfills we have developed a stochastic Lagrangian travel time modeling framework to simulate landfill water and mass balances in order to quantify the emission potential of waste bodies. The parameters in the model are calibrated using time series measurements of leachate volumes pumped from the drainage system and bi-weekly chemical analyses of chloride concentrations in pumped leachate. Measuring pumped leachate volumes and leachate quality is standard procedure for landfill operators in the Netherlands and as such obtaining these time series is much easier and cheaper than taking samples from the landfill for analysis in the laboratory. The source term in the model after calibration is considered to be the emission potential. Long-term extrapolations using the calibrated model provide insight how the emission potential impacts future leachate quality. The generic feasibility and applicability of the proposed concept for quantifying the water balance and the leaching of conservative solutes is demonstrated using data from four different waste bodies.

2. Theory and Methods

In order to develop the model equations we hypothesize that the chloride concentration in (pumped) leachate is mainly controlled by dilution of highly concentrated base flow from the waste body with infiltrating water originating from rainfall. We assume that the waste body is a causal system for leachate production and solute transport. This implies that the output of the system at any given time depends only on the input and the system's past behavior and consequently, the flow of water and transport of solutes through the waste body can be modeled using travel time probability distributions. In this paper we assume that the travel time probability density functions (pdf) are constant in time. The approach we follow is similar to the one described by Benettin et al. (2015).

If we follow a water parcel that enters the waste body at time t_{in} and exits the waste body at time t_{ex} then the total time in the waste body ($T_T = t_{ex} - t_{in}$) at any moment in time can be characterized by its age (or residence time) indicated as T_R and the time it will still remain in the waste body before it exits the waste body (its life expectancy) indicated as T_E. Residence time and life expectancy are related to the total travel time T_T by:

$$T_T = T_R + T_E. \tag{1}$$

Each day as the water parcel moves through the waste body, its residence time increases with 1 day and its life expectancy decreases with one day which can be written as:

$$\frac{dT_R}{dt} = 1, \quad \frac{dT_E}{dt} = -1. \tag{2}$$

Equation 2 can be seen as a celerity with unit value, where the sign determines which property is described.

2.1. Water Balance

The upper boundary of the landfill is its surface where water can enter as rainfall and leaves as evapotranspiration. The lower boundary consists of the drainage system where water is pumped out of the landfill as leachate. To simplify the problem we assume that we can model the landfill as a one-dimensional 2-layered column, where the first layer represents a cover layer and the second layer is the waste body.

The water storage in the landfill is defined as:

$$S_w = \frac{V_w}{A_{lf}} = S_{cl} + S_{wb},$$

in which V_w is the is the volume of water per unit area and A_{lf} is the surface area of the landfill and S_{cl} and S_{wb} are the water storage in the cover layer and waste body respectively.

2.1.1. Water Balance of the Cover Layer

The water balance of the cover layer links water entering the landfill as rain and leaving the landfill as evapotranspiration to the amount of water infiltrating in to the waste body:

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$$\frac{dS_{cl}(t)}{dt} = q_{rf}(t) - q_{ev}(t) - q_{\inf}(t), \tag{3}$$

where S_{cl} is the storage in the cover layer.

The infiltration flux is assumed to be a non-linear function of the storage in the cover layer.

$$q_{\inf} = -K_{cl}(S_{eff})^{b_{cl}} \tag{4}$$

where S_{eff} is the effective storage which ranges from zero to one and is defined as:

$$S_{eff} = \frac{S_{cl} - S_{cl_{\min}}}{S_{cl_{\max}} - S_{cl_{\min}}}$$

where K_{cl} is the hydraulic conductivity of the cover layer (m d^{-1}), $S_{cl_{\max}}$ is the maximum achievable storage in the cover layer, $S_{cl_{\min}}$ is the minimum storage in the cover layer above which water will still freely drain and b_{cl} is a dimensionless empirical parameter which is larger than 0. When b_{cl} is less than 1, drainage from the cover layer predominantly occurs at low effective storage values, whereas if it is larger than 1, drainage predominantly occurs at high effective storage values.

The actual evapo-transpiration is calculated from the potential evapotranspiration:

$$q_{ev} = E_{pot} \;\; C_f \;\; f_{red}, \tag{5}$$

where E_{pot} is the potential evaporation [m/day], C_f is an empirical crop factor which is assumed to be a landfill specific constant and f_{red} is a factor allowing evapo-transpiration to be reduced in order to prevent the storage in the cover layer to become negative.

This model assumes that flow is caused by gravity only, that is, gradients in the hydraulic head of the soil do not drive water flow. The magnitude of flow is strongly controlled by the storage in the cover layer.

2.1.2. Water Balance of the Waste Body

The water balance of the waste body is calculated as:

$$\frac{dS_{wb}(t)}{dt} = q_{\inf}(t) - q_{leach}(t), \tag{6}$$

where q_{leach} is the leachate flux from the waste body to the drainage system.

We can rewrite Equation 6 as a function of life expectancies using a probability distribution of life expectancies $p_{S_{wb}}(T_E, t)$ using:

$$\frac{dS_{wb}(T_E,t)}{dt} = \frac{\partial S_{wb}(T_E,t)}{\partial t} + \frac{dT_E}{dt}\frac{\partial S_{wb}(T_E,t)}{\partial T_E},$$

to get

$$\frac{dS_{wb}(T_E,t)}{dt} = q_{\inf}(t)p_{q_{\inf}}(T_E,t) - q_{leach}(t) \tag{7}$$

where

$$q_{leach}(t) = S_{wb}(0,t) \tag{8}$$

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which states that the leachate flux is equal to all the water present in the waste body with a life expectancy of 0 at time t. Please note that after we have solved for $S_{wb}(T_E,t)$ we can calculate $p_{S_{wb}}(T_E,t)$ with:

$$p_{S_{wb}}(T_E,t)=\frac{S_{wb}(T_E,t)}{S_{wb}(t)}.$$

In order to numerically solve Equation 7, we need to discretize along life expectancies (T_E). T_E can range from 0 to infinity. To simplify implementation we chose to discretize T_E in a discrete number of daily values from $T_{E,0}$ to $T_{E,n_{tt}}$. $S_{wb}(T_{E,i},t)$ represent water storage cells with a life expectancy $T_{E,i}$ at time t. $S_{wb}(T_{E,n_{tt}},t)$ represents a bulk cell containing all water with a life expectancy larger than n_{tt} days. All water with $T_E > T_{E,n_{tt}}$ is assumed to be added to the storage in the bulk of the waste body S_{bulk}:

$$S_{bulk}(t)=S_{wb}(T_E \geq T_{E,n_{tt}},t) \tag{9}$$

The consequence of this choice is that an additional water flux needs to be added to the model the rate of change in $S_{bulk}(t)$. We call this flow, base flow and assume that it is a function of S_{bulk}. The base flow (q_{bF}) controls the leachate flow from the landfill in prolonged drought periods, however, it cannot continue indefinitely because of the finite amount of water stored in the bulk of the waste body. To take this finite amount in to account, we apply a gamma distribution function in order to allow q_{bF} to reduce gradually after the bulk storage reaches a critical level:

$$q_{bF}(S_{bulk})=q_{bF_0}\frac{f_{bF}(S_{bulk})}{S_{bF}}, \tag{10}$$

where

$$f_{bF}(S_{bulk})=\frac{x^{\sigma_{bF}-1}e^{-(S_{bulk}-S_{bulk,\min})}}{\Gamma(\sigma_{bF})}$$

where $S_{bulk,\min}$ is the minimal storage in the bulk where the base flow drops to zero, S_{bf} (m) is a scaling factor for the bulk storage and σ_{bF} (m) determines the shape of the base flow function.

Including the base flow in Equation 7 leads to:

$$\frac{\mathrm{dS_{wb}(T_E,t)}}{\mathrm{d}t}=q_{\mathrm{inf}}(t)p_{q_{\mathrm{inf}}}(T_E,t)+q_{bF}(S_{bulk}(t))\,p_{q_{bF}}(T_E,t)-S_{wb}(0,t) \tag{11}$$

where we have two distinct sources for the water traveling through the waste body: (a) water infiltrating from the cover layer, q_{inf} and (b) the base flow released from the bulk of the waste, q_{bF}.

The probability distribution $p_{q_{\mathrm{inf}}}(T_E,t)$ describes the life expectancies along a large number of trajectories in the waste body along which water is moving. Following Rosqvist and Destouni (2000), we assume that the ensemble of the life expectancies of all particles infiltrating from the cover layer can be described with a bimodal log-normal probability density function. For this paper we assume that this bimodal probability distribution function is time invariant.

$$p_{q_{\mathrm{inf}}}(T_E)=\beta p_{q_{\mathrm{inf}},fast}(T_E)+(1-\beta)p_{q_{\mathrm{inf}},slow}(T_E) \tag{12}$$

$$p_{q_{\mathrm{inf}},i}(T_E)=\frac{1}{T_E\sigma_i\sqrt{2\pi}}\exp\left(\frac{-(\ln(T_E)-\ln(\tau_i))^2}{2\sigma_i^2}\right) \tag{13}$$

In these, $p_{q_{\mathrm{inf}},fast}(T_E)$ and $p_{q_{\mathrm{inf}},slow}(T_E)$ are log-normal probability distribution functions for fractions of water experiencing fast flow and slow flow respectively (indicated with index i in Equation 13) where β is the fraction of water following the fast flow probability distribution function.

The probability distribution function for the life expectancies of the base flow is assumed to be a time invariant gamma distribution, in which Γ is the gamma function and a_{bF} is a value between 0 and 1:

$$p_{bF}(T_E) = \frac{x^{a_{bF}-1}e^{-x}}{\Gamma(a_{bF})} \tag{14}$$

where x is a normalized life expectancy of the water released from the bulk waste defined as:

$$x = T_E/T_{E,\text{norm}} \tag{15}$$

As stated before, assumptions underlying this approach are that the flow in the waste body is considered to be a causal process and that both travel time distributions are assumed to be time invariant. This implies that the flow occurs along specific paths or streamlines and that the flow rates in these paths remain constant in time. Harman (2015) shows that it is relatively simple to relax the assumption of time independent pdfs, for example, by making T_E a function of the storage.

2.1.3. Water Balance of the Drainage Layer

In the landfills analyzed for this paper, leachate is actively pumped from the drainage system by an automatic system that maintains the water level between a minimum and a maximum value. As a consequence, water levels in the drainage system are nearly constant and we can assume that the flux from the drainage system is identical to the flux entering the drainage system:

$$q_{drain} = q_{leach} \tag{16}$$

2.2. Solute Mass Balance

In order to demonstrate the concept we chose to consider only conservative solutes for this paper. This implies that the mass flux is fully controlled by water flow. Because the probability distribution of life expectancies implicitly takes account of the dispersion that occurs as water flows through the system we neglect solute diffusion as a separate process because it is very slow. The solute flux can therefore be written as:

$$\boldsymbol{q}_M = \boldsymbol{q}_w\, c \tag{17}$$

The solute mass balance of the cover layer can be calculated as:

$$\frac{\mathrm{d}M_{cl}(t)}{\mathrm{d}t} = c_{rain}(t)q_{rf}(t) - c_{cl}(t)q_{\text{inf}}(t). \tag{18}$$

The solute mass balance can be defined with:

$$\frac{\mathrm{d}M_{wb}(T_E,t)}{\mathrm{d}t} = c_{\text{inf}}(t)q_{\text{inf}}(t)p_{q_{\text{inf}}}(T_E,t) + c_{bulk}(t)q_{bF}(S_{bulk}(t))\,p_{q_{bF}}(T_E,t) - M_{wb}(0,t) \tag{19}$$

where M_{cl} and M_{wb} are the total mass of conservative species present in the cover layer and waste body ($\mathrm{kg/m^2}$), respectively. As we only consider old landfills which no longer accept waste and we assume that the concentration of conservative solutes in rain in the Netherlands is much lower than those found in landfill leachate we take influx of solutes with rainfall to be zero. In the waste body each water parcel with a specific life expectancy is associated with a specific mass ($M_{wb}(T_E,t)$ similar to the storage in the waste body. The concentration of conservative species for the cover layer is:

$$c_{cl}(t) = \frac{M_{cl}(t)}{S_{cl}(t)},$$

and the concentrations of the water parcels in the waste body are:

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$$c_{wb}(T_E,t)=\frac{M_{wb}(T_E,t)}{S_{wb}(T_E,t)}.$$

2.3. Solution Algorithm for Cover Layer

Implementing the equations for the cover layer as a differential equation results in a model that requires quite a lot of time to solve. In order to have a fast model which allows for a large number of runs in a Monte Carlo simulation framework, we chose to simulate the flows for the cover layer with an algorithmic implementation based on the equations in paragraph 4.1.1. Rainfall data and potential evapotranspiration data are available as daily average fluxes. The implementation is shown in Algorithm 1 using a time step Δt of 1 day.

Algorithm 1. Implementation of the Water Balance Algorithm for the Cover Layer

1. Estimate infiltration flux with Equation 4 and estimate the new storage

$$S_{cl_{est_{n+1}}}=S_{cl_n}+\left(q_{rf_{n+1}}-q_{\inf_n}+q_{Ev_{n+1}}\right)\Delta t. \tag{20}$$

2. If the estimated amount of water in the cover layer is larger than the maximum available storage capacity, $S_{cl_{est_{n+1}}}>S_{cl_{\max}}$, we need to increase the amount of infiltration by short circuiting the flow to the waste body and and then recalculating $S_{cl_{est_{n_1}}}$ with the corrected $q'_{\inf_n}$

$$q'_{\inf_n}=q_{\inf_n}+(S_{cl_{\max}}-S_{cl_{est_{n+1}}})/\Delta t, \tag{21}$$

$$S_{cl_{est_{n+1}}}=S_{cl_n}+\left(q_{rf_{n+1}}-q'_{\inf_n}+q_{Ev_{n+1}}\right)\Delta t. \tag{22}$$

3. However if ($S_{cl_{est_{n+1}}}<0$ and $S_{cl_n}>S_{cl_{\min}}$) then we need to limit the amount of infiltration (there is not enough water in the cover layer to sustain infiltration) and perhaps also reduce the amount of evaporation:

$$q'_{\inf_n}=(S_{cl_{\min}}-S_{cl_n})/\Delta t \tag{23}$$

after which we again calculate $S_{cl_{est_{n+1}}}$ using equation 22.

4. If the estimated storage after correction is still negative, ($S_{cl_{n+1}}<0$), we need to limit the amount of evaporation and then recalculate $S_{cl_{est_{n+1}}}$

$$q'_{Ev_{n+1}}=q_{Ev_{n+1}}+S_{cl_{n+1}}/\Delta t, \tag{24}$$

$$S_{cl_{est_{n+1}}}=S_{cl_n}+\left(q_{rf_{n+1}}-q'_{\inf_n}+q'_{Ev_{n+1}}\right)\Delta t. \tag{25}$$

This approach implicitly implements the f_{red} term in Equation 5.

5. All conditions should now be fulfilled so we have a new update of the storage in the cover layer:

$$S_{cl_{n+1}}=S_{cl_{est_{n+1}}} \tag{26}$$

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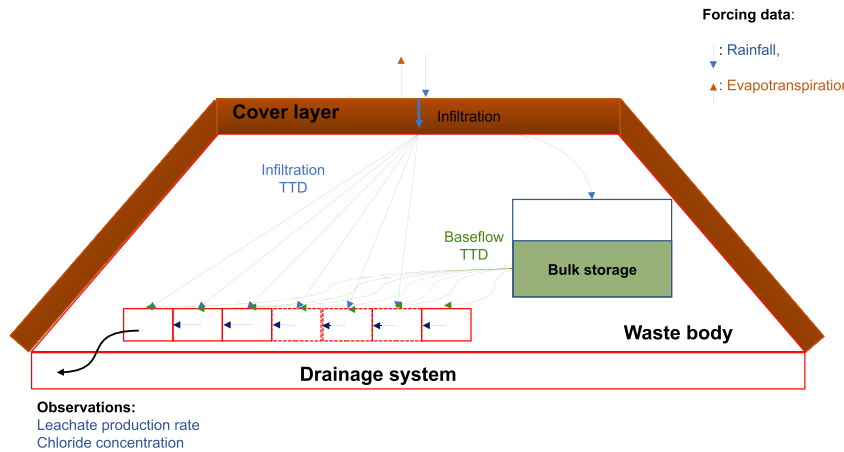


Figure 1. Illustration of the conceptual model of the landfill system. The cover layer allows rain water to be buffered so that evaporation can also occur on days without rainfall. Water subsequently infiltrates in to the waste body. In the waste body the infiltrated water is distributed over a discrete number of life-expectancy cells and the remainder is added to the bulk. On a daily basis water in the cell with a life expectancy (T_E) of zero is emptied in the drainage system from where it is immediately removed as leachate.

2.4. Solution Algorithm for the Waste Body

In order to solve Equation 11 we discretize it over both time dimensions where we use a daily time step d$t = 1$ day and for each time step, the life expectancy is distributed over $n_{tt} + 1$ values ranging from 0 to n_{tt}. This approach is illustrated in Figure 1. Each day, water infiltrating from the cover layer is distributed among the cells in the waste body using $p_{q_{\text{inf}}}(T_E)$ and water flowing from the bulk as base flow using $p_{bF}(T_E)$.

At $t = 0$, all cells are initialized with an initial amount of storage S_{ini}. Then every daily time step, all cells are shifted in life expectancy, that is, the cell with $T_E = 1$ becomes 0, the cell with $T_E = n_{tt}$ becomes $n_{tt} - 1$ days and the cell with $T_E = n_{tt} - 1$ is filled with water from the bulk waste depending on the base flow.

2.5. Model Calibration Using Bayesian Inference

Before we can use this model to simulate leachate production rate and quality we need to quantify the parameters. The parameters can be obtained by history matching of simulated leachate volumes and leachate concentrations to those obtained from measurements. We inferred the values of the parameters with the Multiple-try DREAM(ZS) package Laloy and Vrugt (2012), implemented in pyDREAM Shockley et al. (2018). DREAM (Vrugt, 2016) applies a Bayesian inference scheme to obtain the distribution of model parameters ($\boldsymbol{\theta}$) which optimally describe the measured data in a probabilistic framework. Bayesian inference,

$$p(\boldsymbol{\theta}|\hat{\boldsymbol{y}}) \propto p(\boldsymbol{\theta}) \cdot L(\boldsymbol{\theta}|\hat{\boldsymbol{y}}), \tag{27}$$

allows us to calculate the joint posterior probability distribution ($p(\boldsymbol{\theta}|\hat{\boldsymbol{y}})$) of the set of parameters using the measured data. The posterior distribution is calculated using the prior distribution of the parameters ($p(\boldsymbol{\theta})$) and the likelihood of the parameters given the measured data ($L(\boldsymbol{\theta}|\hat{\boldsymbol{y}})$).

For the likelihood function we applied the generalized likelihood function proposed by Schoups and Vrugt (2010):

$$L(\boldsymbol{\theta}|\hat{\boldsymbol{y}}) = -n \ln \frac{2\sigma_\xi \omega_\xi}{\xi + \xi^{-1}} - \sum_{t=1}^{n} \sigma_t - c_\beta \sum_{t=1}^{n} |a_{\xi,t}|^{2/(1+\beta)}. \tag{28}$$

For a detailed description and explanation of the parameters in this function we refer to Schoups and Vrugt (2010). We chose to use the generalized likelihood function because it allows for an improved handling of residual errors which can be correlated, heteroscedastic and non Gaussian with varying degrees of kurtosis and skewness. As a result, this approach allows for a correct statistical description of the data and residual errors, without the need for

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separating the different error sources. In Equation 28, we defined the measurement error as $\sigma_t = \sigma_0 + \sigma_1 y_t(\boldsymbol{\theta})$, $a_{\xi,t}$ is an independently and identically distributed random error with zero mean and unit standard deviation, described by a skew exponential power (SEP) density using parameters ξ and β to account for non-normality, scalars ω_β, σ_ξ, and c_β are derived from values of ξ and β which are a skewness and kurtosis parameter respectively and $\boldsymbol{\phi} = \{\phi_1, \ldots, \phi_4\}$ stores coefficients for an auto-regressive model of error residuals.

The generalized likelihood function is based on an additive non-linear regression model:

$$\mathbf{Y} = \mathbf{E} + \mathbf{e}$$

where $\mathbf{Y}$ is a vector of n observations, $\mathbf{E}$ is a corresponding vector of expected values; and $\mathbf{e}$ is a vector of zero mean random errors or residuals. The vector $\mathbf{e}$ includes measurement error, model input, model structural errors. In order to account for heteroscedastic errors, Schoups and Vrugt (2010) suggest to include multiplicative bias factors in order to account for systematic deviations in model predictions:

$$E_t = Y_{h,t}(\mathbf{X}|\boldsymbol{\theta}_h)\mu_t. \tag{29}$$

In this equation we assume that expected values can be modeled with a mass-balanced base flow model h, which yields simulated values $\boldsymbol{Y}_h$ as function of an observed input $\boldsymbol{X}$ and a vector of model parameters $\boldsymbol{\theta}_h$. In this equation the simulated flow $Y_{h,t}$, and bias factor μ_t vary as a function of time. Schoups and Vrugt (2010) suggest to amplify the non-linearity in the response of the leachate production using

$$\mu_t = \exp(\mu_1 Y_{h,t}), \tag{30}$$

but we found that we obtained the best results by not including this bias factor so we kept μ_1 to zero.

As suggested by Vrugt (2016), we include σ_0, σ_1, β, ξ, $\boldsymbol{\phi}$ and $y_{\min}$ as so-called nuisance variables in the inference together with all the other unknown parameters.

The generalized likelihood function was applied to both the times series of leachate production volumes and concentration data. The prediction of the cumulative total was constrained by adding a third normal likelihood term based on the cumulative leachate production over the inference period as a likelihood based on a sum of squares:

$$L_{cum}(\boldsymbol{\theta}|\hat{y}_{cum}) = -\frac{1}{2}\ln(y_{cum} - \hat{y}_{cum})^2. \tag{31}$$

The total liklihood, L_{tot} is the sum of the three likelihood values.

2.6. Boundary Conditions

The model is driven by daily rainfall and evaporation data which we downloaded from the Royal Dutch Meteorological Institute (KNMI, n.d.).

2.7. Initialization of the Model

Initial values for the model states need to be defined before we can keep track of the change in states which are driven by the varying boundary conditions. The important states are the storage in the cover layer, S_{cl}, the storage in the waste body, S_{wb} and the solute mass in the cover layer and waste body respectively, M_{cl} and M_{wb}. The model is started in the past well before measurements become available so that the effect of the initial conditions have been minimized by the seasonally varying boundary conditions. For the scenarios presented here, we start the simulation on the first of January 2003. The model is driven by daily precipitation and potential evapotranspiration data.

In order to facilitate a physical interpretation of the initial storage states we relate them to the average water filled porosity and heights of the cover layer and waste bodies. In addition we estimate the initial mass present in the

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cover layer and waste body using an average concentration. The effect of initializing with average values will become smaller over time due to the cyclic seasonality in the meteorological boundary conditions.

The initial states are calculated with:

$$S_{cl} = \theta_{w_{cl}} * H_{cl} \tag{32}$$

$$S_{wb} = \theta_{w_{wb}} * H_{wb} \tag{33}$$

$$M_{cl} = S_{cl}\ c_{cl} \tag{34}$$

$$M_{wb} = S_{wb}\ c_{wb} \tag{35}$$

where subscripts cl and wb indicate cover layer and waste body. $\theta_{w_{cl}}$ and $\theta_{w_{wb}}$ are the volumetric water contents in the cover layer and waste body [-], H_{cl} and H_{wb} are the thickness of the cover layer and waste body $[m]$. M_{cl} and M_{wb} are the solute masses in the cover layer and waste body per unit landfill area. The maximum saturation of the cover layer is then parameterized using the maximum volumetric water content ($\theta_{w_{cl},\max}$) which is equal to the porosity of the cover layer. In order to ensure that the minimum storage in the cover layer is always less the maximum storage, it is initialized as a fraction of $\theta_{w_{cl},\max}$: $f_{w_{cl},\min}$. The saturation of the cover layer is initialized as to be half the difference between $S_{cl_{\max}}$ and $S_{cl_{\min}}$, and the saturation of the waste body was initialized directly. The minimum bulk storage, $S_{bulk_{res}}$ is parameterized in a similar manner with $f_{w_{wb},\min}$.

Each life expectancy cell and the bulk storage in the waste body are initialized with the same initial concentration from which the initial mass present in the waste body is calculated. The amount of mass removed every time step with the leachate is the amount of mass present in the cell with a life expectancy of 0 days. Mass can only enter the life expectancy cells from the bulk with the base flow. The mass in the bulk is updated every time step with the amount removed with the base flow. The mass in the life expectancy cells remains constant with time, infiltrating water from the cover layer only leads to dilution of the concentration.

3. Site Specific Data and Prior Distributions of Unknown Parameters

3.1. Landfills

All data are from two landfills which are currently part of the Natural Biodegradation Research Program on Dutch Landfills (Stichting Duurzaam Storten, 2017). The Wieringermeer landfill is near Medemblik and the Braambergen landfill is near Almere, both in the Netherlands. Details for these landfills are given in Table 1. Both landfills are operated by Afvalzorg N.V.

Geo-referencing available as-built drawings to background maps and recent high resolution areal photographs in a GIS package, allowed us to estimate the surface area of the basal drainage system and the heights and surface areas of the landfills. The heights of the basal drains have been measured in 2016. As the topography of the sites is variable, we estimated the volume of the waste body from the GIS derived data and then calculated the average height of the waste body by dividing the volume by the area of the basal drainage system. Background data for the four landfill cells can be found in Table 1.

Detailed monitoring of produced leachate volumes and leachate quality is carried out in the context of the biodegradation research program by the landfill operator since March 2012.

Data available for model calibration and verification were the cumulative leachate production measured every 15 min from 14 June 2012–1 November 2024 and chloride concentrations measured in a commercial laboratory over the same period. Laboratory analyses were performed on leachate samples that were taken once every 2 weeks.

By testing different attempts to infer the parameters from the data, we found that the best results were obtained when cumulative leachate production is transformed to weekly leachate production rates by differentiation of the cumulative production. This transformation allows the model to capture the weekly dynamics in the data.

Rainfall and potential evaporation data are downloaded from automatic weather stations operated by the Royal Dutch Meteorological Institute (KNMI, n.d.). For the Wieringermeer landfill we used the data from the Berkhout

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Table 1
General Background Information on the Landfill Cells

Town	Braambergen Almere	Wieringermeer Medemblik
Compartment ID	11N, 11Z and 12	VP06
Area basal drainage system (m^2)	**11N:** 34,802	28,355
	11Z: 35,188	
	12: 30,000	
Time in operation	1,999–2008	1,992–1,998
Total amount of waste [ton]	1,216,723	281,083
Volume of landfill cell (m^3)	**11N:** 345,426.2	323,094
	11Z: 388,981.9	
	12: 315,254.4	
Average Height of the landfill (m)	**11N:** 9.9	12.2
	11Z: 11.1	
	12: 10.5	
Current landfill cover	Soil, incinerator bottom ash, jet grout (1.5 m)	Soil (1.5 m)
Landfill gas extraction	36 gas wells	2 gas wells + 1 shared
Bottom liner	Combination of mineral (50 cm sand bentonite) and 2 mm HDPE foil	Single 2 mm HDPE foil
Leachate drainage and collection	3 separate drainage systems for **11N**, **11Z** and **12** (3 pump pits)	Separate drainage system for compartment 6, single pump pit
Aeration system	Installed between Nov 2016-Jan 2017 and expanded in 2022 **11N**: well spacing: ca. 20 m, after expansion about 10 m (total number: **11N**: 65, after expansion 113) **11Z** well spacing: ca. 15m after expansion about 7 m (total number: 114 after expansion 163) **12** well spacing: ca. 20m (total number: 56) filter length: 2m depth filter: 1 m above the top of the drainage system	Installed in Oct 2016 well spacing: ca 14 m total number gas wells: 109 filter length: 2 m depth filter: 1.4 m above the top of the drainage system

station, for Braambergen we used the data from the Lelystad station. Daily rainfall, and calculated reference evapo-transpiration were used for the water balance analysis.

Between October 2016 and February 2017 a large number of wells were installed at both landfills through which the waste body is aerated. As the aim of aeration is to ultimately improve leachate quality, the filters of the wells are installed deep in the waste body (about 1–2 m above the top of the drainage system. In 2023 additional wells were installed at Braambergen.

3.2. Prior Distribution Ranges

In order to use Bayesian inference we require prior distributions of uncertain model parameters. We chose to initialize the optimization with uniformly distributed priors over a predefined search range (Table 2). The initial ranges were defined based on the expected physical values and sometimes by trial and error. In this last case, when it became apparent during the optimization that the initial prior was too constrained, the boundaries of the distribution were extended. For priors where variation is expected to vary across orders of magnitude, the ranges were initialized using the log-10 values of the parameters.

The number of finite travel times (n_{tt}) was set to be equal 1,825 days (or 5 years). The model bias factor μ_1 in Equations 29 and 30 was set to zero as first inference attempts indicated that model bias was not important.

In order to minimize the effect of the initial parameters on the calibration with measured data we started the model on 1 January 2003. This 'burn-in' time, allows for the base flow from the bulk that initiated on 1 January 2003, to

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Table 2
Priors for the Parameter Distributions Used in the Bayesian Inference

Parameter	Minimum	Maximum	^{10}log
Cover layer			
C_f	0.75	1.5	–
$\theta_{w_{cl},\max}$	0.3	0.5	–
$f_{w_{cl},\min}$	0.0001	1	–
K_{cl}	−5	3	x
b_{cl}	0	8	–
$c_{ini_{cl}}$	−4	−4	x
Waste body			
τ_{fast}	1	730	–
σ_{fast}	−5	2.5	x
$\Delta\tau_{slow}$	0	9,125	–
σ_{slow}	−5	3	x
β_f	0	1	–
$\theta_{wb_{ini}}$	0.0	0.5	–
$f_{wb_{\min}}$	0.0	0.5	–
bF_0	−5	−2	x
$c_{ini_{wb}}$	2	6	x
S_{bF}	0	15	–
σ_{bF}	0	15	–
a_{bF}	−9	0	x
t_{norm}	0	1,825	–
Generalized likelihood			
σ_0	−8	2	x
σ_1	−8	2	x
μ_1	0		–
β	−1	1	–
ξ	0.1	10	–
$\phi_{1,leachate}$	−1	1	–
$\phi_{1,conc}$	−1	1	–
$[\phi_2, \phi_3, \phi_4]$	[0, 0, 0]		–

Note. Priors are uniform distributions. The column^{10} log indicates which parameters have a range defined by the^{10} log values. Parameters with only a minimum value have not been inferred, the given values are used as a constant. The parameters for the generalized likelihood function are the same for both the leachate flow and the concentration data, except for the correlation parameter ϕ_1 which were maximized based on trial and error.

have moved completely across all 1,825 cells before the results are compared to any measurement values. As such the solute mass and volume of water in the travel time cells are by then fully constrained by the base flow from the bulk waste 5 years earlier.

The model was calibrated using measured leachate volumes and chloride concentrations from the first of January 2014 to the 31st of December 2020. The remaining available data from the complete data set from 12 June 2012 until 1 November 2024 were used to assess the model performance beyond the calibration range.

Calibration was initially started allowing the pyDREAM to randomly sample from the prior distributions. Once the inference had converged, pyDREAM was restarted with the final values of the 3 chains as an initial guess until the Gelman Rubin criterion indicating convergence was met (Vrugt (2016)). The data were analyzed using the final distributions from this last optimization. The convergence and consequently the parameter distributions were assessed using the final 50% of the length of each chains Vrugt (2016). The optimal parameter set is the Pareto optimal of the three likelihoods calculated for leachate cumulative outflow, leachate outflow rate and leachate concentration.

4. Results and Discussion

4.1. Simulated Leachate Outflow Rate and Leachate Concentration Values

After convergence in pyDREAM we may assume that all likelihood values in the final parameter set are samples from the distribution of likelihood values in the model that fit the measurements best. Because the inference is carried out in a hyperspace with 29 dimensions, different parameters can be highly correlated with each other. This is illustrated in Figure S1 in Supporting Information S1 for some of the parameters in the converged set for the Braambergen 11N waste body that have a Pearson's correlation coefficient larger than 0.75. The presence of a strong correlation between parameters is an indication that the range of some parameters can cover the complete prior-range. The parameter inference procedure has sampled the correlation in the posterior joint probability distribution. As a result, we cannot use averaged parameter values from the posterior joint probability distributions. Instead, we need to select individual parameter vectors from the total converged distribution of parameters.

In order to provide insight in how well the model is able to describe the measured data we decided to present model estimations based on the posterior likelihood for parameters vectors where the density is 1, and close to 0.95, 0.5, and 0.05 from the converged distribution. The cumulative distribution of likelihood values shown Figure S2 (Supporting Information S1) for the four waste bodies analyzed for this paper. The likelihood values corresponding to the probability quantiles of the lines in the following graphs are reported in the legends of the figures.

The results of the simulated values of leachate production and leachate chloride concentration are compared with measured values for the Braambergen 11N waste body in Figure 2. In the Supporting Information (Figure S3 in Supporting Information S1) we present similar figures for the Braambergen 11Z and 12 and the Wieringermeer VP06 waste bodies.

The generalized likelihood model of Schoups and Vrugt (2010) allows us to calculate a simulated measurement error with the forward model. For all sites the model is able to describe cumulative leachate production and

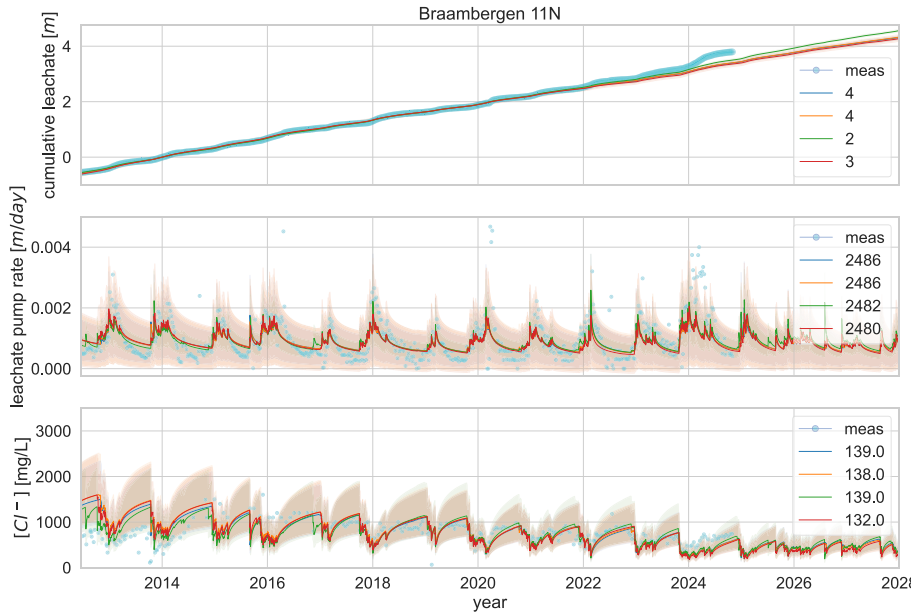


Figure 2. Simulated and measured values of cumulative leachate production (CL [m]), leachate pump rate (LPR [m/day]) and leachate chloride concentration (conc $[kg/m^3]$ for Braambergen 11N. The four colors are the results of four scenarios corresponding to distinct values of likelihood from the converged parameter set. The shaded areas are the 95% confidence intervals estimated from the generalized likelihood model. The legends give the likelihood of the parameter set for the three objective functions used for optimization.

leachate flow dynamics with similar accuracy. The uncertainty estimated with the 95% confidence intervals is able to capture the spread in the measurement data for the data set used for the calibration.

In the generalized likelihood model of Schoups and Vrugt (2010), heteroscedasticity is explicitly accounted for by assuming that the measurement error increases linearly with the expected value:

$$\sigma_t = \sigma_0 + \sigma_1 E_t.$$

The inferred parameters in the generalized likelihood model ($\sigma_{0,leachate}$, $\sigma_{1,leachate}$, $\sigma_{0,conc}$, and $\sigma_{1,conc}$) of which the log10 values are reported in Table 3, allow us to calculate the estimated measurement error for the simulated leachate production rates and leachate concentrations. For a leachate production rate of 1×10^{-3} m/day the measurement error parameter set with the highest likelihood will be 0.72×10^{-3} m/day or about 72% of the expected value. This implies that the approximate 95% confidence interval ranges between -0.41×10^{-3} and 2.41×10^{-3} m/day. The negative value is a consequence of the simplified approach for estimating the confidence interval.

For the concentration data this calculation is less straight forward because the measurement error is estimated using the log10 transform of the measured concentration data. The measurement error for the log10 of the concentration for the highest likelihood with an expected value of 1,000 mg/L is 0.11, or about 4% of the log10 transformed concentration. This leads to a 95% confidence interval between 612 and 1,634 mg/L. Similar values can be estimated for the other waste bodies as is graphically shown in Figure S3 (Supporting Information S1).

Although the uncertainty in the simulated values is significant, the estimates of the expected values give a good description of both measured time series. Please note that the calibration was carried out using data that were measured between 1-1-2014 and 31-12-2020.

The estimates of the leachate production rates do not capture the extremes in the measured data. This is due to several reasons. The first is because the optimal parameter set is a pareto optimum of both leachate production rates and chloride concentrations. The simulation represented by the red line in Figure S3 (Supporting Information S1) for the Braambergen 11Z waste body is a clear example, with a high likelihood for the concentration

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Table 3
Statistics and Optimal Parameter Values After Optimization With DREAM(ZS), Braambergen 11N, Number of Samples in Converged Parameter Set = 60,000

	Mean	Std	Min	25.00%	50.00%	75.00%	Max	*1*	0.975	0.5	0.025
C_f	0.98	0.08	0.80	0.93	0.98	1.04	1.17	1.06	1.03	0.88	0.98
$\theta_{w_{cl,\max}}$	0.31	0.01	0.30	0.31	0.31	0.32	0.38	0.32	0.31	0.32	0.31
$f_{w_{cl},\min}$	0.19	0.03	0.11	0.17	0.20	0.22	0.26	0.20	0.22	0.23	0.25
$^{10}\log K_{cl}$	1.76	0.66	−0.53	1.26	1.76	2.28	2.99	2.15	1.20	2.17	−0.08
b_{cl}	3.48	1.35	0.85	2.67	3.21	3.80	8.00	2.90	2.00	3.46	1.19
τ_{fast}	297.04	191.65	26.05	135.26	241.12	453.54	727.53	244.97	171.36	162.45	140.90
$^{10}\log\sigma_{fast}$	0.44	0.09	0.18	0.36	0.44	0.51	0.69	0.40	0.36	0.41	0.39
$\Delta\tau_{slow}$	5092.93	2058.14	1007.65	3182.48	5063.49	6673.43	9112.41	7063.72	6855.75	1933.23	2796.92
$^{10}\log\sigma_{slow}$	−1.86	1.57	−4.97	−3.10	−1.94	−0.55	0.94	−1.07	−2.71	−3.01	−4.33
β_f	0.71	0.14	0.33	0.61	0.70	0.81	0.99	0.78	0.68	0.73	0.71
$\theta_{wb_{ini}}$	0.45	0.03	0.36	0.43	0.45	0.47	0.50	0.46	0.43	0.42	0.43
$S_{\min}$	0.38	0.07	0.17	0.33	0.38	0.44	0.50	0.38	0.35	0.45	0.40
$^{10}\log\, bF_0$	−1.90	0.23	−2.73	−2.03	−1.86	−1.73	−1.50	−1.89	−1.65	−1.86	−2.09
$^{10}\log c_{ini_{cl}}$	−0.49	2.26	−4.00	−2.39	−0.74	1.00	4.87	−3.48	−2.91	0.31	−3.70
$^{10}\log c_{ini_{wb}}$	3.39	0.05	3.30	3.35	3.38	3.41	3.60	3.38	3.41	3.41	3.40
S_{bF}	7.47	4.28	0.28	3.12	8.25	11.11	14.99	10.14	14.19	9.80	9.69
σ_{bF}	1.80	0.48	1.11	1.47	1.69	1.95	3.34	1.45	1.45	1.67	1.15
$^{10}\log a_{bF}$	−4.76	2.39	−8.99	−6.80	−5.05	−2.69	−0.50	−5.77	−4.50	−2.50	−7.16
$T_{E,\text{norm}}$	1265.17	391.84	5.84	1024.45	1333.88	1566.78	1824.89	1010.26	1122.62	1345.83	1500.61
$^{10}\log\sigma_{0,leachate}$	−3.63	0.04	−3.78	−3.65	−3.63	−3.61	−3.55	−3.63	−3.63	−3.69	−3.64
$^{10}\log\sigma_{1,leachate}$	−0.35	0.13	−0.75	−0.43	−0.35	−0.26	0.05	−0.43	−0.36	−0.63	−0.38
$\beta_{leachate}$	0.94	0.05	0.71	0.90	0.95	0.98	1.00	0.99	0.98	0.97	0.74
$\xi_{leachate}$	1.24	0.05	1.08	1.20	1.23	1.27	1.40	1.25	1.22	1.22	1.28
$\phi_{1,leachate}$	0.66	0.03	0.55	0.64	0.67	0.69	0.70	0.67	0.65	0.68	0.61
$^{10}\log\sigma_{0,conc}$	−1.03	0.05	−1.16	−1.06	−1.02	−0.99	−0.91	−1.01	−1.00	−0.96	−1.06
$^{10}\log\sigma_{1,conc}$	−5.16	1.68	−8.00	−6.63	−5.07	−3.68	−1.95	−5.45	−6.26	−4.43	−2.46
β_{conc}	0.93	0.05	0.75	0.91	0.95	0.97	1.00	0.97	0.97	0.95	0.78
ξ_{conc}	0.93	0.09	0.69	0.87	0.92	0.99	1.22	0.90	1.03	1.11	1.01
$\phi_{1,conc}$	0.59	0.07	0.36	0.54	0.59	0.64	0.70	0.59	0.53	0.67	0.58
L_{tot}	2569.35	4.88	2536.62	2566.29	2569.90	2572.43	2580.20	2580.20	2576.75	2569.90	2561.41

data, but a lower one for the leachate data. An important reason for this ambiguity lies in the fact that the model is an initial boundary value problem in which many of the waste body properties cannot vary with time. Early attempts, where first only leachate production data were used in the objective criterion, gave better fits of measured leachate production values, however attempts to subsequently describe the concentration data with fixed optimal parameters for the leachate production rate simulation led to poor results for the concentration data (results not shown). This implies that the assumption of purely convective flow for chloride is not completely true or that the parameters in the model vary with time. When inferring the parameters from both time series, leachate production rates need to be smoothed in the model to a certain extent. Another example of the initial boundary condition problem can be seen in the early predictions of the concentration data (before the start of the calibration period in 2014) where the simulated concentrations poorly describe the measured values for Braambergen 11N, 12 and Wieringermeer waste bodies.

The second reason is related to the quality of the measurement data. Leachate levels in the pump-pits of the waste body cells are allowed to vary over a narrow bandwidth of 10 cm. When the maximum level is reached, the pump will be switched on, when the minimum level is reached it switches off. During pumping, flow is cumulatively

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recorded. Since, the start of monitoring in April 2012, several problems were encountered with the pumps causing them to be switched off leading to a zero flow. As a consequence, the drainage system buffered the leachate. As soon the issues were fixed, the pumps quickly pumped the excess water until the set-points were reached. Pumping excess water led to temporarily much higher flow rates. In order to minimize this effect in the data, flow rates were obtained by taking backward differences of the cumulative data over a period of 7 days.

Because measurements of $q_{rf}(t)$ and $q_{leach}(t)$ were used to calibrate the model, the uncertainty in the water balance is mainly associated with the estimation of $q_{ev}(t)$. In the approach we used, the final estimate of $q_{ev}(t)$ is determined by multiple (correlated) parameters in the model. For most of the time $q_{ev}(t)$ is equal to the estimated potential evapotranspiration, but there are moments when evaporation became zero due to insufficient water present in the cover layer.

The posterior distributions of the model parameters indicate the model sensitivity of the system to the parameter values within the optimal likelihood parameter set. Figure 3 gives examples of posterior cumulative parameter distributions (in black) compared to the prior distributions in blue: the left column shows the inferred distributions for C_f, b_{F0}, and $c_{ini_{wb}}$ which are examples that have narrow distributions compared with the prior ranges given in Table 2. This narrow distribution implies that the measured data contains sufficient information to infer these parameters. The total water balance depends strongly on the crop factor, C_f, because the surface area of the waste body is fixed and the crop factor is the only parameter that can limit or enhance the evapotranspiration. Outflow concentrations strongly depend on the amount of solute mass present in the waste body, which is controlled by the initial concentration $c_{ini_{wb}}$ and the base flow, b_{F0}, which constrains the lowest flow rate during dry periods.

The parameters in the right column of Figure 3 are examples of poorly inferred parameters because the posterior distribution is very similar to the uniform prior distribution in Table 2. The outflow concentration does not depend on the initial concentration in the cover layer, $c_{ini_{cl}}$, in 2003. The simulation results show that any conservative solute in the cover layer is quickly removed. The posterior distribution can also be similar to the prior when the parameter is highly correlated with another one, a good example of this is the distribution of the mobile fraction in the cover layer, β_f which is highly correlated with τ_{fast} as shown in Figure S1 (Supporting Information S1). The last example of a poorly inferred parameter is the posterior distribution for $\Delta\tau_{slow}$ which does have a narrower range than the prior, however the final parameter range is still uniform over a wide range. The reason for this is that the inferred values cause the τ_{slow} value in Equation 13 to be larger than $n_{tt} = 1825\ days$. Given the way the model is implemented, any value larger than n_{tt} would lead to the same result.

4.2. Error Model

In order to check if the parameters in the error model are correctly inferred we follow the approach used by Schoups and Vrugt (2010) were different aspects of the residuals are evaluated. Figure 3 presents the results of this analysis for the Braambergen 11N waste body. For the error model we assume that the errors are heteroscedastic, the left plots show the residuals as a function of the expected values of measured leachate production rates and concentrations. The errors are nicely distributed around zero indicating that there is no bias in the results. The middle plots show that the distributions of errors are well described using the inferred parameters in the Skewed Exponential Power distribution of the generalized likelihood model. Clearly the error model does not follow a normal distribution. Finally, the autocorrelation in the residuals is adequately captured with the autocorrelation parameter even though the range for this parameter was constrained by a maximum value of 0.7. In addition, the different chains show similar results demonstrating that the final parameter set is indeed from a converged distribution (see Figure 4).

4.3. Extrapolation to 2066

The model allows us to make predictions of how emissions vary in the future while taking the uncertainty in the inferred model parameters in to account. The results for the Braambergen 11N waste body are shown in Figure 5, for the other waste bodies we refer to the Supporting Information S1, Figure S4. For all waste bodies, simulated results for selected parameter sets lie close to each other in the time range used to infer the parameters, but before and after the measurement time range, the results can diverge. This most clearly seen in the plot of the cumulative leachate production because small differences in simulated cumulate over time. For the time range used for the parameter inference these small differences are compensated, so the results for the different parameter sets do not

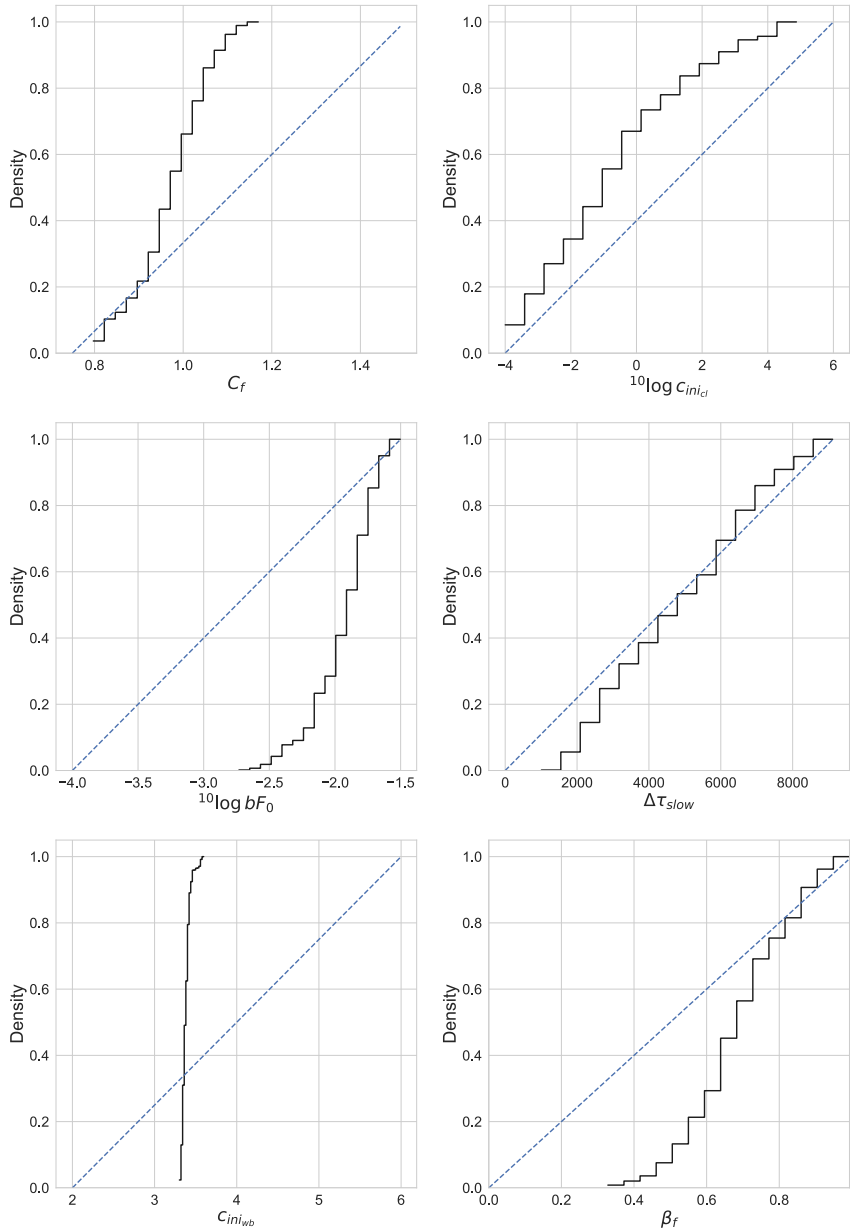


Figure 3. Posterior (black) and prior (dashed blue) cumulative distributions of selected parameters for Braambergen 11N. The left column gives examples of sensitive parameters that have converged to narrow posterior distributions, the right column gives examples parameters which are highly correlated with other parameters or which are not sensitive and therefore are close to the prior.

diverge from each other. Similar effects also occur for leachate production rates and leachate concentration data. However, as the effects do not cumulate as quickly as for the cumulative leachate production, it will take a much longer time series to see the effects in the graphs.

The simulated cumulative leachate production starts to deviate significantly from the measured cumulative flow after 2022 and in spring 2024 we see that measured flow rates fall above the 95% intervals. This is due to the fact the past years have moved from exceptionally dry to exceptionally wet in a very short time. An additional factor is that in 2022 additional wells were installed on Braambergen.

One of the most important assumptions in developing this approach is that the probability density functions of the travel time distributions do not change with time. It is likely that this assumption is too strict. Apparently, the

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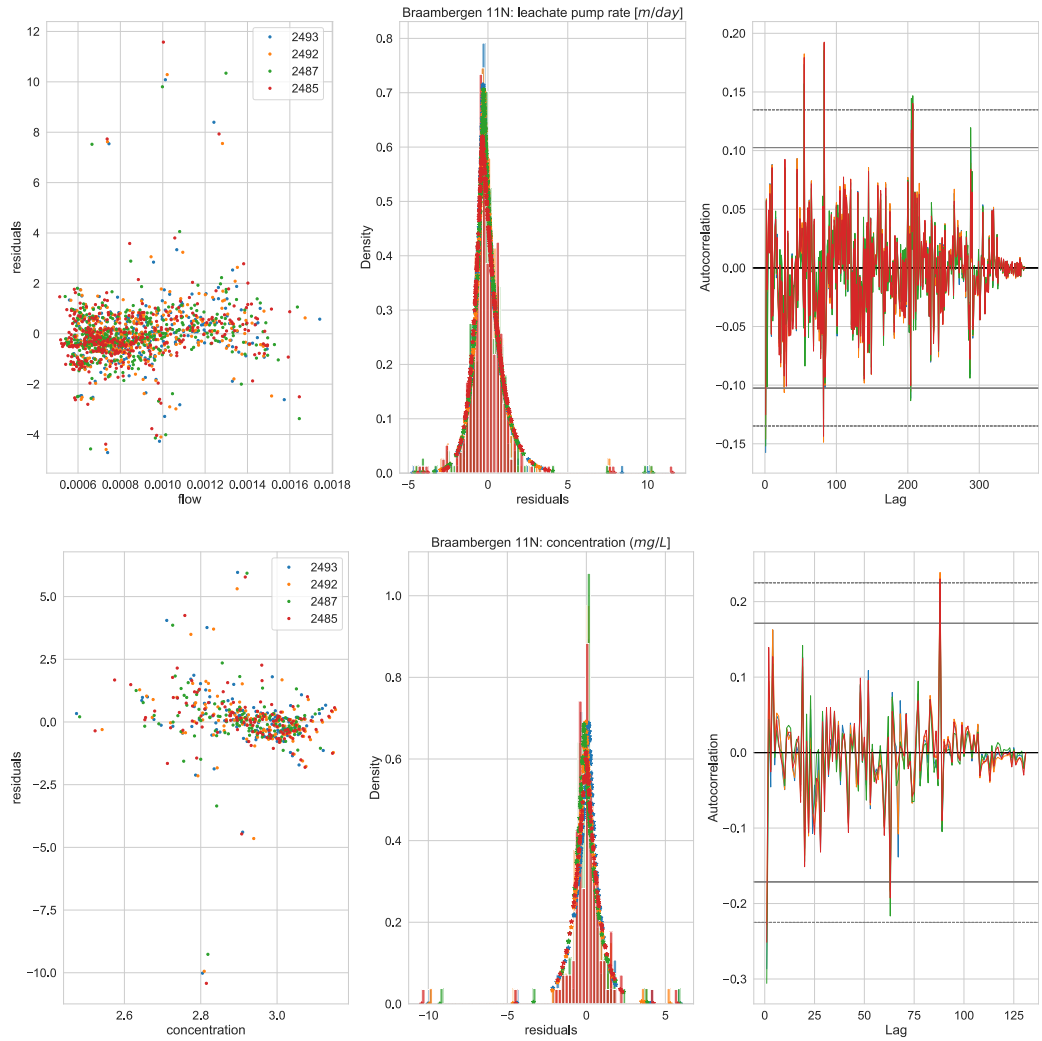


Figure 4. Braambergen 11 N. Plots of the residuals as a function of leachate production rate or concentration, distribution of the errors and auto-correlation in the errors for the flow data (top row) and concentration data (bottom row).

waste body is not able to store more water as rainfall increases, instead preferential flow to the drainage system seems to increase as well. Measurement artifacts also play a role. Because of the excess amount of water due to heavy rainfall, the landfill operator had to reduce the discharge to the water treatment plant by reducing the pump rate from the drainage system for a couple of weeks. The reduced flow of water may have led to a higher leaching of chloride.

In order to capture time dependent changes in the properties of the waste body and boundary conditions other approaches are required than used for this paper. Parameter distributions can be adjusted so that they become time dependent. This could be done by making them depend on the storage in the waste body as suggested by Harman (2015) or by inferring parameters and states in time using a particle filter as suggested by (Wang & Heimovaara, 2023).

The long-term predictions (Figure 5) indicate that chloride is gradually leached from the waste body and the concentration varies with the seasonal variation in infiltration. All scenarios (see also Figure S4 in Supporting Information S1) indicate that water storage in all waste bodies reach a long-term dynamic steady state where base-flow is compensated by storage from infiltration with life-time expectancies above n_{tt} or 1,825 days.

The concentration in the leachate is controlled by chloride mass and amount of water draining from the bulk volume of the waste body as base flow. The base flow rate is controlled by the volume of water stored in the bulk

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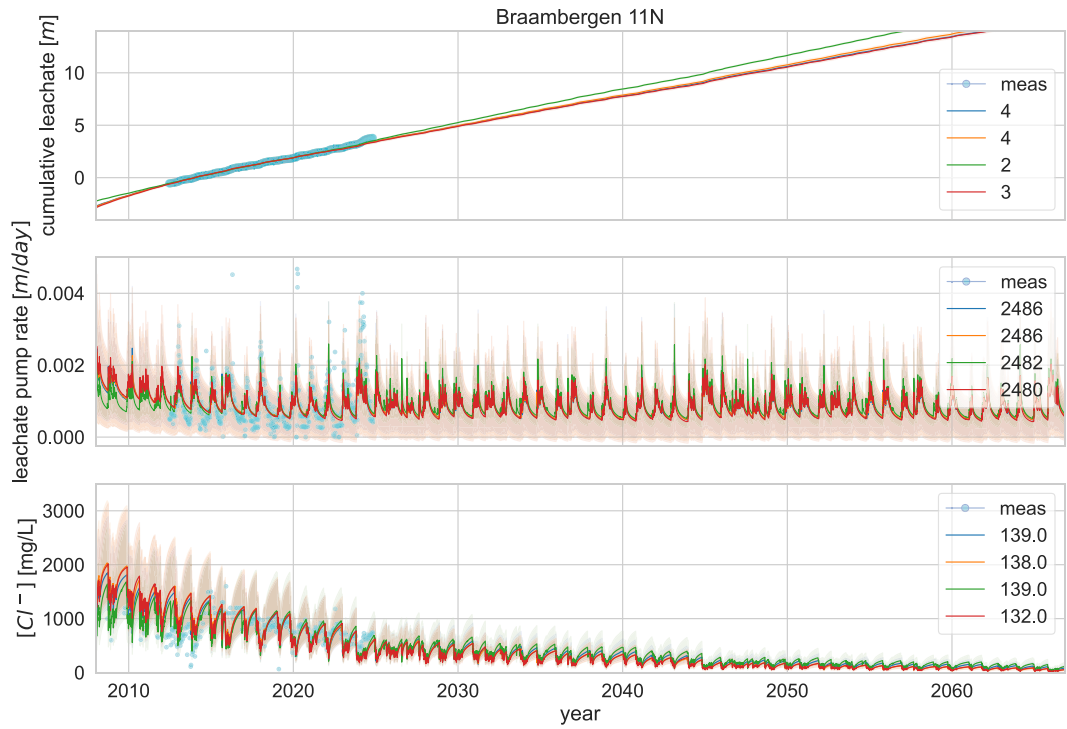


Figure 5. Long term extrapolation of cumulative leachate production (CL [m]), leachate pump rate (LPR [m/day]) and leachate chloride concentration (conc $\left[\mathrm{kg/m^3}\right]$ for Braambergen 11N. The scenarios are identical to the ones presented in Figure 2.

volume. Figure 6 shows the base flow as function of the bulk storage, Figure 7 the simulated base flow over time and Figure 8 shows the bulk concentration which is the ratio of the solute mass and storage. Each parameter set results in base flows with a different magnitude, however as the model is simulating both the water balance and the chloride mass-balance, final outcomes are very similar (see Figures 2 and 5). The differences in magnitudes for the base flow are caused by the fact that concentration is the ratio of solute mass over water storage. A higher concentration leads to a higher water mass, which therefore will lead to higher bulk storage values and therefore a different base flow function to achieve similar base flow mass rates. A clear indication of the mass balance are the similar magnitudes of the variations in the bulk storage (S_{bulk}) in Figure 8.

The oscillations in the base flow (Figure 6) can be explained by the seasonal variation in the infiltration leading to a variation in the bulk storage (Figure 8) and the slope of the base flow function (Figure 6).

4.4. Life Expectancy Distributions

In Figure 9, cumulative density functions are plotted for the life expectancy time distributions used to partition the water from the infiltration flux from the cover layer and the base flow from the bulk. Until a life expectancy of 2,500 days, the probability density functions for q_{inf} are completely determined by the fast flow fraction for all scenarios except the green one. Apparently the slow fraction only has an impact on water with a life expectancy which is much larger than 2,500 days. Given the fact that all water with a life expectancy older than $n_{tt} = 1825$ days is added to the bulk, the results imply that about 40% of the infiltrating water is added to the bulk of the waste body and that about 20% of the infiltrating water will have left the waste body as leachate after about 45 days. The same is true for the green scenario as the jump occurs after 1,900 days.

The cumulative density function for the base flow indicates that in all scenarios, except for the 50% probability scenario (green with a likelihood of 2487) are directly added to the cell with a life expectancy of 1,825 days which is consistent with convective transport with the water.

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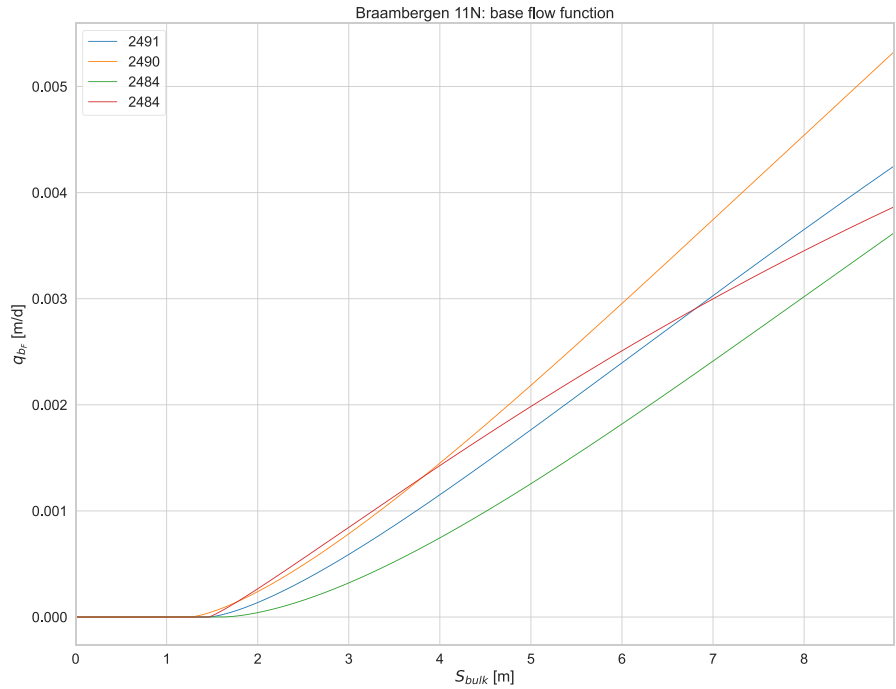


Figure 6. Base flow (b_F) functions for Braambergen 11N using Equation 10.

Because 20% of the water infiltrating from the cover layer has a life expectancy of less than 45 days, leachate concentration dynamics are dominated by this water moving preferentially through the waste body. This preferential flow explains why in winter concentrations are low and in summer concentrations are high. In the Netherlands, evapo-transpiration is high in summer leading to no or very low infiltration fluxes from the cover layer and solute present in cells with short life expectancy is not diluted. In winter evapo-transpiration is very low, leading to high infiltration fluxes which significantly dilute the solute present in the cells with short life expectancy.

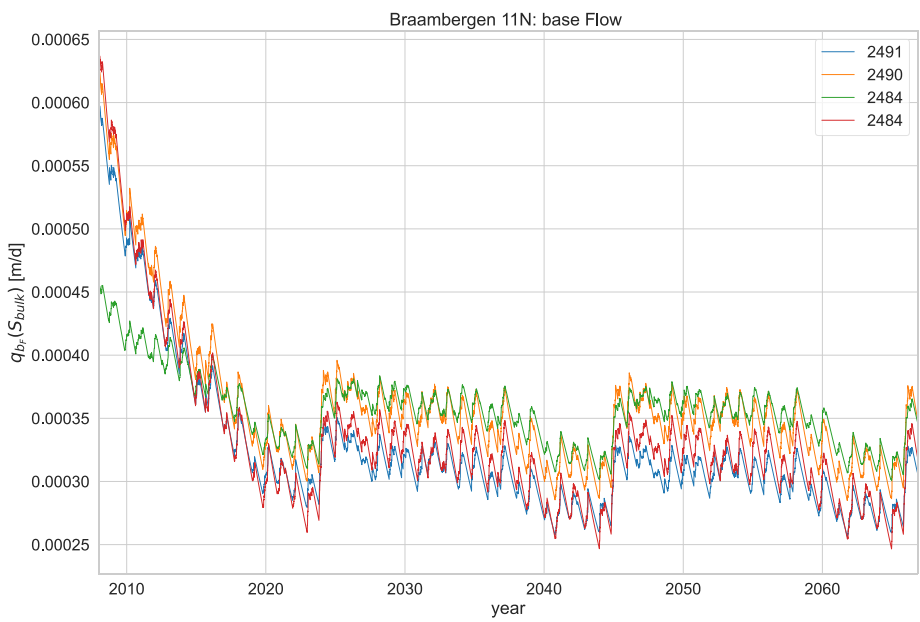


Figure 7. Simulated base flow (b_F) for Braambergen 11N.

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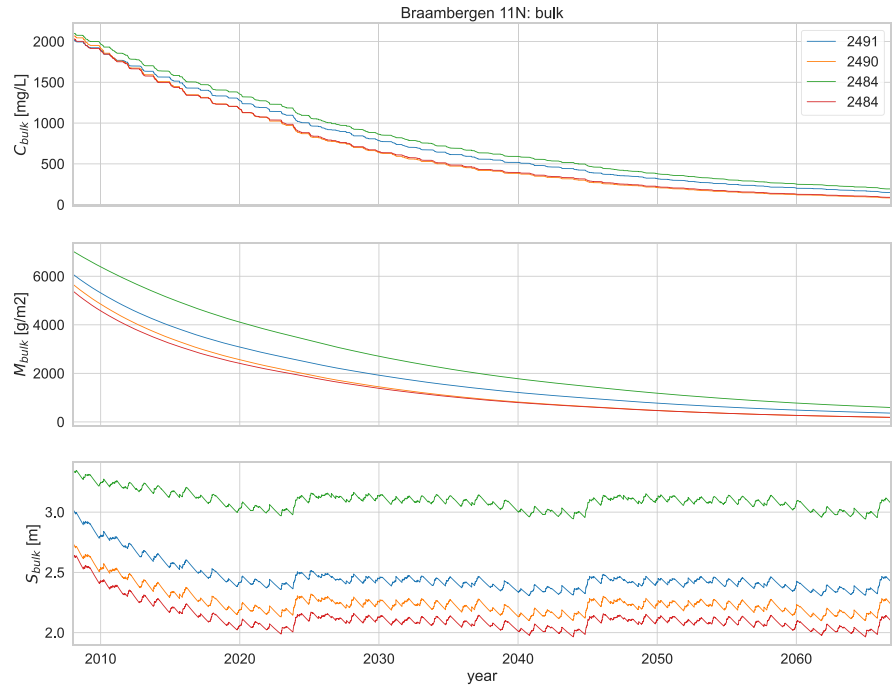


Figure 8. Simulated chloride concentration, mass and total storage in the bulk of the waste body for Braambergen 11N.

4.5. Emission Potential

The model keeps track of the mass balances of water and chloride in the waste body. The dynamics in the long term leachate production rates and leachate chloride concentrations are controlled by the mass present in the bulk. The only source for chloride in the leachate is the mass present at initialization, water is added via precipitation and subsequent infiltration in to the waste body. These assumptions lead to a gradual decrease in chloride mass which then leads to a gradual reduction in leachate concentrations as well.

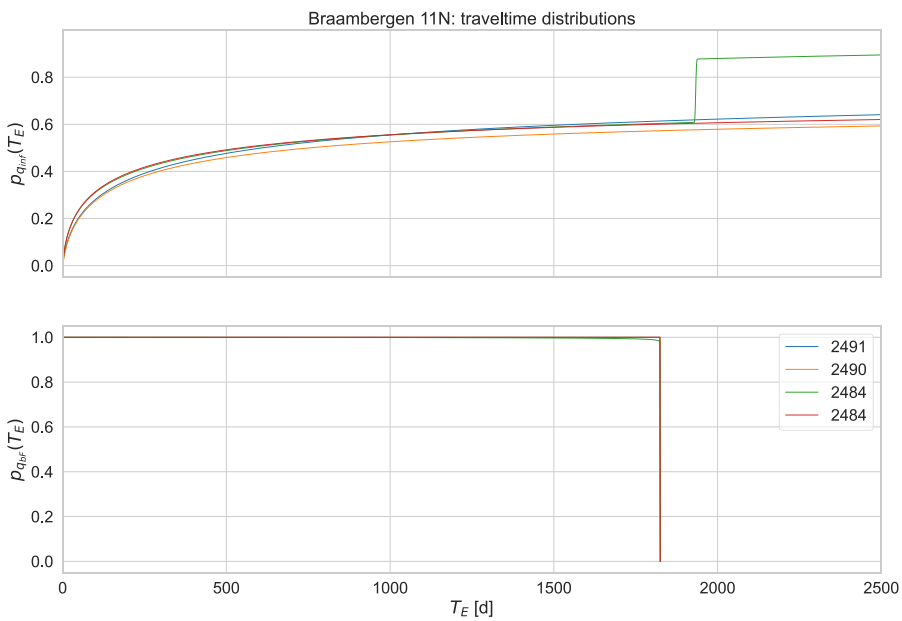


Figure 9. Cumulative densities of the travel time distributions for the infiltration flux from the cover layer (q_{inf}) using Equation 12 and the base flow from the bulk (q_{bF}) using Equation 14.

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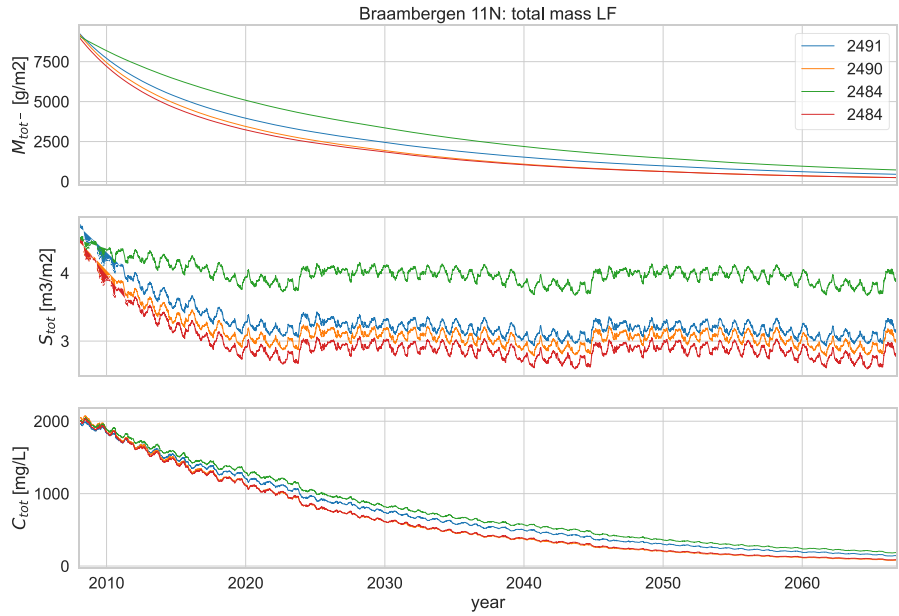


Figure 10. Total chloride mass, total storage and solute concentration in the waste body of Braambergen 11N.

Figure 10 shows the simulated totals of chloride mass, water storage and corresponding chloride concentrations for the waste body of Braambergen 11N. Clearly the mass shows an exponential decrease with time, which is to be expected. For the Braambergen 11N case, the difference in estimated total mass, varies from about 9,200 ± 100 g/m^2 in 2008 to 510 ± 250 g/m^2 in 2066. The corresponding emission from 2008 to 2066 ranges from 8,364 tot 9,018 g/m^2.

The leachate volume in the waste body decreases from 4.5 m to values between 2.6 and 4 m. The concentration is the ratio of the mass and the storage. As long as base flow occurs, the total mass in the waste body will decrease. The rate of decrease is controlled by the magnitude of the base flow and the concentration in the bulk. Similar patterns have been found for the other waste bodies in this study as well.

In 2018 a number of samples were taken from Braambergen 11N while drilling holes for gas injection wells in the waste body. These solid samples were sent to the laboratory for further analysis. The chloride measurements for these samples ranged from 287 to 540 mg/kg dry waste. Assuming an average waste body height of about 10 m and a dry bulk density of 1,600 kg/m^3 this would imply values ranging from 4,592 to 8,640 g/m^2. The values in Figure 10 range from 3,560 to 5,436 g/m^2. Although these numbers should be considered with care, because of the uncertainties related to the total mass of waste and water content, the magnitude and range of the values are however, very similar.

These results indicate that our approach provides insight in the mass controlling long-term emissions from waste bodies. The total mass in Figure 10 shows the emission potential of this waste body as function of time. This mass controls the concentration in the leachate and as no new mass is added to the waste body it also will control future emissions.

5. Implications for Managing Landfill After Care

The model and parameter inference approach based on life-expectancy modeling is a viable approach to describe measured time series of leachate production rates and leachate concentration dynamics. Because the parameter inference approach provides us with uncertainty estimates, we also obtain insight in the uncertainty of the simulated values. The inferred parameters allow us to understand the uncertainty in the parameters controlling the emission of solutes from the waste body. The model allows us to make sense of the measured variations in leachate concentration data without having the need to smooth the data.

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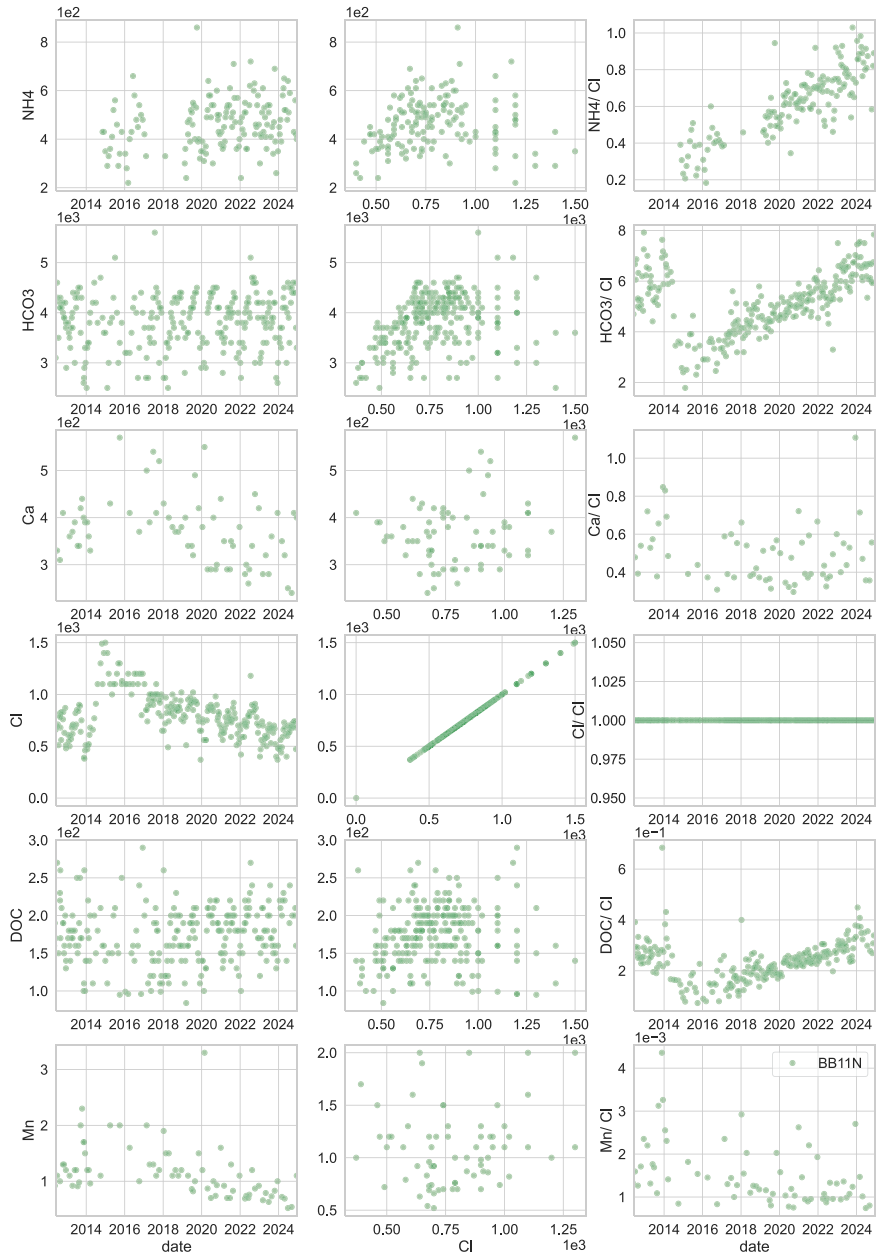


Figure 11. Time series of reactive parameter concentrations in the leachate of Braambergen 11N. The left columns shows the measured time series, the middle column shows the correlation with the measured chloride concentrations and the right column shows the time series of concentrations normalized to chloride.

An important result is that this approach can provide minimum and maximum estimates of leachate concentrations over time which can be used to assess the necessity of landfill after-care measures. In addition the inferred parameter distributions allow for an estimate of amount of mass in the waste body that is controlling the long-term leachate concentrations. This information is essential for understanding long term future risk associated with leachate emissions.

The approach we present currently only estimates the water balance and the emission of conservative solutes such as chloride which is a necessary first step to assess the emission of reactive compounds. We illustrate this in Figure 11 where time series of a selection of reactive parameters are shown. Normalizing all measurements by the chloride concentrations will illustrate the impact of dilution by preferential flow. If dilution has a significant impact, normalizing by chloride will remove a lot of variation from the time series. This is clearly seen for the

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time series of ammonium (NH4), bicarbonate (HCO3), and dissolved organic carbon (DOC) in the right column in Figure 11. A strong indication of non-conservative behavior is the increasing trend in these three time series. For calcium (Ca) and manganese (Mn) the behavior is different, the impact of dilution is much less clear.

The non-conservative behavior of these parameters is controlled by a multitude of processes. NH4, DOC and HCO3 are to a large extent controlled by the hydrolysis of solid organic matter in the waste body, where the dissolved compounds are further degraded under a range of redox conditions present in the waste body. Since 2018, the Braambergen 11N waste body has been aerated by the landfill operator by over extracting landfill gas from the waste body which effectively pulls in oxygen from the ambient air. As a result, in part of the waste body aerobic degradation can occur, leading to a significant increase in the CO_2 pressure. The behavior of HCO3 is also impacted by dissolution and precipitation of a wide range of carbonate minerals which are strongly influenced by the partial CO_2-pressure in the waste body. In anaerobic landfills the partial CO_2-pressure is in the order of 0.5 bar and in aerobic parts of the waste body it can be higher. Pumping of leachate from the leachate system leads to a large amount of turbulence in the pump-pit causing the leachate to mix with the ambient air, thus rapidly lowering the CO_2-pressure, which causes a significant precipitation of carbonate minerals in the pump-pit. This is probably the reason why the calcium concentrations do not seem to be influenced by dilution, they are most likely controlled by the solubility of calcium carbonate in the pump-pit. Manganese is a very redox sensitive parameter and it is soluble under anaerobic conditions. The time series of chloride normalized Mn concentrations implies that leaching is to a certain degree conservative.

Clearly, assessing emission potential from time series of reactive parameters is not straightforward. However, knowing the impact of dilution after assessing the water balance and the emission of chloride provide insights in the net effect of hydrolysis and degradation on the concentration of for example, NH4. Such insights will guide the development of reactive transport models with which we can assess the long term behavior of chemical compounds distributed over the solid mineral, solid organic, liquid and gas phases present in the waste body. The models will need to include processes such as dissolution and precipitation of minerals, hydrolysis of organic matter, sorption to reactive surfaces and the biological degradation of organic compounds under a wide range redox conditions. Such reactive transport models need to include both transport with the flowing water, as well as transport of the landfill gas migrating through the waste body.

The results presented in this paper clearly demonstrate that concentrations of chloride in leachate are dominated by dilution with water infiltrating from the cover layer and quickly moving via preferential path ways to the drainage system. Transport of mass from the bulk of the waste body to the drainage system is a relatively slow process. Dilution is a dominating mechanism reducing the actual leachate concentrations compared with the solute concentrations present in the waste body.

Environmental protection criteria are related to the actual concentrations in the leachate and if these are consistently below accepted values, landfill after care can be reduced (Brand et al., 2016; Dijkstra et al., 2018). Quantification of the emission potential is an essential step in assessing if the leachate concentrations comply with environmental protection criteria under a wide range of scenarios under the constraint of the boundary conditions close to the ones used for quantifying the model parameters.

Enhancing preferential flow by engineered measures in the waste body, may reduce these concentrations even further because the amount of water being stored in the bulk will decrease. This then leads to a decrease in the release rate from the bulk because of a decrease in storage. However the decrease in emission potential will slow down as well. When relying on such engineered measures it is important to ensure that the engineered solutions are robust and remain operational over extended periods of time under a range of varying boundary conditions.

Extreme scenarios such as flooding of the landfill may have to be taken in to account as well as these may lead to enhanced leaching (Laner et al., 2009; Nicholls et al., 2021). Emission potential estimates obtained by applying the methods proposed in this paper are a good starting point in evaluating the consequences of such extreme events.

This methodology requires long-term time series of leachate production rates and leachate concentration values in order to infer the parameters. Leachate production rates and leachate concentrations are parameters that landfill are obliged to measure in order to be compliant with the regulations. For the Wieringermeer and Braambergen landfills the landfill operator, Afvalzorg, did increase the measurement frequency significantly. When applying

the approach to new data sets one can start using the posterior distributions obtained published with this paper, instead of starting with fresh uninformative priors.

6. Summary and Conclusions

A model has been developed for simulating leachate production rates and leachate concentrations using a mass balance approach combined with a stochastic travel time approach based on life time expectancies. The model is one dimensional and consists of two layers. The first layer is a reservoir model for the cover layer, the second layer a stochastic life expectancy model. The model is driven by measured rainfall and potential evapotranspiration and is calibrated using measured leachate production rates and leachate concentrations. Posterior parameter distributions are inferred using a Bayesian MCMC approach implemented in PyDREAM (Shockley et al., 2018) where the objective functions are based on the generalized likelihood model of Schoups and Vrugt (2010). The model has been applied to analyze data sets obtained from two different landfills and a total of four waste bodies.

We also propose to use emission potential as a term to describe the amount of mass that can be released from the waste body under realistic meteorological conditions. This emission potential is the source term for a conservative solute (chloride) in a modeling framework that can describe measured leachate flux and leachate concentration. Quantifying the water balance and conservative leaching is a necessary first step before evaluating the leaching of more reactive compounds.

The model with posterior parameter distributions can describe the measured time series of leachate production rates and leachate chloride concentrations. In addition uncertainty bandwidths using inferred measurement errors can be determined as well. Model simulations can be carried out to extrapolate leachate production and leachate concentration in to the future allowing for assessment of the future development of concentration and leachate production volume.

The hydrological parameters, travel time distributions and stagnant zone properties derived with the approach presented in this paper form the basis of a reactive transport model setup in which both conservative and reactive substances can be estimated simultaneously.

The results indicate that the waste bodies that have been studied, have reached seasonal steady state until 2022, where total water storage in the waste body oscillates around a constant value. From 2022 onward, the measured cumulative leachate production is larger than simulated. This implies that using time independent life-expectancy probability distributions is too strict.

The oscillations in leachate production rates and leachate concentrations are controlled by infiltration rates from the cover layer and the life time expectancy distribution. Leachate concentrations depend strongly on the simulated base flow which is controlled by the storage in the bulk of the waste body where life expectancy of water is longer than 1,825 days.

Emission potential is a combination of the total mass present in the waste body and the expected future behavior of the base flow. The model can be used to plot the future development of the two parameters controlling leachate concentrations being total solute mass and total water storage for different climate forcing scenarios. The total mass is a quantification of the emission potential. The results of such simulations can be used to assess different landfill after care scenarios and therefore it allows us to estimate leachate concentrations and the expected emission over a predefined time period.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The software and data including documentation used for generating the results in this paper are available on the 4TU. ResearchData repository (Heimovaara & Wang, 2024): https://doi.org/10.4121/ade0d39f-8b07-4e48-8726-f900cf27141e.

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Micropollutants characteristics, fate, and sustainable removal technologies for landfill leachate: A technical perspective

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ABSTRACT

Waste disposal in landfills has gained momentum in the last few decades as it is one among the easy and cost-effective method for waste management for the accelerating global population. Heterogenous nature of the waste ending up in landfills makes it difficult to predict the fate of these pollutants making it difficult for its bio-monitoring and specific treatment. Among the major issues associated with landfill treatment, liquid percolation from this heterogenous waste substrate collectively referred as leachate poses the greater risk to environment through soil and ground water pollution. The diversity of micropollutants presents in landfill leachates ranging from microbial pathogens, pesticides, microplastics, pharmaceuticals and other harmful chemicals calls for crucial attention towards improving methods used for their treatment and removal. This review summarizes the key components of landfill leachates with specific emphasize on micropollutant content of leachate. Further the features of most recent and advanced technologies that were successfully explored for micropollutant removal from landfill leachates are presented in this review.

1. Introduction

Rapid industrialization, population growth and urbanization has triggered the generation of huge amounts of diverse waste materials often ending up in landfills as their final destination in its life cycle. This heterogeneous waste undergoes various physical, chemical and biological changes in landfills resulting in the liberation of more toxic micropollutants especially in the leachates originating from these landfill disposals [1]. Landfill leachates are produced due to a variety of processes in the landfills that include the release of inherent water content in the waste, percolation of rainwater through waste and enzymatic along with physicochemical degradation of the waste [2]. Irrespective of the mode of its origin, landfill leachates contain substantial amounts of micropollutants like organic compounds, pesticides, toxic residues, pathogens, heavy metals, dyes, microplastics and other harmful compounds that can pollute the soil and groundwater. These pollutants cause severe environmental pollution due to accelerated chemical oxygen demand (COD), presence of dyes and high nitrogen content due to ammonia and nitrogenous compounds [3]. High degree of variability is observed in landfill leachates based on the seasons, storage period and other geographical features [4]. Although the landfill leachate treatment is not a relatively new concept as it encompasses many conventional and currently existing technologies. But these methods cannot individually be recommended as fully effective in removing the micropollutants from

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landfill leachates [5]. This calls for development of integrated strategies and improvement of existing technology to cater to the heterogeneous nature of landfill leachates. Understanding the precise composition of the micropollutants in the landfill leachate is crucial to devise techniques for their removal and further treatment [6]. Despite several research endeavours related to landfill leachate treatment a wide knowledge gap still exists in this concept when these techniques are applied for onsite treatment over a long period of time. The performance and reproducibility of the results obtained in a laboratory scale when applied to the onsite treatment is one among the major challenges to the researchers working in this domain [7].

Taking into consideration the importance of this concept, the presented work critically reviews the emerging techniques and integrated approaches that can be used for the removal of micropollutants from the landfill leachates. This review work focuses equally on the compositional aspect of micropollutants to suggest and recommend the strategies for their mitigation. Further the limitations of each of the existing technologies and their possible improvement for revolutionizing the field of landfill leachate treatment is presented under various sections. Furthermore, the challenges and future directions in technological perspective for landfill leachate treatment are addressed.

2. Composition and characteristics of landfill leachate

During last decade, several countries in the world have seen continuous commercial and industrial growth to satisfy the need of affluent lifestyle which resulted into increased municipal and solid waste generation. Most commonly the municipal waste is dumped into landfill as it is the considered an economic option available. Leachate is generated when the inherent water present in the waste deposited in the landfills oozes out or when rain water mixes with the waste in landfills and percolates the soil to contaminate the nearby water sources. Landfill leachate is one of the major pollution caused by open dumping of municipal waste as the landfills are not engineered to collect liquid leachate [8,9]. The organic compound rich wastes in landfills goes through series of chemical and biological modifications. In new landfills which contains high amount of biodegradable waste, initially enters an anaerobic fermentation stage and produces volatile fatty acids (VFAs) [10]. Under high moisture content, acid fermentation takes place and releases free volatile fatty acids. This phase is known as acidogenic phase [11]. During the maturation phase of the landfill, methanogenic microbes grow and convert the volatile fatty acids into biogases like methane and carbon dioxide [12]. At this phase, the concentration of degradable organic matters is lower than the non-biodegradable matters [13]. As different types of wastes are dumped over the years, the different layer will be on different phases of conversion [14]. The characteristics of landfill leachate greatly depend on types of the wastes, state of decomposition, age of landfill, and the climate condition [15].

2.1. Characteristics of landfill leachate

Designing a treatment strategy for landfill leachate primarily requires an in-depth understanding about the composition and physicochemical characteristics of landfill leachate. This analysis serves as important checkpoints to evaluate the efficiency of the designed process, durability and reproducibility. There are different parameters to characterize the landfill leachate such as biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), pH, heavy metals and suspended solids [16]. The state of oxidation of carbon and biodegradability of organic compounds can be indicated by the ratio of BOD, COD and COD to TOC [17]. The composition of waste, seasons, temperature, precipitation and moisture content can alter the characteristics of leachate [11,18]. While oxidation reduction potential, concentration of metals, total and volatile suspended solids remains unaffected by seasonal changes, decreased COD and dissolved oxygen (DO) concentration results from high temperature in summer [19]. The landfill leachate composition and characteristics can be greatly affected by the age of landfill. Landfill older more than ten years is referred to as old while landfill between 5 and 10 years and older than 5 years are known as medium and young landfill respectively [20]. In new landfill leachate, low molecular weight organic compounds are present in high concentration. It has low pH and biodegradability index is also high. In addition, it contains several plasticizers and endocrine disruptors [21–23]. In stored landfill leachate (depending on their composition), high molecular weight components like humic acids and fulvic acid are present in high concentration, which increases the pH and decreases the biodegradability index. Stored landfill leachate contains low concentration of heavy metals as increased pH in stored landfill leachate reduces heavy metals solubility [14,24]. Some of the dissolved organic matter present in landfill leachate can absorb UV rays and light. This produces a dark color solution and it is known as chromophore dissolved matter [25,26]. Humic acids, fulvic acid and hydrophilic faction can be recovered when landfill leachate is treated with resin (combination of XAD-8 and cation exchanger) as the solubility of landfill leachate differs greatly [27]. The fourth fraction can be hydrophobic aromatic compounds which can interact with chlorine to produce by-products. Biodegradable compounds such as simple carbon chain structures are originated from initial decomposition of organic matter while the non-biodegradable components of landfill leachates are formed by condensation and polymerization of by-products from biodegradation [28,29]. Recently, pollutants like endocrine disrupting chemicals, personal and pharmaceutical care products such as antibiotics, stimulants, anti-inflammatory and beta blockers have been identified in landfill leachate. In addition to that disinfectants, their by-products and antibiotic resistance genes are also identified in landfill leachates which are considered to be a great threat to human health [30].

2.2. Composition of landfill leachate

Landfill leachate is composed of percolated rainwater, inherent water in waste, and water from the waste biodegradation. It contains dissolved organic matter, heavy metals, salts, chlorinated aliphatic and pesticides [31]. The detailed composition of municipal solid waste leachate is presented in Table 1.

Dissolved organic matter in landfill leachate is composed of various organic compounds such as low molecular weight volatile fatty acids, humic acid and fulvic acid [34].

Dissolved organic matter is a major portion of landfill leachate and it is a complex mixture. Therefore, it may affect the leachate composition.

Table 1
Composition of municipal solid waste leachate [32,33].

Components	Range	Unit
pH	7.29–8.61	mg/L
COD	580–1821	mg/L
BOD	76–701	mg/L
Total suspended solids	191–740	mg/L
Volatile suspended solids	72–329	mg/L
Total nitrogen	95–401	mg/L
Organic nitrogen	29–46	mg/L
Ammonia nitrogen	66–364	mg/L
Total phosphorus	1.4–15.7	mg/L
Magnesium	126–419	mg/L
Calcium	192–430	mg/L
Chlorides	490–1190	mg/L
Volatile dissolved solids	1248–2175	mg/L
Total dissolved solids	2969–6384	mg/L
Cadmium	0.022–0.13	mg/L
Zinc	0.22–0.435	mg/L
Chromium	0.05–0.08	mg/L
Mercury	0.005–0.017	mg/L
Ethylbenzene	2.4–89	μg/L
Xylene	9.3–225	μg/L
Toluene	0.3–182	μg/L

The composition of dissolved organic matter present in the leachate varies with the different phases of leachate biodegradation in the landfill. The concentration of fulvic acid varies from 6 to 30 % in aerobic and anaerobic leachates. Isolation and purification of leachate can help in better characterization of dissolved organic matter present [35]. Dissolved organic matter from leachate polluted groundwater showed the presence of fulvic acid (49 %), humic acids (8 %) and hydrophilic components (25 %) [11]. Leachate contains 95 % of low molecular weight volatile fatty acids and 1.3 % of high molecular weight acids [36]. In addition, it contains several volatile amines and alcoholic compounds. It has been observed that during the during methanogenesis compounds such as volatile fatty acids, amines and alcohols were absent.

Leachate also consists of humic substances which estimate about 60 % [37]. Composition of landfill leachate mixed with soil and water was observed to have high concentration of carbon, hydrogen, sulphur with low concentration of phenolic groups.

Maturation and stabilization of landfill can affect the concentration and composition of inorganic macro-components. During methanogenic phase with a pH range of 6.5–7.5, the concentration of magnesium (40–350 mg/L), calcium (20–600 mg/L), manganese (0.03–45 mg/L), iron (3–280 mg/L) and dissolved organic matter was low [38]. This is due to a high pH of the leachate. The sulphate concentration reported was low because methanogenic bacteria can reduce sulphate into sulphide. The concentration of chloride, potassium and sodium remain unchanged in methanogenic and acidogenic phases as the effects of sorption, precipitation and complexation on these compounds are negligible [39].

Ammonia and nitrogen are two important inorganic compounds present in landfill leachate. In leachate, ammonia is mainly generated from decomposition of proteins [40]. Ammonia is recalciterant to degradation. Therefore, it is present in high concentration in leachate. A study showed that the ammonia concentration was not reduced even after 30 years of aging of the landfill [41].

Heavy metals present in landfill leachate are low in concentration. The low concentration of heavy metal is due to sorption and precipitation of these heavy metals. Studies have shown that waste rich in organic matter harbours methanogenic bacteria which can absorb these heavy metals [42]. The anionic components such as sulphides (originated from reduction of sulphate) and carbonates are typically present in landfill. These sulphides and carbonates can interact and precipitate the cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu) and lead (Pb) [43,44]. Carbonates are present in high amount in landfill which have higher solubility to metals than sulphides although sulphide precipitation dominates the heavy metals immobilization. But it is not capable of chromium precipitation. Chromium is only precipitated by hydroxides. At neutral or high pH hydroxides and phosphates can also form precipitates with heavy metals. Sorption to colloids and complexation with inorganic and organic ligands are also known mechanisms for heavy metals immobilization. According to, a study reported that colloidal fraction is highly associated heavy metals. It was observed that significant concentration of chromium, lead and zinc are found in colloidal fraction [45].

Municipal solid wastes are the main source of xenobiotic compounds. Over last two decades, the concentration of xenobiotic compounds entering landfill has significantly decreased. Though countries with fewer restriction have seen presence of broad ranges of xenobiotic compounds [46]. The composition of xenobiotic compounds also varies with age, waste composition and landfill technologies. Mono-aromatic hydrocarbons such as benzene, xylenes, toluene, ethylbenzene and halogenated hydrocarbons like trichloroethylene and tetrachloroethylene are most abundantly found in landfill leachate In contrast, phenols and cresols are found in minor concentrations (in μgL^{-1}) [47]. Pesticides are class of xenobiotic compounds found in landfill leachate. Out of twenty one different pesticides identified in landfill, Mecoprop, Bentazon, 2-methyl-4-chlorophenoxyacetic acid (MCPA) are most commonly found along with chlorpropham, ametryn, dichlobenil, atrazine, hexazinon. Different surfactant used in shower gel and laundry detergents like benzene and naphthalate sulfonate are present in leachate in a concentration ranging from 1 to 10 mg/L [48]. Another type of surfactants, alkylphenol polyethoxylated and their metabolites are also found in landfill. Different phthalates like di-ethyl-phthalate, di-(2-hexylethyl)-phthalate, di-*n*-butyl-phthalate and their common metabolite phthalic acids are reported to be present in mg/L concentration in leachate [46]. The concentration of gasoline additive, methyl-tert-butyl-ether (MTBE) present in leachate was 30-35 $\mu g\ L^{-1}$. Synthetic cyclic ethers such as dioxanes and dioxolans with high odor and low odor intensity are generated from disposed coating and painting products and alkyle resin like materials. Adsorbable Organic Halogen (AOX) was present in the range of 200-5000 $\mu g\ L^{-1}$ [49,50].

3. Micropollutants & contaminants present in landfill leachate

Leachate is aroused from physicochemical changes in solid wastes that are hazardous and even have the potential to cause cancer [51]. Therefore, leachate is known as refractory wastewater and includes a wide range of pollutants in high concentrations. It is understood that inadequate management accompanies chemical generation. Leachate can be toxic, mutagenic, genotoxic, and have estrogenic effects which results in substantial harm to the ecosystem, including human beings [52]. Studies reveal that leachate has a complex chemical composition which may additionally contain several micropollutants in addition to common contaminants already present [53].

Landfill leachate contains a variety of micropollutants, including synthetic compounds like- phthalic acid esters (PAEs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs), pesticides, microplastics (MPs), *per*- and polyfluoroalkyl substances (PFAS), cleaning detergents, microplastic, steroids, etc. [22,54]. Despite being exist in very lower concentrations ($\mu g\ L^{-1}$ to $ng\ L^{-1}$ or even lower), micropollutants still significantly adversely affect ecosystems, the economy, and humans [55]. Fig. 1 represents various micropollutants and their toxic effects on humans.

Although modern landfills are well constructed to minimize environmental harm. However, the production of landfill leachate being full of resistant micropollutants is an unavoidable side effect and contaminates the neighbouring aquatic systems [56]. Some of the most reported micropollutants are discussed in detail below.

3.1. Phthalate esters

Phthalic acid diesters (PAEs), known as phthalates, are lipophilic compounds widely engaged in many cosmetics and personal care product These include nail paints, shampoo, deodorants, hair gels, body wash etc. They are also added to plastics to increase the malleability and flexibility of polymer chains (like making vinyl plastics synthesis). Besides that, they are used in paper coating, paints, and adhesives-making industries [21]. Actually, the production of PAEs began in 1920 and increased after 1950, as a result of the increased use of polyvinyl chloride (PCV) in transparent bags, plastic toys, medical appliances, construction, and insulation materials [57]. Among diverse applications, plastics industry currently uses roughly 65 % of all phthalates and it uses most frequently the phthalates having high molecular weight (HMWPs) [58]. Since phthalates favour physical binding instead of chemical. They leak and migrate into the environment and pose substantial risk to the environment [59]. These substances exhibit environmental stability, lyophilic characteristics, and a propensity for bioaccumulation [60]. In addition, the polymer matrix's strong environmental resilience guarantees years of possible phthalate release from completed goods.

PAEs pose a major risk because the landfills lack suitable environmental protection systems (such as leachate collection systems). Further, their widespread existence and resistance to degradation lead

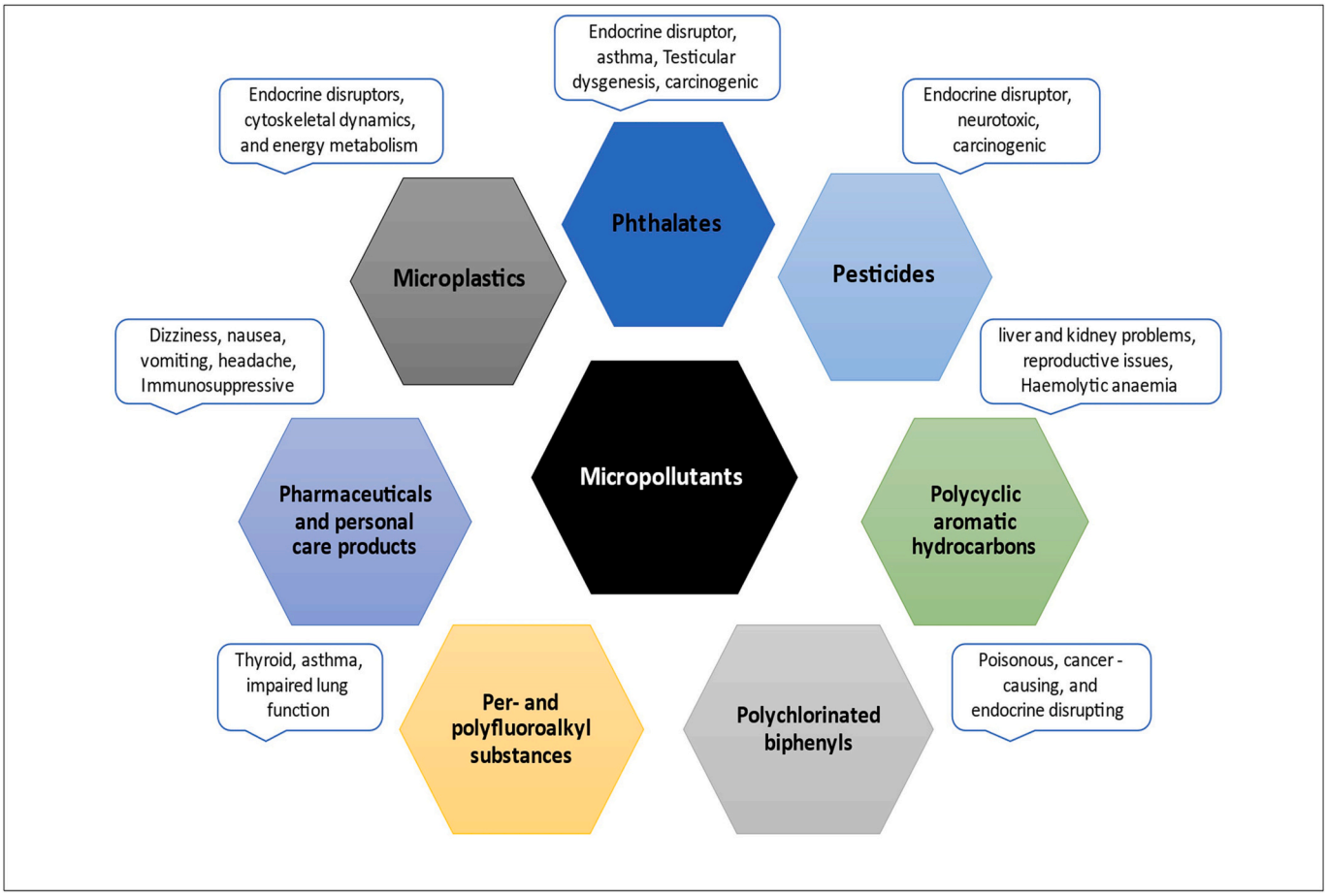


Fig. 1. Types of micropollutants present in landfill leachate and their harmful impacts on human beings.

to accumulation in aquatic habitats. Consequently, PAEs exposure not only risks the aquatic animals, it impacts their entire aquatic ecosystem including microorganisms, seaweed, fish, and invertebrates in seawater or limnetic zones [61]. Although it is believed that PAEs have low acute toxicity, but their breakdown products such as phthalic acid monoesters (PMEs) are harmful to animals [57]. They are detected in the gastrointestinal tract, and are regarded as endocrine disruptor (ED) chemicals by several environmental agencies like the US Environmental Protection Agency (USEPA) as well as European Environmental Agency (EEA) [62]. Besides the digestive system, they can be absorbed by the respiratory system, and some being more lipophilic including the most prevalent di (2-ethylhexyl) phthalate (DEHP) which can be absorbed through the skin [63]. After entering the body, they reach blood, and can cross the placental barrier [64].

Several PAEs, such as DEHP, dimethyl phthalate (DMP), diethyl phthalate (DEP), and dibutyl phthalate (DnBP) are recognised as hazardous micropollutants in different countries. Mohammadi et al., studied the leachate samples in Bushehr port (Iran) and reported a prohibitive range of PAEs of about 3.27 mg/ L, where DBP and DEPH are recorded as the most abundant ones [65]. Similarly, Kotowska et al., reported the presence of DEHP with the maximum concentrations up to 143 mg/ L in almost all the wastewater samples studied in Poland [66].

3.2. *Microplastics*

Microplastics (MPs) (<5 mm in size) are ubiquitous in landfill leachates and may enter the surrounding environments [67]. Depending upon their origin, MPs can be divided into- primary and secondary MPs. Primary MPs are intentionally produced of small-sized plastic, which can be traced in medications, textiles, cosmetics, and personal care goods. Whereas secondary MPs are produced as a result of the breakdown of massive plastic debris [68]. MPs are heterogeneous in nature and their characteristics are critical for their diffusion in the environment and bioavailability [69]. There are many studies coverings the prevalence, nature, sources, and effects of these MPs. MPs exert both direct and indirect negative impacts on living beings. These include disruption to the endocrine, cytoskeletal, and metabolism [60]. A research group investigated the impacts of polystyrene (PS) MPs in marine medaka (*Oryzias melastigma*) and observed tissue damage, sex-specific reproductive disruption, and transgenerational effects in the fish [70]. In another study, PS MPs exposure in mice resulted in excessive production of ROS, which lead to abnormal patterns of skeletal muscle regeneration, with suppressed myogenic differentiation of myosatellite cells and their redirection towards adipogenic differentiation [71]. Similar to this, repeated oral administration of polyethylene (PE) MPs to mice, results in higher neutrophils cells levels in the blood, tissue damage, disturbed immunological response, and altered numbers of live births, sex composition, and body weight of offsprings [72]. In another study, mice exposed to PE MPs during the gestation period caused metabolic disorders in the offsprings [73].

It is observed that substantial release of MPs into the environment generally happens due to improper waste management and anthropogenic activities. As a result, lot of plastic end up being buried in landfills and emerge as a significant source of microplastic pollution [74]. The plastic waste accumulated in these landfills is exposed to harsh environmental conditions. With complex biochemical reactions and physical changes such with varying pH (ranging from 4.5 to 9) MPs are transformed to harmful products [75]. All these actions cause the plastics to break into MPs resulting in smaller plastic debris.

However, the waste treatment management sector has not given

much consideration to the existence of MPs pollution. Research has not only examined the concentrations of MPs in leachates, but also assessed their risk towards ecosystem [51]. Mohammadi et al., reported an abundance of MPs with a size of >1000 μm in the leachate samples in Iran [65]. Su et al., observed a greater concentration (4.0–13.0 items L^{-1}) of MPs in leachate in Shanghai, China [76]. In the same region, polyethylene and polypropylene were the predominant polymers in landfills. The plastic dumped in these landfills lingers for decades, and the sizes vary between 100 and 1000 mm [77]. Despite their high levels, no study has looked at their long-term impacts on the environment.

3.3. Pesticides

Globally, around 1.2–2.5 million tons of pesticides are applied annually in agricultural system against the attack of fungi and other pest infestation [78]. They are used commercially as well as in domestic pest control. Their traces are found in landfills, incinerators, and composting plants. Pesticides include a variety of synthetic chemicals. The organochlorine pesticides possess slow degradation, high toxicity on living organisms, and long-range transmission capabilities. Therefore, these pesticides are banned in developed countries. But they are still used in several developing countries [79]. Nowadays, the use of pyrethroids has been growing over time, due to their superior effectiveness and less hazardous nature as compared to the previous insecticides like- organophosphate (OP), organochlorine (OC), and carbamates [80]. As a result, they became one of the three main groups of pesticides in 2015, controlling roughly 38 % of the market worldwide. The pyrethroids market stood at $1633.03 million globally in 2016 [80].

Numerous pesticides act as endocrine disruptors (EDs), neurotoxicants, immunotoxins, and carcinogens for both animals and humans. Pesticides like OCs, OPs etc., contribute to various life-threatening diseases like Alzheimer's and amyotrophic lateral sclerosis, but primarily to Parkinson's disease [81]. The pesticide exposure also leads to a higher incidence of coronary heart diseases, childhood brain tumours, and acute lymphocytic leukemia [82].

It is noticed that pesticide along with persistent chemicals, is frequently dumped as general garbage in municipal landfill sites without even prior separation or sufficient pre-treatment. During degradation into wastes, these toxic compounds get transported via leachate [83]. Currently, pesticides are leading emerging organic compounds, threatening aquatic life and the environment [84]. Varnosfaderany et al., studied the concentration of OCPs in the different samples of Zayandehrud River in Iran, and recorded high levels of total OCP concentrations ranging from 0.1 to 51.5 ng gL^{-1} dry weight in surface as well as in core sediments [85]. A research group investigated the prevalence of pesticides in the landfill leachate in Al Amirat, in Muscat. Numerous OCPs, including gamma benzene hexachloride (γ-BHC), delta hexachloride (δ-BHC), aldrin, heptachlor epoxide, endosulfan alpha, dichlorodiphenyldichloroethylene (Pp DDE), endrin, endosulfan beta, Dichlorodiphenyldichloroethane (Pp DDD) and endrine ketone were recorded from the samples. The two pesticides with the highest concentrations were endosulfan sulphate (range: 0.011–0.016 mg/L) and endrin aldehyde (0.003–0.063 mg/L). Although exceedingly low, their concentrations could hardly be ignored [86]. In another study of Al-Ghabawi landfill in the Ghabawi area, Jordan revealed the presence of DDTs (ranged from 2.16 μgL^{-1} to 3.38 μgL^{-1}), along with other OCPs in trace amounts in the leachate sample [87].

Fenton oxidation process is employed to remove a combination pf pesticides like chlorpyrifos, atrazine and chlorfenvinphos and observed to have seventeen fold increase in the removal of these micropollutants as compared to other conventional methods [88]. In another study with alachlor 33 %(*w*/w), degradation of the pesticide micropollutant was achieved using ozonation process [89].

3.4. Pharmaceutical and personal care products

Pharmaceuticals and personal care products (PPCPs) are regarded as emerging organic contaminants (EOCs), and have raised concerns among environmentalists. PPCPs with expiration dates are disposed of in landfills and accumulate in leachates. They generally exist in trace quantities between ng L^{-1} and g/L in drinking water, groundwater, surface water, wastewater, and other aquatic environments [90]. However, it is recorded that the majority of PPCPs exert adverse physiological effects, even at this low concentration [91]. The ongoing discharge of PPCPs into the environment could have unintended negative impacts on ecological species by contaminating water supplies for a longer period of time [92]. Once ingested, the PPCPs in the environment have the potential to bio-accumulate in living beings and have negative impacts. The harmful effects include antibiotic resistance, endocrine disruptions, and primary productivity inhibition [61]. As a result, it has become pertinent to consider their occurrence, distribution, migration, transformation, and potential dangers in our environment.

Yu et al., studied the effect of seasonal variations, like rain, on the levels of PPCPs in leachate from China and recorded a significant difference in the PPCPs concentration with 17.0 μg L^{-1} in the months from April to September, while only 3.8 μg L^{-1} in the remaining months [93]. Similarly, total PPCPs range from 0.39 to 349 μg L^{-1} was reported in the landfill leachates in Shanghai [90]. Interestingly, caffeine is also a commonly reported compound, with high concentrations in different water matrices. Its concentration generally ranges between 1 and 174 μg L^{-1} in surface water bodies, and sometimes reaches to 499 μg L^{-1} in Indian wastewater samples [94]. Similarly, in Japanese streams, caffeine concentration is reported to be around 5.3 μg L^{-1} [95]. Irrigation water source in Saudi Arabia is also tested with high concentrations of caffeine (21 μg L^{-1}), diclofenac (1.4 μg L^{-1}), paracetamol (3.1 μg L^{-1}), and diazinon (1 μg L^{-1}) [96]. The reported studies demonstrate that the micropollutants are not managed properly and reaches to the landfill leachate.

3.5. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are another category of common pollutants released into the environment via landfill leachate and generally originate from both natural and anthropogenic activities. They are originated from pyrolysis, car exhaust, and coal refinement processes [97]. These typically have two or more fused aromatic benzene rings, imparting lipophilic nature with comparatively high desorption activation energy. Based on their structures, PAHs can be divided into low and high molecular weight [98]. The water solubility of PAHs decreases almost linearly with increasing molecular mass. PAHs are also employed in manufacturing plastic goods, cosmetics, personal care items, and pesticides. However, their high mutagenic, carcinogenic, and teratogenic potential has drawn much attention in water, air, and soil pollution research. The data suggest that carcinogenicity potential increases with escalating molecular weight.

Additionally, they are suspected of being EDs and weakening the immune system [99]. They persist in nature for quite a long time due to their high chemical stability and resistance. These are bio-recalcitrant and have lower aqueous solubility, which did not let traditional physicochemical and biological processes to remove them. Furthermore, presence of low molecular weight contaminants hinders their removal [100]. Ates and Argun recorded the hazardous level of 10–58 μg L^{-1} PAHs in leachate present in Konya province, Turkey [101]. Similarly Qi et al., found the concentration of 5.81–1263 μg L^{-1} in the landfill leachate in China [102].

3.6. Per- and polyfluoroalkyl substances

Per- and polyfluoroalkyl substances (PFAS), are a large family of synthetic fluorinated compounds employed in an extensive range of

commercial applications since the 1950s. These possess exceptionally high thermal and chemical stability and are found extensively in municipal landfills. From landfilled wastes, the PFAS infiltrate the leachate through a chain of diverse physical, chemical, and biological processes. This process is common in landfill settings and can contaminate nearby soil and groundwater which is a threat to both human health and ecosystems [103]. Thus, the management of PFAS becomes challenging, mainly due to their widespread usage and recalcitrant degradation.

It is understood that the strongest bond in PFAS is the carbon and fluorine bond which is due to the extremely electronegative characteristic of fluorine. Thus, C—F chain segment the molecule shows high resistivity towards degradation [104]. Among the different PFAS, the most researched PFAS are- perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). The MSW leachates can have PFOA concentrations in the range of 10 μg L^{-1} and PFOS about 1 μg L^{-1} in the United States [105], and in Europe [106].

PFAS began to draw the attention of scientific communities, regulatory organizations, and the general public in the late 1990s, because of their widespread occurrence [107]. The exposure of PFAS can leads to thyroid, asthma, impaired lung function, negative impacts on immune system responses, testicular tumours, and cancers of the liver and renal, kidney etc. [108]. As a result, the USEPA issued a drinking water health advice of 70 ng L^{-1} for the total of PFOA and PFOS, effective from May 2016 [109]. It is predicted that between 563 and 638 kg of PFAS is getting transferred from American landfills to the influent of municipal wastewater treatment plants (WWTPs) in 2013 [105]. It is noticed that the conventional leachate treatment processes are not good enough for the entire degradation of PFAS [110].

3.7. Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants with bioaccumulation potential in living beings. PCBs usually occur as a mixture of chlorinated biphenyl molecules containing 1–10 chlorines per molecule. There are 209 possible congeners of PCBs. They are persistent, lipophilic, hydrophobic, and prone to long-range transport of synthetic chemicals used in electrical equipment until the 1970s. After that, PCBs are also utilized in transformer cooling oils, lubricants in oils and greases, dielectric fluids of capacitors, insecticides, heat transfer fluids, preservatives, and impregnating agents [111]. Their wide use is the reason behind high PCB concentration detection in chlorinated goods or as by-products during the manufacture of solvents and polymer resins [112]. Environmental PCB exposure is a serious health problem due to its poisonous, cancer-causing, and endocrine-disrupting properties [113]. In the 1960–70s, there was a growing understanding of their environmental presence, and the health threats to life resulted in a federal ban on their sales and manufacture in 1979. Presently, roughly 100 t of PCBs is anticipated to be present only in Norway [114]. Tracking the release of PCB is a complicated task because the chief PCB sources might not reflect prior but rather an accidental generation. The Stockholm Convention mentions PCBs as compounds that may be generated and accidentally released from anthropogenic sources. Thus, it can be concluded that PCB issue might not get resolved without a more profound comprehension of its occurrence and fate during recycling and disposal. Table 2 discusses about the various

Table 2
A list of emerging micropollutants found in the landfill leachate.

Sr. no.	Micropollutants	Toxic effects	Country	Concentration (μg L^{-1})	Reference
1.	Phthalates				
	Diethyl phthalate (DEP)	Asthma, antioxidants enzymes alteration	Poland	<LOD-14.5	[66]
	Di(2-ethylhexyl) phthalate (DEHP)	Endocrine disruptor	Poland	73.9	[57]
			Poland	Up to 536	[115]
	Di-*n*-butyl phthalate (DBP)	Affect kidney and liver health.	China	Up to 83.3	[116]
	Dimethyl phthalate (DMP)	Testicular dysgenesis, obesity, asthma, antioxidants enzymes alteration	Poland	2.46–24.6	[66]
2.	Microplastics	Disruptions to the endocrine system, cytoskeletal dynamics, and energy metabolism	China	235.4[a]	[117]
			China	0.42 to 24.58[a]	[77]
			Serbia, Bosnia, and Herzegovina	640–2160	[118]
3.	Pesticides				
	Organochlorine pesticides	Endocrine disruptors, neurotoxicants, and carcinogens	China	0.03–0.20	[102]
	Endrin aldehyde	Immunotoxins and carcinogens	Oman	3–63	[86]
4.	Pharmaceuticals & personal care products				
	Diclofenac	Gastrointestinal problems	India	898	[119]
	Sulfamethazine	Dizziness, nausea, vomiting, headache	China	16	[102]
	Sulfadiazine	Breathing difficulty	China	0.23	[90]
	Camphor	Liver damage	USA	62.4	[120]
	Ibuprofen	Nausea, vomiting, heartburn, Immunosuppressive	India	136	[119]
	Caffeine	Increase in anxiety and disturbs sleeping	Saudi Arabia	21	[96]
			India	499	[94]
	Bisphenol A	Endocrine disruptor	Serbia, Bosnia and Herzegovina	700-2720	[118]
5.	Polyaromatic hydrocarbons (PAHs)				
	Acenaphthylene		Turkey	58.47	[101]
	Acenaphthene	Eye and skin irritation.	Turkey	25.40	[101]
			Kenya	1.0	[121]
	Naphthalene	Haemolytic anaemia	Kenya	0.06	[121]
	Benzo(*a*)pyrene	Reproductive issues	France	0.051	[122]
6.	Per- and polyfluoroalkyl substances				
	Perfluorooctanoic acid (PFOA)	Thyroid, asthma, impaired lung function	USA	10	[105]
	Perfluorooctanesulfonic acid (PFOS)	Testicular tumours and cancers of liver	USA	1	[105]
7.	Polychlorinated biphenyls (PCBs)	Poisonous, cancer-causing, and endocrine-disrupting	Oman	500–1400	[86]

LOD - limit of detection.
[a] Item/L.

micropollutants, their toxic effects, origin and determined concentrations.

4. Critical analysis on micropollutant removal technologies and future direction

The heterogeneous nature of the micropollutants present in the leachate makes it inevitable to use efficient and integrated strategies for the removal of micropollutants.

The major technologies used for the removal of micropollutants from landfill leachate are summarized in Fig. 2. Each of the listed technologies have the characteristic features and associated limitations that require critical focus in future to make them sustainable methods for micropollutant removal from landfill leachate.

4.1. Electrochemical treatment

Electrochemical oxidation method was reported to be a highly efficient method for the mineralization of micropollutants as it does not produce or leaves any toxic waste residues after the treatment period [123]. The efficiency of method depends upon the choice of electrodes. Although conventionally used anodes were also efficient but they contain critical raw materials (CRMs) that were highly prone to corrosion, low efficacy, easily deactivation. Therefore, newly introduced boron doped diamonds (BDD) contributed in high mineralization efficiency. Various studies have reported the removal of harmful pollutants such as polychlorinated dibenzo-p-dioxins and dibenzofurans, polychlorobiphenyls, polycyclic aromatic compounds, organochlorine pesticides by electrochemical method. A recent study carried out electrochemical treatment of leachate collected from municipal waste with the help of boron doped diamond (BDD) anodes [124]. The study reported the removal of >95 % poly- and perfluoroalkyl substances (PFAS) [125]. The collected samples treated with membrane bioreactor (MBR) such as raw leachate and leachate with no ammonia content were operated at the current densities between 200 and 800 A/m^2. It was reported that the absence of ammonia does not have any significant impact on mineralization process. Moreover, study reported the removal of 17 PFAS with estimated value ($\sum$17PFAS = 3456 ng L^{-1}). The maximum removal of PFAS was observed at 800 A/m^2. MBR treatment significantly enhanced the energy efficiency of ELOX leachate treatment. Another study reported the elimination of methiocarb and bisphenol-A through electrochemical method [126].

4.2. Fenton-like oxidation process

Heterogenous Fenton process is recently introduced process for the treatment of landfill leachate. A recent study used Iron Molybdophosphahate (FeMoPO) as a catalyst at dose of 1.75 g/L with pH 2, Hydrogen peroxide (H_2O_2) concentration 9 mM which was capable of removing 84.9 % COD and 71 % TOC using Box-Behnken response surface design [127]. Another study by Singa et al. [128] used Photo-Fenton oxidation process using Fe^{2+} and H_2O_2 as oxidizing agent. It was observed that maximum COD removal of 68 % was observed at the dosages of Fenton reagents i.e., H_2O_2 hydrogen peroxide and Fe^{2+} were optimum at 0.09 mol/L and 0.03 mol/L respectively. In a study, zirconia supported copper catalyst (Cu/ZrO_2) in heterogenous Fenton oxidation was used [129]. It was observed that employed process showen high catalytic activity with catalyst dose of 200 mg/L at temperature of 70 °C with pH 5 and 30 mL/L dose of H_2O_2 dose for the time period of 150 min. A study carried out the removal of numerous micropollutants including polycyclic aromatic hydrocarbons (PAHs), phthalates, alkylphenols and pesticides using Fenton and ozone oxidation process [130]. The Fenton and ozone oxidation process was carried out at different doses and reaction time. It was observed that employed process was able to eliminate di-(2-Ethylhexyl) phthalate, 4-nonylphenol and 4-tert-octylphenol by 5–100 % but its efficiency reduced for PAHs including four and more ring members. Another study carried out the degradation of methylparaben using Fenton, photo-Fenton and electro-Fenton process [131]. It was observed that electro-Fenton process exhibited excellent results. Thetarget pollutant was removed in 10 min by using $Ti/Ru_{0,3}$ $Ti_{0,7}O_2$ as cathode where as other methods show degradation in 20 and 16 min by Fenton and photo-Fenton process respectively. The optimum conditions in electro-Fenton process were 4 mg/L Fe^{2+}, j = 25 mA/cm^2 and 0.05 mol/l sodium sulfate. A study, utilized landfill effluent with high COD and investigated processes such as electro-Fenton (EF) and 24hotoelectron-Fenton processes in a continuous-flow reactor using boron-doped diamond anode (Nb/BDD) [131]. The results showed the COD removal of about 66 %, 68 % and 89 % with an energy consumption of

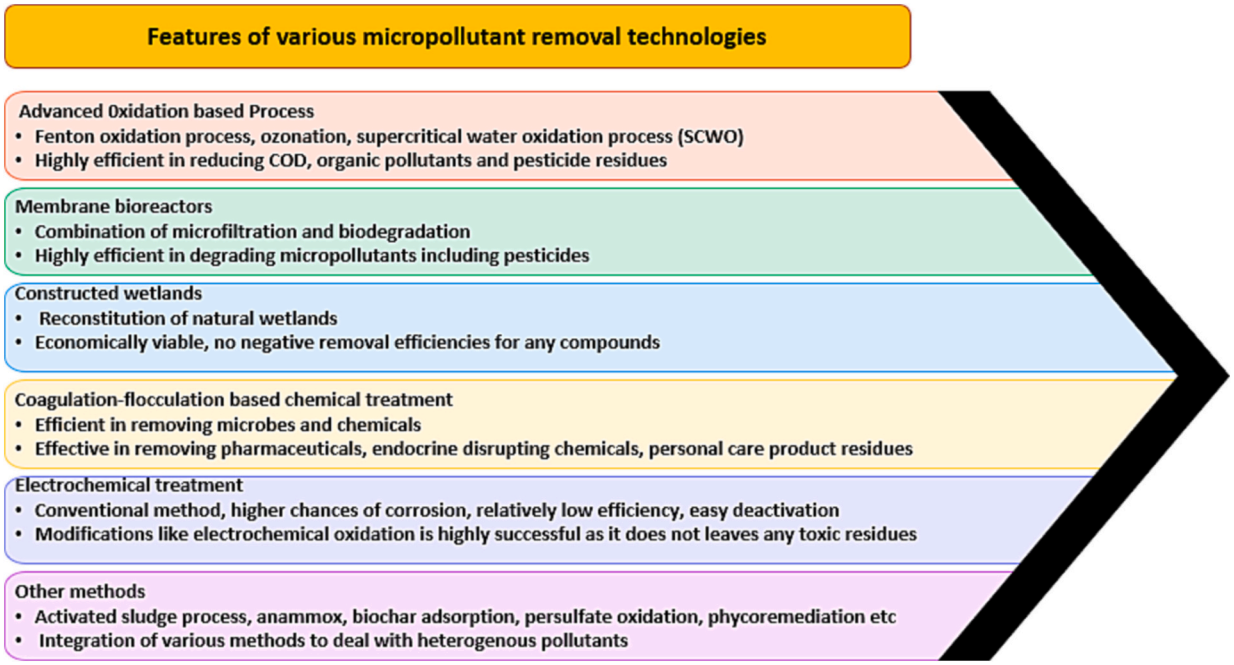


Fig. 2. Technologies for removal of micropollutants from landfill leachate.

19.41, 17.61 and 17.59 kWh kg COD^{-1} for electro-Fenton, photo electro-Fenton-UVA and photo electro-Fenton -UVC respectively during 4 h procedure. The byproducts formed during the process were the acetic and formic acids as well as NO_2^-, NO_3^-, and NH_4^+. A study carried out the biological and chemical degradation of fluconazole, clotrimazole, climbazole, and epoxiconazole by activated sludge. In the study, two novel Gram-negative bacterial strains- *Stenotrophomonas maltophilia* AsPCl2.3 and *Pseudomonas monteilii* LB2 were used. The method used UV treatment, Fenton reaction, and their combination [132]. It was observed that Fenton reaction easily removed all of target pollutants whereas biological method efficiently removed only climbazole. Similarly, another study carried out batch pilot plant experiments to study efficacy of Powdered Activated Carbon (PAC)-Activated Sludge (AS) tank for the removal of micropollutants [133]. It was reported that PAC with 2.5 mg dose contributed to 80 % pollutant removal. The characterization of removed organic matter was done with size exclusion chromatography coupled with organic carbon detection (SEC-OCD).

4.3. Ozonation

Ozonation is emerging as another productive candidate in oxidative treatment of landfill leachate. A study carried out the ozonation of atrazine, bisphenol A, carbamazepine and alachlor by semi-continuous method [134]. It was found that 0.95 g of ozone was consumed for the removal of >99 % of target pollutants bisphenol A, carbamazepine. A high ozone reactivity was observed during the process i.e., kO3 > 10^4 M^{-1} s^{-1}. The study also suggested that it is not authenticated to predict micropollutants level with hydroxyl formation yield. Yang and his co-workers proposed UVA254-based model for sensing of micropollutants using different spectroscopic measurements. Ozone based oxidative process application in high dissolved organic matter (DOM) was performed in a study [135]. The study was carried out using advanced oxidation process aided with heterogeneous catalyst along with O_3/H_2O_2 process for enhancement of indirect oxidation. It was reported that O_3/H_2O_2 process was more energy-efficient as compared to others. The catalytic process exhibited its efficiency when the chemical oxygen demand (COD) removal was <35 %. In another study introduced advanced oxidation process called as hybrid sono-electrocoagulation process for landfill leachate treatment [136]. Response surface methodology (RSM) and central composite design (CCD) approaches were used to study pH, reaction time, direct electrical current in developed process. It was observed that under the optimum conditions of pH: 5.7 with 80 min reaction time and 1.9 A direct current approximately 86 % COD was removed. A study employed packed bubble column for landfill leachates treatment and developed new method for biotransformation through ozonation [137]. The ozone columns were packed with lava rocks or metal pall rings (LBC or MBC). It was observed that with 8.35 mg dose of ozone, there was 32 % and 46 % COD removal in MBC and LBC. The highest O_3 utilization efficiency (89 %) and hydroxyl radical (OH) exposure rate (3.0×10^{-10} M s) were observed in LBC with lowest energy consumption (E_{EO}) for COD removal of 18 kWh/m^3. A recent study carried out the heterogeneous catalytic ozonation of landfill waste using Fe incorporated Ni − induced C−Al_2O_3−framework ($_{Ni}$CAF) composite [138]. Fe−$_{Ni}$CAF catalyst was synthesized for efficient catalytic ozonation. It was observed that at 4 g·L^{-1} dose of Fe−$_{Ni}$CAF, there was 100 % COD removal even at high concentration of pollutants. The efficacy of Fe−$_{Ni}$CAF/O_3 process was enhanced by the addition of hydrogen peroxide (H_2O_2) and peroxymonosulfate (PMS) due to the generation of hydroxyl radical (•OH) and singlet oxygen ($^1O_2$). A study carried out the ozonation of ^{14}C labelled micropollutants and converted them into ^{14}C labelled transformation products. $^{14}CO_2$ traps introduction shown that partial mineralization in all compounds except propyl-labelled bisphenol A and *O*-methyl labelled naproxen [139]. It was observed that after ozonization micropollutants shown high adsorption at powdered activated carbon. But adsorption rate decreased if high level of ozone dose was used during ozonation. A research group studied the impact of ozonation on adsorption properties of pollutants [140]. The studies revealed that ozonation decreases affinity of organic pollutants towards the activated carbon through site competition. They combined nitrification-Anammox, O_3/H_2O_2, and a granular activated carbon filtration (GAC) processes for the removal of total nitrogen, COD and micropollutants such as atrazine, alachlor, carbamazepine, and bisphenol A. The results revealed that there was >90 %, 80 % and 95 % removal of total nitrogen, COD and micropollutants respectively.

4.4. Supercritical water oxidation process (SCWO)

Degradation of naphthalene using supercritical water oxidation process (SCWO) was carried out in a recent study [141]. It was observed that employed method caused >98 % mineralization of naphthalene with the production of derivatives of aldehyde, propanoic acid, benzene acetic acid and benzo-furan as by products.

4.5. Constructed wetland for micropollutant removal

Constructed wetlands (CWs) are reconstitution systems of natural wetlands that are well-known for the betterment of water quality. A consortium of water, microorganisms, substrates, and plants can act simultaneously to either reduce or eliminate distinct compounds (pollutants) during the treatment. Micropollutants (MPs) have been inviting the attention of the scientists as they mostly present in trace amounts, and even after undergoing conventional treatments they ultimately end up in aquatic resources [142]. Aquaculture farms are potent sources of MPs because of the medications and artificial feeds used for aquatic animals. Influents, effluents and aquatic food products contain MPs whose removal is crucial to run an environmentally sustainable aquaculture [143]. Although both are capable of degrading organic MPs but advanced oxidation technologies are expensive than CWs. With this regard, CWs are opted due to their low cost of implementation, operation, and maintenance. Although CWs consume space and time, they sound interesting and safe due to the absence of toxic intermediate products. As study performed the removal of the European Union's eight priority micropollutants (polycyclic aromatic hydrocarbons) by three different treatment methods [144]. About 48 % of removal efficiency was achieved with CWs. No negative removal efficiencies for any compounds were reported in CWs by the authors. CWs performed relatively better than the stabilization ponds in eliminating the priority MPs. An interesting piece of research was accomplished [145] in which the distribution of MPs and lipids in various compartments of a two-stage Vertical Flow Constructed Wetland in France was investigated [145]. This would aid the operators to better understand the infiltration processes in the sludge treatment plants and develop strategies to specifically manage sludge. Most of the MPs were found in the top layers of the plant and their diffusion and settlement at the bottom lines was unavoidable.

Removal efficiency of acetaminophen (ACT) in hospital wastewater by vertical flow CWs and peroxidase enzymes generated by certain plants was studied in a study [146]. ACT is one of the major MPs in hospital wastewater as it is one of the highly prescribed drugs. *Scirpus validus*, a plant that generates peroxidase enzymes, was thoroughly checked for its capability to alleviate MPs' stress along with a pilot scale CW. Results showed that the vertical flow CW treatment plant removed initial high concentrations of ACT and nutrients to a recommended level for drinking purposes. The wastewater discharged finally met the standards of Thailand and Vietnam. A study monitored urban stormwater treatment and removal of heavy metals by CWs in all the seasons [147]. Removal efficiencies of MPs were more than97 percentage during most of the seasons. CWs can resolve the diffusion of MPs into the environment as the technology is decentralized with coexisting physical, chemical and biological processes. A vertical flow constructed wetlands (CW) was used with combination of substrates, i.e., gravel, sand, pine bark, zeolite and expanded clay to treat landfill leachate [148]. The

wetland systems were planted with *Phragmites australis*. It was observed that developed system removed heavy metals such as Zn, Ni, Cu, Cr by >50 % with total nitrogen reduction of about 70 %.

4.6. Advanced oxidation process

One of the robust and efficient means of removing the micro-pollutants (MPs) in the leachates, which are hitherto difficult to be eradicated by conventional means, is by exploiting the power of oxidation. Some of the recommended processes making use of this strategy include ozonation, powder activated carbon (PAC), granular activated carbon (GAC) and advanced oxidation processes (AOPs) [55]. Each of these specific techniques has its own merits and demerits. Though GAC helps adsorption and physical removal of most of the OMPs, its efficiency is dependent on the frequency of regeneration of GAC. The problem with ozonation is the generation of harmful by-products whose removal may require additional treatment later [149].

A recent study has revealed the successful removal of sixteen micropollutants, including alkylphenols and phthalates (both of which arising from the plastic waste, detergent packages and cosmetics), polycyclic aromatic hydrocarbons (PAHs) and few insecticides. The degradation potential was found t excellent, except for PAHs with four or more rings in their structure. Even though removal efficacy was found better for Fenton oxidation when compared to ozonation, the former showed more degradation products of higher molecular weight [88].

A broad range of organic micropollutants can be efficiently degraded by advanced oxidation processes (AOP) to increase the potability of water by ensuring the breakdown of complex organic material into smaller carbon chains containing more assimilable organic carbon (AOC). But this method has a few limitations - i) more AOC can potentially attract more bacterial growth ii) undesired by-products like bromate and nitrate, products of incomplete mineralization of OMPS etc. will be formed. A large-scale study conducted in the Netherlands combining AOP and Managed aquifer recharge and recovery (MARR) (has established that both these techniques complement each other in OMP removal, without compromising on the inorganic chemistry and biological stability of water. Hence the above method could be exploited as a promising technology for reducing the MPs in drinking water [150].

AOP is a recent approach in Europe, where the existing common methods for OMP removal include GAC and ozonation [151]. One of the first countries to implement legal regulations on the level of micro-pollutants in wastewater treatment plant effluents, was Switzerland. In their strategy, it is envisaged that such an advanced treatment method must have a very strong scientific basis, technical and economic feasibility, and societal acceptability. Therefore, only such holistic and sustainable approaches would turn out to be successful. The removal of OMPs by way of a tertiary water treatment was studied for four months in Germany In the process two methods were applied including: AOP (making use of Hydrogen peroxide and UV rays) and GAC with OMP removal efficiencies of about 76 % and 90 % respectively. Though the latter method had higher removal efficacy in the first few weeks, it showed a diminishing efficacy rate with time, whereas the AOP method when optimized at 40 ppm hydrogen peroxide and 10 kJ/m^2 UV-C light showen excellent OMP removal efficacy to the tune of almost 97 %. The low resource requirement and possible reuse of Hydrogen peroxide in the later stages, makes this approach more in line with circular economy [152].

Apart from OMPs, several metals contribute to inorganic MPs in wastewater, the removal of which are also being investigated. Chitosan was successfully used for removal of MPs owing to its properties like miscibility with other polymers, good hydrophobicity, biodegradability and low toxicity [153]. Another successful strategy was recently reported which made use of β–CD–CS–EDTA (a cross-linking polymer based on β-cyclodextrin (CD), chitosan (CS) and EDTA) for the removal of both OMPs and heavy metal ions simultaneously from wastewater [154].

4.7. Membrane bioreactors

Membrane bioreactors which combine biodegradation and micro-filtration have been useful for treating old landfill leachates particularly when conventional processes turn inefficient. It is deemed more efficient due to separation by filtration instead of gravity and longer sludge retention time. Improved decomposition of MPs was observed in MBR systems due to their ability to maintain higher sludge concentrations thereby enhancing removal efficiencies [155]. With a view to understand the MP behavioural dynamics during MBR removal, modeling studies were carried out on sorption and biodegradation by calibrating various parameters [156]. First generation MBRs were costlier owing to their configuration wherein the membrane modules were located outside the aerobic tank used to supply oxygen for the microbes doing the biodegradation. The positive traits of this system include easier module replacement, cleaning and maintenance [156]. Later, different types of integrated and hybrid MBR configurations were successfully tested. One such hybrid MBR with nanofiltration capability was used for the treatment of textile industry effluent [157] and an electrically enhanced MBR was used for the removal of metals and organics [158].

Anaerobic-aerobic bioreactors result in lesser footprint when compared to the aerobic systems. Some of the specific advantages include handling large variation in organic loading, easier switching to non-working mode in case of lower load, conversion of 90 % biodegradable organics into biogas, generation of lower biomass and ability to tolerate high quantities of organics and fats [159]. An aerobic -anaerobic MBR was shown to successfully remove the pesticide atrazine from waste water [160]. Successful removal of MPs by utilizing the membrane biofouling layer was demonstrated using MBRs which were hitherto not possible by ultrafiltration or microfiltration membranes. MP removal efficiency of such a system was found to be dependent on the microbial flora forming the biofilm on the membrane surface [161]. The efficacy of MBRs depends on the type and composition of wastewater to be treated. Hence more experiments need to be performed to evaluate the performance of high retention and hybrid MBRs with a view to suit each country's requirements based on factors like scaling up, economic feasibility and long term sustainability.

4.8. Coagulation-flocculation based chemical treatment

Among the various MPs' removal processes, coagulation-flocculation has been playing a vital role in controlling the pollutants and microbes. It involves destabilization of particles in water/wastewater by neutralizing the particle charges, followed by agglomeration to end up with filterable and settleable macro-flocculants [162]. Coagulants and flocculants are organic/inorganic chemicals being used for the above mentioned process. The dissolved organic matter of leachate can influence the microbial community, changes the transport behavior of heavy metals, interact with different inorganic matter, leads to membrane fouling and decreases the effluent quality of the coagulation process [18]. A research group optimized and predicted the appropriate coagulant dose to eliminate organic MPs using four mathematical models based on turbidity and related environmental parameters [163]. Another research group performed preliminarily sorption potential of three different categories of MPs (pharmaceutical, endocrine-disrupting and personal care) on to polystyrene and polyethylene, which are widely used microplastics in recent times [164]. Microplastics serve as transport vehicles for MPs in the natural ecosystem and food chain. Researchers treated this sorption process with a coagulation method to remove the microplastics. Sorption of antihypertensive drugs (valsartan and losartan) with polystyrene was evident. No sorption of bisphenol A, parabens and sulfamethoxazole was observed. Addition of ferrous sulphate or magnesium sulphate was effective for polystyrene removal. Appreciable removal of polyethylene was obtained when magnesium sulphate was added. An elaborative study revealed that the removal efficiency was more notable with polystyrene (92.4 %) than

polyethylene (72.1 %). Similarly, another research group tried the addition of several coagulants and flocculants to raw wastewater which led to 66.6 to 97.3 % of microplastic transfer to the floating or settled sludge, ensuring effective microplastic removal in the primary clarifier [165]. Positive impact of aqueous solution of polyaluminium chloride resulted in 90 % removal. Authors concluded that this process of coagulation and flocculation would reinforce the safe usage of the sludge in the agricultural sector.

Combined effect of activated carbon with coagulants and polymers in treating municipal wastewater both in lab scale and in pilot plant scale was evidenced [166]. The MPs (suspended solids based) removal percentage was 84.40–91.30 % with activated carbon alone that increased to 88.90–93.60 % by addition of coagulant. The process became more viable by addition of polymer (flocculant). It was observed that as the size of flocs increased it made its separation easier. Combined sewer overflows (CSO) consist of overspill of untreated sewer wastewater during wet weather conditions. They act as reservoirs of different MPs. A study conducted by [167] consisted of coagulation, flocculation and sedimentation processes, followed by ozonation to enhance the primary treatment of CSO. The treated effluents exhibited insignificant levels of acute toxicity, enabling the feasibility of the combinations to treat such overflows with maximum removal of MPs. Geosmin and 2-methylisoborneol (2-MIB) are problematic algal MPs which are categorized as taste and odor compounds in drinking water treatment plants. Cyanobacteria and actinomycetes are the causative agents of such algal MPs. A researcher reported the effective application of powdered activated carbon (using ball mill) and permanganate oxidation combined with coagulation to control the taste and odor of MPs in conventional drinking water treatment plants [168]. The process results in simultaneous adsorption of MPs. Pilot scale trials in drinking water treatment plants revealed the suitability of the experiments with maximal adsorption. Coagulation-flocculation process also plays an inevitable role in the leather industries. One of the key wet-end processes in tanneries is dyeing which threatens the ecological equilibrium and increases chemical oxygen demand of tannery effluents. Another researcher group achieved significant dye removal in tannery wastewater, using coagulation-flocculation along with adsorption processes [169]. A novel activated carbon compound was prepared by pyrolysis (microwave-assisted) of an organic naive precursor extracted from the sludge of the tannery wastewater treatment plant and reached 85.2 % dye removal.

A study reported the use of a coagulation-flocculation process for the pre-treatment and removal of various micropollutants including surfactants and pharmaceuticals such as cationic surfactants, phenols and pharmaceuticals such as 5-methylbenzotriazole, ibuprofen, carbamazepine, and metoprolol [170]. This method involves the use of plant-based materials such as tannin-based product and use of tannin coagulant for nitrogen recovery using membrane contactor technology. Response Surface Methodology (RSM) was used for standardization of reaction conditions such as pH 7.3. This technology reported the removal of Iron (Fe) (92 %), Titanium (Ti) (91 %), Chromium (Cr) (68 %), Aluminium (Al) (52 %), Barium (Ba) (48 %) and Vanadium (V) (44 %). The employed combined technology also assisted the removal of TP, TOC and TN of 47 %, 15 %, and 4 % respectively and NH_3–N removal increased by 20 %. Another processes known as sequential coagulation and electro-oxidation (EO) processes were employed to treat landfill leachate and complex wastewater using Box-Behnken design of RSM [171]. This method involved the use of poly aluminium chloride (PAC) as a coagulant to reduce the high pollutant concentration before electro-oxidation process. In the electro-oxidation process multi-metal oxide doped Ti (MMO/Ti), Pt doped Ti (Pt/Ti), and graphite were used as anode and stainless steel was used as cathode. It was observed that method in which Pt/Ti anode was used under 1.25A current and pH 5, COD, UV_{254}, and CN removal efficiencies were observed to be 52.8, 68.1, and 85.6 % respectively.

4.9. Other methods

The complex and heterogeneous nature of micropollutants in landfill leachates calls for advanced and modified treatment processes that can effectively remove these pollutants with greater degree of reproducibility and sensitivity. Such methods are often combinations of conventional treatment methods or optimized processes derived from these traditional treatment processes. Nevertheless, each of these treatment strategies has their own advantages and limitations in removal of micropollutants from landfill leachates as summarized in Table 3.

Table 3
Comparison of treatment techniques used for micropollutant removal from landfill leachate.

Method	Advantages	Limitations	References
Activated sludge process	Compatible with any volume of leachate, Easy to implement and maintain	High energy and capital investment, Requires regular monitoring	[172]
Rotating biological contactors (RBC)	Low energy consumption, Relatively simple	High capital investment, Low performance efficiency	[173]
Anaerobic ammonium oxidation (Anammox)	Low cost technique	Long start up time	[174]
Biochar adsorption	Waste valorisation technique High efficiency in removing micropollutants	High power and energy investment for biochar formation	[175]
Persulfate oxidation	Broad range of pollutants can be targeted, Accelerated reaction speed	High cost of electrodes used, Short service life of electrode	[176]
Aerobic methane oxidation coupled to denitrification	Alternative solution for nitrogen removal of NO_3 and NO_2	High initiation and maintenance cost, Difficulty in process optimization	[177]
Membrane biofilm reactor	Most efficient in carrying out oxidation and reduction reaction for wide array of pollutants	Difficulty in controlling the growth of complex microbial community in biofilm	[178]
Sequential batch reactor	Flexibility in operation, High biomass retention, Resistance to shock loads	Automatic operation facilities, Excellent process control	[179]
Moving bed biofilm reactor	Can tolerate high amount of ammoniacal nitrogen content	High cost	[180]
Photo fenton process	Complete mineralization of organic contaminants in leachate	Precise optimization of process is difficult	[181]
Nanofiltration	Stability in operation, Efficient in removing dissolved organic matter	Limited life span of membranes, High maintenance cost	[182]
Phycoremediation	Eco Friendly method Relatively low cost	Sensitive to pH and temperature fluctuations	[183]
Electrocoagulation	Minimal operating cost, Improved efficiency of coagulation	High energy expenditure, Building up of toxic substances	[184]

5. Conclusion and future perspectives

The heterogenous nature of micropollutants present in the landfill leachates makes their removal and treatment a herculean task. Variability in the amount and nature of these micropollutants makes it difficult to define a single method for the treatment of these micropollutants. Conventional methods for removal of micropollutants although cost effective may not be sound enough to treat the emerging micropollutants due to the continuous change in waste ending up in landfills. Another major concern is to achieve a stable performance of the advanced technologies currently used for micropollutant removal with respect to varying season and geographical location. The influence of other physicochemical parameters in the vicinity of the landfills also needs careful consideration while designing advanced technique for micropollutant removal from landfill leachates. The issue related to sludge disposal and management should also be a focus area of research as sludge accumulation is often unavoidable during the leachate treatment. The success of any advanced treatment technology depends on its reproducibility, affordability, and performance durability. Development of integrated strategies connecting multiple existing technologies can open new avenues in dealing with the concern associated with heterogeneity of landfill leachates. Finally, the life cycle assessment of these treatment methods and their timely modification and improvement is also essential steps for the success of any micropollutant removal technologies.

Declaration of competing interest

It is declared that all the authors are mutually agreeing to submit this manuscript to the journal. It is also declared that co-authors do not hold any conflict of interest that may affect the publication of this manuscript.

Data availability

No data was used for the research described in the article.

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National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate

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Supporting Information

ABSTRACT: Landfills are the final stage in the life cycle of many products containing per- and polyfluoroalkyl substances (PFASs) and their presence has been reported in landfill leachate. The concentrations of 70 PFASs in 95 samples of leachate were measured in a survey of U.S. landfills of varying climates and waste ages. National release of PFASs was estimated by coupling measured concentrations for the 19 PFASs where more than 50% of samples had quantifiable concentrations, with climate-specific estimates of annual leachate volumes. For 2013, the total volume of leachate generated in the U.S. was estimated to be 61.1 million m^3, with 79% of this volume coming from landfills in wet climates (>75 cm/yr precipitation) that contain 47% of U.S. solid waste. The mass of measured PFASs from U.S. landfill leachate to wastewater treatment plants was estimated to be between 563 and 638 kg for 2013. In the majority of landfill leachate samples, 5:3 fluorotelomer carboxylic acid (FTCA) was dominant and variations in concentrations with waste age affected total estimated mass. There were six PFASs that demonstrated significantly higher concentrations in leachate from younger waste compared to older waste and six PFAS demonstrated significant variation with climate.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs) are used in many consumer products including baking papers, microwave popcorn bags, carpet, upholstery, medical garments, food contact paper, nonstick cookware, dental floss, and outdoor clothing.[1−4] Many of these products are disposed in landfills at the end of their useful life and the presence of PFASs in landfill leachate is well documented, though the range of concentrations varies widely.[5−10] For example, the reported range of perfluorooctanoic acid (PFOA) concentrations in U.S. landfill leachate (n = 13) was 0.15−9.2 μg/L.[6,9] For Chinese landfill leachate, concentrations of PFOA have been reported to be as high as 214 μg/L.[5] The range of reported PFAS concentrations in landfill leachate is not surprising given the heterogeneity of municipal solid waste (MSW)[11] and the range of PFAS content on various products.[1−4,12]

The mass release of PFASs from landfills to wastewater treatment plants (WWTPs) is of interest as the U.S. EPA recently established advisory levels for perfluorooctanesulfonic acid (PFOS) and PFOA of 0.07 μg/L in drinking water.[13,14] WWTPs are not known to attenuate PFOA and PFOS, and previous studies have shown higher effluent PFOA and PFOS concentrations compared to the influent concentrations, with the transformation of precursor compounds during the biological treatment process as the likely source of the increase.[15−19] The mass of PFASs in collected leachate sent to WWTPs is a function of both leachate concentrations and leachate volume. Leachate volume will depend on the climate (i.e., rainfall rates, evapotranspiration) as precipitation is the major source of infiltration to landfills. Busch et al. (2010) documented ∼90 kg/yr release for 44 PFASs in treated leachate from all German landfills (∼1700 landfills).

Given the heterogeneity of waste disposed in landfills, there are many potential sources of variability in leachate PFAS concentrations. Concentrations could be influenced by infiltration volume (i.e., climate) as well as waste age and seasonal variability in infiltration. In addition, some landfills accept WWTP biosolids that have been reported to contain PFASs.[17] Previous studies on PFASs in leachate did not assess variations in concentrations based on climate.[5−10] The potential for leachate PFAS concentrations to change with time as concentrations of phased-out PFASs decrease (i.e., PFOA- and PFOS-based products) has not been evaluated. Benskin et al.

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(2012) demonstrated temporal PFAS concentration variations for a single landfill with one average waste age, with variations largely attributed to increases of C5, C6, C8, and C10 PFCAs and 8:2 fluorotelomer carboxylic acid (FTCA) during the spring months. However, no studies identified have evaluated the effect of climate or waste age on PFAS concentration.

The objective of this study was to characterize leachate PFAS concentrations in U.S. landfills operated in different climates and containing MSW of different ages, and to use concentration data with independent estimates of leachate volumes to estimate the mass of PFASs released from U.S. landfills. In addition, temporal variability was examined using samples collected from two landfills that were sampled five times over two-years.

MATERIALS AND METHODS

Site Selection and Descriptions. Prior to selecting a landfill for inclusion, landfill operators completed a questionnaire with information on waste sources and waste age, operating characteristics, and potential sample locations. Landfills were selected to include sites in different climates and containing refuse of different ages. Climate categories were adopted from the U.S. EPA which categorizes landfills based on annual precipitation: arid (<38 cm), temperate (38−75), and wet (>75).[18] The average waste age associated with a leachate sample (Table 1) was calculated from the mean of the date of initial waste placement and the sampling date (2013). This calculation of average waste age is imperfect because it assumes equal waste placement annually, but it allows for some analysis of the effect of waste age.

All participating landfills were publicly owned, the implication of which is that they were receiving primarily MSW and in some cases biosolids, but were less likely to accept a range of industrial wastes relative to privately owned facilities. Ultimately, 95 samples were collected from 18 landfills (Table 1), either directly from a valve after flushing, or using a polyethylene baler for leachate obtained from manholes and ponds. Most landfills were sampled twice, with approximately 6−16 months between samples, but two landfills (T and U) were sampled five times over a two-year period to examine temporal variability. Landfills H and N were only sampled once due to collection and shipping limitations.

The emphasis of the sampling strategy was to collect leachate as it leaves the landfill for offsite treatment at a WWTP. At some landfills, leachate was collected at additional locations to obtain samples from individual landfill cells to increase the size of the data set and/or to obtain waste-age specific leachate samples. To ensure that all landfills were weighted equally, all data from cells of the same waste age was averaged so that only one value is reported for each landfill at each time point.

Sample Collection and Storage. Landfill operators were provided with self-contained sampling kits with return shipping instructions. Sample collection took place from February 2013 to December 2014, with the majority of sample collection in 2013. Leachate was collected in a 1-L HDPE container and then poured into a 50 mL sample tube, sealed with parafilm, and frozen overnight onsite when possible. After freezing, samples were shipped on ice overnight to Oregon State University (OSU) for analysis. For Landfill O, the samples were shipped the same day as a freezer was not available.

For quality control, each sample kit included duplicate field and trip blanks (i.e., sampling containers with DI water only). Trip blanks remained sealed during sampling while field blanks were opened during sample collection to assess potential background contamination during sampling.

Table 1. Site Characteristics for U.S. landfills sampled

landfill[a]	number of sampling events	total samples collected	climate[b]	years of waste disposal	average waste age[c] (years)
K	2	10[d]	arid	1996−Present	9
L	2	2	arid	1970−Present	22
M	2	2	arid	1966−Present	24
E	2	2	temperate	1988−Present	13
F	2	4[e]	temperate	1993−2001	10.5
G	2	8[f]	temperate	1999−Present	7.5
T	5	10[g]	temperate	1975−Present	19.5
B	2	2	wet	1981−Present	16.5
H	2	2	wet	1998−Present	8
I	2	2	wet	1989−Present	12.5
J	2	2	wet	1996−Present	9
N	1	1[h]	wet	1998−Present	8
O	2	4[i]	wet	1970s−Present	>15
P	2	4[j]	wet	1970s−Present	>15
Q	2	2	wet	2001−Present	6.5
R	2	8[k]	wet	1977−Present	18.5
S	2	4[l]	wet	1997−Present	8.5
U	5	26[m]	wet	1980−Present	17
total		95			

[a]Landfills A, C, and D are not shown because these landfills were closed before 1980 and the data were not included in the national inventory. [b]"Arid" < ~38 cm of precipitation a year, "Wet" > ~75 cm a year, and "Temperate" precipitation between 38 and 75 cm a year as in reference23. [c]Average waste age was calculated as 2013 minus the initial waste placement date divided by two. [d]For Landfill K, the average concentration of the five cells at each time point were used in the national inventory model. [e]For Landfill F, the average concentration of the two cells at each time point were used in the national inventory model. [f]For Landfill G, the average concentration of the four cells at each time point were used in the national inventory model. [g]For Landfill T, only the four samples collected in March and October 2013 were used in the national inventory model. [h]For Landfill N, concentrations for the single sample were entered twice in the national inventory model. [i]For Landfill O, the average concentration of the two cells at each time point were used in the national inventory model. [j]For Landfill P, the average concentration of the two cells at each time point were used in the national inventory model. [k]For Landfill R, only the samples collected from the onsite lagoon were used in the national inventory model. [l]For Landfill S, the average concentration of the two cells at each time point were used in the national inventory model. [m]For Landfill U, only the samples collected from the onsite tank collected in February and October 2013 were used in the national inventory model.

Micro-Liquid−Liquid Extraction (Micro-LLE) and Liquid Chromatography Tandem Mass spectrometry

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(LC-MS/MS). Samples were analyzed for the aqueous concentrations of 70 PFASs comprising 14 compound classes (Supporting Information (SI) Table S1) using previously described methods for leachate analysis by LC/MS/MS.[6] Briefly, leachate samples were centrifuged, titrated to pH 7−8, and extracted with trifluoroethanol and ethyl acetate. Then, 900 μL of the extract was injected, using orthogonal column chemistries to separate classes of compounds and tandem mass spectrometry for individual compound detection and identification. Method detection limits were at low to subng/L levels. Analytes were divided into four tiers based on the availability of standards: quantitative (Qn), semiquantitative (Sq), screening (Sc), and qualitative (Ql). Quantitative (Qn) analytes (n = 29) had analytical standards, the measured accuracy fell within 90−110%, and precision was ≤20% RSD. Semiquantitative (Sq) analytes (n = 7) had analytical standards, but the measured accuracy did not fall within 90−110% and/or the precision was ≥20% RSD. Only a commercial reference material was available for qualitative (Ql) analytes (n = 16). No reference material was available for screening (Sc) analytes (n = 18) but whose composition fell within homologous series of compounds that differed only in chain length. For PFASs in the Sc and Ql categories, concentrations were estimated assuming equal molar response factors to structurally similar, quantifiable PFASs. Leachate samples were analyzed concurrently with samples presented in Allred et al. (2015) and Lang et al. (2016).

Quality Control. Concentrations in all 69 trip and field blanks were less than the limit of quantification (<LOQ) for all 70 PFASs measured, except for low level contamination in one field blank sample, from the first sampling event at Landfill Q (<3 ng/L for all compounds). The absence of quantifiable levels of PFASs in the blanks indicates that concentrations measured in the samples were attributable to the leachate and not background contamination.

Data Analysis of PFAS Concentrations. For the national inventory, the 70 PFASs were categorized into three groups based on the number of samples with concentrations above the LOQ. This grouping was implemented because a large number of PFAS concentrations were < LOQ. Individual PFASs were assigned to group 1 if over 50% of all samples were > LOQ. Mean concentrations were calculated for group 1 PFASs, as a majority of concentrations were at quantifiable levels. PFASs were assigned to groups 2 or 3 if the fraction of samples > LOQ was 20−50% or <20%, respectively. To evaluate the contribution of group 2 PFASs, maximum likelihood concentrations were calculated as outlined in Gibbons and Coleman (2001), with the equation in the SI. Group 3 compounds are presented graphically in the SI, but a mean was not calculated.

Leachate PFAS concentrations were analyzed to evaluate whether there were significant differences attributable to climate or average waste age (greater than or less than 10 years). For waste age evaluation, an average age of 10 years was selected because this resulted in two sample populations with similar numbers of samples in each group. To estimate national release, a separate mean concentration was used for each climate and waste age category for each PFAS.

Estimate of Mass Flow of PFASs in U.S. Landfill Leachate. eq 1 was used to estimate the mass release of individual PFASs in leachate from U.S. landfills in wet climates. This equation was repeated for landfills in temperate and arid climates, with the sum of the three climates equal to the total mass release for an individual PFAS in U.S. landfill leachate.

$$M_{p,\mathrm{wet}} = (\bar{x}_{\mathrm{p},<10,\mathrm{wet}} \times \mathrm{WIP}_{<10,\mathrm{wet}} + \bar{x}_{\mathrm{p},>10,\mathrm{wet}} \times \mathrm{WIP}_{>10,\mathrm{wet}}) \times \mathrm{LG}_{\mathrm{wet}}/\mathrm{SA} \quad (1)$$

where, $M_{\mathrm{p,wet}}$ is the mass release of PFAS p from landfills in wet climates (kg/yr), $\bar{x}_{\mathrm{p,a,wet}}$ is the average concentration of PFAS p for the set landfills with average waste age a, (i.e., >10 years or <10 years) from landfills in wet climates, $\mathrm{WIP}_{\mathrm{a,wet}}$ is the total mass of waste contained in U.S. landfills in Tg (1 Tg = 10^6 kg) from landfills in wet climates with waste age a, LG_c is the leachate generation rate for landfills in wet climates (m^3/ha-day), and SA is average mass of waste per surface area for U.S. landfills (Tg/ha). PFAS mass release was estimated for 2013, which was the year when most leachate samples were collected. The leachate generation rate was derived for three climate categories, as leachate generation varies with precipitation. SA was calculated for all U.S. landfills as it was not expected to vary with climate.

The probable range for the national release of total PFASs calculated here was estimated using a Monte Carlo analysis, which reflects uncertainties in PFAS concentrations and in predictors of leachate volume (LG_c and SA). For the Monte Carlo analysis, the total mass release of group 1 PFASs in U.S. landfill leachate was estimated as the sum of eq 2, repeated for landfills in wet, temperate, and arid climates. Group 1 PFASs defined as screening (Sc) or qualitative (Ql) in the LC-MS/MS method were not included in eqs 2 and 3. Group 2 PFASs were not included in the total release, as their average concentrations are only maximum likelihood estimates.

$$M_{\mathrm{T,wet}} = (\bar{x}_{\mathrm{T},<10,\mathrm{wet}} \times \mathrm{WIP}_{<10,\mathrm{wet}} + \bar{x}_{\mathrm{T},>10,\mathrm{wet}} \times \mathrm{WIP}_{>10,\mathrm{wet}}) \times \mathrm{LG}_{\mathrm{wet}}/\mathrm{SA} \quad (2)$$

where, $M_{\mathrm{T,wet}}$ is the total PFAS mass released to WWTP from landfills in wet climates, and $\bar{x}_{T,a,wet}$ is the average of the total measured group 1 PFAS concentrations for the set of n landfills in wet climates and each waste age (eq 3).

There are two methods that can be used to calculate the total, average PFAS concentration for a given climate and waste age category ($\bar{x}_T$). One alternative is the average of the total PFAS concentration from each landfill, which is not the same as the sum of the average concentration for each PFAS. To calculate M_{T} in eq 2, the sum of the group 1 PFAS concentrations from each landfill was used as in eq 3. This is because the total measured PFASs at each landfill was judged to be a more accurate estimate of total release than summing the average concentrations of individual PFASs.

$$\bar{x}_{\mathrm{T,a,c}} = \frac{\sum_l \sum_{\mathrm{p}} x_{l,\mathrm{p,a,c}}}{n_{\mathrm{a,c}}} \quad (3)$$

where, $\bar{x}_{\mathrm{T,a,c}}$ is the average of the sum of the measured group 1 PFAS concentrations for the set of n landfills in climate c and waste age a, $\sum_l \sum_p x_{\mathrm{l,p,a,c}}$ is the sum of the total group 1 PFAS concentrations from landfill n in climate c with waste age a, and $n_{\mathrm{a,c}}$ is the number of landfill samples analyzed in climate c with waste age a.

The Monte Carlo analysis was conducted with 10 variables including the total PFAS concentration for waste that is less than and greater than 10 years in age in each of three climates (6), the leachate generation rate in each climate (3) and the waste mass per surface area (1). To ensure model convergence,

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Table 2. Per- and Polyfluoroalkyl Substances Grouped Based on the Percent of Total Samples Analyzed above The LOQ[a]

Percent of Samples > LOQ	
>50%	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, 6:2 FTCA, 8:2 FTCA, 3:3 FTCA[c], 5:3 FTCA, 7:3 FTCA, PFBS, PFPS[c], PFHxS, PFOS, 6:2 FTSA, 8:2 FTSA[d], MeFBSAA[d], MeFPeSAA[e], MeFHxSAA[e], MeFHpSAA[e], MeFOSAA, EtFBSAA[e], EtFPeSAA[e], EtFHxSAA[e], EtFOSAA
20−50%	10:2 FTCA, 6:2 FTUCA, 8:2 FTUCA, 9:3 FTCA[e], PFHpS[c], 4:2 FTSA[d], FBSAA[e], FPeSAA[e], FHxSAA[e], FHpSAA[e], EtFHpSAA[e]
<20%	PFUnDA, PFDoDA, PFTriDA, PFTeDA[d], PFPeDA[c], PFHxDA[d], PFHpDA[c], PFOcDA[d], 4:2 FTCA[e], 4:2 FTUCA[e], 10:2 FTUCA[e], PFNS[c], PFDS, FOSAA[d], 4:4 PFPIA[e], 4:6 PFPIA[c], 6:6 PFPIA, 6:8 PFPIA, 8:8 PFPIA, 4:4 diPAP[c], 4:6 diPAP[e], 6:6 diPAP, 6:8 diPAP[c], 8:8 diPAP, 8:10 diPAP[c], 10:10 diPAP[c], 6:2 FTMAP[c], 6:2/8:2 FTMAP[c], 8:2 FTMAP[c], 8:2/10:2 FTMAP[c], 10:2 FTMAP[c], 8:8 SAmPAP[c]

[a]Full compound names and their abbreviations are listed in Table S1. [b]PFASs defined in Allred et al. (2014) as quantitative based on standard availability unless otherwise specified (n = 29). [c]PFASs defined in Allred et al. (2014) as qualitative based on standard availability and therefore not included in the national release model (n = 16). [d]PFASs defined in Allred et al. (2014) as semiquantitative based on standard availability (n = 7). [e]PFASs defined in Allred et al. (2014) as screening based on standard availability and therefore not included in the national release model (n = 18).

Table 3. Mean Concentrations (μg/L) for Group 1 PFASs Used in the Mass Release Model[a,b]

	wet		temperate		arid	
μg/L	<10 yrs. (n = 14)	>10 yrs. (n = 12)	<10 yrs. (n = 2)	>10 yrs. (n = 6)	<10 yrs. (n = 2)	>10 yrs. (n = 4)
PFBA	0.9 ± 1	1 ± 0.9	0.3 ± 0.01	1 ± 0.9	1 ± 0.3	0.3 ± 0.2
PFPeA	1 ± 1	0.8 ± 0.8	0.2 ± 0.01	0.9 ± 0.9	0.9 ± 0.04	0.3 ± 0.1
PFHxA	2 ± 2	1.8 ± 1.9	0.5 ± 0.1	2 ± 2	3 ± 0.1	0.6 ± 0.3
PFHpA	0.8 ± 0.8	0.6 ± 0.6	0.2 ± 0.04	0.6 ± 0.4	1 ± 0.1	0.1 ± 0.1
PFOA	1 ± 2	1 ± 1	0.2 ± 0.001	0.7 ± 0.6	1 ± 0.05	0.1 ± 0.04
PFNA	0.1 ± 0.1	0.1 ± 0.	0.01 ± 0.002	0.02 ± 0.01	0.1 ± 0.002	0.005 ± 0.003
PFDA	0.1 ± 0.1	0.05 ± 0.1	0.005 ± 0.003	0.01 ± 0.01	0.02 ± 0.001	0.003 ± 0.004
6:2 FTCA	0.9 ± 0.5	0.6 ± 0.7	1 ± 0.5	0.5 ± 0.4	3 ± 1	0.1 ± 0.1
8:2 FTCA	0.2 ± 0.2	0.1 ± 0.2	0.1 ± 0.03	0.1 ± 0.1	0.4 ± 0.01	0.01 ± 0.01
5:3 FTCA	4 ± 6	3 ± 3	4 ± 0.9	4 ± 3	15 ± 1	0.4 ± 0.4
7:3 FTCA	0.9 ± 1	0.4 ± 0.6	0.1 ± 0.02	0.2 ± 0.2	0.9 ± 0.4	0.03 ± 0.03
PFBS	0.5 ± 0.8	0.3 ± 0.5	0.02 ± 0.005	0.03 ± 0.02	0.3 ± 0.04	0.01 ± 0.01
PFHxS	0.3 ± 0.3	0.4 ± 0.2	0.1 ± 0.01	0.3 ± 0.2	0.5 ± 0.005	0.02 ± 0.01
PFOS	0.1 ± 0.2	0.1 ± 0.1	0.01 ± 0.001	0.1 ± 0.1	0.2 ± 0.05	0.003 ± 0.003
6:2 FTSA	0.2 ± 0.1	0.3 ± 0.6	0.03 ± 0.003	0.1 ± 0.1	0.3 ± 0.01	0.005 ± 0.009
8:2 FTSA	0.1 ± 0.	0.03 ± 0.05	0.001 ± 0.0002	0.03 ± 0.1	0.1 ± 0.05	0.0003 ± 0.0005
MeFBSAA	0.6 ± 0.6	0.4 ± 0.6	0.4 ± 0.1	0.2 ± 0.2	0.8 ± 0.01	0.04 ± 0.06
MeFOSAA	0.2 ± 0.3	0.2 ± 0.2	0.005 ± 0.003	0.1 ± 0.2	0.04 ± 0.01	0.001 ± 0.002
EtFOSAA	0.1 ± 0.2	0.1 ± 0.2	0.0003 ± 0.0004	0.1 ± 0.3	0.04 ± 0.01	0.001 ± 0.001
total	15 ± 16	11 ± 12	7 ± 1	11 ± 9	29 ± 1	2 ± 0.8

[a]One standard deviation is presented for each mean concentration. [b]Climates: "arid" less than ~38 cm of precipitation a year, "wet" above ~75 cm a year, and "temperate" annual precipitation between 38 and 75 cm a year.

10 000 realizations were conducted on the total PFAS mass flow (eq 2).

RESULTS AND DISCUSSION

The results for group 1 PFASs are presented first, as these were the only data used quantitatively for the national inventory. Results for group 1 PFASs are followed by the results for group 2 and 3 PFASs. As presented below, group 2 PFASs were less <1% of the total estimated PFAS release to landfill leachate.

PFASs Present above the Detection Limit in >50% of Samples (Group 1). The PFASs assigned to group 1 (i.e., >50% of samples exhibited quantifiable concentrations) belong to the PFCAs, FTCAs, PFSAs, fluorotelomer sulfonic acid (FTSAs), n-methyl fluoroalkyl sulfonamido acetic acids (MeFASAAs) and n-ethyl fluoroalkyl sulfonamido acetic acid (EtFASAAs) compound classes (Table 2). The widespread presence of C4−C10 PFCAs and C4, C6, and C8 PFSAs in the sampled leachate is consistent with previous observations of these PFASs in leachate[5−10] and as residuals on PFAS-treated products.[1−4,12] The presence of FTSAs, FTCAs, EtFASAA, and MeFASAAs in leachate is less well-documented. With the exception of FTSAs, these polyfluorinated substances are described as "intermediate environmental transformation products," as opposed to surfactants used on products.[12]

The mean concentrations for group 1 PFASs are presented in Table 3. The standard deviations are often greater than the mean and reflect considerable variability in each sample population (Table 3). Given the heterogeneity of landfills and the numerous factors that influence PFAS release to leachate (e.g., sorption, preferential flow paths of leachate through waste, uneven distribution of PFAS-containing products in landfills), this is not surprising.

Of the 19 group 1 compounds quantified, there were four for which all concentrations were > LOQ (i.e., C6−C8 PFCAs and PFHxS). For the remaining 15 compounds, the mean concentration across all landfill samples was essentially the same whether a value of the LOQ, 50% of the LOQ or 0 was used to calculate the mean (SI Table S4). The low effect of the substituted LOQ value on the mean concentrations is due to the small percentage of group 1 samples with a LOQ result and the low LOQs compared to measured concentrations. To

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calculate a mean concentration for cases in which samples were < LOQ, the concentration was assumed to be 50% of the LOQ.

The mean concentrations of group 1 PFCAs and FTSAs, PFBS, and PFHxS reported here are comparable to previously published concentrations for untreated landfill leachate.[15−19] The major difference in the PFAS concentrations reported here is the addition of 5:3 FTCA. This compound was not measured in the majority of previous landfill leachate studies, but the data in Table 3 shows that the mean 5:3 FTCA concentration is at least three times higher than PFOA and PFOS combined for leachate from all climates. While mean MeFOSAA and EtFOSAA concentrations reported here are less than previously reported,[15−19] the mean concentration of MeFBSAA reported here was higher. These changes in FASAA concentrations correspond to the switch to shorter chain compounds.

PFAS Concentration Variations with Waste Age. Analysis of variations in PFAS concentrations as a function of average waste age was examined for the 19 group 1 PFASs defined as quantitative or semiquantitative in the LC/MS/MS method (Table 2). For this analysis, data from all climates was combined and an unpaired two-sample Student's t test was performed on the log-transformed PFAS concentrations as a function of average waste age. There were only six PFASs that demonstrated significantly different means ($P < 0.05$) for older waste compared to younger waste (PFNA, 8:2 FTCA, 5:3 FTCA, PFBS, MeFBSAA, MeFOSAA, SI Table S5), with higher concentrations in leachate from younger waste in all cases. This could be due to decreases in concentrations with time or to changes in the types of PFASs used on products. For example, manufacture of PFBS and PFNA based products increased as alternatives to PFOS and PFOA products, and both PFBS and PFNA were higher in younger leachate.[12] Similar concentrations for old and new waste indicates that release from a given waste mass will continue for many years following placement.

PFAS Concentration Variations with Climate. When log-transformed group 1 PFAS concentrations were compared using analysis of variance (ANOVA), the means of six compounds were found to be statistically different based on climate (PFNA, PFDA, PFBS, PFOS, 6:2 FTSA, and MeFOSAA - SI Table S6). For all PFASs that differed by landfill climate, the largest concentrations were measured in leachate from wet climates, suggesting that leaching governed release for these compounds. Mean 5:3 FTCA concentrations for landfill leachate from wet, temperate, and arid climates were 2.1 ± 3.0, 4.1 ± 5.0, and 5.2 ± 7.6 μg/L, respectively (SI Table S6). While the mean 5:3 FTCA concentration was highest for the arid climate leachate, the large standard deviations masked any potential effect of climate on PFAS concentration.

Mass Disposed and Leachate Volume Estimates for U.S. Landfills in 2013. For estimates of the total mass of waste in U.S. landfills, 1980 was selected as the base year given the assumption that waste disposed after 1980 was managed in engineered landfills, which include leachate collection systems, though some landfills were operated without liners through the early 1990s.[20] Previous estimates for annual waste disposal in U.S. landfills demonstrate considerable variability, with annual disposal estimates varying from 150 to 284 Tg in 2013 (SI Figure S1).[11,24−26] The Powell et al. (2015) estimate for annual disposal was adopted here as it is the most recent and is the only one that utilizes certified reports from landfill operators for the majority of the data. For the years prior to 1990, the Powell et al. (2015) estimate was decreased at the rates described by the U.S. EPA.[11] For years after 1990, the Powell et al. (2015) estimate was assumed to be linear between the years where the mass was provided. The fraction of waste generated in each climate region was adopted from published estimates of disposal rates for each region (SI Figure S2).

For landfills in wet climates, leachate generation rates (SI Figure S3) were estimated using data from annual landfill operating reports to state agencies (n = 27), published data (n = 12), data provided by some of the landfills that participated in this study (n = 7) and data obtained from a consulting engineer (n = 6).[27,28] The wide distribution of leachate generation rates is likely due to variability in landfill geometry and operating conditions, which are known to affect infiltration into a landfill. Leachate generation rates for temperate and arid climates are summarized in SI Table S2.

The mass of waste contained per landfill surface area was estimated using landfill operating reports to state agencies (n = 18)[28] and data obtained from a consulting engineer (n = 95 - SI Table S3). The mass of waste contained per surface area was assumed to be constant across climates based on standard landfill operating practice. As such, the data were aggregated (SI Figure S4).

For 2013, the estimated total volume of leachate generated in the U.S. was 61.1 million m^3/yr (Table 4). Landfills in wet climates generated the majority of leachate in the U.S. (79%), even though only 47% of the waste is generated in this climactic region (Table 4). It is recognized that this estimate of leachate volume does not consider leachate that is recirculated to the waste and thus not sent off-site for treatment. Estimates of total leachate recirculation were not available but judged to be on the order of 10−20% of leachate generation in wet climates.

Table 4. Mean Values for Leachate Generation and the Mass of Waste Per Surface Area, Total Waste in Place for United States Landfills, And the Estimated Volume of Leachate Generated in 2013

	leachate generation (m^3/ha-day)[a]	mass per surface area (Tg/ha)[a]	total waste in place[b] (Tg)	volume of leachate for 2013 (million m^3/yr)
arid	0.04 ± 0.03	0.14 ± 0.098	1492	0.10
temperate	2 ± 3	0.14 ± 0.098	2602	13
wet	5 ± 5	0.14 ± 0.098	3648	48
total				61.1

[a]One standard deviation is presented for leachate generation and mass of waste per surface area. [b]Waste disposed from 1980−2013.

Annual PFAS Mass Release in U.S. Landfill Leachate. The national inventory of PFAS mass release based on eq 1 is given in Figure 1. The majority of estimated PFAS mass release was attributable to PFCAs (291 kg/yr) and FTCAs (285 kg/yr), with lower releases of PFSAs and their precursors (84 kg/yr). Both 5:3 FTCA and 6:2 FTCA were previously identified products of anaerobic 6:2 fluorotelomer alcohol (FTOH) degradation.[29] Whereas Buck et al. (2011) lists FTCAs as biotransformation intermediates, a recent publication demonstrates that FTCAs were present on Japanese consumer products.[30] PFAS release from arid climates was <1% of the total mass release. Although mean PFAS concentrations were statistically similar in different climates, the low leachate volume in arid climates resulted in low mass release (Figure 1). Total release of the seven group 1 PFASs defined as qualitative and screening was estimated to be ∼56 kg PFAS/yr, but these

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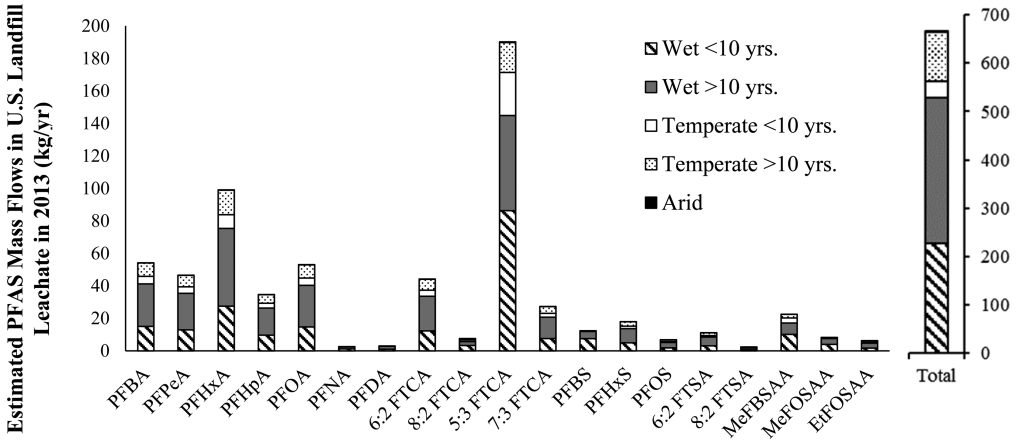


Figure 1. Group 1 PFAS release in U.S landfill leachate for 2013 demonstrating a dominance of compounds with five fluorinated carbons (PFHxA and 5:3 FTCA). Releases were calculated from mean concentrations in each climate and age category (Table 3). The individual columns are based on eq 1 while the total is based on eq 2.

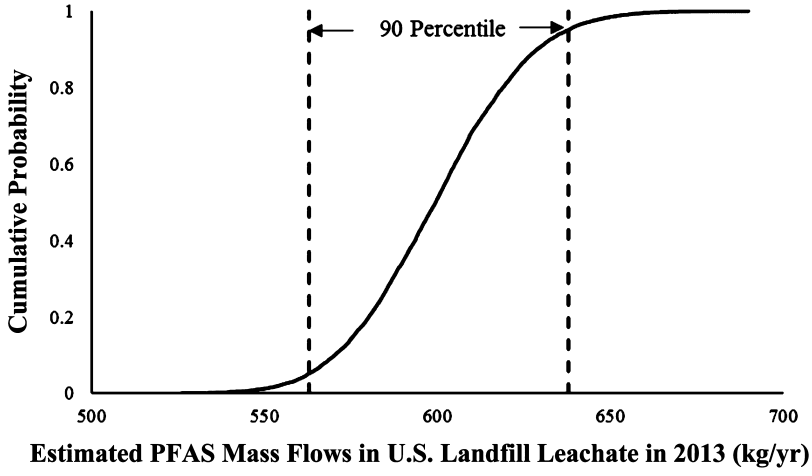


Figure 2. Distribution for total PFAS release in 2013 created using a Monte Carlo analysis with eq 2 and the distributions in SI Table S7.

compounds were not included in Figure 1 or the national release model as concentrations were not quantitative.

A Monto Carlo analysis was conducted to evaluate the uncertainty associated with the point estimate developed using eq 1. Model parameter distributions are described in SI Table S7 and Figure S7. The 90-percentile range for total group 1 PFASs of 563 to 638 kg/yr (~600 kg/yr with one significant figure - Figure 2). Since total oxidable precursor assays or total fluorine analyses were not completed in the current study, the actual inventory of PFASs in U.S. landfill leachate is likely higher than presented here, due to the presence of unmeasured PFASs.

PFASs Present above the Detection Limit in 20−50% of Samples (Group 2). Eleven PFASs were placed in group 2 (Table 2). The two classes of PFASs with the largest representation in group 2 were FASAAs and long chain FTCAs, but one PFSA, one unsaturated fluorotelomer carboxylic acid (FTUCA) and one FTSA were also present. The presence of a compound in group 2 indicates that the PFAS could be present in landfill leachate, but its presence is not widespread. Maximum likelihood estimates for group 2 PFASs that were quantifiable (10:2 FTCA, 8:2 FTUCA, and 4:2 FTSA, Table 5) are low relative to concentrations for group 1 PFASs (Table 3). The inclusion of group 2 PFASs added only ~1 kg/yr to PFAS mass flows (Figure 1).

Table 5. Concentration Ranges and Maximum Likelihood Estimates for Group 2 PFASs (20−50% of the Results Were > LOQ)

μg/L	concentration ranges	maximum likelihood estimate[a]
10:2 FTCA	ND−0.3	0.004
8:2 FTUCA	ND−0.2	0.005
4:2 FTSA	ND−0.02	0.001

[a]Maximum likelihood estimate calculated using methods outlined in Gibbons & Coleman (2001) using all samples (n = 95).

Long chain FTCAs are less likely to be present in leachate compared to their more soluble, shorter chain homologues, which were present in >50% of the leachate samples (group 1 − Table 2). FASAAs were present in a lower number of samples (group 2) compared to MeFASAAs and EtFASAA,s which were present in the majority of samples (group 1, Table 3). This is consistent with the lower production and use of FASAAs relative to the production of N-MeFASAAs and N-EtFASAAs derivatives.[31]

PFASs below the Detection Limit in the Majority of Samples (Group 3). There were 32 PFASs defined as group 3 PFASs because they were present in less than 20% of leachate samples (Table 2). Data for group 3 PFASs are only presented graphically (SI Figure S5) because the fraction of results that

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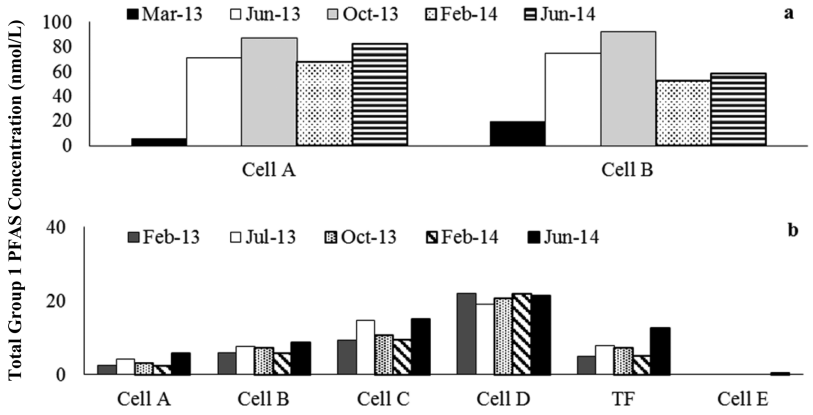


Figure 3. Total group 1 PFAS concentrations measured at (a) Landfill T and (b) Landfill U. The maximum whole method variability for the compounds in group 1 PFASs was 20%. For Landfill T, leachate was collected from two distinct areas with waste placement dates of 1975−1990 (Cell A) and 1990-present (Cell B). For Landfill U, Cell A contained the oldest waste (1980−1988) with each subsequent cell containing younger waste (Cell B: 1988−1993, Cell C: 1993−1998, Cell D: 1999−2014, and Cell E: 2014-present). Samples were also collected from a tank farm (TF), which collects and stores all leachate from Cells A−E prior to discharge for wastewater treatment. The leachate flows for Landfill U during the sampling period are presented in SI Figure S6.

were quantifiable was too low for a mean to be calculated. Long chain PFCAs (>C11), diPAPs, and PFPIs were present at quantifiable levels in <20% of landfill leachate samples. One explanation for this is the sorption of these PFASs to several materials known to be present in MSW.[32] Since diPAPs were previously identified on food contact paper,[2] a product that is typically landfilled in the U.S., their absence in the majority of landfill leachate does not imply that they are not entering landfills, but rather that they are not being released to the aqueous phase. Allred et al. (2015) reported that diPAPs were present in the leachate in anaerobic laboratory scale landfill reactors filled with a single MSW sample, but concentrations were depleted by day 200 in both live and abiotic reactors. The PFPIs are less likely to be present in MSW initially, as their primary use is pesticides.[12]

Temporal PFAS Concentration Variations. Five samples were collected over 17 months at Landfills T and U to evaluate temporal variability. The variability illustrated in Figure 3 is useful when considering the degree to which PFAS concentrations are representative of a landfill. At both Landfills T and U, variations appeared to be consistent with time across the landfill cells. For example, the March 2013 samples had the lowest group 1 PFAS concentrations in both Cells A and B, although the cells were physically separate, and Cell A had not accepted waste since 1990, whereas Cell B was accepting waste when sampled (Figure 3). Similar variations in PFAS concentrations in separate cells suggest that climate (i.e., rainfall) as opposed to internal processes in the buried waste was responsible for variations in concentrations (Figure 3). This contrasts the conclusion presented above that most PFASs concentrations were not statistically different based on the climate of the landfill sampled (SI Table S6). Benskin et al. (2012) also noted temporal changes for one landfill with increases over time in most of the PFASs analyzed as part of that study. The coefficients of variation (CV = stnd. dev./mean) for total PFAS concentrations in leachate from Cells A and B at Landfill T and Cells A to E at Landfill U were 53, 46, 37, 13, 33, 30 and 27%, respectively. In general, these values are lower than the variability in leachate samples between landfills (Table 3).

IMPLICATIONS AND LIMITATIONS

The estimate of total PFAS mass release in landfill leachate developed here (~600 kg/yr) represents the mass in collected leachate that was sent to wastewater treatment in 2013. Since 5:3 FTCA was the largest contributor to overall PFAS release in leachate, future work is needed to identify FTCA precursors in landfills and to estimate the attenuation of FTCAs during wastewater treatment. This study demonstrates that PFAS release from waste is slow relative to the quantities manufactured and applied to consumer products annually.[12] There are many reasons for the slow release including sorption, low PFAS solubility, bonding to polymers that are at most slowly degradable, and relatively low infiltration rates and subsequent waste flushing. However, the waste buried today will continue to release PFASs at similar rates for many years following placement (>10 yrs.). The slow release agrees with previous reports of PFASs release from MSW and MSW components (i.e., carpet and clothing).[21,22]

There are several limitations associated with the ~600 kg/yr estimate, and it is important to recognize other sources of PFASs that are attributable to landfills. First, there were 1540 landfills in the U.S. in 2013 and the estimated release is based on PFAS concentrations from 18 sites in different regions of the U.S.[33] Mass release is a function of both concentration and leachate volume. While leachate volume was estimated for the entire U.S. population of landfills, the extent to which the sampled landfills resulted in representative average PFAS concentrations is unknown, though variability in concentration data was incorporated in the Monte Carlo analysis.

The estimated release is based on ionic, nonvolatile PFASs quantified by LC-MS/MS and does not include volatile gas-phase PFASs typically measured by gas chromatography/mass spectrometry (GC/MS) (i.e FTOHs). Washington et al. (2014) reported that the degradation of fluorotelomer based polymers produced mostly volatile PFASs measured with GC-MS (>10 fold) compared to the nonvolatile PFASs measured by LC-MS/MS. An estimate of total PFAS release from landfills that includes volatile PFASs, would likely be higher than the estimates for leachate release of PFASs measured with LC-MS/MS alone, as presented here. Inclusion of additional new PFASs

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that can be measured with LC-MS/MS would further increase the estimate of release presented here.[34,35]

In the U.S., some MSW landfills likely receive waste from PFAS manufacturing and utilization facilities. This would include landfills near facilities that manufacture various PFASs and send their nonhazardous waste to MSW landfills, as well as facilities that utilize PFASs on their products and dispose of scrap material to an MSW landfill (e.g., carpet, textiles). For example, the total concentration of 12 PFASs in a Minnesota landfill that received wastewater treatment sludge from a 3 M manufacturing facility was 136 μ/L, as compared to the totals presented in Table 3 of 2−29 μ/L.[36] No landfill sampled in this study disclosed acceptance of waste from PFAS, carpet, or textile manufacturing.

An additional source of PFAS release to the environment is associated with unlined landfills. In 1988, there were an estimated 6000 landfills in the U.S., many of which did not have leachate collection systems such that leachate was released to the subsurface.[37] While some of these landfills later received low permeability covers that would reduce leachate flows, unlined landfills likely represent a significant source of PFASs to groundwater. Finally, there are other persistent organic pollutants in landfill leachate that may not be fully attenuated during leachate treatment and thus represent an additional source or surface water contamination.[38]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05005.

Additional details regarding the PFASs analyzed and their acronyms, data for evaluation of changes in group 1 PFAS means with varying values substituted for a < LOQ result, group 1 PFAS concentration variations with climate and waste age, PFAS concentration correlations, and data used to estimate the annual leachate volume generated in the U.S. (PDF)

All PFAS concentration data for each landfill, the LOQ for each compound and the release for each compound (XLSX)

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Notes

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Review

A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants

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ABSTRACT

Poly- and perfluoroalkyl substances (PFAS) comprise more than 4,000 anthropogenically manufactured compounds with widescale consumer and industrial applications. This critical review compiles the latest information on the worldwide distribution of PFAS and evaluates their fate in wastewater treatment plants (WWTPs). A large proportion (>30%) of monitoring studies in WWTPs were conducted in China, followed by Europe (30%) and North America (16%), whereas information is generally lacking for other parts of the world, including most of the developing countries. Short and long-chain perfluoroalkyl acids (PFAAs) were widely detected in both the influents (up to 1,000 ng/L) and effluents (15 to >1,500 ng/L) of WWTPs. To date, limited data is available regarding levels of PFAS precursors and ultra-short chain PFAS in WWTPs. Most WWTPs exhibited low removal efficiencies for PFAS, and many studies reported an increase in the levels of PFAAs after wastewater treatment. The analysis of the fate of various classes of PFAS at different wastewater treatment stages (aerobic and/aerobic biodegradation, photodegradation, and chemical degradation) revealed biodegradation as the primary mechanism responsible for the transformation of PFAS precursors to PFAAs in WWTPs. Remediation studies at full scale and laboratory scale suggest advanced processes such as adsorption using ion exchange resins, electrochemical degradation, and nanofiltration are more effective in removing PFAS (~95–100%) than conventional processes. However, the applicability of such treatments for real-world WWTPs faces significant challenges due to the scaling-up requirements, mass-transfer limitations, and management of treatment by-products and wastes. Combining more than one technique for effective removal of PFAS, while addressing limitations of the individual treatments, could be beneficial. Considering environmental concentrations of PFAS, cost-effectiveness, and ease of operation, nanofiltration followed by adsorption using wood-derived biochar and/or activated carbons could be a viable option if introduced to conventional treatment systems. However, the large-scale applicability of the same needs to be further verified.

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Abbreviations

6:2 Cl-PFAES/ F-53B	6:2 chlorinated polyfluoroalkyl ether sulfonate	$Cl\text{-}C_6F_{12}\ OCF_2CF_2SO_3^-$
ADONA	Dodecafluoro-3H-4,8-dioxanonanoat	$C_7H_{12}O_4HNH_4$
di-SAmPAP	Perfluorooctane sulfonamidoethanol-based phosphate diester	–
EtFOSAA	Ethyl perfluorooctane sulfonamidoacetic acid	$C_8F_{17}SO_2N(C_2H_5)CH_2CO_2H$
FOSA	Perfluorooctane sulfonamide	$C_8F_{17}SO_2NH_2$
FOSAA	Perfluorooctane sulfonamidoacetic acid	$C_nF_{2n+1}\text{-}\ SO_2NCH_2CO_2H$
FOSE	Perfluorooctane sulfonamidoethanol	$C_nF_{2n+1}.SO_2NHCH_2CH_2OH$
FTCA	Fluorotelomer carboxylic acid	$C_nF_{2n+1}\text{-}CH_2COOH$
FTS	Fluorotelomer sulfonate	$C_nF_{2n+1}\text{-}CH_2CH_2SO_3^-$

(*continued on next page*)

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FTSA	Fluorotelomer sulfonic acid	C_nF_{2n+1}-$CH_2CH_2SO_3H$
FTUCA	Fluorotelomer unsaturated carboxylic acid	C_nF_{2n+1}-CF=CHCOOH
GenX/ HFPO-DA	Heptafluoropropylene-oxide-dimer-acid	$C_4HF_7O_3$
MeFOSAA	Methyl perfluorooctane sulfonamidoacetic acid	$C_8F_{17}SO_2N(CH_3)CH_2CO_2H$
n:2 FTOH	n:2 Fluorotelomer alcohol	C_nF_{2n+1}-CH_2CH_2OH
n:3 Acids	n:3 Saturated acids	C_nF_{2n+1}-CH2CH2COOH
N-EtFOSA	N-ethyl perfluorooctane sulfonamide	$C_8F_{17}SO_2N(C_2H_5)H$
NMeFOSA	N-methyl perfluorooctane sulfonamide	$C_8F_{17}SO_2N(CH_3)H$
PBSF	Perfluorobutane sulfonyl fluoride	$C_4F_9SO_2F$
PFAA	Perfluoroalkyl acids	–
PFBA	Perfluorobutyric acid	$C_4HF_7O_2$
PFBS	Perfluorobutanesulfonate/ sulfonic acid	$C_4F_9O_3$-SO_3^-/SO_3H
PFCA	Perfluorocarboxylic acid	C_nF_{2n+1}-COOH
PFDA	Perfluorodecanoic acid	$C_{10}HF_{19}O_2$
PFDPA	Perfluorodecylphosphonic acid	$C_{10}H_2F_{21}O_3P$
PFDS	Perfluorodecane sulfonate/sulfonic acid	$C_{10}F_{21}O_3$- SO_3^-/SO_3H
PFHpA	Perfluoroheptanoic acid	$C_7HF_{13}O_2$
PFHpS	Perfluoroheptanesulfonate/ sulfonic acid	$C_7F_{15}O_3$- SO_3^-/SO_3H
PFHxA	Perfluorohexanoic acid	$C_6HF_{11}O_2$
PFHxPA	Perfluorohexanephosphonic acid	$C_6H_2F_{13}O_3P$
PFHxS	Perfluorohexanesulfonate/ sulfonic acid	$C_6F_{13}O_3$- SO_3^-/SO_3H
PFNA	Perfluorononanoic acid	$C_9HF_{17}O_2$
PFOA	Perfluorooctanoic acid	$C_8HF_{15}O_2$
PFOPA	Perfluorooctanephosphonic acid	$C_8H_2F_{17}O_3P$
PFOS	Perfluorooctane sulfonate/sulfonic acid	$C_8F_{17}O_3$- SO_3^-/SO_3H
PFPeA	Perfluoropentanoic acid	$C_5HF_9O_2$
PFPeS	Perfluorpentanesulfonate/ sulfonic acid	$C_5F_{11}O_3$- SO_3^-/SO_3H
PFPrA	Perfluoropropionic acid	$C_3HF_5O_2$
PFSA	Perfluorosulfonate/sulfonic acid	C_nF_{2n+1}- SO_3^-/SO_3H
POSF	Perfluorooctane sulfonyl fluoride	$C_8F_{17}SO_2F$
PTFE	Poly tetrafluoroethylene	–
PVDF-CTFE	Poly vinylidene fluoride-co-chlorotrifluoroethylene	–
PVDF-HFP	Poly vinylidene fluoride-co-hexafluropropylene	–
TFA	Trifluoroacetic acid	$C_2HF_3O_2$
TFMS	Trifluoromethane sulfonic acid	CF_3SO_3H

1. Introduction

Per- and polyfluoroalkyl substances (PFAS), a class of artificially manufactured compounds, have been extensively used in various industrial and commercial products from the mid-twentieth century (Wang et al., 2017). Comprised of a hydrophobic fluorinated alkyl chain at one end and a hydrophilic functional group at the other (Arvaniti et al., 2014), PFAS (C_nF_{2n+1}-R; R: Functional group) (Meng et al., 2020, Buck et al., 2011) have high thermal and chemical stability owing to the strong C-F bonds (Mulabagal et al., 2018). This unique combination of physical and chemical properties, along with the hydrophobic and lipophobic moieties, make PFAS extremely suitable as water and oil repellants and friction resistants (Kwiatkowski et al., 2020). Due to the desired performance and production suitability, PFAS are manufactured massively for wide-scale industrial (manufacturing of paper, textiles, pesticides, leather, medical aids, oil, and minerals, metal plating etc.) and consumer applications (food packaging, cosmetics and personal 'care products, paints, inks, non-stick cooking utensils, surfactants, firefighting foams, and several other waterproof products) (Gagliano et al., 2020; Ji et al., 2020; Wang et al., 2017; Lu et al., 2017; Kotthoff et al., 2015). The general purpose of treating consumer products with PFAS is to impart an extended service life and durability. This practice, in turn, results in prolonged exposure of humans, wildlife, and the environment to PFAS (Herzke et al., 2012).

Although PFAS have been used widely since the 1950s, it was only after the first report of PFAS in wildlife and human serum in the early 2000s that scientific studies on the properties, occurrence, environmental fate, and health effects of PFAS accelerated (Cousins, 2015). Over the past few decades, PFAS have been widely detected in the environment (Nakayama et al., 2019), and they are ubiquitous in almost all aquatic matrices such as drinking water, surface water, groundwater, and coastal water (Wei et al., 2018). Humans can be exposed to PFAS through drinking water and dietary intake (Domingo & Nadal, 2019, Sunderland et al., 2019, Wei et al., 2018). Studies have reported that several acute as well as chronic human diseases, such as thyroid, asthma, anxiety, obesity, pediatric allergies, hyperuricemia, peroxisome proliferation, immune toxicity, kidney disorders, liver damage, and cardiovascular diseases, may be associated with PFAS exposure (Ruan et al., 2019, Jian et al., 2017, Suja et al., 2009). Other studies have demonstrated toxic effects, such as immunotoxicity, carcinogenicity, and hormonal disorders, of some perfluoroalkyl carboxylic acids (PFCAs) on animals (Poothong et al., 2020, Rand & Mabury, 2017).

Today, more than 4,000 PFAS are manufactured and used worldwide, including both conventional (e.g., PFOA and PFOS) and alternative PFAS (short-chain PFAS and newly identified fluorinated replacements of conventional PFAS) (Pan et al., 2019). Anticipating long-term exposure effects due to their persistent and bioaccumulative nature (Ateia et al., 2019a, (Wang et al., 2016), conventional PFAS were voluntarily phased out (Wang et al., 2014b, Krafft & Riess, 2015) due to regulations (e.g., US EPA drinking water guideline for PFOA and PFOS: 70 ng/L) (Li et al., 2020, Ateia et al., 2019b, Pan et al., 2019). Still, many studies have reported high levels of conventional PFAS in WWTP effluents (>100 ng/L) (Table 2 and 3). Alternative PFAS have also been detected abundantly in WWTPs by several studies with concentrations up to some hundred ng/L (Table 2 and 3). Short-chain PFAS, being highly mobile, are detected in all ecosystems (Brendel et al., 2018) and can be equally toxic as their longer-chain counterparts (Li et al., 2020).

The occurrence of PFAS in WWTPs has been reviewed earlier by Arvaniti & Stasinakis, 2015. However, more than 100 new monitoring studies have been published since 2015. Some involve aspects not covered earlier, such as the effect of different treatment stages of a WWTP on removal efficiencies and the transformation of PFAS precursors to perfluoroalkyl acids (PFAAs) during wastewater treatment, that allows a better understanding of the fate of PFAS in WWTPs. Overall, this article aims at providing a systematic overview of the up to date knowledge on the occurrence, fate, transformation, and removal of PFAS in WWTPs.

First, the sampling and analysis methods adopted in monitoring studies are discussed, followed by the global occurrence data of different types of PFAS in the influents and effluents of WWTPs. The removal efficiencies and mechanisms are then discussed in detail, emphasising the fate of PFAS in a full-scale treatment plant and the transformation of PFAS precursors during treatment. This comprehensive review on the levels and fate of conventional and alternative PFAS in WWTPs, along with their removal at different scales, allows the identification of research gaps. Those are compiled in the last section, along with suggestions for future research concerning alternative PFAS (especially ultra-short chain PFAS and PFAS precursors), transformation mechanism of PFAS precursors, and large scale applications of laboratory tested PFAS treatment techniques.

Table 1
Common sampling and analysis practices reported in the recent literature.

Process	Practices	References (selected)
Sampling		
Type	Grab and/or **Composite***	(Table 3)
Containers	**Polypropylene/High density polyethylene bottles**	(Nakayama et al., 2019, Nguyen et al., 2019, Stroski et al., 2019, Chen et al., 2018, Wang et al., 2018b, Elmoznino et al., 2018, (Chen et al., 2017b) Shi et al., 2015)
	Glass bottles	(Kibambe et al., 2020, Nakayama et al., 2019 Ciofi et al., 2018)
Preservation		
Refrigeration	**-20 to 4°C**	(Wang et al., 2020c, Nakayama et al., 2019, Wang et al., 2019a, Zhou et al., 2019, Wang et al., 2018b, Elmoznino et al., 2018, Houtz et al., 2018, Ciofi et al., 2018, Dauchy et al., 2017)
Acidification	Hydrochloric acid	(Nguyen et al., 2019)
	Nitric acid	(McCord et al., 2018)
	Formic acid	(Tian and Sun, 2019)
Other chemical addition	Formaldehyde	(Kibambe et al., 2020)
Time	**1 to 30 days between extraction and/or analysis**	(Zhou et al., 2019, Wang et al., 2018b, Elmoznino et al., 2018, Ciofi et al., 2018, Houtz et al., 2018)
Sample clean-up		
Filter material	**Polypropylene filter**	(Elmoznino et al., 2018)
	Glass fibre	(Wang et al., 2020c, Kibambe et al., 2020, Zhou et al., 2019, Jiawei et al., 2019, Coggan et al., 2019a, Wang et al., 2019a, (Chen et al., 2017b))
Solid-phase extraction	**Weak anion exchange cartridges**	(Wang et al., 2020c, Coggan et al., 2019b, Pan et al., 2019, Munoz et al., 2019, Björnsdotter et al., 2019, Zhou et al., 2019, Mullin et al., 2019, Pan et al., 2019, Jiawei et al., 2019, Houtz et al., 2018, Chen et al., 2018, Eriksson et al., 2017, Boiteux et al., 2016)
	Hydrophilic-lipophilic balance (HLB)	(Wang et al., 2020c, Pan et al., 2019, Mulabagal et al., 2018, Hopkins et al., 2018)
Sonification and Centrifugation	–	(Letcher et al., 2020, Singh et al., 2019, Nguyen et al., 2019)
Analysis		
Equipment	**Ultra/High performance LC MS/MS**	(Al Amin et al., 2020, Letcher et al., 2020, Kibambe et al., 2020, Nakayama et al., 2019, Zhou et al., 2019, Coggan et al., 2019b, Munoz et al., 2019, Nguyen et al., 2019, Elmoznino et al., 2018)

* The practices in **bold** are recommended for precise analysis of PFAS at trace concentrations by EPA method 537.1, Al Amin et al., 2020, Tian and Sun, 2019 and other references cited in this section.

2. Sampling and Analysis

Measuring PFAS at environmentally relevant concentrations (ng/L) comes with a series of associated challenges from sampling to analysis. The sampling, laboratory, and analytical components (e.g., sample collection equipment and containers, laboratory consumables, analytical grade water and solvents, sample preparation, and analytical instruments can potentially cause background interference owing to the ubiquitous presence of PFAS (Al Amin et al., 2020, Misa and Kennedy, 2018). Table 1 summarizes the commonly practised sampling and analytical procedures applied when monitoring PFAS in wastewaters.

Ideally, glass and fluoropolymer containers should be strictly avoided while collecting and storing samples (Lath et al., 2019). This is because of the tendency of PFAS to adsorb onto glass surface (Tian and Sun, 2019) and contamination from fluoropolymer (e.g., PTFE (Polytetrafluoroethylene)) containers (Chen et al., 2018) may result in inaccurate analysis. While recent studies have mostly used either polypropylene or high-density polyethylene (HDPE) bottles for the collection of samples (Table 1), the consequences of using glass containers on quantification remain ambiguous (Kibambe et al., 2020, Nakayama et al., 2019, Ciofi et al., 2018). Cleaning all the sampling equipment and containers with tap water followed by triple rinsing with ultra-pure water and methanol can reduce background contamination (Elmoznino et al., 2018).

It is essential to carefully consider the variableness for a WWTP (e.g., diurnal, seasonal) and representativeness of a sample without which the evaluation of PFAS is of the least value (Liu et al., 2020, Gallen et al., 2018, Berger et al., 2011). Many recent studies have relied on composite sampling for observing the presence of PFAS in WWTPs (Table 3). Grab samples (Wang et al., 2020c, Elmoznino et al., 2018) could be considered less representative as they fail to take into account the diurnal variations in wastewater flow and may not be apt to understand the diversity in PFAS' quality and quantity during the treatment. Though acidification (Kibambe et al., 2020, Nguyen et al., 2019) and refrigeration (Zhou et al., 2019, Dauchy et al., 2017) of biologically active samples, such as wastewater and sludge, can reduce the biodegradation potential of PFAS (precursors) (Tian and Sun, 2019), the excess protons in acidic water could lead to the adsorption of PFAS onto the container surface upon acidification (Ateia et al., 2019b). Most studies refrigerated samples at $\leq$ 4°C (Table 1), as recommended by Standard Methods (EPA 537.1, 2018, D-7979-19, 2019), to ensure the preservation of target PFAS until analysis.

The typically low concentrations of PFAS in wastewater (Table 3), along with the high levels of organic matter and inorganic salts, may result in inaccurate quantification of the target compounds (Liu et al., 2020, Al Amin et al., 2020, Huset et al., 2011). Hence, clean-up and concentration of wastewater are vital steps prior to PFAS analysis. Despite the capability of glass fibre, cellulose acetate, nylon, etc., to adsorb or release PFAS (Tian and Sun, 2019), filtration using glass fibres prior to extraction is often applied (Table 1). As polypropylene filters can also retain long-chain PFAS (Elmoznino et al., 2018), future studies could rely on centrifugation for pre-cleaning wastewaters (Table 1). At present, solid-phase extraction (SPE) using weak anion exchange (WAX) ad-

sorbents is the primary sample clean-up approach for wastewater matrices (Table 1 and Table 4), as WAX cartridges have shown better recoveries for short-chain PFAS than other polymeric cartridges such as Hydrophilic-Lipophilic Balance (HLB) (Pan et al., 2019, Mullin et al., 2019, Hopkins et al., 2018, Taniyasu et al., 2005).

Analytical sensitivities using direct injection has greatly improved over the last few years (< 1 ng/L), which can overcome the contamination risks associated with sample manipulation during SPE (Nakayama et al., 2019, Ciofi et al., 2018). Most studies have used Ultra/High-performance liquid chromatography to analyse PFAS with the mass spectroscopy usually operated in negative electron ionisation mode as most target PFAS are anionic (Nakayama et al., 2019). While the predominantly used reversed-phase chromatography columns work well for most anionic PFAS, separation of highly polar short-chain PFAS (especially ultra-short chain, C<4) is challenging (Tian and Sun, 2019) due to their higher solubility and poor retainability (Yeung et al., 2017). Since the prevalent detection techniques are not capable of detecting a wide range of precursors due to inadequate sensitivities and the unavailability of reference standards (Pan et al., 2019), further studies must adopt the total oxidisable precursors assay (TOPA) technique to analyse PFAS (Al Amin et al., 2020, Houtz et al., 2018). Blank samples, e.g., field, transport, procedural blanks, are necessary to ensure maximum accuracy (Liu et al., 2020, Houtz et al., 2018, Wang et al., 2018b, Chen et al., 2018, Shi et al., 2015). The emerging approach to evaluating PFAS contamination in wastewater is to implement complementary target and nontarget analyses. While the target analyses can quantify known PFAS, nontarget analyses are recommended to fully elucidate the types of PFAS that are present in a sample, including PFAS that are unexpected or unknown, by means of high-resolution mass spectrometry (HRMS) (Jacob et al., 2021).

While sample preservation and preparation are performed with maximum vigilance in the majority of studies, sampling is often not reported in detail. A special emphasis should be placed on the collection of contamination-free samples as it can be critical in trace analysis of PFAS (Feng et al., 2019, Concha-Graña et al., 2018, Berger et al., 2011). Some of the essential elements of sampling were unclear from the literature, such as standard deviations and limitations of sampling methods undertaken (Lorenzo et al., 2019). Hence, detailing the critical aspects of sampling, such as the type of sampling, duration and frequency of sample collection samples, procedure and duration of storage, and precautions necessary to minimize background contamination, would help guide future monitoring studies.

3. Occurrence of PFAS in WWTPs

3.1. Global distribution of monitoring studies

PFAS have been monitored in wastewaters worldwide (Table 2), but the geographical distribution of studies conducted over the last decade is largely unequal (Fig. 1). The majority of studies were conducted in China (31%), followed by Europe (30%) and North America (16%), whereas very limited data is currently available for other parts of the world, including Africa, Oceania, or South America. Emissions and occurrence of PFAS are expected to be higher in more urbanized and industrialized regions, which is a possible rationale behind the high number of studies in China (Wang et al., 2015c). Conversely, lesser studies are expected for countries with lower manufacturing output, such as Australia, where PFAS issues are mostly associated with the use of imported products usage (Coggan et al., 2019b). However, detection of significant amounts of PFAS (maximum reported concentrations of 440 ng/L in influents and 560 ng/L in effluents) in WWTPs around Australian regions (Gallen et al., 2018), together with recent developments in analytical capabilities, might have triggered many recent investigations in Australia (Table 2). At present, no/little information is available regarding the occurrence, fate and transformation of PFAS in WWTPs of least developed and developing countries (except China). Similar to other persistent organic pollutants, PFAS tend to move around the Earth through atmospheric and/or oceanic diffusion (Lam et al.,2017) due to their long-range mobility (Wang et al., 2019c). The data gaps regarding the occurrence and fate of PFAS in WWTPs in several parts of the world limits our understanding of their global production, usage, and transport. Although the lesser number of studies have been conducted in some countries, such as South Korea or Germany, in comparison to China or U.S., a larger number of WWTPs (>70) (Kwon et al., 2017, Ulrich et al., 2016) have been surveyed in a single study for some countries. Hence, comparison of countries based solely on the number of monitoring studies does not present a complete picture of PFAS occurrence considering the variableness in conducting monitoring studies worldwide and lack of such details in many studies.

3.2. PFAS monitored in WWTPs

To date, very few compounds among the vast PFAS family have been monitored. Perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates/sulfonic acids (PFSAs) largely dominate (Letcher et al., 2020, Ruan and Jiang, 2017), whereas there is no data for a significant proportion of PFAS. Out of more than 4,000 PFAS currently present in the global market (Wang et al., 2017), most studies so far have focussed largely on two long-chain PFAS, which have been used for the longest time: PFOS and PFOA (Cohen Hubal, 2019). The production of long-chain PFAS has greatly decreased in the last two decades as a consequence of voluntary initiatives (e.g. PFOA, PFOS and related compounds phased out by 3M in 2000 (Krafft and Riess, 2015), national (e.g. PFOA production ban in Norway in 2013 (Li et al., 2020), and international restrictions (e.g. inclusion in the Stockholm convention in 2009 (Buck et al., 2011) (Askeland et al., 2020), Szabo et al., 2018). However, the proportional distribution of different PFAS detected in WWTPs worldwide indicates PFOA and PFOS were monitored and found in about 70% of studies (Fig. 2). The inability of natural environmental conditions to degrade these recalcitrant PFAS (Blum, 2015) with long half-lives (PFOS: >41 years and PFOA: >92 years) (Szabo et al., 2018, Olsen et al., 2008) could be a possible reason for their prevalence long after phasing out from the year 2000 onwards (Houtz et al., 2016, Krafft and Riess, 2015, Wang et al., 2009). Another long-chain PFAS, PFNA (C9), has also been reported in more than 40% of studies, after being previously detected in a wide range of consumer products and human samples (Kotthoff and Bücking, 2018).

An unfortunate consequence of these efforts to reduce contamination by conventional PFAS is the increased production and use of shorter chain (C4-C6) PFAS, which are now ubiquitous at relatively elevated concentrations in WWTPs (Phong Vo et al., 2020).

A significant proportion (40%) of studies reported short-chain PFAS (C≤6, e.g. PFBA, PFBS, PFHxS, and PFPeA) with the exception of PFHxA (C6), which was found in 69% of the total studies (Fig. 2). PFHxA has been extensively used as an alternative to PFOA over the last decade, which explains its increased occurrence in WWTPs (Shan et al., 2014). The detection of the above-mentioned short-chain PFAS in WWTPs is consistent with the studies reporting PFHpA, PFHxA, PFPeA, PFBA, and PFBS as the most widely found short-chain PFAS in the environment (Li et al., 2020) and PFHxS as the most widely used compound in stain and water repellent products (Wang et al., 2015a, The Danish Environmental Protection Agency, 2015). Despite their pervasive occurrence in WWTPs and other environmental media worldwide, no regulatory measures are in place regarding short-chain PFAS, which could be attributed to

Table 2
Global Distribution of PFAS in WWTPs from studies published during 2011-2020.

Regions	Number of WWTPs	PFAS detected	References
China			
Yanghe River, North China	6	PFBA, PFOA, PFOS	(Zhou et al., 2019)
Guangzhou province	3	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFHxS, PFOS	(Jiawei et al., 2019)
Wenzhou	-[#]	6:2 Cl-PFAES	(Wang et al., 2019c)
Daling river basin, Northern China	3	PFBA, PFOA, PFBS	(Wang et al., 2019a)
-	-	TFA, PFBA, 6:2 Cl-PFAES	(Chen et al., 2019)
Jiangsu Province	-	PFOA, PFSAs, H-PFCAs, Cl-PFCAs	(Wang et al., 2018b)
Qingdao City and Jiaozhou Bay	1	PFHxA, PFOA, PFNA, PFHxS, PFOS, FTCAs, FOSA, di-SAmPAP	(Wang et al., 2018a)
Guanting Reservoir	6	PFBA, PFPeA, PFHxA, PFOA, PFBS, PFOS	(Chen et al., 2018)
Liaoning Province, Shandong Province, Chinese Bohai Sea	-	PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS, FOSAA	(Chen et al., 2017a)
Wuxi City, Jiangsu Province	12	4:2, 6:2, 8:2 and 10:2 FTOHs	(Chen et al., 2017b)
Guangzhou City, South China	3	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFOS	(Pan et al., 2016)
-	-	PFOS, 6:2 Cl-PFAES, 6:2 and 8:2 FTSAs	(Ruan et al., 2015)
Xihe River	-	PFBA, PFOA, PFBS	(Wang et al., 2015b)
Yingcheng, Hubei	-	PFHxA, PFHpA, PFOA, PFOS	(Du et al., 2015)
Shanghai	2	PFPrA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Zhang et al., 2015)
Jinan, Shandong	-	C4-C7, C9-C11, PFOA	(Shi et al., 2015)
Taihu Lake	-	PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS	(Guo et al., 2015)
Jiangsu Hi-tech	1	PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Shan et al., 2014)
Beijing, Shanghai, Guangzhou	28	PFPrA, PFBA, PFHxA, PFOA, PFNA, PFOS	(Zhang et al., 2013c)
Tianjin	6	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS	(Sun et al., 2012)
Shanghai	25	PFPrA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Yan et al., 2012)
Shenyang	4	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS, 8:2 FTUCA	(Sun et al., 2011b)
Canada			
-	20	Sidechain fluorinated polymer (C4-C8)	(Letcher et al., 2020)
Cambridge Bay, Victoria Island	1	PFOA, PFNA, PFDA, PFBS, PFOS	(Stroski et al., 2019)
-	20	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS. PFOS	(Guerra et al., 2014)
Ontario	1	PFBA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFSs and PFSAs (C 4, 6, 8, 10)	(Vierke et al., 2013)
USA			
-	-	PFHxA, PFBS, PFOS	(Ateia et al., 2019a)
North Carolina	-	GenX	(Tian and Sun, 2019)
Long Island Sound	12	PFPeA, PFHxA, PFOA, PFOS	(Elmoznino et al., 2018)
Oakdale, Minnesota	-	PFBA, PFPeA, PFHxA, PFOA, PFOS	(Scher et al., 2018)
San Franciso Bay, San Jose Santa Clara, East Bay Dischargers Association, East Bay Municipal Utilities District, Central Contra Costa, Palo Alto, San Mateo, Fairfield Suisun, San Francisco Airport Industrial (SFO)	8	PFBA, PFPeA, PFHxA, PFOA, PFNA, PFBS, PFHxS, PFOS, PFHxPA, PFOPA, 6:2 and 8:2 FTS, MeFOSAA, EtFOSAA	(Houtz et al., 2016)
Washington	4	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFOS	(Furl et al., 2011)
Pennsylvania, Maryland, Delaware	3	PFPeA, PFHxA, 6:2 and 8:2 FTOH, 6:2 FTS	(Wang et al., 2011)
Australia			
-	19	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFDS, 6:2 and 8:2 FTS, 6:2 Cl-PFAES	(Coggan et al., 2019b)
-	2	PFBA, PFPeA, PFHxA, PFOA, PFBS, PFOS, 6:2 FTS	(Nguyen et al., 2019)
-	14	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS	(Gallen et al., 2018)
Melbourne	1	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFPeS, PFHxS, PFOS, PFDS, 6:2 FTS	(Szabo et al., 2018)
Queensland	2	PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Thompson et al., 2011)
Europe			
-	1	PFBA, PFPeA, PFHxA, PFOA, PFDA, PFBS, 6:2, 8:2 and 10:2 FTOH, 6:2 FTCA, 6:2 and 8:2 FTUCA, 5:3 acid	(Gremmel et al., 2017)
Netherlands			
Dordrecht	-	GenX	(Brandsma et al., 2019)
Papendrecht	-	PFBA, PFPeA, PFHxA	(Gebbink et al., 2017)
Switzerland			
-	45	PFCA (C4-C8), PFBS, PFOS	(Alder and van der Voet, 2015)
Zurich	20	PFOS	(Sun et al., 2011a)
Sweden			
-	-	TFA, TFMS	(Björnsdotter et al., 2019)
-	13	PFHxA, PFOA, 6:2 FTSA	(Gobelius et al., 2018)
Henriksdal, Gässlösa, Umeå	3	PFBA, PFPeA, PFHxS, PHHpA, PFOA, PFNA, PFBS, PFHxS, PFOS, 6:2 and 8:2 FTSAs, FOSA/FOSEs, FTCA/FTUCAs	(Eriksson et al., 2017)
Bromma, Bollebygd, Umeå	3	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, PFDS	(Filipovic and Berger, 2015)
Italy			
Trissino (Vicenza Province)	-	PFOA, PFOS, other PFAS	(Domingo and Nadal, 2019)
Milan	6	C4-C7, PFOA, PFOS	(Castiglioni et al., 2015)

(*continued on next page*)

Table 2 (*continued*)

Regions	Number of WWTPs	PFAS detected	References
South Korea			
Hyung-san River, Gyeongju and Pohang	3	PFHxA, PFBS, PFOS	(Seo et al., 2019)
Seoul, Incheon, Daejeon, Daegu, Busan, Gwangiu	81	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS, N-EtFOSA	(Kwon et al., 2017)
-	25	PFHxA, PFBA, PFBS, PFHxS	(Kim et al., 2016)
Japan			
Osaka	-	PFHxA	(Brendel et al., 2018)
Germany			
-	1	PFOA, PFHxS, 6:2 and 8:2 FTS	(Gremmel et al., 2017)
Halle	-	PFHxA, PFOA, PFNA, PFBS, PFOS	(Shafique et al., 2017)
Bavaria	71	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, PFDS, PFOSA	(Ulrich et al., 2016)
River Alz	-	ADONA	(Wang et al., 2013)
Hesse	5	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Llorca et al., 2012)
South Africa			
Gauteng Province	3	PFBA, PFPeA, PFHxA, PFOA, PFDA, PFHxS, PFOS	(Kibambe et al., 2020)
Spain			
Albufera Natural Park, Valencia	-	PFPeA, PFHxA, PFOA, PFHxS, PFOS	(Pico et al., 2012)
Alzira, Loja, and Cuenca	16	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFHpS, PFOS	(Campo et al., 2014)
France			
North France	1	PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, 6:2 and 8:2 FTSA, 6:2, 8:2, 10:2 and 12:2 FTOH	(Dauchy et al., 2017)
Nancy	1	PFOA, PFOS	(Pasquini et al., 2014)
India			
Chennai	-	PFOA, PFOS	(Sunantha and Vasudevan, 2016)
Kenya			
Bungoma, Busia, Kakamega, Kisumu, Kisii, Mumias	6	PFHxA, PFOA, PFNA, PFDA, PFHxS, PFOS, PFDS, PFOSA	(Chirikona et al., 2015)
Vietnam			
Hanoi	-	PFOA, PFOS	(Duong et al., 2015)
Red River	-	PFOA, PFNA, PFDA, PFOS	(Duong et al., 2015)
Thailand			
Bangkok	2	PFBA, PFHxA, PFHpA, PFOA, PFNA, PFBS, PFOS	(Tabtong et al., 2015)
Central and Eastern Thailand	2	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS	(Kunacheva et al., 2011)
Nigeria			
Lagos, Oyo, Ogun	10	PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS	(Sindiku et al., 2013)
Finland			
Turku, Espoo, Helsinki, Porvoo	4	PFHxA, PFOA, PFDA, PFOS	(Perkola and Sainio, 2013)
Greece			
Athens, Mytilene	2	PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFHpS, PFOS	(Arvaniti et al., 2012)

[#] No information available

the limited knowledge about their toxic effects and human exposure pathways. Recent literature suggests, shorter-chain PFAS might behave similarly in terms of persistence and bio-accumulation as their longer-chain counterparts (Ateia et al., 2019b) and can be equally hazardous as observed during experiments on animals (Sunderland et al., 2019). It is noteworthy that PFHxS, having similar toxicity potential as PFOA (Szabo et al., 2018), has been proposed for inclusion as a persistent organic pollutant (POPRC-15/1) under the Stockholm Convention (Kotthoff and Bücking, 2018). The relative lack of information regarding levels of short and ultra-short chain PFAS in wastewaters is particularly concerning as the demand for short-chain PFAS, especially in developing countries, is likely to increase their release into the environment in the coming years (Li et al., 2020).

The occurrence of precursors of PFAS and their fate in WWTPs is least studied, which calls for future research in this field as the production of precursors of PFAS outweighs that of PFCAs and PFSAs (Letcher et al., 2020). PFAS precursors (e.g., FTOHs) are widely used for manufacturing of various products such as fabrics, papers, surfactants, water and stain-resistant products, and firefighting foams (Lewis et al., 2016, Liu et al., 2015, Shi et al., 2015 Wang et al., 2012), and, hence, eventually make their way to WWTPs (Zhang et al., 2013b), where they can transform into PFAAs (Brendel et al., 2018, Houtz et al., 2016). Recently, two new side-chain polymers (perfluorooctane sulfonamide-urethane polymer and perfluorobutane sulfonamide-urethane polymer), which could potentially transform into polyfluorinated sulfonamides (e.g. FBSA and FOSA) and then short-chain PFSAs (e.g. PFBS), were reported for the first time in Canadian WWTP sludge with maximum concentrations of 105 and 2,051 ng/g d.w respectively (Letcher et al., 2020). Perfluoroalkyl ether acids (PFESAs and PFECAs) and fluorotelomer acids (FTSA and FTCA) are two main classes of PFAS which are widely used as alternatives to conventional PFAS in electroplating, processing aids, metal surface treatment, plastics manufacturing, etc. (Wang et al., 2019c, Wang et al., 2015d), and, hence, they are likely to be present in WWTPs. However, very few studies have evaluated the occurrence and fate of such compounds in WWTPs. Hence, the role of WWTPs as point sources of alternative PFAS to the aquatic environment requires deeper investigations.

Table 3
Influent and effluent concentrations for different PFAS categories, together with the associated sampling details.

Compounds	Influent (ng/L)	Effluent (ng/L)	[5]Removal efficiency (%)	Grab	Composite (Duration)	Country	Remarks	References
ΣPFAS	10 to 15	14 to 24	-40 to -60	✓	–	Jordan	[1]Ef>In	(Shigei et al., 2020)
	–	110	–	✓	(24 h)	Australia	–	(Coggan et al., 2019b)
	–	538	–	–	–	China	–	(Jiawei et al., 2019)
	*d	*d	–	✓	–	China	–	(Wang et al., 2018b)
	–	83	–	–	–	China	–	(Wang et al., 2018a)
	–	103 to 443	–	–	–	China	–	(Chen et al., 2016)
	20 to 232	16 to 234	-1 to +20 -	–	(24 h)	China	[2]Poor removal	(Pan et al., 2016)
	2	3	-50	–	–	Thailand	Ef>In	(Tabtong et al., 2015)
	–	130±20	–	–	(24 h)	Canada	–	(Vierke et al., 2013)
	0 to 91	0 to 107	-8	✓	–	China	Ef>In	(Zhang et al., 2013c)
	–	219	–	✓	–	USA	–	(Furl et al., 2011)
	761	903	-19	✓	–	Thailand	Ef>In	(Kunacheva et al., 2011)
	55	94	-71	✓	–	Australia	Ef>In	(Gallen et al., 2018)
ΣPFAA	81±25	–	–	–	(24 h)	Australia	–	(Nguyen et al., 2019)
ΣPFCA	930	780	+16	✓	–	China	Poor removal	(Wang et al., 2020c)
	20	40	-100	–	(7 days)	Sweden	Ef>In	(Eriksson et al., 2017)
	–	137	–	–	(24h)	Italy	–	(Castiglioni et al., 2015)
	–	1,580	–	–	–	Switzerland	–	(Alder and van der Voet, 2015)
ΣPFSA	490	260	+47	✓	–	China	Poor removal	(Wang et al., 2020c)
	5	6	-20	–	(7 days)	Sweden	Ef>In	(Eriksson et al., 2017)
	–	5	–	–	(24 h)	Italy	–	(Castiglioni et al., 2015)
Ultra-short chain compounds								
PFPrA	17±2	14±2	+18	✓	–	China	Poor removal	(Zhang et al., 2015)
Short-chain compounds								
PFBA	5	4	+20	✓	(24 h)	Spain	Poor removal	(Lorenzo et al., 2019)
	130	490	-277	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
	24	20	+17	–	–	China	Poor removal	(Zhou et al., 2019)
	–	19	–	✓	–	USA	–	(Houtz et al., 2016)
	–	>800	–	–	–	China	–	(Wang et al., 2015b)
PFPeA	2	1	+50	–	(24 h)	Spain	[3]Ef<In	(Lorenzo et al., 2019)
	3	2	+33	–	–	China	Poor removal	(Zhou et al., 2019)
	200	1,690	-745	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
	–	32	–	–	(24 h)	USA	–	(Elmoznino et al., 2018)
	–	10	–	✓	✓	USA	–	(Houtz et al., 2016)
	27	76	-181	–	(24 h)	Greece	Ef>In	(Arvaniti et al., 2012)
PFHxA	2	3	-50	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	4	4	0	–	–	China	Poor removal	(Zhou et al., 2019)
	–	18	–	–	–	China	–	(Jiawei et al., 2019)
	350	1,370	-291	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
	–	27	–	–	(24 h)	USA	–	(Elmoznino et al., 2018)
	10	18	-80	✓	–	Australia	Ef>In	(Gallen et al., 2018)
	–	21,200	–	✓	(24 h)	France	Poor removal	(Dauchy et al., 2017)**
	–	24	–	✓	–	USA	–	(Houtz et al., 2016)
	7±2	13±200	-86	–	(24 h)	Sweden	Ef>In	(Filipovic and Berger, 2015)
	–	911 to 10,300	–	–	–	China	–	(Shan et al., 2014)
	–	4	–	–	(24 h)	Finland	–	(Perkola and Sainio, 2013)
	20±2	42±4	-110	✓	–	China	Ef>In	(Zhang et al., 2015)
	6	10	-67	–	–	USA	Ef>In	(Xiao et al., 2012)
PFBS	#n.d	17	–	–	(24 h)	Spain	[4]n.d in In but present in Ef	(Lorenzo et al., 2019)
	3	2	+33	–	–	China	Poor removal	(Zhou et al., 2019)
	1 to 195	1 to 186	-9 to +5	–	(24 h)	China	Ef>In to Poor removal	(Pan et al., 2016)
	–	3	–	✓	–	USA	–	(Houtz et al., 2016)
	–	>1,500	–	–	–	China	–	(Wang et al., 2015b)
	39 ± 1	386 ± 43	-890	✓	–	China	Ef>In	(Zhang et al., 2015)
Long-chain compounds								
PFHpA	2	20	-900	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	60	940	-1,467	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
PFOA	3	65	-2,067	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	6	6	0	–	–	China	Poor removal	(Zhou et al., 2019)
	–	431	–	–	–	China	–	(Jiawei et al., 2019)
	100	110	-10	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
	–	36	–	–	(24 h)	USA	–	(Elmoznino et al., 2018)
	5	22	-340	✓	–	Australia	Ef>In	(Gallen et al., 2018)
	3 to 12	4 to 13	-33 to -8		(24 h)	China	Ef>In	(Pan et al., 2016)
	–	23	–	✓	–	USA	–	(Houtz et al., 2016)
	3	8±1	-167	–	(24 h)	Sweden	Ef>In	(Filipovic and Berger, 2015)
	12	–	–	–	–	Kenya	–	(Chirikona et al., 2015)
	10	10	0	–	(24 h)	France	Poor removal	(Pasquini et al., 2014)
	–	29	–	–	(24 h)	Finland	–	(Perkola and Sainio, 2013)
	204 ± 10	341 ± 16	-67	✓	–	China	Ef>In	(Zhang et al., 2015)
	2 to 91	13 to 107	-550 to -18	–	–	China	Ef>In	(Zhang et al., 2013c)
	7	11	-57	–	–	USA	Ef>In	(Xiao et al., 2012)
	92	100 to 145	-33	–	–	China	Ef>In	(Sun et al., 2012)
	26,000	28,000	-8	✓	–	China	Ef>In	(Sun et al., 2012)

(*continued on next page*)

Table 3 (*continued*)

Compounds	Influent (ng/L)	Effluent (ng/L)	[5]Removal efficiency (%)	Grab	Composite (Duration)	Country	Remarks	References
PFNA	–	9	–	✓	–	USA	–	(Houtz et al., 2016)
PFDA	n.d*	3	–	✓	(24 h)	Spain	n.d in In but present in Ef	(Lorenzo et al., 2019)
PFHxS	7	18	-157	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	–	28	–	–	–	China	–	(Jiawei et al., 2019)
	–	5	–	✓	–	USA	–	(Houtz et al., 2016)
	430	500	-16	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
PFHpS	2	3	-50	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	2,950	1,450	+51	✓	(3 days)	USA	Ef<In	(Houtz et al., 2018)
	7	NA	–	–	–	USA	–	(Xiao et al., 2012)
PFOS	11	35	-218	–	(24 h)	Spain	Ef>In	(Lorenzo et al., 2019)
	–	35	–	–	–	China	–	(Jiawei et al., 2019)
	–	18	–	–	(24 h)	USA	–	(Elmoznino et al., 2018)
	6 to 11	3 to 23	-109 to +50	–	(24 h)	China	Ef>In	(Pan et al., 2016)
	–	15	–	✓	–	USA	–	(Houtz et al., 2016)
	2±1	1	+50	–	(24 h)	Sweden	Ef<In	(Filipovic and Berger, 2015)
	–	28	–	–	(24 h)	Finland	–	(Perkola and Sainio, 2013)
	1 to 32	1 to 67	-109	–	–	China	Ef>In	(Zhang et al., 2013c)
	2 to 176	1 to 75	+50 to +57	✓	–	China	Ef<In	(Sun et al., 2012)
Precursor compounds								
6:2 FTS	2,400	4,790	-100	✓	(3 days)	USA	Ef>In	(Houtz et al., 2018)
	–	3	–	✓	–	USA	–	(Houtz et al., 2016)
8:2 FTS	700	330	+53	✓	(3 days)	USA	Ef<In	(Houtz et al., 2018)
FTSA	4	3	+25	–	(7 days)	Sweden	Poor removal	(Eriksson et al., 2017)
6:2 FTAB	8,712,250	4,228,250	+51	✓	(24 h)	France	Ef<In	(Dauchy et al., 2017)**
M4	1,459,500	85,000	+94	✓	(24 h)	France	Ef<In	(Dauchy et al., 2017)**

The removal efficiency of the wastewater treatment (% Removal) is based on the reported effluent and influent concentrations (negative values indicate an increase in PFAS concentration during the treatment).

[1] Ef>In: Concentration of compound in effluent > Concentration of compound in influent; Removal efficiency (%) < 0

[2] Poor removal: 0 ≤ Removal efficiency (%) < + 50

[3] Ef<In: Concentration of compound in effluent < Concentration of compound in influent; Removal efficiency (%) ≥ + 50

[4] n.d in In but present in Ef: Not detected in influent but present in effluent

[5] Removal efficiencies (%) are calculated from the influent and effluent concentration values, which were rounded to the nearest whole numbers.

** The influent and effluent concentrations (ng/L) are the average of concentrations of PFAS in the homogenization pool (Table S4, (Dauchy et al., 2017)) and effluent (Table S7, (Dauchy et al., 2017)) respectively, during May, July, October, December 2013.

* d: Detected

n.d: Not detected

3.3. Concentrations of PFAS in influents

Table 3 summarises the concentrations (ng/L) of different PFAS classes detected in the influent of WWTPs across the world. PFAAs tend to be more abundant and present at higher concentrations in WWTPs relative to other classes of PFAS. According to Filipovic & Berger (2015), industrial wastes are a primary source of PFAAs found in WWTP. For instance, Gallen et al. (2018) suspected a local industry to be responsible for high levels (444 ng/L) of PFAAs found in the influent of a WWTP. Similarly, influents receiving wastes from an electroplating industry carried elevated PFAS content with short-chain PFAAs (C4-C8), accounting for more than 60 % of the total PFAS (Jiawei et al., 2019). In some studies conducted prior to 2015, PFOA concentrations were as high as 92–66,000 ng/L in WWTP influents (Sun et al., 2012). The lower levels of PFOA typically reported after 2015 (3–100 ng/L) (Kim et al., 2021, Lorenzo et al., 2019, Zhou et al., 2019, Gallen et al., 2018, Houtz et al., 2018, Pan et al., 2016), can be attributed to the united efforts undertaken to reduce the production of conventional PFAS (see section "PFAS monitored in WWTPs" above).

Following PFOA, PFHxA has been the second most abundant in terms of occurrence in WWTP influents. Dauchy et al. (2017) found PFHxA at an unusually elevated concentration (~4,000 ng/L) in the influent of a WWTP that received raw effluents from a fluorochemical manufacturing plant. The technical performance of short-chain PFAS being lower than long-chain PFAS (Ateia et al., 2019b) larger quantities of short-chain PFHxA are typically required to achieve similar performance as long-chain PFOA. This, in turn, can lead to the massive production and abundance of PFHxA (Shan et al., 2014). More studies elucidating the reason behind such a high prevalence of PFHxA and tracking its sources to WWTPs are needed.

In addition to short (C6-C4) and long (C>6) chain PFAAs, PFSAs (C9-C4) have also been detected at significant levels (up to 1,500 ng/L) in WWTP influents (Table 3). The abundance of PFOS in domestic wastes (Chen et al., 2012) and the use of PFBS as an alternative to conventional PFAS (Liang and Chang, 2019) have been stated earlier. Studies regarding ultrashort (C2-C3) chain PFAS in WWTPs are scarce, which could be attributed to the difficulty in analysing three or fewer carbon PFAS (see the section on sampling and analysis). Björnsdotter et al. (2019) confirmed the presence of TFA (C2) and PFPrA (C3) at concentrations as high as 14,000 and 53,000 ng/L in landfill leachates and groundwater samples, respectively. Another study in China detected PFPrA (17 ng/L) in the influent of a WWTP (Zhang et al., 2015). These findings highlight the need for a further investigation of WWTPs as potential sources of such ultrashort chain PFAS to groundwater and/or landfills.

Precursors of prevalent PFAS have been found at elevated concentrations in influents of some WWTPs (Table 3). Unlike PFAAs, the precursors' concentrations systematically decreased from influent to effluent (Dauchy et al., 2017, Houtz et al., 2018), probably due to their transformation into PFAS or other compounds during treatment (Chen et al., 2017b). In some cases, the precursors were reported in the influent but not in the effluent. For instance, Houtz et al. (2018), for the first time, reported two new classes of fluorotelomer thioether surfactants (FTSHCs) and fluorotelomer thioether alkylamido hydroxyl carboxylate (FTSAHCs) in the influent but did not find those in the effluent. Other new PFAS, e.g., 6:2 fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) and 6:2 fluorotelomer sulfonamide propyl N,N dimethylamine (M4), have

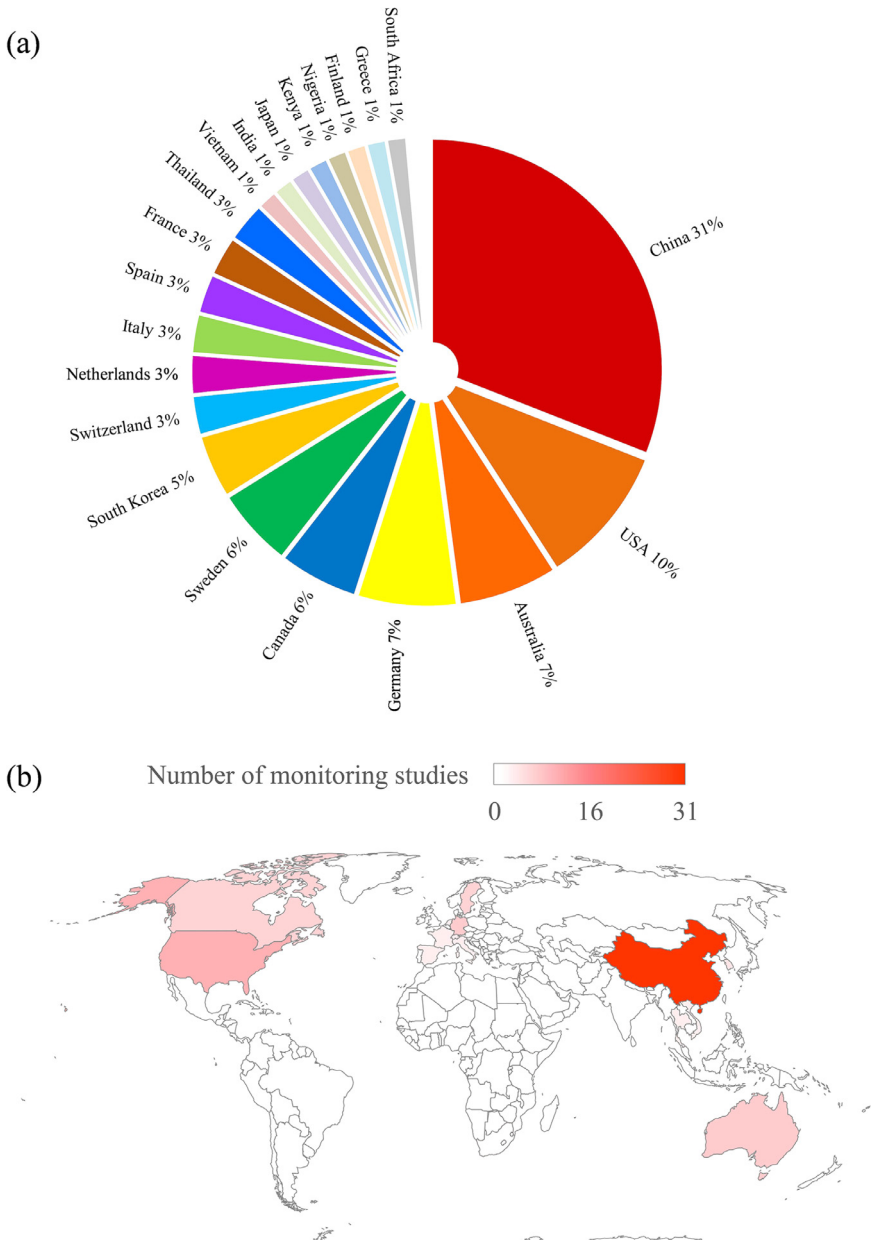


Fig. 1. Geographical distribution of studies monitoring PFAS in WWTPs during 2011–2020 in proportions (a) and number of studies across the globe (b).

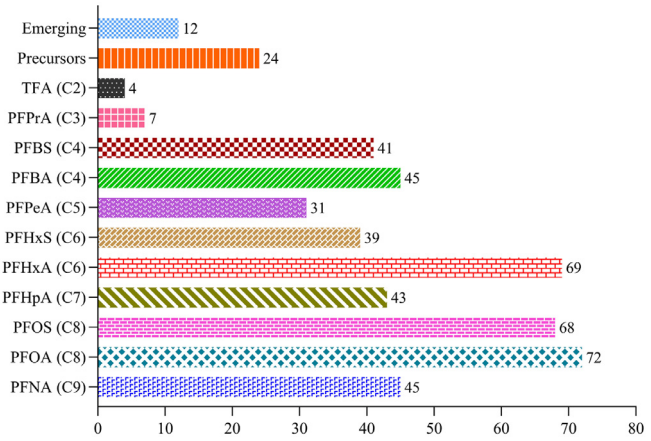


Fig. 2. Proportional distribution of selected PFAS found in monitoring studies. *Abundance of PFAS (%) was calculated based on 74 studies monitoring PFAS in WWTPs, E.g. PFHxA was detected in 69% of studies.

been reported at high concentrations (Table 3) in influent of a WWTP receiving effluent from a fluorochemical manufacturing facility (Dauchy et al., 2017). Thus, more monitoring studies involving new classes of PFAS and their precursors are recommended to understand their occurrence and fate in WWTPs.

Most monitoring studies conducted to date have focused on the occurrence of PFAS in the effluents than in influents of WWTPs. However, more work on PFAS in the influents could add to the existing knowledge about the source of newly discovered precursors to influents.

3.4. Concentrations of PFAS in effluents

Knowing the levels of PFAS in the effluents of a WWTP allows characterisation of the discharge into the environment. Effluents with comparatively lesser background matrix effect are easier to analyse than influents. This could be a possible reason behind the availability of more data on PFAS in effluents than

in influents (Table 3). High levels (1,100 ng/L) of PFAS has been detected in the effluents of WWTPs receiving wastes from industries (Castiglioni et al., 2015). WWTP effluents are significant point sources of PFAS to various environmental matrices, which receive wastewaters either through direct discharge (surface and coastal water) or application of recycled wastewaters (groundwaters, soils, and vegetation). Elmoznino et al. (2018) found WWTP effluent in the Long Island South, USA, to be a source of PFAAs to major tributary rivers. Similarly, a study conducted in the state of Washington, USA, suspected the effluent (about 200 ng/L of PFAAs) from a WWTP as the source of contamination to the surface water downstream (Furl et al., 2011). Inadequate removal or rather elevated levels of PFAS in the effluents has been observed in most of the studies (Table 3). For instance, in a recent study, Shigei et al. (2020) noticed that the combined concentration of three PFAS, i.e. PFPeA, PFOA, and PFNA, increased six times from influent to effluent. Similarly, the concentrations of short-chain PFAS, such as PFBA, PFPeA, and PFHxA, are often larger in the effluent than in the influent (Lorenzo et al., 2019, Houtz et al., 2018, Gallen et al., 2018, Filipovic et al., 2015, Arvaniti et al., 2012), which is much likely due to the degradation of precursors into recalcitrant shorter chain PFAS (Chen et al., 2017b). On the other hand, the concentration of longer chain PFAS (C>9) and precursors in the effluent decreased for some cases, which could be due to their sorption onto activated sludge (Zhou et al., 2019, Sun et al., 2012) and/or degradation to short-chain PFAAs (Zhang et al., 2015).

Houtz et al. (2018) suggested adsorption onto sludge and/or degradation to be responsible for the absence of novel PFAS precursors (FTSHCs and FTSAHCs), in the effluent in spite of their detection in the influent. Another study reported high removal (>80%) for two new fluorotelomer compounds: 6:2 FTAB and M4 in the final effluent after treatment (Dauchy et al., 2017). The actual reason behind the substantial elimination of such newly found PFAS in effluents is unclear and needs further research. However, an exception was observed in the case of a PFAS precursor, 6:2 FTS, whose concentration doubled after treatment (Houtz et al., 2018). Emerging PFAS, such as the ones mentioned above, have comparable levels of residue as their longer-chain counterparts and can potentially cause similar impacts as long-chain PFAS (Ruan and Jiang, 2017). Hence, in-depth investigation of newly discovered precursors and fluorinated compounds in terms of their occurrence and fate in WWTP would be helpful in better understanding such contradictory observations.

3.5. PFAS in biosolids

The occurrence of PFAS in biosolids and its consequences are often overlooked (Letcher et al., 2020), although biosolids and sludge from secondary treatment are notable routes for PFAS emission into the environment (e.g. groundwater, soil, vegetation etc.) (Ebrahimi et al., 2021, Stoiber et al., 2020, Zhang et al., 2013). PFCAs, PFSAs, precursors (e.g. FTOHs) (Guerra et al., 2014), and novel fluorinated polymers (Letcher et al., 2020) have been detected in biosolids worldwide, including North America, Europe, Africa, Asia, and Australia (Moodie et al., 2021). A recent study in Australia reported significant levels of PFAS (up to 910 ng/g) in biosolids (Moodie et al., 2021), despite the usage of imported products, rather than PFAS using/manufacturing industries, being predominantly responsible for the generation of PFAS wastes (Coggan et al., 2019b). Regulating various operational parameters (e.g., solid retention time, temperature) and solution chemistry (e.g., pH) have shown to reduce the PFAS loads in the effluent due to enhanced partitioning of PFAS into sludge (Ebrahimi et al., 2021, Zhang et al., 2013) (Section 4.1). However, these techniques result in the accumulation of PFAS in biosolids which could eventually leach into the environment (Rodríguez-Varela et al., 2021, Moodie et al., 2021, Guerra et al., 2014). Further research indicating the effects of various process parameters on the leaching and/or release of PFAS from biosolids into the environment is required.

PFAS enriched biosolids are disposed to landfills (Stoiber et al., 2020, Fuertes et al., 2017) which could be responsible for the abundance of PFAS (10 to 416,000 ng/L), including short and ultra-short chain compounds (Björnsdotter et al., 2019), in landfill leachates throughout the world (Hamid et al., 2018). Concerns regarding the long-term release of PFAS from solid waste disposal facilities and associated risks are emerging due to observed emissions of PFAS from landfills into various environmental matrices (Wang et al., 2020a). While incineration of PFAS loaded wastes and evaporation of volatile PFAS (primarily precursors, e.g. FTOHs) can discharge PFAS (including harmful fluorinated greenhouse gases) into the atmosphere (Stoiber et al., 2020, Wang et al., 2020a, Hamid et al., 2018), leaching of PFAS can contaminate the groundwater and soil (Moodie et al., 2021, Stoiber et al., 2020). The potential of commercial landfills to release PFAS into the air, water, and soil require immediate attention. Moreover, treating landfill leachates through WWTPs is widely practised (Stoiber et al., 2020). Hence, PFAS could be just transferring between wastewater and solid waste treatment facilities rather than getting removed from the environment, and hence more research is needed in this field.

4. Removal of PFAS through wastewater remediation techniques

The type of treatment and the physicochemical characteristics of PFAS significantly affect their removal efficiencies and composition (Kibambe et al., 2020, Ateia et al., 2019b, Chen et al., 2018, Rahman et al., 2014). Table 4 summarizes the various treatment techniques and their effectiveness for the removal of PFAS from wastewater, along with the effect of the background matrix. A drastic increase in the concentrations of PFAS from influent to effluent has been observed in many studies (Table 3) and is discussed in more detail in the following section.

4.1. Full-scale treatment

4.1.1. Conventional WWTPs: Overview

Very few studies have investigated the levels of PFAS at various stages of a WWTP (Kibambe et al., 2020, Wang et al., 2019a, Zhou et al., 2019). The design, capacity, and operating conditions such as hydraulic and sludge retention time, feed concentrations, temperature, flow rate, and mixed liquor suspended solids decide the fate of PFAS in a WWTP (Kibambe et al., 2020). For instance, longer retention time and higher temperature led to the formation of PFAAs, which increased their levels in the effluent (Guerra et al., 2014). On the other hand, unique operating parameters of higher mixed liquor suspended solids (5,000 mg/L) and longer sludge retention time (45 days) enhanced the removal of PFAS from the aqueous phase significantly in a WWTP using recirculation of activated sludge (Kibambe et al., 2020). Other factors such as the source of wastewaters (domestic, industrial, urban runoff and/or agricultural), climatic conditions, and atmospheric depositions influenced the concentrations of different PFAS and their removal from the aqueous phase in WWTPs (Ratola et al., 2012).

Along with process and external factors, the type of PFAS is also crucial. For example, PFAAs, the most abundant class of PFAS, which are usually present in anionic forms, are non-volatile and recalcitrant to biodegradation (Ateia et al., 2019b). Whereas neutral PFAS, which are mainly precursors such as FTOHs and perfluoroalkyl sulfonamidoethanols, are volatile and/ semi-volatile (Wang et al., 2021 (Ateia et al., 2019b), Hamid et al., 2018) and hence, can be released into the atmosphere from WWTPs

Table 4
Overview of treatment techniques tested for the removal of PFAS from wastewater at the laboratory scale (Lab), pilot or full scale.

Treatment	Target PFAS	Scale	Initial conc.	Details	Mechanism	Time	Efficiency (%)	Matrices effect	References
Electrochemical degradation	ΣPFAS	Full	1,642 μg/L	*Electrodes:* boron doped diamond (BDD) anode and stainless-steel cathode, *Current density:* 50 mA/cm^2 *Pre-treatment of WW:* SPE*	Decarboxylation and defluorination of PFCA carboxyl radical by OH radical oxidation	10 h	~ 100	TOC: removal > 90%	(Gomez-Ruiz et al., 2017)
Adsorption	PFOS	Full	146 ng/L	*Sludge:* 45 days aged *Pre-treatment of WW:* SPE	adsorption onto activated sludge	–	94	–	(Kibambe et al., 2020)
Adsorption	ΣPFAS	Full	200 ng/L	*Pre-treatment of WW:* SPE	adsorption onto activated sludge	–	82	–	(Kibambe et al., 2020)
Biological filtration	ΣPFAS	Full	18.5 ng/L	*Pre-treatment of WW:* SPE	–	–	41	–	(Kibambe et al., 2020)
Biological deodorization of raw water	ΣPFAAs	Full	208 ng/L	Biologically induced deodorization to raw influent *Pre-treatment of WW:* SPE	–	–	-70	–	(Wang et al., 2019a)
Adsorption	C3 to C11 PFCAs, C4, C6, C8 PFSAs, and C8 FOSA	Pilot	3 to 5 μg/L	*Adsorbent:* biochar filtration (BF), BF with active biofilm and BF with inactive biofilm *Pre-treatment of WW:* SPE	Hydrophobic interaction and hydrophilic functional groups interaction	22 weeks	58, 42, and 22	*Biofilm:* decreased availability of adsorption sites *Protein:* led to lower removal of PFOS and PFOA than carbohydrate content	(Dalahmeh et al., 2019)
Adsorption	PFAA (PFPeA, PFHxA, PFOA and PFOS)	Pilot	4 to 18 ng/L	*Adsorbent:* granular activated carbon *Pre-treatment of WW:* SPE	Hydrophobic interactions	–	61	*Biomass:* pore blockage	(Inyang and Dickenson, 2017)
Adsorption	GenX	Lab	70 ng/L to 5 mg/L	*Adsorbent:* purolite® A860, strongly basic anion exchange (IX) resin *Pre-treatment of WW:* microfiltration and ultrafiltration	Ion exchange	10 min	100	*Organic ions:* pore diffusion *Inorganic ions:* limited the availability of adsorption sites	(Dixit et al., 2020a)
Adsorption	PFOA, PFOS, PFBA, PFBS, and GenX	Lab	10 μg/L	*Adsorbent*: anionic ion exchange (IX) resin *Pre-treatment of WW:* SPE	Ion exchange	–	99	Organic and inorganic ions: competed with PFAS for adsorption sites	(Dixit et al., 2020b)
Adsorption	PFOA and PFOS	Lab	–	*Adsorbent:* anionic ion exchange resin (IX) *Pre-treatment of WW:* SPE	Ion exchange	40 min	70	*Organic matter:* more NOM required more dosage of resin	(Dixit et al., 2019)
Adsorption	ΣPFAS: PFOA, PFOS, PFBA, PFBS, GenX, ADONA, F-53B & other	Lab	1,000 ng/L	*Adsorbent:* DMAPAA-Q hydrogel polymers *Pre-treatment of WW:* SPE	Hydrophobic interaction: long-chain PFAS and PFSA Electrostatic interaction: other PFAS	< 2 h	100	*Inorganic anions:* adsorption of short-chain PFAAs decreased by an increase in anion concentrations which compete for adsorption sites and/or salt-out PFAS	(Ateia et al., 2019a)
Adsorption	PFOA	Lab	150 mg/L	*Adsorbent:* 1/19-MF-VT, Fe_3O_4 nanopowder and fluorinated vermiculite mixed at a ratio (mass) of 1:19 *Pre-treatment of WW:* centrifugation	Fast and selective adsorption for PFOS due to the fluorophilicity of C–F chains	4 h	98	–	(Du et al., 2017)

(*continued on next page*)

Table 4 (*continued*)

Treatment	Target PFAS	Scale	Initial conc.	Details	Mechanism	Time	Efficiency (%)	Matrices effect	References
Adsorption	PFAA (PFOA or PFBA)	Lab	1 µg/L	*Adsorbent:* biochar *Pre-treatment of WW:* SPE	Intra-particle diffusion	7 days	0 to 94	*Organic ions:* blockage of adsorption sites to PFOA.	(Inyang and Dickenson, 2017)
Adsorption	PFHxA, PFHpA, and PFOA	Lab	314, 364, and 828 mg/L	*Adsorbent:* bamboo-derived activated carbon *Pre-treatment of WW:* filtration	Hydrophobic interaction	33.5 h	< 80	*Divalent cations:* (Ca^{2+} and Mg^{2+}) neutralized negative surface charges of adsorbents forming bridges between PFAS	(Du et al., 2015)
Adsorption	PFHxA, PFHpA, and PFOA	Lab	314, 364, and 828 mg/L	*Adsorbent:* resin IRA67 *Pre-treatment of WW:* filtration	Anion exchange	33.5 h	< 80	*Anions:* decreased PFCAs solubility by salt-out effect, promoted the formation of PFCAs micelles, decreased removal of PFCAs by SO_4^{2-}	(Du et al., 2015)
Adsorption	PFHpA, PFHxS	Lab	5 µg/L	*Adsorbent:* WWTP sludge	Bridging effect, physisorption and coagulation	3 days	–	*Divalent cations:* bridging effect *Trivalent ions:* coagulation and adsorption	(Wang et al., 2015a)
Electrical degradation	PFOA	Lab	62 ng/L	*Electrodes:* boron-doped diamond (BDD) anode and Fe10MnC cathode	Cathodic electro-Fenton and anodic oxidation	4 h	96	–	(Wang et al., 2019b)
Algae and aerobic degradation	PFHxPA, PFOPA and PFDPA	Lab	100 µg/L	Biodegradation: Desmodesmus subspicatus and aerobic microorganisms in wastewater effluent *Pre-treatment of WW:* ultrasonication and centrifugation	–	> 10 days	0	–	(Llorca et al., 2018)
Photocatalysis	PFOA	Lab	30 mg/L	*Catalysts:* titanium dioxide (TiO_2), Indium Oxide (In_2O_3) and Gallium Oxide (Ga_2O_3); UV light source: UVB *Pre-treatment of WW:* filtration	In_2O_3 and Ga_2O_3: direct hole oxidation TiO_2: indirect oxidation of hole from OH radicals	180 min	0 to 23	–	(Lopes da Silva et al., 2017)
Nanofiltration (NF) and electrochemical degradation of NF concentrate	PFHxA	Lab	60 to 200 mg/L and 870 mg/L	*Filter:* DowFilm NF270 membrane (pressure: 20 bar) *Electrodes:* bipolar boron doped diamond electrode *Current density:* 50 A/m^2	Diffusion and electrochemical oxidation	1 h total recirculation and 1.5 h	99 and 98	–	(Soriano et al., 2017)
Aerosol based separation	6:2 FTSA	Lab	8.5 mg/L	*Design:* fritted glass set-up; pore diameter - 16-40 µm, solution: 0.2 M H_2SO_4 *Pre-treatment of WW:* LLE**	Transport of PFAS to the surface with the help of air bubbles generated in aqueous solution followed by the formation of PFAS enriched aerosols and their subsequent removal	< 1 h	~ 100	Higher ionic strength led to higher removal of 6:2 FTSA	(Ebersbach et al., 2016)

* SPE: Solid Phase Extraction
** LLE: Liquid-Liquid Extraction

(Fuertes et al., 2017). To date, the knowledge regarding the emission of volatile and/or semi-volatile PFAS from WWTPs into the atmosphere and the impact of various treatment processes is limited. Due to the complex wastewater matrix, biological and physicochemical reactions, and the unique properties of PFAS, WWTPs directly or indirectly serve as either source or sink for various PFAS (Chen et al., 2018). Hence, the efficiency of different treatment processes in removing PFAS and their formation in WWTPs needs further study.

4.1.2. Adsorption

In general, adsorption and biodegradation are the two processes responsible for the removal of contaminants from the aqueous phase in WWTPs. However, PFAS (long, short, ultra-short chain and other new alternate PFAS) are least susceptible to biodegradation due to the strong C-F bond (513 ± 10 kJ mol^{-1}) (Rodríguez-Varela et al., 2021), and hence adsorption onto sludge is the primary mechanism for their removal from the aqueous phase in WWTPs (Kibambe et al., 2020). The distribution coefficient (K_d) is an important parameter to evaluate the distribution of PFAS between sludge (adsorption onto sludge) and wastewater (dissolved phase) during wastewater treatment (Li et al., 2021). Factors like pH and composition of the wastewater and the structure of PFAS influences the partitioning of PFAS (Wang et al., 2020b). For example, with a decrease in pH (9 to 2), the PFAS partitioning to sludge intensified, resulting in increased sorption onto sludge in acidic conditions (Ebrahimi et al., 2021). The chemical structure of PFAS, especially the length of the carbon chain, dictates the partition behaviour of that PFAS between liquid and solid phases (Mussabek et al., 2019). For instance, the hexagonal ring structure of perfluoroethylcyclohexane sulfonate was associated with enhanced adsorption onto sediments (Liu et al., 2019b) while the ether bonds present in ADONA was detrimental for its adsorption onto suspended particles (Sun et al., 2016).

Studies suggest short-chain PFAS tend to partition to aqueous phase while long-chain PFAS partitions to the solid phase in the aquatic environment (Coggan et al., 2019b). A similar trend was observed in WWTPs where partitioning of PFAAs to sludge increased with an increase in chain length (Li et al., 2021, Mussabek et al., 2019, Coggan et al., 2019b, Pan et al., 2016) owing to the strong affinity of hydrophobic compounds to organic matter (Li et al., 2021). Moreover, the type of functional group in a PFAAs also influences its adsorption onto sludge. Wang et al. (2015a) found the K_d of PFHxS to be higher than that of PFHpA, suggesting a stronger affinity of more acidic sulfonate group towards organic content in the sludge than that of carboxylate groups (Arvaniti et al., 2014, Chen et al., 2012). Further studies utilizing K_d for understanding the effect of PFAS structure on its adsorption onto sludge could generate new insights. Very few studies have investigated the influence of PFAS headgroup charge (anionic, cationic, and zwitterionic) on its partitioning at liquid-liquid and solid-liquid interfaces (Ebrahimi et al., 2021, Xiao et al., 2019, Brusseau & Van Glubt, 2019). While most PFAS being anionic are partitioned to the sludge through hydrophobic and/or London−van der Waals interactions, cationic and zwitterionic compounds may be electrostatically attracted to negatively charged sites in the sludge along with other forces mentioned above (Xiao et al., 2019). The organic and inorganic matter present in wastewater is also crucial for predicting the partitioning behaviour of PFAS (Ebrahimi et al., 2021) in wastewater-sludge system which is discussed in later sections (4.2.1.1 and 4.2.1.2). As controlling the PFAS loads to influent may be gradual and is not a viable option at present, optimization of the process parameters, such as maintenance of lower pH and monitoring and regulating organic and inorganic fractions in wastewater to enhance PFAS partitioning to sludge, could be beneficial.

The partition behaviour of PFAS between water and solids (e.g. sediments, suspended particles, and soils) have been studied more in coastal, surface and groundwater systems (Wang et al., 2020b, Lee et al., 2020, Liu et al., 2019ab, Mussabek et al., 2019, Li et al., 2019, Dong et al., 2018) in comparison to wastewater and sludge in WWTPs (Ebrahimi et al., 2021, Li et al., 2021, Wang et al., 2015a, Coggan et al., 2019b). In addition, most of the previous studies have focused on the two legacy PFAS, i.e., PFOA and PFOS (Liu et al., 2019b). Insights on the partition behaviour of short/ultra-short chain and precursor PFAS between sludge-wastewater and effects of treatment type on their partition are insufficient. Further studies on K_d of sludge-wastewater systems can provide a better understanding of the fate, bioaccumulation, adsorption mechanism and transport of PFAS during and after treatment.

4.1.3. Transformation

Biological remediation techniques (e.g. aerobic/anaerobic digestion, biological filtration) applied during wastewater treatment influence the transformation of PFAS precursors in WWTPs, which ultimately affects the concentrations of PFAS in effluents (Chen et al., 2012). While typical WWTP may remove longer chain PFAAs from wastewater as a result of their adsorption onto sludge, shorter chain PFAS are formed during treatment (Houtz et al., 2016, Guerra et al., 2014). Short-chain PFAS are more persistent than their long-chain counterparts, resulting in longer-term occurrence (Li et al., 2020). Therefore, future studies should focus on the effective remediation of shorter chain PFAS from wastewaters using cost-effective, robust techniques with practical applicability.

Numerous studies have reported the formation of PFAAs after secondary stage (especially, anaerobic/anoxic/oxic oxidation) treatment (Table 3) (Wang et al., 2019a, Zhou et al., 2019, Houtz et al., 2018, Chen et al., 2012). FTOHs and fluorotelomer sulfonates (FTS) constitute a significant class of PFAS precursor compounds that can degrade into perfluoroalkyl acids (PFAAs) ($C \geq 4$), when undergoing aerobic and anaerobic treatment (Hamid et al., 2020a, Hamid et al., 2020b, Zhou et al., 2019, Coggan et al., 2019b, Chen et al., 2018, Hamid et al., 2018, Liu et al., 2015). Biodegradation of FTOHs to PFCAs through microbes has been well studied in laboratories (Chen et al., 2017b). Fluorotelomer carboxylic acids (FTCAs) and unsaturated fluorotelomer carboxylic acids (FTCUAs) are other intermediary compounds derived from fluorotelomer precursors of PFAS, which can eventually lead to the formation of PFAAs as end products (Hamid et al., 2018). The transformation of PFAS precursors to product PFAS in WWTPs is shown in Table 5.

While many studies have revealed the transformation of PFAS precursors into perfluoroalkyl carboxylic acids (PFCAs), $C \geq 4$, the ability of precursors to transform into ultrashort-chain PFCAs (C2-C3) remains unexplored. A few studies suggested that ultrashort-chain PFCAs (e.g., trifluoroacetic acid (TFA) and perfluoropropionic acid (PFPrA)) are usually generated at fluoropolymer manufacturing industries (Chen et al., 2019), but overall knowledge regarding the degradation of ultra-short chain PFAS from their respective precursors in WWTPs is limited.

A significant rise in the levels of PFAS for WWTPs applying biological deodorization to raw influent (Wang et al., 2019b) enunciates the need for evaluating the effect of specific microorganisms used for deodorization methods which caused ~70 % increase in the concentrations of PFAS. Aerobic treatment also has the potential to degrade PFAS precursors (Zhang et al., 2013b), which was confirmed by Guerra et al. (2014), who observed high levels of PFAAs in the secondary sludge of a WWTP adopting aerobic oxidation. Zhang et al., (2015) also reported a significant increase of PFAS in the final effluent of a WWTP using sequencing batch reactor system. Overall, PFAS precursors' transformation to PFAAs was prominent in WWTPs applying biological treatment methods

Table 5
Transformation of PFAS precursors to PFAS.

Product	Transformation	Matrix	Precursors	References
TFA, $C_2HF_3O_2$	Biochemical treatment	Landfill Leachate	Unknown C2–C4 PFAA precursors	(Wang et al., 2020a)
	Aerobic biotransformation	Landfill soil	6:2 FTOH	(Sun et al., 2020)
	Thermolysis (~400°C to ~650°C)	Landfill Leachate	PVDF-HFP, PVDF-CTFE and PTFE	(Cui et al., 2019)
	Reaction with $^{\bullet}$OH radicals	Industrial by-product	Semifluorinated alkanes [SFAs, F(CF2) n(CH2) mH]	(Wang et al., 2014b)
PFPrA, $C_3HF_5O_2$	Biochemical treatment	Landfill Leachate	Unknown C2–C4 PFAA-precursors	(Wang et al., 2020a)
PFBA, $C_4HF_7O_2$	Aerobic and anaerobic biotransformation	WWTP sludge, landfill leachate	8:2 FTOH	(Hamid et al., 2020a, Li et al., 2018, Yu et al., 2018, Yu et al., 2016)
	Aerobic biotransformation	WWTP sludge, landfill leachate	6:2 FTOH	(Sun et al., 2020, Yu et al., 2018)
	Aerobic biotransformation	Landfill Leachate	6:2 FTS	(Hamid et al., 2020a, Hamid et al., 2020b)
	Hydrothermal liquefaction (HTL) enhanced biotransformation	WWTP sludge	8:2 FTUCA, 7:3 FTCA and 8:2 FTS	(Yu et al., 2020)
	Aerobic biotransformation	Landfill Leachate	4:2 FTOH, 2-(trifluoromethyl) acrylic acid (TFMAA)	(Sun et al., 2020)
	Biochemical treatment	Landfill Leachate	Unknown C2–C4 PFAA-precursors	(Wang et al., 2020a)
	Photodegradation	WWTP effluent	2H,2H,3H,3H Perfluoroundecanoic acid (2H,2H,3H,3H-PFUnDA)	(Liu et al., 2019a)
	Thermolysis of persulfate ($S_2O_8^{2-}$)	WWTP effluents	8:2 FTCA	(Wang et al., 2018a)
	Reaction with $^{\bullet}$OH radicals, photodegradation and/or biodegradation	WWTP sludge	6:2 fluorotelomer based and PBSF based alternatives	(Wang et al., 2013)
	Biotransformation	WWTP sludge	5:3 acid (C5F11CH2CH2CO2H)	(Wang et al., 2012)
PFPeA, $C_5HF_9O_2$	Aerobic biotransformation	Landfill leachate	6:2 FTS	(Hamid et al., 2020b)
	Aerobic biotransformation	Landfill Leachate	4:2 FTOH	(Sun et al., 2020)
	Photodegradation	WWTP effluent	2H,2H,3H,3H-PFUnDA	(Liu et al., 2019a)
	Aerobic and anaerobic biotransformation	WWTP sludge	8:2 FTOH	(Li et al., 2018, Yu et al., 2018, Yu et al., 2016)
	Thermolysis of persulfate ($S_2O_8^{2-}$)	WWTP effluents	8:2 FTCA	(Wang et al., 2018a)
	Photodegradation	WWTP effluent	6:2 FTUCA	(Anumol et al., 2016)
	Biotransformation	WWTP effluent	POSF	(Wang et al., 2014a, Wang et al., 2014b)
	Biotransformation	WWTP sludge	5:3 acid (C5F11CH2CH2CO2H)	(Wang et al., 2012)
PFHxA, $C_6HF_{11}O_2$	Aerobic and anaerobic biotransformation	WWTP sludge, landfill leachate	8:2 FTOH	(Hamid et al., 2020a, Yu et al., 2018, Yu et al., 2016, Zhang et al., 2013b)
	Aerobic biotransformation	WWTP sludge, landfill leachate	6:2 FTOH	(Sun et al., 2020, Yu et al., 2018, Lewis et al., 2016, Zhang et al., 2013b)
	Aerobic biotransformation	Landfill Leachate	6:2 FTS	(Hamid et al., 2020a, Hamid et al., 2020b)
	Hydrothermal liquefaction (HTL) enhanced biotransformation and ozonation	WWTP sludge and WWTP effluent	8:2 FTUCA	(Yu et al., 2020, Glover et al., 2018)
	Hydrothermal liquefaction (HTL) enhanced biotransformation	WWTP sludge	7:3 FTCA and 8:2 FTS	(Yu et al., 2020)
	Photodegradation	WWTP effluent	2H,2H,3H,3H-PFUnDA	(Liu et al., 2019a)
	Degradation	Air	Fluorotelomer acrylate polymers	(Seo et al., 2019)
	Thermolysis of persulfate ($S_2O_8^{2-}$)	WWTP effluent	C8 PFAA precursors, 8:2 FTCAs	(Wang et al., 2018a, Ye et al., 2014)
	Ozonation	WWTP effluent	6:2 FTUCA	(Glover et al., 2018)
	Biotransformation	–	POSF	(Wang et al., 2014a)
	Reaction with $^{\bullet}$OH radicals, photodegradation and/or biodegradation	Biota	6:2 fluorotelomer based and PBSF based alternatives	(Wang et al., 2013)

(*continued on next page*)

Table 5 (*continued*)

Product	Transformation	Matrix	Precursors	References
PFHpA, $C_7HF_{13}O_2$	Aerobic biotransformation	WWTP sludge, landfill leachate	8:2 FTOH	(Hamid et al., 2020a, Yu et al., 2018, Yu et al., 2016)
	Aerobic biotransformation	Landfill leachate	6:2 FTS	(Hamid et al., 2020b)
	Photodegradation	WWTP effluent	2H,2H,3H,3H-PFUnDA	(Liu et al., 2019a)
	Ozonation	WWTP effluent	6:2 FTUCA and8:2 FTUCA	(Glover et al., 2018)
	Biotransformation	–	POSF	(Wang et al., 2014a, Wang et al., 2014b)
	Biotransformation	WWTP sludge	PFCAs, 7:3 acids (C7F15CH2CH2CO2H)	(Wang et al., 2012)
PFOA, $C_8HF_{15}O_2$	Aerobic and anaerobic biotransformation	WWTP sludge, landfill leachate	8:2 FTOH	(Hamid et al., 2020a, Li et al., 2018, Yu et al., 2018, Yu et al., 2016, Zhang et al., 2013b, Gauthier & Mabury, 2005)
	Aerobic biotransformation	Landfill leachate	6:2 FTS	(Hamid et al., 2020b)
	Oxidation	WWTP effluent	8:2 FTCA	(Wang et al., 2018a, Ye et al., 2014)
	Anaerobic biotransformation		6:2 FTOH	(Zhang et al., 2013b)
PFNA, $C_9HF_{17}O_2$	Aerobic biotransformation	WWTP sludge	8:2 FTOH	(Yu et al., 2018, Yu et al., 2016)
	α-oxidation	WWTP effluent	8:2 FTCA	(Wang et al., 2018a)
6:2 FTCA, 6:2 FTUCA	Aerobic and anaerobic biotransformation	WWTP sludge, landfill leachate	6:2 FTOH	(Lewis et al., 2016, Zhang et al., 2013b)
8:2 FTCA, 8:2 FTUCA	Aerobic and anaerobic biotransformation	WWTP sludge	8:2 FTOH	(Zhang et al., 2013b)
5:3 acid (C5F11CH2CH2CO2H)	Aerobic and anaerobic biotransformation	WWTP sludge, landfill leachate	6:2 FTOH	(Lewis et al., 2016, Zhang et al., 2013b, Wang et al., 2012)
7:3 acid (C7F15CH2CH2CO2H)	Aerobic and anaerobic biotransformation	WWTP sludge	8:2 FTOH	(Zhang et al., 2013b, Wang et al., 2012)
PFBS, $C_4F_9SO_3H$	–	WWTP effluent	FOSA	(Wang et al., 2018a)
	Oxidation	WWTP sludge	NMeFOSA, FOSA, and diperfluorooctane sulfonamidoethanol-based phosphate	(Ye et al., 2014)
	Chemical degradation	Industrial by-product	PBSF	(Wang et al., 2013)
PFOS, $C_8HF_{17}SO_3H$	Biotransformation	WWTP sludge	FOSA	(Land et al., 2018)
	Oxidation	WWTP effluent	NMeFOSA, FOSA and diperfluorooctane sulfonamidoethanol-based phosphate	(Ye et al., 2014)
	Aerobic and anaerobic biotransformation	WWTP sludge	N-ethyl perfluorooctane sulfonamido ethanol (N-EtFOSE)	(Rhoads et al., 2008)
5:2 FTOH	Biotransformation	WWTP sludge	6:2 FTOH	(Lewis et al., 2016)

(Houtz et al., 2018), which are likely to break only the C-C bond resulting in the formation of shorter chain PFAS (Gagliano et al., 2020). The weaker adsorption of PFAS onto primary sludge than secondary sludge could be due to the hindrance from background ions (see section 4.2.1.2). The enhanced transformation of PFAS precursors during biological treatment could also be responsible for the higher detection of PFAS in the final effluent after secondary treatment (Zhang et al., 2015). Microorganisms could gain energy for their growth from thermodynamically favoured reductive defluorination (Arvaniti and Stasinakis, 2015) provided strong electron donors are available to facilitate such reactions. Thus, future studies should focus on the performance of anaerobic microorganisms capable of degrading PFAS.

The efficiency of biological filters in removing PFAS from wastewater is dependent on various parameters such as sludge age and thickness. Biological filters are inefficient in removing short-chain PFAS ($C \leq 6$) from wastewater. Observed removal efficiencies of about 60% for PFOA and $< 20\%$ for PFAAs ($C \leq 6$) by biological filtration confirmed the inability of microbial degradation to remove shorter chain PFAS (Kibambe et al., 2020). When thickened, the biofilm can act as both aerobic (outer layer) and anaerobic (inner layer), which could be possibly influencing PFAS rejection (Kibambe et al., 2020). Biological activated carbon filters using granular activated carbon (GAC) perform more efficiently than biological filters in PFAAs removal from wastewater due to the strong ability of GAC to adsorb PFAAs ($C > 7$) (Pramanik et al., 2017). Though biological filters/biological activated carbon filters showed considerable removal for PFAAs (~50 %) (Kibambe et al., 2020, Wang et al., 2019a), activated sludge treatment outperformed both with $\geq$ 90 % removal efficiency (Kibambe et al., 2020, Castiglioni et al., 2015).

Further investigation to understand the effects of different biological treatments on the fate of PFAS precursors, long-chain, short-chain and ultra-short chain PFAS are necessary for drawing tangible inferences. In addition to WWTPs, landfills are also important sites where PFAS precursors can transform into PFAS. The biotic conditions prevailing at landfills and subsequent biochemical treatment of landfill leachates are favourable for this transformation to occur (Hamid et al., 2020a, Sun et al., 2020, Wang et al., 2020a). Discharging leachates into WWTPs and dumping WWTP sludge in landfills are common practices, which may contribute towards PFAS levels in both media (Seo et al., 2019, Hamid et al., 2018). To our knowledge, there are no insights available on this interrelation to date, which requires further investigation.

4.2. Lab-scale investigations

4.2.1. Adsorption

Among all the processes explored for the remediation of PFAS from wastewater, adsorption is the most studied at the laboratory scale (Table 4). Adsorption using ion exchange resins has shown promising results with $\geq$ 99 % removal efficiency for PFAS along with dissolved organics (>90%) (Dixit et al., 2021, Dixit et al., 2020a). However, results obtained at high initial concentrations (5–1,000 mg/L) of PFAS in synthetic and spiked wastewaters are not necessarily applicable to lower and more realistic concentrations (<1,000 ng/L). The formation of nitrosamine precursors during regenerating amine-based anion exchange (IX) resins documented earlier is also concerning (Flowers and Singer, 2013). Biochar, on the other hand, successfully removed PFAS at a lower concentration (1,000 ng/L) (Inyang and Dickenson, 2017). Biochar filtration post-secondary treatment (after removal of most of the organic matter) could facilitate the removal of PFAS through adsorption (Dalahmeh et al., 2019). Modification of biochar surfaces to improve PFAS adsorption, especially for short-chain PFAS, should also be further studied. Other novel adsorbents, such as hydrogel polymers and magnetic fluorinated adsorbents, showed excellent results in minimum time (2–4 h) (Ateia et al., 2019a, Du et al., 2017). However, the applicability of these adsorbents at large scale treatment facilities with lower concentrations of PFAS and complex background matrix needs to be confirmed.

4.2.1. 1 Role of PFAS carbon chain length

To date, the effect of alkyl chain length on PFAS adsorption have been investigated mostly with activated carbon, biochars, and resins in aqueous and/or synthetic wastewater solutions (Gagliano et al., 2020). Hydrophobic interactions have been found to be the most prominent mechanism responsible for the adsorption of PFAS onto various adsorbents (Ateia et al., 2019a, Dalahmeh et al., 2019, Du et al., 2014). Hydrophobicity of perfluoroalkyl compounds, in turn, depends on the length of the carbon chain; with an increase in the length of the carbon chain from C5-C15, the hydrophobicity and, hence, their adsorption onto sludge increases (Zhang et al., 2013a). Shorter chain PFAS, being less hydrophobic and more water soluble, are less likely to get adsorbed onto the sludge in WWTPs (Brendel et al., 2018, Zhang et al., 2013a). Hence, the length of the carbon chain of a PFAS plays a crucial role in the adsorption behaviour of that compound. As wastewater has a different composition (organic and inorganic matter) from other aquatic matrices (e.g. surface, coastal and/or groundwater) (Phong Vo et al., 2020), PFAS interacts differently with adsorbents in wastewater. Hence, more studies are required to understand the role of chain length during adsorption of PFAS onto sludge in wastewater matrix. The interaction by short and long-chain PFAS with sludge has been studied using activated carbons and polymers, which suggest short-chain PFAS interact with organic matter through electrostatic repulsions (Dalahmeh et al., 2019) and pore blockage, while long-chain PFAS tend to have hydrophobic interactions (Gagliano et al., 2020). Since organic matter constitutes a major fraction of sludge, the adsorption mechanism between short/ultra-short chain PFAS and sludge could be studied further, as discussed in 4.1.2.

4.2.1. 2 Role of background matrices

Earlier reviews have discussed in detail the interaction between inorganic and organic ions and organic contaminants (Kah et al., 2017). The organic matter (e.g., proteins, lipids, carboxylic and amino acids, natural and/or dissolved organic matter (Gagliano et al., 2020) present in wastewater (Ebrahimi et al., 2021, Liu et al., 2020) impact the adsorption of PFAS onto sludge in WWTPs (Zhang et al., 2019). Only a few studies have investigated the role of organic ions on PFAS removal, among which most are concentrated on the effect of humic and fulvic acids (Banks et al., 2020), and least is known about the impact of dissolved organic matter on PFAS removal from wastewater. (Dixit et al., 2020b) found organic matter (natural organic matter, humic acid and fulvic acid from surface water) had a negative impact (~ 55% decrease in adsorption capacity) on the adsorption of PFAS using ion exchange (IX) resins as organic ions caused blockage of pores through diffusion and competed with PFAS for adsorption sites (Dixit et al., 2021, Dixit et al., 2019). On the contrary, Wang et al. (2015a) found that the adsorption of PFAS to sludge reduced significantly after the removal of organic matter from the sludge through thermal treatment. Hence, the authors suggested that PFAS has a higher affinity for sludge from secondary treatment with higher biomass. Zhang et al. (2013a) observed that protein in the sludge had a positive effect on the adsorption of PFAS and deduced that certain amide groups present in proteins could possibly be aiding the adsorption of PFAS onto sludge. While another study found protein

in the wastewater influent led to lower removal of PFOS and PFOA (Pramanik et al., 2017).

Similar to organic ions, inorganic ions can have both positive and negative effects on the adsorption of PFAS (Kah et al., 2020, Banks et al., 2020, Zhang et al., 2019). Divalent cations, such as Ca^{2+} and Mg^{2+}, can form cation-bridge between the negatively charged PFAS and sludge, thereby improving adsorption (Zhang et al., 2013a). In contrast, monovalent cations present in wastewater, such as Na^{+}, have been found to hinder the adsorption of PFAS (Arvaniti et al., 2014). Anions, such as SO_4^{2-}, PO_4^{3-}, NO_3^{-}, Cl^{-}, and CrO_4^{-}, strongly compete with PFAS for adsorption sites (Dixit et al., 2021, Ateia et al., 2019a), thereby interfering with the adsorption of PFAS on sludge (Deng et al., 2010). Ateia et al. (2019a) observed a rapid decrease (10–20 %) in the adsorption of short-chain PFCAs with an increase in anion concentrations. Whereas, high background anions in the real wastewater matrix caused the salting-out effect, which compensated the hindrance by SO_4^{2-} by reducing the solubility of PFAS (Du et al., 2015).

Such conflicting observations in terms of the effect of organic and inorganic ions on the treatment of PFAS in wastewater (Table 4) generates scope for more research on the impacts of different types of organic compounds and inorganic ions (cations and anions) on the removal of short-chain PFAS and precursors at environmentally relevant concentrations (<1,000 ng/L) (Ateia et al., 2019a). Further, the effect of co-existing PFAS in the presence of background ions is yet to be explored. Indeed, the rate of adsorption decreased significantly when three PFCAs (C6, C7 and C8) were treated simultaneously in wastewater with resins, which was attributed to the competitive adsorption between short and long-chain PFAS (Du et al., 2015). To date, most studies have investigated the effects of organic and inorganic ions separately on individual PFAS in aqueous solutions at concentrations not relevant to the environment. Outcomes of the simultaneous effects of various organic and inorganic ions on the removal of co-existing short-chain (<C4) PFAS and/or precursors would be relevant for real-world conditions. Further, the chemical interactions between various ions and PFAS, leading to the differences in adsorption behaviour, could provide useful mechanistic insights.

4.2.2. Other treatment techniques

Advanced treatment processes like adsorption, electrochemical degradation, nanofiltration, and reverse osmosis (Dixit et al., 2020a, Ateia et al., 2019a, Wang et al., 2019b, Soriano et al., 2017) are comparatively more effective than conventional processes (Kibambe et al., 2020, Wang et al., 2019a) in terms of PFAS removal. For example, a WWTP based on conventional treatment showed negative removal (-27 %) for PFAS, whereas a WWTP using advanced treatment (reverse osmosis) achieved 86 % removal (Tabtong et al., 2015). Similarly, a membrane bioreactor system was found to be more effective in removing long-chain PFCAs than conventional activated sludge treatment (Pan et al., 2016). However, it is noteworthy that some treatments like ozonation, UV, chlorination and sand filtration have been found ineffective in removing PFAS (Gagliano et al., 2020, Pan et al., 2016).

Nanofiltration (NF) has been efficient (>98%) in removing PFAS along with dissolved organic carbon and mineral hardness from drinking water (Franke et al., 2021). The efficiency of NF in removing PFAS while simultaneously achieving other water quality targets in wastewater needs validation by further studies. A study that conducted NF followed by electrochemical degradation could achieve ~ 99 % removal of C6 PFAA in less than 3 h for PFAS concentrations <1,000 mg/L (Soriano et al., 2017). Similarly, electrochemical treatment processes using electrodes like boron-doped diamond anode and stainless-steel cathode could achieve >95% degradation of PFAS with high and low initial concentrations of 1,642 µg/L (Gomez-Ruiz et al., 2017) and 62 ng/L (Wang et al., 2019b) within 10 h. Hence, the application of electrochemistry for degradation of short-chain PFAS and PFAS precursors at lower concentrations could be explored more rather than combining it with other techniques.

Treatment trains should involve processes that are not efficient individually, while their combined efficiency is higher in terms of PFAS removal along with the ease of operation and cost-effectiveness. For instance, ozonation (Wang et al., 2019b) and photocatalysis (Lopes da Silva et al., 2017) were ineffective in removing PFAAs from wastewater matrix individually, while the combination of ozonation and photocatalysis led to the degradation of PFAS as the reactions between $^{\bullet}OH$ and PFAAs precursors can initiate degradation reactions forming recalcitrant shorter chain PFAS (Wang et al., 2019a, Wang et al., 2018a, Huang et al., 2016). Similarly, efficient treatment (>98%) of PFAS from drinking water using NF followed by subsequent adsorption of PFAS (85–99%) from NF concentrate (Franke et al., 2021) calls for more study using such treatment train practices for effective remediation of PFAS in wastewaters.

Another unique aerosol-based separation technique for remediation of precursor 6:2 FTSA achieved ~100 % removal within 1 h (Ebersbach et al., 2016). However, the initial concentration of the spiked PFAS in wastewater was unrealistically high (~ 10 mg/L), which is one common limitation in experimental studies published to date (Table 4). More experimental data carried out at realistic concentrations (<1,000 ng/L) (Li et al., 2020) and involving short-chain PFAS (C < 4), and matrix effects are needed. The knowledge regarding the treatment of PFAS precursors from wastewater at environmentally relevant concentrations is also limited.

5. Conclusions and research recommendations

5.1. Conclusions

The lack of monitoring data from many parts of the world limits our understanding of the global distribution of PFAS. The inaccessibility of advanced analytical facilities and the need to meet more pressing wastewater quality issues in many developing countries could be responsible for the dearth of PFAS monitoring studies in these regions. Ultra-short chain PFAS, precursors of PFAS, and new generation replacements of conventional PFAS are understudied, which could be attributed to their analytical method limitations and the complexity of TOPA and non-target analysis. The relative ease of PFAS analysis in effluents, having lower background interference than in influents, could be responsible for fewer studies of PFAS in influents than effluents. The partitioning of longer chain PFAS to sludge and the transformation of precursors to shorter chain PFAAs during biological treatment influence the concentrations of PFAS in the sludge and the effluents. The release of volatile compounds is a possible route for the transfer of precursors from wastewater to air and remains unexplored currently. While most studies monitored the removal of PFAS from the aqueous phase (effluents), their fate after partitioning to sludge and/or biosolids is relatively unexplored, which compels us to think if the mere shifting of PFAS loads from one phase to the other has been misunderstood as removal to date.

5.2. Research recommendations

- The limited information about PFAS levels in developing and least developed countries necessitates future studies in these regions.

- To date, no study has critically reviewed the sampling procedures despite it being critical in monitoring PFAS, considering the high risk of background contamination.
- Monitoring ultra-short chain PFAS, precursors of PFAS, and new generation PFAS in wastewater and studying their transformation pathways is required as some of these compounds can exhibit similar persistence and bioaccumulating capabilities as their longer-chain counterparts.
- More monitoring data for PFAS in the influents could add to the existing knowledge about the sources of short-chain PFAS and newly discovered PFAS precursors in WWTPs.
- While adequate studies reveal PFAS precursors' transformation into perfluoroalkyl carboxylic acids (PFCAs), C $\geq$ 4, the likelihood of precursors to transform into ultrashort-chain PFCAs (C2-C3) remains unexplored.
- Investigating the degradability (e.g., biodegradation, photodegradation, ozonation, etc.) of synthetic precursor compounds at a laboratory scale could help better understand the mechanisms responsible for their transformations and effective treatments.
- The effects of different biological treatments, especially the effects of aerobic and anaerobic microbes, on PFAS precursors' transformation to PFAAs need to be explored.
- The reported rise in the levels of PFAS after the application of biological deodorization in WWTPs necessitates studying the effects of specific microorganisms used for the deodorization process.
- More mass balance studies of PFAS and their precursors in WWTPs, accounting for masses in all three phases, are advised as their removal reported in WWTPs so far could be simply the result of a transfer of mass load from one phase to another within a WWTP.
- The common practice of discharging landfill leachates into WWTPs and dumping WWTP sludge and/or biosolids in landfills necessitates studying the fate of PFAS throughout such interconnected systems.
- The combined effects of various organic (e.g. humic and fulvic substances, lipids and proteins, and natural and/or dissolved organic matter) and inorganic ions (cations, anions, and zwitterions) on the removal of co-existing short-chain PFAS and precursors need further studies due to the real-world implications.

Declaration of Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Letter

Landfill Gas: A Major Pathway for Neutral Per- and Polyfluoroalkyl Substance (PFAS) Release

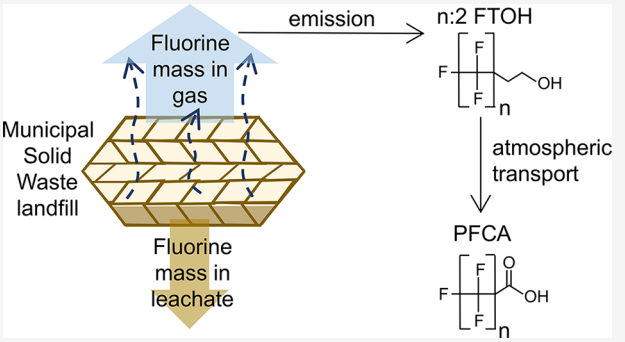
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ABSTRACT: The undisclosed and ubiquitous use of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in consumer products has led to a growing issue of environmental pollution, particularly within the solid waste community, where the fate of volatile (neutral) PFAS in landfilled refuse is not well understood. Here, three municipal solid waste landfills in Florida were assessed for neutral PFAS in landfill gas and ionic PFAS in landfill leachate to compare the relative mobility between the two pathways. Landfill gas was directly sampled using a high volume, XAD-2 resin based sampling approach developed for adsorption and analysis of 27 neutral PFAS. Across sites, 13 neutral PFAS were identified from fluorotelomer alcohol (FTOH), fluorotelomer olefin (FTO), secondary FTOH, fluorotelomer acetate (FTOAc), and fluorotelomer methyl acrylate (FTMAc) classes; however, FTOHs dominated concentrations (87−97% total neutral PFAS), with most detections surpassing utilized calibration levels. Even under conservative assumptions, the mass of fluorine leaving in landfill gas (32−76%) was comparable to or greater than the mass leaving in landfill leachate (24−68%). These findings suggest that landfill gas, a less scrutinized byproduct, serves as a major pathway for the mobility of PFAS from landfills.



KEYWORDS: *volatile, emissions, GC, fluorotelomer alcohol*

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1. INTRODUCTION

Widespread per- and polyfluoroalkyl substance (PFAS) contamination has been a mounting environmental concern due to their chemical persistence and toxicity to human and biotic health.[1−4] While numerous industries are being confronted with PFAS-related management challenges, the burden of remediation and PFAS removal has often fallen on downstream industries—namely, the solid waste sector.[5−9] Discarded, PFAS-laden consumer products including textiles, wood products, and packaging and commonly landfilled industrial byproducts like MSW incineration ash and wastewater biosolids are known contributors to PFAS loading in landfills.[10−16] Existing research suggests most discarded PFAS mass is retained within landfills[9,17] with liquid-phase byproducts of waste decomposition, leachate and gas condensate, currently considered prevalent pathways for PFAS mobilization.[2,7,9] However, the extent of PFAS release to another major byproduct, landfill gas (LFG), has remained largely unscrutinized.

The bulk of PFAS characterization studies focus on nonvolatile/semivolatile (ionic) perfluoroalkyl acids (PFAAs) measured in liquid and solid matrices, in part because of a high presence and awareness of these species within the PFAS community but largely because analytical capabilities for ionic PFAS measurement are better established.[18−21] Volatile (neutral) PFAS are also utilized in consumer products[13,22−27,27] and have been determined in a few studies on ambient air surrounding landfills and near wastewater treatment plants,[28−32] but a lack of volatile analytical standards and latency in methodological development has hindered the progression of gas phase research in environmental matrices. Whereas PFAS characterization in leachate is established, concentrations ranging from thousands to tens of thousands of nanograms per liter are commonly encountered;[33−38] only two studies characterize volatile PFAS directly in LFG.[39,40] Titaley et al. identified fluorotelomer alcohol (FTOH), fluorotelomer acrylate (FTAc) and fluorotelomer olefin (FTO) homologues in LFG with combined concentrations ranging from 4,600 to 14,000 ng m^{-3} across three landfills. Goukeh et al., only assessing FTOHs, identified higher combined concentrations than Titaley et al., finding ∼18,000 ng m^{-3} (sum of 6:2 and 8:2

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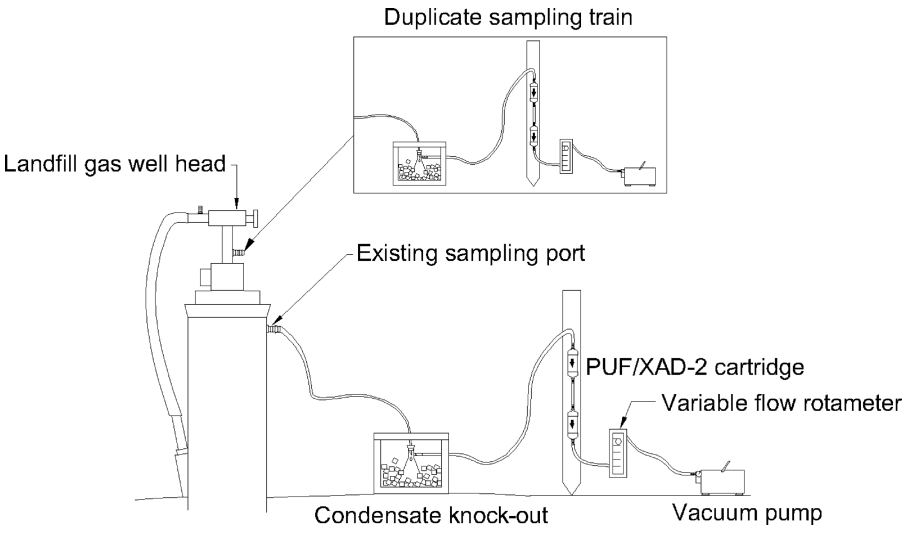


Figure 1. Developed system for sampling neutral PFAS directly from landfill gas well heads.

FTOH) in the one LFG sample examined. These studies suggest PFAS variability in LFG, which motivates further investigation, deploying higher sampling volumes[39] and larger analyte lists[40] to understand the potential presence of other neutral PFAS and distribution among landfills of different regions, compositions, and sizes.

With the ongoing development of PFAS regulation,[19] understanding the partitioning behavior of PFAS in major repositories like MSW landfills grows increasingly critical to minimize environmental and human risk. Unlike leachate, LFG is not always captured by collection systems, and management varies broadly across landfills, ranging from no treatment (i.e., passive venting) to some treatment (i.e., flaring, LFG to energy projects), but current treatment, if any, is not intended for PFAS.[41,42] Emerging research suggests the toxicity of volatile species (specifically 6:2 FTOH) to be significantly higher than their ionic counterparts via the inhalation pathway (a main route of exposure for volatile compounds).[43−47] Further, degradation of neutral species to ionic PFAAs once emitted to the atmosphere is well established.[48−58] The potential for long-range atmospheric transport of PFAS from landfills underscores the importance of considering neutral species and their fate during management to prevent further environmental contamination of highly scrutinized PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). As the only studies on LFG primarily identified FTOHs in LFG, the magnitude and significance of other neutral species remains unclear.

Here, LFG was sampled directly from gas well heads at three MSW landfill locations in Florida using a higher volume sampling protocol. XAD-2 resin sandwiched between polyurethane foam (PUF) was utilized for PFAS capture, then samples were analyzed for 27 volatile/semivolatile (neutral) PFAS via targeted gas chromatography high resolution mass spectrometry (GC-HRMS). To contextualize release in the gas phase, leachate was also collected at each landfill and analyzed for ionic PFAS (n = 93) using ultrahigh pressure liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). The observed LFG and leachate concentrations were normalized on a mass of fluorine basis to compare the potential mobility in gas versus leachate matrices. This study provides foundational data critical for understanding the role of landfills in anthropogenic PFAS release and for informing LFG management.

2. METHODS AND MATERIALS

For brevity, materials and methods associated with ionic PFAS analysis in landfill leachate are provided in section 1 of the Supporting Information (Tables S-1 through S-4).

2.1. Standards and Reagents. Targeted neutral PFAS (≥97% purity, n = 27) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada), SynQuest Laboratories (Alachua, FL), and Chiron (Stiklestadveien, Trondheim, Norway). Nine classes of neutral PFAS (perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonamidoethanols (FASEs), fluorotelomer acetates (FTOAcs), fluorotelomer methyl acrylates (FTMAcs), fluorotelomer iodides (FTIs), fluorotelomer secondary alcohols (sFTOHs), FTOHs, FTAcs, and FTOs) were measured using eight isotopically labeled internal standards (IS) from FASA, FASE, FTOH, and FTMAc classes for quantitation (Table S-5).

2.2. Sample Preparation and Collection. Polyvinyl chloride (PVC) cartridges filled with 4−5 g of Amberlite XAD-2 resin retained between two polyurethane foam (PUF) discs were utilized for PFAS capture.[29,59,60] Before use, XAD-2 sorbent was made PFAS-free through sequential Soxhlet extractions.[61] All cartridge components, sampling vessels, and tubing were sonicated in a mixture of Liquinox and PFAS-free water, rinsed, and then sonicated in methanol and methanol rinsed before use. Once dried and assembled, cartridges were stored in individually sealed polyethylene bags at 4 °C until sampling.

As neutral compounds were the focus of this investigation, aerosolized/particulate-bound PFAS were not specifically targeted for capture; however, a condensate collection system was included to prevent moisture interference. The developed sampling system (Figure 1) consisted of a condensate knockout (borosilicate, barbed Erlenmeyer flask contained in a cold box), two PUF/XAD-2 cartridges (installed in-series), a rotameter for flow control, a portable vacuum pump, and PFAS-free Tygon tubing. Before each sampling event, gas well head connection to the larger landfill gas collection system was disabled to create a neutral to positive pressure, workable for flow through the sampling system, then gas composition/

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Table 1. Average Concentrations (n = 2) of 13 Neutral PFAS (ng m^{-3}) from Three Municipal Solid Waste Landfills in Florida (Site Characteristics Are Provided in Table S-9)[a]

	concentration (ng m^{-3})					
analyte	landfill 1	E	landfill 2	E	landfill 3	E
4:2 FTOH	220		ND		57	
6:2 FTOH	*>9,900*	**170,000**	*>6,000*	**22,000**	*>6,500*	**62,000**
8:2 FTOH	*>6,800*	**200,000**	*>6,000*	**140,000**	*>6,500*	**740,000**
10:2 FTOH	*>5,100*	**14,000**	*>3,000*	**23,000**	*>5,000*	**120,000**
12:2 FTOH	860		1,400		5,000	
5:2 sFTOH	*>2,900*	**8,800**	*>1,700*	**9,000**	*>1,900*	**5,900**
7:2 sFTOH	320		*>1,300*	**13,000**	*>1,400*	**11,000**
8:2 FTO	2,500		1,300		550	
10:2 FTO	650		840		540	
12:2 FTO	97		580		160	
8:2 FTOAc	610		90		490	
10:2 FTOAc	99		19		140	
6:2 FTMAc	3,800		56		150	

[a]Concentrations of 6:2, 8:2, and 12:2 FTOH and 5:2 and 7:2 sFTOH consistently exceeded the upper limit of developed calibration ranges; therefore, both a minimum concentration (assuming the highest calibration concentration) and a maximum extrapolated concentration are provided. Italicized values denote a minimum concentration. Column "E" presents average maximum concentrations. "ND" denotes non-detect measurements. FTAcs, FASAs, FASEs, FTIs, and 8:2 FTMAc were not detected in any samples. Analyte acronyms and details are provided in Table S-5.

temperature was recorded using an Optimax Biogas analyzer (MRU Instruments, Humble, TX). Duplicate sampling trains were connected to existing gas well sampling ports. Approximately 1,200 L was sampled through each train at a flow rate of 5 L min^{-1}. After sampling, PUF/XAD-2 cartridges were sealed and individually stored at ≤4 °C for transport/storage. Quality control (QC) procedures are provided in the SI, section 2.

2.3. Extraction and Analysis. Spent XAD-2 from each cartridge was weighed and transferred to a 50 mL polypropylene centrifuge tube and vortexed, and approximately 2 g aliquoted for extraction. Samples were spiked with a mixture of mass labeled IS (Table S-5), rotated end-over-end for 18 h in 4 mL of 75/25% (v/v) ethyl acetate and methanol, and centrifuged for 10 min at 4,000 rpm. Supernatants were transferred to 15 mL centrifuge tubes, and the extraction process was repeated, combining supernatants from the two-fold extraction. Extracts were concentrated to 3 mL via gentle nitrogen evaporation, aliquoted, and stored no more than 30 days at −20 °C until analysis. QC details are provided in the SI, section 2 (Table S-6 and Figure S-1).

Targeted analysis of 27 neutral PFAS by positive chemical ionization (PCI) with selected ion monitoring (SIM) was conducted using a Thermo Scientific TRACE 1310 gas chromatograph coupled to a Thermo Scientific Orbitrap Exploris GC 240 mass spectrometer (GC-HRMS; see SI, section 2 for details regarding GC separations and instrumentation). A 12-point external calibration curve (from 1 to 2,000 pg μL^{-1}) was developed for quantitation, prepared through serial gravimetrically derived dilutions of primary stock solutions. A mixture of mass labeled IS at concentrations of 150 pg μL^{-1} was added to each calibration level. When a labeled standard was not available for a compound, a labeled standard with a similar retention time or structure was utilized for quantitation (Table S-5).

3. RESULTS AND DISCUSSION

Unexpectedly, several neutral PFAS concentrations in LFG exceeded the implemented calibration levels. Because of considerable exceedance for some compounds, dilution would reduce IS below instrument detection; therefore, in instances where sample concentrations exceeded calibration limits, two concentrations are presented (Equation S-1): a minimum value which assumes the highest calibration concentration and a maximum extrapolated concentration. Fluorine mass release calculations utilize minimum values, preventing overextrapolation while providing a conservative estimate for leachate comparison. Even under these assumptions, substantial concentrations of neutral PFAS, higher than those previously observed, were identified. Future assessments should deploy shorter sampling durations to refine findings.

3.1. Neutral PFAS in Landfill Gas. Except for 4:2 FTOH in one landfill, 13 PFAS were detected in duplicate samples across the three sites (site characteristics are provided in Table S-9). Observed concentrations are displayed in Table 1. At minimum, combined concentrations of neutral PFAS in LFG ranged from 22,000 to 33,000 ng m^{-3}. Considering extrapolated values, total concentrations ranged from 210,000 to 940,000 ng m^{-3}, an order of magnitude higher than those previously reported in LFG.[39]

3.1.1. FTOHs and sFTOHs in Landfill Gas. Like previous studies on LFG and air surrounding landfills, FTOHs dominated neutral PFAS concentrations;[28,31,32,39,40] however, extrapolated concentrations in this study surpassed previous reports in LFG, in some cases by 2 orders of magnitude, and were more comparable (although much lower) to concentrations recently identified in soil vapor near a PFAS manufacturing facility.[55] While there are uncertainties given the degree of extrapolation, the magnitude of FTOHs found in this study compared to existing research suggests fundamental differences potentially related to sampling methodology (e.g., much larger sampling volumes) and/or sampled landfill characteristics (e.g., waste type, age, air intrusion), although these data were not available for comparison. Across the three sites, 6:2, 8:2, and 10:2 FTOH, combined, made up 87 to 97% of total concentrations, but 8:2 FTOH alone constituted 50 to 79%. The shortest and longest analyzed homologues, 4:2 and

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12:2 FTOH, were significantly lower in concentration (Table S-10). This is supported by previous FTOH distributions determined from source fluoro-telomer polymers[62] and observations in LFG, urban air, and air surrounding wastewater treatment/landfill sites.[28−31,39,40,63] Concentrations of 12:2 FTOH were of similar magnitude to those in Titaley et al., but 4:2 FTOH has not been detected in LFG, suggesting MSW landfills to be a previously unidentified potential source of atmospheric 4:2 FTOH.[39]

Secondary FTOHs have not been targeted in gas-phase landfill research but have been identified in condensate associated with LFG collection systems.[37] As intermediary byproducts of 6:2 and 8:2 FTOH biodegradation to PFAAs, 5:2 and 7:2 sFTOH, were unsurprisingly elevated, they were at least an order of magnitude lower than respective parent FTOH homologues.[64−66] All detections of 5:2 sFTOH and two out of three detections of 7:2 sFTOH were above calibration, combined sums attributed to 2 to 10% of total concentrations.

3.1.2. Other Neutral PFAS in Landfill Gas. Other neutral PFAS fell within acceptable calibration ranges and together accounted for 0.22 to 1.9% of total concentrations. FTO homologues have been encountered in other LFG and ambient air studies, but in past assessments 8:2 and 10:2 FTO were below limits of quantitation and 12:2 FTO concentrations were consistently an order of magnitude higher than those reported here.[39,59] To the authors' knowledge, 8:2 and 10:2 FTOAc and 6:2 FTMAc have not been determined in LFG. FTOAcs are not commonly assessed analytes but are associated with fluoropolymer textile treatments and have been identified in one indoor air study from Japan.[67,68] Similarly, 6:2 FTMAc has only been analyzed in a few studies on cosmetics and wastewaters but at lower concentrations.[69−71]

3.2. Comparative Fluorine Mass Release between Landfill Byproducts. Normalizing PFAS concentrations on a fluorine basis allows comparisons to be drawn between different matrices and PFAS types (e.g., gas−liquid, neutral−ionic, precursor−terminal). This methodology is widely used to assess the "mass balance" of PFAS within systems, given that the long-term environmental fate of measurable PFAS is transient, whereas the mass of fluorine is conserved.[17,72,73]

Here, the same approach is utilized to compare the PFAS mobility in leachate versus LFG pathways. Neutral (Table 1, minimum values) and ionic (Table S-4) PFAS concentrations in LFG and leachate from this study were individually normalized to a mass of fluorine (Equation S-2) using compound specific fluorine mass fractions (Table S-8). Summed fluorine masses in leachate and LFG were then scaled according to site-specific annual generation volumes reported for each landfill (Table S-9).[41] A caveat of this comparison is the absence of measurements for neutral species in leachate and ionic species in LFG; however, the literature suggests FTOHs (the dominant neutral class identified) predominantly exist in the gaseous phase, while PFAAs exist in liquid or particulate phases.[28,74] Subsequent research should assess neutral and ionic compounds in both matrices to validate findings and further elucidate the PFAS behavior in landfills.

Even utilizing minimum concentrations observed in LFG, equal magnitudes of fluorine release are observed between LFG and leachate at each site (Figure 2)—contrasting from existing estimates of PFAS mass flow from landfills.[9] Existing

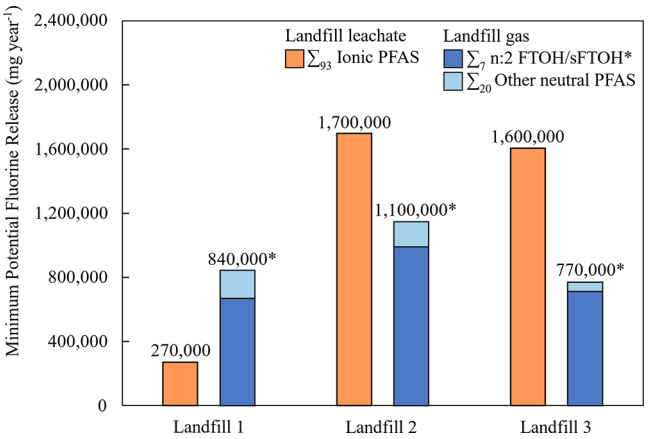


Figure 2. Annual fluorine mass release in landfill leachate versus landfill gas (LFG) from three municipal solid waste landfills in Florida. Fluorine masses in leachate are derived from ionic PFAS ($\sum_{93}$ PFAS) concentrations measured in leachate from each site (Table S-4) multiplied by the annual leachate generation volume and scaled using each detected compound's fluorine mass fraction (Tables S-8, S-9). The same methodology was applied for neutral PFAS ($\sum_{27}$ PFAS) in LFG by using the average of minimum concentrations (Table 1). Asterisked (*) values denote input FTOH/sFTOH concentrations which were above calibration levels developed for this study and therefore assumed to be at the highest calibration concentration. Consequently, these findings should be viewed as minimum values which conservatively estimate the magnitude of PFAS mobility in leachate versus LFG.

estimates, based on limited data, suggest that most PFAS mass mobilized from landfills releases through leachate (~62%).[9] However, our data from Landfill 1, showing over 76% fluorine release in LFG, along with substantial masses released by LFG in Landfills 2 and 3 (at minimum 40% and 32%, respectively), indicate that LFG may serve as an equal, likely greater, conduit of PFAS mobility from landfills than leachate, concurring with previous reactor studies on FTOH volatilization and neutral/ionic PFAS assessments of select waste materials.[17,75,76]

At least 79 to 92% of the fluorine mass in LFGs were derived from FTOH/sFTOH classes, with minimal contribution from FTOs, FTOAcs, and FTMAcs. In this conservative assessment, fluorine from LFG surpassed leachate in only Landfill 1. Although actual fluorine emission from LFG is higher than reported here, the elevated ratio of gas-to-leachate generation at Landfill 1 likely caused this difference (Table S-9). Landfill 2, the largest site, demonstrated the highest combined fluorine release from leachate and LFG, followed by Landfill 3, and then Landfill 1, corresponding to descending waste mass in place at each location.

4. IMPLICATIONS

This study provides fundamental data about neutral PFAS in LFG from MSW landfills. Unexpectedly, FTOH/sFTOH detections in LFG from this study exceeded implemented calibration levels; subsequent research should deploy shorter sampling durations. Regardless, even under more conservative assumptions these findings suggest that LFG, largely unscrutinized for PFAS, contains similar or greater magnitudes of PFAS compared to leachate, mostly attributed to midlength FTOH homologues. As landfills can be viewed as unabating PFAS repositories, the significance of LFG management in mitigating the long-term, long-range atmospheric transport of

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neutral PFAS, and subsequently derived PFAAs, cannot be understated. Unlike landfill leachate, LFG collection systems (when in place) are not fully efficient, collecting an estimated ~50−70% of generated biogases.[77] Though this is a considerable collection efficiency of biogas and presumably neutral PFAS, management of captured LFG fractions varies globally, from no treatment to degrees of carbon filtration and thermal treatment (i.e., flaring, advanced renewable natural gas technologies). Because the feasibility of PFAS destruction through thermal treatment remains unclear, research is needed to determine the treatment/removal efficiency of existing LFG management technologies. Considering the range of LFG capture efficiency, the retention and emission of neutral PFAS via fugitive emissions (i.e., migration through the waste layer) should also be examined, along with the role of landfill waste type, age, and temperature in neutral PFAS variability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.4c00364.

Acronyms, structures, and instrumental parameters for neutral PFAS via GC-HRMS and ionic PFAS via LC-MS/MS; detailed QC information and results; and fluorine mass balance/extrapolation details and assumptions (PDF)

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Notes

The authors declare no competing financial interest.

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Landfill leachate treatment process is transforming and releasing banned per- and polyfluoroalkyl substances to UK water

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Landfills are a known source of PFAS pollution. Many have environmental permits allowing the discharge of treated leachate to controlled waters. In this article we compared leachate data for 17 PFAS from 17 different landfill sites across the UK. The results show that the landfill leachate treatment process (designed to improve water quality) is generating the banned PFAS; PFOA and PFOS. Approximately 80% of locations tested showed an increase in PFOS, with an increase of 1,335% in one sample. The highest concentrations of PFOS and PFOA in treated leachate were 2,460 ng L^{-1} and 26,900 ng L^{-1}, respectively. When compared against the environmental quality standard of 0.65 ng L^{-1} for PFOS this leachate could pose a significant concern. Landfill leachate treatment has proven effective for a wide range of different pollutants, but this research shows in several instances that it is not appropriate for PFAS remediation.

KEYWORDS

per- and polyfluoroalkyl substances, PFAS, PFOS, PFOA, landfill leachate, waste water treatment, effluent

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) are persistent environmental pollutants of global concern. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) were the first two PFAS to be listed under the Stockholm convention (Secretariat of the Stockholm Convention (UNEP), 2008). There is currently widespread contamination of PFOS and PFOA which is impacting the marine environment, freshwater environments and drinking water (Kurwadkar et al., 2022). PFOS and PFOA are not readily removed by conventional drinking or waste-water treatment processes, and growing evidence has shown that PFOA and PFOS can be generated from precursor compounds in chemical and biological processes. Xiao et al. (2012) identified a significant increase (up to 1,200%) in the wastewater concentrations of perfluorohexanoic acid (PFHxA) and PFOA at 22 out of 37 wastewater treatment plants. Similar increases have also been observed in other biological wastewater treatment plants (Guo et al., 2010; Schultz et al., 2006; Takagi et al., 2011; Xiao et al., 2012), and during the drinking-water disinfection processes (Appleman et al., 2014; Boiteux et al., 2017; Dauchy et al., 2012). Increases of 18–77% of the mass of perfluoroalkyl carboxylic acids PFCAs, including PFOA, have been reported after disinfection of ozone or chlorine. The authors concluded that this was caused by the transformation of unidentified precursors in surface water and other legacy precursor compounds (Boiteux et al., 2017).

These increases in PFAAs have been identified in a wide number of different treatment processes all over the globe. A survey of 15 U.S. water treatment plants, identified that the concentration of PFOA and PFOS in water was consistently higher after chemical disinfection treatments (Appleman et al., 2014). Similarly, increases in PFOA and PFOS concentrations in drinking-water processes have been reported in Japan, which was attributed to the transformation of precursor compounds (Takagi et al., 2011). The extremely strong carbon-fluorine bond makes PFAS inherently persistent to the biological treatment, with studies showing that the biological landfill leachate treatment process also resulted in elevated total PFAS concentrations in leachate after aeration (Fuertes et al., 2017; Solo-Gabriele et al., 2020). This indicates biotransformation of precursor compounds [such as fluorotelomer alcohols (FTOHs), fluorotelomer sulfonates (FTSs) and polyfluoroalkyl phosphate esters (PAPs)] in leachate to produce perfluoroalkyl acids (PFAAs) (Liu et al., 2021).

While this process has been studied in some global regions, to the best of our knowledge it has never been investigated or reported in the UK. The UK has a long industrial history where a large proportion of chemical waste was disposed of in landfill sites. Many of these are historic landfills, where, according to the Environment Agency definition, there is no pollution prevention and control permit or waste management license currently in force (Gov.UK, 2024). Climate change is resulting in more severe weather events and as a result the UK is experiencing increased frequency and severity of rainfall and coastal erosion. This is already putting pressure on these landfill sites, with nearly one in ten historic coastal landfill sites in England already at risk of erosion (Brand et al., 2018). Many of these historic landfill sites are also located within drinking water protection zones (Brand and Spencer, 2023) and so it is imperative that we understand the potential risk of PFAS from our industrial legacy.

Once a landfill operator in the UK has treated the leachate, they are legally allowed to discharge their waste directly into controlled waters via a Discharge to Water permit, this includes hazardous landfills (Gov.UK, 2024). Given that the treatment process has the potential to generate banned PFAS it is imperative we understand these risks further.

2 Methodology

In this study we evaluated leachate data from 17 landfill locations across the UK to identify if they are likely to be a significant source of PFAS to the environment. All data obtained for this report was obtained by an ENDS Report Freedom of Information Request. The data was collected by third-party contractors and formed part of a UK government analysis into landfill leachate for PFAS as part of a wider DEFRA-funded research project on persistent organic pollutants (Environment Agency, 2021). The data collected came from a range of operational, closed and historical landfills in England, they are predominantly classified as non-hazardous, accepting municipal solid wastes. All samples were collected between 2021–2022. The locations of the landfill sites and sample collection dates were not provided, we were informed this was because the contractors provided the Agency with an anonymized dataset. Where on-site leachate treatment facilities were available, raw and treated leachate (final effluent) samples were collected. The treatment facilities used biological, chemical, and physical technologies, the most commonly used in the UK landfill industry is biological sequence batch reactors (SBR) with alkaline-dosing. As the data set was anonymized we were unable to identify which technology was used at each location.

In total we obtained results for 48 samples. This included 32 raw samples and 16 treated samples from 17 different landfill sites, plus three blank samples. Duplicate samples were obtained from 4 locations (Landfills 1, 2, 6, & 11). Samples were prepared using solid phase extraction and quantified using isotope labeled internal standards, with analysis by HPLC-MS/MS (high pressure liquid chromatography coupled to a triple quadrupole mass spectrometer). Results were reported for 17 PFAS (perfluorooctyl sulphonate (PFOS), perfluorooctanoic acid (PFOA), 5: 3 fluorotelomer carboxylic acid (5, 3 FTCA), 6: 2 fluorotelomer sulphonate (6, 2 FTSA), 8: 2 fluorotelomer alcohol (8, 2 FTOH), perfluoropentyl sulphonate (PFPeS), perfluoroheptyl sulphonate (PFHpS), perfluoropentanoic acid (PFPA), perfluoroheptanoic acid (PFHpA), hexafluoropropylene oxide-dimer acid (HFPO-DA) (Gen-X), F53B (two components), perfluorobutyl sulphonate (PFBS), perfluorobutanoic acid (PFBA), perfluorononanoic acid (PFNA), perfluorohexanoic acid (PFHxA), perfluorohexyl sulphonate (PFHxS), perfluoroethylcyclohexane sulphonate (PFECHS)) with limits of detection of 0.065 ng L^{-1} for PFOS and PFOA. Data is presented in the Supplementary information.

As the data was obtained from a variety of different landfill sites, we urge caution comparing data between different locations. However, in this study we are focused on identifying overall trends and identifying relative trends in raw and treated leachate. These paired raw and treated samples were analyzed at the same time which facilitates this type of data analysis.

3 Results and discussion

Concentrations of all 17 PFAS in the raw leachate ranged from 1 ng L^{-1} to 87,100 ng L^{-1} (Table 1). The highest concentration for any PFAS in a treated sample was for perfluorobutyl sulphonate (PFBS), which was detected at a concentration of 44,800 ng L^{-1}. PFOS concentrations in the raw leachate samples ranged from 16–320 ng L^{-1} and 15.3–2,460 ng L^{-1} in the treated samples. These concentrations greatly exceed the current environmental quality standards (EQSs) for PFOS. The annual average EQS for inland surface waters is 0.65 ng L^{-1} and the annual average EQS for other surface waters is 0.13 ng L^{-1} (Environment Agency, 2019). The EU Water Framework Directive applies an EQS of 0.65 ng L^{-1} for PFOS in (inland) surface waters (European Union, 2013), with a threshold of 4.4 ng L^{-1} proposed for a group of 24 PFAS in surface and groundwater (European Environmental Bureau, 2023). In England, the Drinking Water Inspectorate's current guidance states that in England the acceptable levels of the two most common types of PFAS - PFOS and PFOA - is 100 ng L^{-1}. In the U.S. the proposed legal limit is 0.004 ng L^{-1} for PFOA and 0.0 2 ng L^{-1} for PFOS. There are currently no guidelines for other PFAS chemicals. There is currently no guidance in England on PFBS, although animal studies following oral exposure to PFBS have shown health effects on the thyroid, reproductive organs and tissues, developing fetus, and kidney (U.S. Environmental Protection Agency, 2024).

Data was reported for 17 Landfill sites, but only 14 locations had data from both raw and treated leachate. This paired data was used to provide a broad assessment of the effectiveness of 14 sites to reduce PFAS concentrations. Only one location (landfill 11) displayed lower concentrations of every PFAS in the treated samples relative to the raw samples. The majority of locations displayed a relative increase in

TABLE 1 Average concentrations and relative difference of the 17 PFAS in raw and treated leachate samples across the 14 paired locations.

		Landfill 1	Landfill 2	Landfill 3	Landfill 4	Landfill 5	Landfill 6	Landfill 7	Landfill 8	Landfill 9	Landfill 10	Landfill 11	Landfill 12	Landfill 13	Landfill 14	Number of locations with an increase	Number of locations with a decrease
PFOS	Raw	193	168	84	83	16	47	169	274	70	317	232	129	320	52		
	Treated	478	258	268	125	15	70	718	342	56	2,460	157	302	603	752	11	3
	x Increase	2.5	1.5	3.2	1.5	1.0	1.5	4.2	1.2	0.8	7.8	0.7	2.3	1.9	14.4		
PFOA	Raw	737	940	15,500	545	10	59	1,310	1,280	538	1,310	2,183	1,014	2,250	533		
	Treated	1,040	1,295	26,900	635	9	44	1,230	862	140	3,670	1,030	1,350	2,350	102	7	7
	x Increase	1.4	1.4	1.7	1.2	0.9	0.7	0.9	0.7	0.3	2.8	0.5	1.3	1.0	0.2		
5:3 FTCA	Raw	193	3,942	5,550	2,770	*0.001*	3.0	1790	1940	3,710	460	3,733	3,428	6,390	1,250		
	Treated	478	13	86	*0.001*	*0.001*	*0.001*	14	92	4.0	750	15	96	41	30	2	11
	x Increase	2.5	0.0	0.0	0.0		0.0	0.0	0.0	0.0	1.6	0.0	0.0	0.0	0.0		
6:2 FTSA	Raw	116	489	532	227	*0.001*	5.0	128	344	129	300	198	1,202	244	291		
	Treated	111	74	1,030	12	*0.001*	1.0	4.0	92	3.0	1800	109	108	101	94	2	11
	x Increase	1.0	0.2	1.9	0.1		0.2	0.0	0.3	0.0	6.0	0.6	0.1	0.4	0.3		
8:2 FTOH	Raw	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	1,630	1,130		
	Treated	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	0	2
	x Increase													0.0	0.0		
PFPeS	Raw	41	123	48	25	*0.001*	8.0	59	47	71	99	88	35	73	60	11	2
	Treated	257	153	103	149	*0.001*	4.0	465	223	86	100	42	157	241	82		
	x Increase	6.3	1.2	2.1	6.0		0.5	7.9	4.7	1.2	1.0	0.5	4.5	3.3	1.4		
PFPHpS	Raw	3.1	8.3	*0.001*	*0.001*	*0.001*	2.0	9.0	10	3.0	17	5.0	*0.001*	14	*0.001*	9	2
	Treated	14	*0.001*	*0.001*	11	*0.001*	4.0	28	14	5.0	89	*0.001*	17	18	*0.001*		
	x Increase	4.5	0.0		11,000		2.0	3.1	1.4	1.7	5.2	0.0	17,000	1.3			
PFPA	Raw	648	662	868	388	*0.001*	9.0	551	676	707	713	800	816	1,350	725	10	3
	Treated	1,680	859	1,210	856	*0.001*	22.5	1,460	1960	235	529	334	1,510	1,510	866		
	x Increase	2.6	1.3	1.4	2.2		2.5	2.6	2.9	0.3	0.7	0.4	1.9	1.1	1.2		
PFPHpA	Raw	336	408	624	256	*0.001*	18	607	572	398	463	459	310	695	362	9	4
	Treated	622	490	715	335	*0.001*	16.5	640	693	109	478	178	559	654	474		
	x Increase	1.9	1.2	1.1	1.3		0.9	1.1	1.2	0.3	1.0	0.4	1.8	0.9	1.3		

(Continued)

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TABLE 1 (Continued)

		Landfill 1	Landfill 2	Landfill 3	Landfill 4	Landfill 5	Landfill 6	Landfill 7	Landfill 8	Landfill 9	Landfill 10	Landfill 11	Landfill 12	Landfill 13	Landfill 14	Number of locations with an increase	Number of locations with a decrease
HFPO-DA (Gen-X)	Raw	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	1.0	2.0	1.0	1.0	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	1	1
	Treated	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	1.0	*0.001*	2.0	1.0	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*		
	x Increase							0.0	2.0								
F53B	Raw	0.11	*0.001*	*0.001*	*0.001*	*0.001*	1.0	1.0	2.0	1.0	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	2	3
	Treated	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	1.5	2.0	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*	*0.001*		
	x Increase	0.0					1.5	2.0	0.0	0.0							
PFBS	Raw	2,140	5,690	24,400	8,100	*0.001*	17	7,740	16,200	2,370	8,850	3,867	29,083	20,600	10,500	9	4
	Treated	18,200	14,200	25,000	9,370	*0.001*	21	10,800	29,400	2,280	6,930	1710	44,800	11,500	10,900		
	x Increase	8.5	2.5	1.0	1.2		1.2	1.4	1.8	1.0	0.8	0.4	1.5	0.6	1.0		
PFBA	Raw	823	4,603	3,010	1940	29	62	1820	1,580	1,080	2,700	1806	1,346	2,850	1,190	7	7
	Treated	3,190	2,150	2,970	2,160	22	61	2,310	2030	395	2,840	871	2090	2,800	1,550		
	x Increase	3.9	0.5	1.0	1.1	0.8	1.0	1.3	1.3	0.4	1.1	0.5	1.6	1.0	1.3		
PFNA	Raw	34	26	47	20	*0.001*	*0.001*	38	87	9	15	36	33	70	17	9	3
	Treated	54	33	76	29	*0.001*	*0.001*	82	43	3	87	17	60	126	52		
	x Increase	1.6	1.3	1.6	1.5			2.2			5.8		1.8	1.8	3.1		
PFHxA	Raw	1,443	1,743	3,240	1,080	13	78	2,320	2010	1880	1810	1806	1,688	4,190	1,350	7	7
	Treated	2,330	1,880	3,400	1,140	12	32	2080	2,150	572	1860	512	2,430	2,800	1,130		
	x Increase	1.6	1.1	1.0	1.1	0.9	0.4	0.9	1.1	0.3	1.0	0.3	1.4	0.7	0.8		
PFHxS	Raw	377	427	188	319	*0.001*	25	452	589	308	969	338	247	576	316	9	3
	Treated	726	362	321	407	*0.001*	37	738	686	141	1,050	140	566	952	316		
	x Increase	1.9	0.8	1.7	1.3		1.5	1.6	1.2	0.5	1.1	0.4	2.3	1.7			
PFECHS	Raw	50	36	16	26	18	62	39	13	4	108	13	41	284	12	8	6
	Treated	69	33	17	33	21	99	20	7	*0.001*	209	13	62	142	*0.001*		
	x Increase	1.4	0.9	1.1	1.3	1.2	1.6	0.5	0.5	0.0	1.9	1.0	1.5	0.5	0.0		

Red shading indicates a relative increase, green shading indicates a relative decrease, grey shading indicates no change. Values in italics represent limit of detection.

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straight chain PFAAs, and a relative decrease in branched PFAS. There were more instances where higher concentrations of PFAS were detected in treated leachate than raw leachate for PFOS, PFPeS, PFPHpS, PFPA, PFPHpA, PFBS, PFNA, PFHxS, and PFECHS. The branched PFAS 5: 3FTCA, 6: 2FTCA and 8: 2FTOH were the only PFAS with more locations displaying a relative decrease in concentrations (Table 1). These results indicate that relative increases in straight chain PFAAs is likely due to precursor transformation during the treatment process (Fuertes et al., 2017; Solo-Gabriele et al., 2020; Liu et al., 2021). This transformation can occur slowly in the environment but appears to be drastically accelerated during treatment at some locations.

When the data is investigated it reveals many instances where the treatment process appears to be increasing the concentrations of the banned PFAS (PFOA and PFOS) (Table 1). Eleven (11) of the 14 paired samples displayed a higher concentration of PFOS in the treated leachate than the raw leachate (Figure 1). In 9 of these samples the PFOS concentrations increased by over 50% and in 6 of the samples the PFOS concentrations increased by over 100%. A paired T-test revealed concentrations of PFOS were significantly higher in the paired treated samples. The results reveal some of the highest ever reported relative potential increases in PFOS concentrations. The concentration in Landfill 14 increased by 1,335%, from 52.4 ng L^{-1} to 752 ng L^{-1}, and in Landfill 10 by 676%, from 317 ng L^{-1} to 2,460 ng L^{-1} (Figure 1).

Seven (7) of the 14 paired samples displayed a higher concentration of PFOA in the treated leachate than the raw leachate (Figure 2). In six (6) of these samples the PFOA concentrations increased by over 50% and in two (2) of the samples the PFOA concentrations increased by over 100%. The highest relative increases were observed in Landfill 10 which displayed a potential increase of 180% from 1,310 ng L^{-1} in the raw sample to 3,670 ng L^{-1} in the treated sample (Figure 2). Despite these cases concentrations of PFOA in treated samples were not statistically significantly higher in the paired samples.

Relative increases in the straight chain PFAAs could not be explained by relative decreased in the 3 branched PFAS alone. As only targeted analysis was performed on the data it was not possible to ascertain what other PFAS were present in the raw leachate, or what degradation products are being generated from the treatment process. These results indicate that there are likely to be many more PFAS in these samples and so further analysis using total PFAS methods and non-targeted analysis would be recommended. Wastewater treatment plants can be effective at improving water quality for a wide variety of pollutants. However, our snapshot of data from UK treatment plants indicates that they are not effective at removing PFAS, and in many instances are generating the banned PFAS (PFOA and PFOS) through precursor transformation. This data was gathered from a targeted monitoring program however, future monitoring efforts would benefit from complimentary non-targeted and total PFAS methods to gain a more complete picture of what is entering our waterways.

4 Conclusion

The results of our study paint a concerning picture for the effectiveness of current efforts to treat PFAS in landfill leachate. As the locations of the landfill sites were not disclosed it is not possible to comment on the direct impact to the environment. However, the highest concentrations of PFOS and PFOA in treated leachate were 2,460 ng L^{-1} and 26,900 ng L^{-1}, respectively. When comparing these against the environmental quality standard of 0.65 ng L^{-1} for PFOS in inland waters, it would indicate that if this treated leachate was to be discharged directly to the environment it would pose a significant

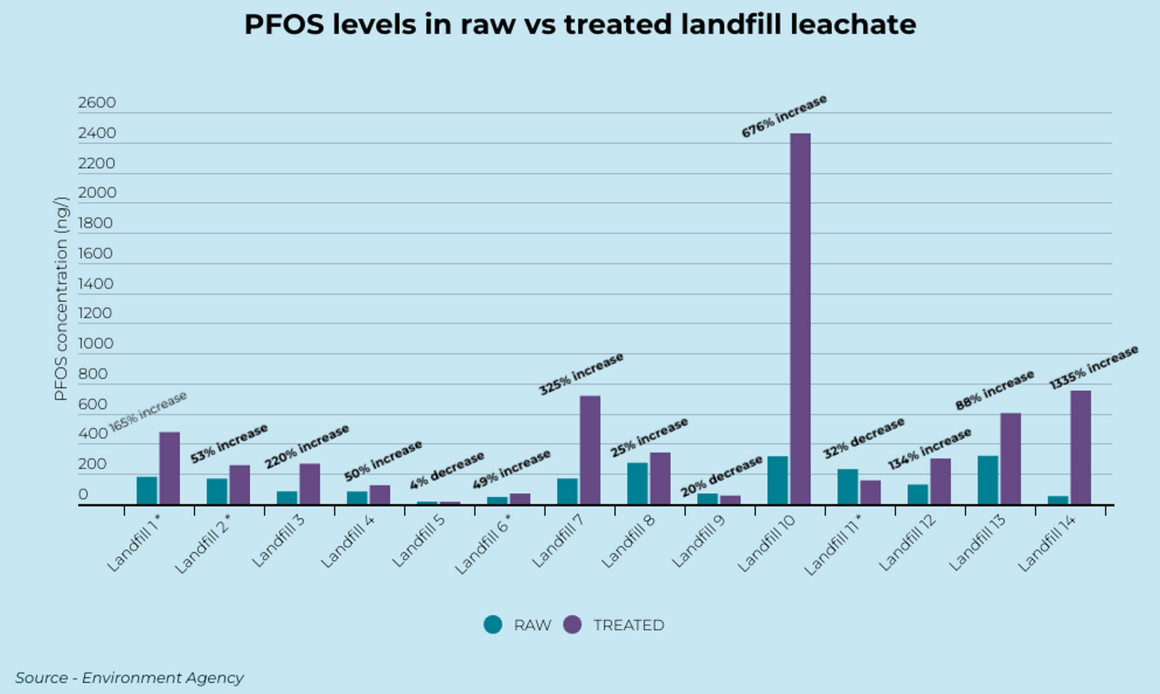


FIGURE 1
PFOS concentrations in raw and treated landfill leachate. *Represents average value for landfills with multiple treated or raw samples.

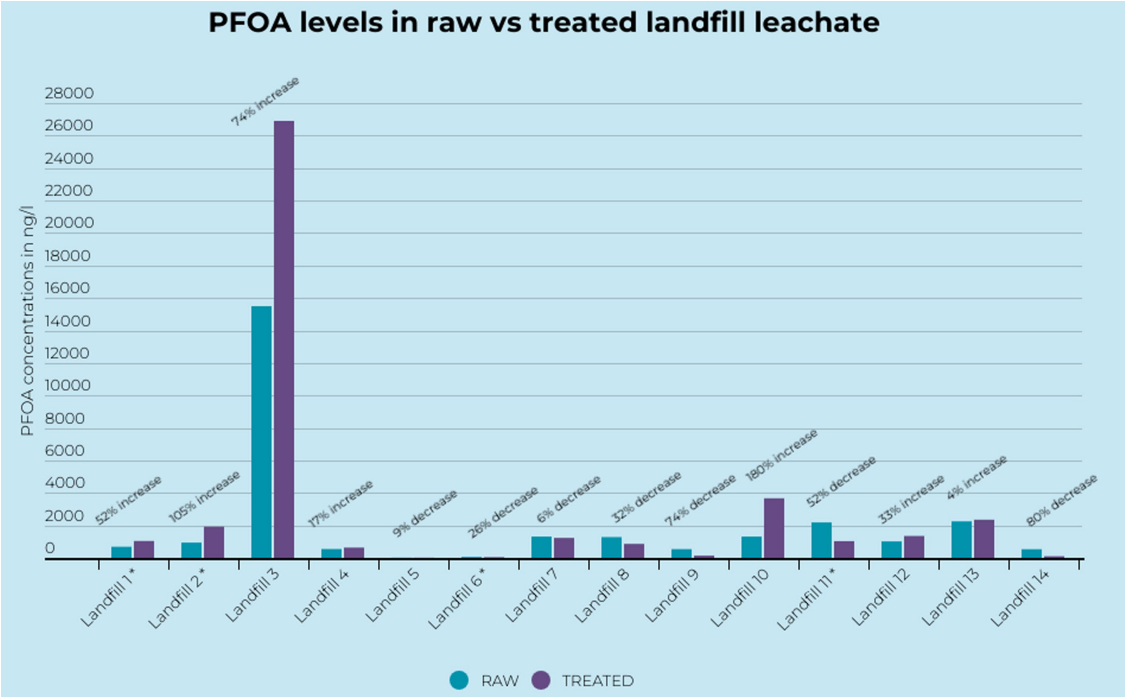


FIGURE 2
PFOA concentrations in raw and treated landfill leachate. *Represents average value for landfills with multiple treated or raw samples.

concern. It was disappointing that spatial and temporal data was not collected by subcontractors (or was removed and anonymized) as this limits what could be interpreted from the dataset. Further monitoring would be strongly recommended to compare the performance of different treatment types, and assess seasonal variation. We hope this manuscript will prompt further research of this nature. This will enable the development and use of the most appropriate technologies for leachate treatment. This information will help support the development of more appropriate monitoring programs and policies, both in the UK and globally.

PFOS and PFOA are listed under the Stockholm convention under Annex B (Restriction) Annex A (elimination) respectively. They pose a significant risk to the environment and PFOA is a class one carcinogen and PFOS is possibly carcinogenic to humans (Group 2B). This study shows that there is an urgent need for further investigation and to upgrade inappropriate leachate treatment works in the UK. In several cases the technology that is designed to protect humans and the environment appears to be doing the opposite and is actively creating considerable amounts of PFOS and PFOA.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

PN: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. DM: Formal analysis, Writing – original draft, Writing – review & editing.

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Conflict of interest

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Supplementary material

The Supplementary material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/frwa.2024.1480241/full#supplementary-material

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Review

A critical review of perfluoroalkyl and polyfluoroalkyl substances (PFAS) landfill disposal in the United States

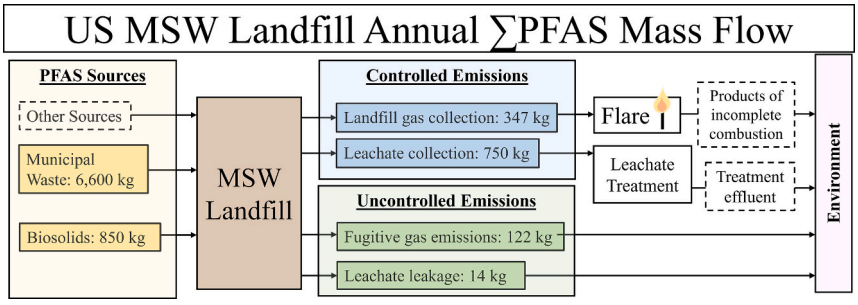
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HIGHLIGHTS

- Solid waste management strategies impact PFAS emissions.
- PFOA has the highest ratio to its respective RSL in C&D and MSW landfill leachates.
- Unlined C&D landfills present a significant source of PFAS to the environment.
- An estimated 7.5 metric tons of PFAS enter MSW landfills annually.
- Annually, 460 kg of PFAS emitted via landfill gas, 750 kg via landfill leachate.

GRAPHICAL ABSTRACT



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ABSTRACT

Landfills manage materials containing per- and polyfluoroalkyl substances (PFAS) from municipal solid waste (MSW) and other waste streams. This manuscript summarizes state and federal initiatives and critically reviews peer-reviewed literature to define best practices for managing these wastes and identify data gaps to guide future

Abbreviations: µg, Microgram; AFFF, Aqueous film-forming foams; C&D, Construction and demolition; diPAP, Polyfluoroalkyl phosphoric acid diesters; FASA, Perfluoroalkane sulfonamide; FASE, Perfluoroalkane sulfonamido ethanol; FTAc, Fluorotelomer acrylate; FTCA, Fluorotelomer carboxylic acid; FTO, Fluorotelomer olefin; FTOH, Fluorotelomer alcohol; H_2S, Hydrogen sulfide gas; HAL, Health Advisory Limit; kg, Kilogram; L, Liter; LFG, Landfill gas; MCL, Maximum Contaminent Level; MeFBSAA, Methyl-n-perfluorobutanesulfonamidoacetic acid; MeFOSAA, Methyl-n-perfluorooctanesulfonamidoacetic acid; mg, Milligram; Mg, Megagram (metric ton); MPCA, Minnesota Pollution Control Agency; MSW, Municipal solid waste; MSWI, Municipal solid waste incineration; NEBRA, North East Biosolids & Residuals Association; NWRA, National Waste & Recycling Association; PFAA, Perfluoroalkyl acids; PFAS, Per- and polyfluoroalkyl substance(s); PFBS, Perfluorobutane sulfonate; PFCA, Perfluoroalkyl carboxylic acids; PFHxA, Perfluorohexanoic acid; PFHxS, perfluorohexane sulfonate; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonic acid; PFPeA, Perfluoropentanoic acid; PFSA, Perfluoroalkyl sulfonic acids; PIC, Product of incomplete combustion; RCRA, Resource Conservation and Recovery Act; RNG, Renewable natural gas; RO, Reverse osmosis; RSL, Regional Screening Limit; SI, Supplementary information; US EPA, United States Environmental Protection Agency; WWTP, Wastewater treatment plant.

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research. The objective is to inform stakeholders about waste-derived PFAS disposed of in landfills, PFAS emissions, and the potential for related environmental impacts. Furthermore, this document highlights data gaps and uncertainties concerning the fate of PFAS during landfill disposal. Most studies on this topic measured PFAS in liquid landfill effluent (leachate); comparatively fewer have attempted to estimate PFAS loading in landfills or other effluent streams such as landfill gas (LFG). In all media, the reported total PFAS heavily depends on waste types and the number of PFAS included in the analytical method. Early studies which only measured a small number of PFAS, predominantly perfluoroalkyl acids (PFAAs), likely report a significant underestimation of total PFAS. Major findings include relationships between PFAS effluent and landfill conditions – biodegradable waste increases PFAS transformation and leaching. Based on the results of multiple studies, it is estimated that 84% of PFAS loading to MSW landfills (7.2 T total) remains in the waste mass, while 5% leaves via LFG and 11% via leachate on an annual basis. The environmental impact of landfill-derived PFAS has been well-documented. Additional research is needed on PFAS in landfilled construction and demolition debris, hazardous, and industrial waste in the US.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) include thousands of unique manufactured chemical compounds with a hydrophobic carbon-fluorine chain and a functional group that may be hydrophilic or hydrophobic. PFAS provides beneficial properties for many consumer products and industrial applications, mostly stick- and stain-resistance and surfactant qualities. PFAS's usefulness has led to a nearly ubiquitous presence in our lives, and PFAS's stability, due to the strength of carbon-fluorine bonds, result in long half-lives and the nickname "forever chemicals."

Human exposure to PFAS has been linked to detrimental health effects which impact all systems, including reproductive effects such as decreased fertility or increased high blood pressure in pregnant women, developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, behavioral changes, increased risk of some cancers, including prostate, kidney, and testicular cancers, reduced ability of the body's immune system to fight infections, including reduced vaccine response; interference with the body's natural hormones and increased cholesterol levels and risk of obesity (reviewed by Fenton et al., 2021). In response to the growing body of evidence identifying PFAS as a significant threat to human health and the environment, the United States Environmental Protection Agency (US EPA) is undertaking research to determine the impact of PFAS via a risk paradigm approach: (1) determine toxicity, (2) understand exposure, (3) assess risk, and (4) find and innovate effective treatment and remediation techniques and strategies. Because PFAS-containing products are disposed of at the end of their useful lives, significant PFAS quantities are managed with solid waste in the US and elsewhere. Properly managing solid waste via containment, treatment, and destruction is essential to protecting our environment and reducing the risk of harmful exposures.

Recognizing the impact of PFAS on human health and the environment, the US EPA released its first provisional Health Advisory Levels (HALs) for PFAS in drinking water in 2009. As analytical capabilities and scientific understanding of PFAS health impacts have improved, the Agency has promulgated additional guidance and risk-based thresholds. For the first time, in 2023, the US EPA proposed enforceable drinking water regulatory limits to reduce human exposure to PFAS (US EPA, 2022d). In April of 2021, the US EPA released the PFAS Strategic Roadmap, which outlines the EPA's commitments to action for 2021 through 2024. Information about US EPA PFAS initiatives is summarized in ***Table S1*** of the Supplementary information (SI), and applicable limits are included in Table 1. The US EPA has also proposed designating PFOA and PFOS as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and is considering adding certain PFAS to the Resource Conservation and Recovery Act (RCRA) list of hazardous constituents (US EPA, 2022b).

At the State level, all the US states except Arkansas, Louisiana, Mississippi, Nebraska, Texas, and Wyoming have dedicated websites providing PFAS-specific information. Some states have banned PFAS-containing products, as summarized in ***Table S2*** (SI). In contrast, others have initiated their own regulatory limits and advisory guidelines, as presented in ***Table S3*** (SI). Eight states have undertaken specific actions and introduced or passed bills targeting PFAS in solid waste (see ***Table S4***, SI). Notably, PFAS regulations are rapidly evolving, and any documentation of state-level PFAS initiatives will likely be outdated quickly.

Confronted with significant quantities of PFAS managed in landfills, the solid waste community struggles to understand the best means to manage PFAS-containing waste streams. Many studies have evaluated PFAS in landfills. However, there is a need for a critical review of the literature that would define the best methodologies for managing these wastes and identify data gaps to guide future research. This manuscript aims to inform the public and stakeholders from the solid waste industry

Table 1
Average concentrations (ng L^{-1}) of select PFAS in landfill leachate and US EPA risk-based thresholds.

Leachate matrix		PFOA		PFOS		PFNA		PFBS		PFHxS		PFHxA	5:3 FTCA
		Mean (n)	DF	Mean (n)	DF	Mean (n)	DF	Mean (n)	DF	Mean (n)	DF	Mean (n)	Mean (n)
MSW		*1400 (284)*	*23*	260 (284)	6.6	69 (234)	1.2	910 (234)	0.1	540 (234)	1.4	2800 (225)	3500 (86)
CDD		*1100 (17)*	*19*	660 (17)	17	50 (17)	0.8	530 (17)	0.1	2200 (17)	5.7	1600 (17)	1400 (17)
MSWI Ash		*800 (40)*	*13*	400 (40)	10	59 (40)	1.1	1400 (40)	0.2	510 (40)	1.3	1300 (40)	700 (40)
HW (Primary)		4900 (24)	81	*4100 (24)*	*102*	530 (24)	8.7	6500 (24)	1.1	12,000 (24)	32	12,000 (24)	NM
HW (Secondary)		*100 (5)*	*1.7*	14 (5)	0.4	40 (5)	0.7	57 (5)	0.01	86 (5)	0.2	440 (5)	NM
	Tapwater RSL (HQ = 1.0)	60		40		59		6000		390		n/a	n/a
EPA limit (ng L^{-1})	Lifetime HAL	0.004		0.020		n/a		2000		n/a		n/a	n/a
	Proposed MCL	4		4		n/a		n/a		n/a		n/a	n/a

(HAL = health advisory level; MCL = maximum contaminant level; RSL = regional screening level; HQ = hazard quotient; DF = average dilution factor required to meet RSL; NM = not measured).
Italicized values represent the controlling dilution factor.

about PFAS entering the waste stream and being disposed of in landfills, potential landfill PFAS emissions, and the related environmental impacts. Furthermore, this document highlights data gaps and uncertainties concerning the fate of PFAS during landfill disposal. Data were compiled and summarized, as described in the Methods section of the SI (***Section S2*** and ***Table S5***), to provide a concise critical review of this evolving research topic.

2. Solid waste management in the United States

A detailed discussion of solid waste management in the US is included in the SI (Section S3). Residents, businesses, and industries in the United States (US) generate significant amounts of solid waste; overall municipal solid waste (MSW) generation in 2018 was 265 million metric tons (US EPA, 2020b). In addition to MSW, significant amounts of construction and demolition (C&D) waste (545 million metric tons), wastewater treatment plant (WWTP) biosolids (2.5 million metric tons), and varied amounts of industrial waste and disaster debris enter the US solid waste management system every year (US EPA, 2020b). Over time, MSW generation in the US has increased. While the fraction of MSW which is landfilled has decreased from over 90% in 1960 to 50% in recent years, the mass of MSW disposed of in landfills reached its highest recorded level at 133 million metric tons in 2018 (see Fig. S1 in the SI). The US's landfill design, monitoring, and classification are identified and regulated according to the RCRA described in the SI's RCRA section. RCRA and its regulations provide requirements for landfill engineering controls based on the type of waste the landfill receives (MSW (Subtitle D), Hazardous (Subtitle C), industrial, construction, and demolition (C&D) debris) as outlined in the SI.

2.1. Sources of PFAS in solid waste

While extensive research has been undertaken to measure PFAS in effluent from waste management activities (particularly landfill leachate), fewer studies have attempted to estimate the PFAS load entering the waste management sector. Coffin et al. (2022) estimated an extractable ∑PFAS concentration in MSW of 50 μg kg^{-1} based on concentrations in MSW screenings reported by Liu et al. (2022a). Estimating PFAS loading to landfills is not only complicated by analytical challenges and the diversity of measurable PFAS, but also by the heterogeneity of MSW and other waste streams (e.g., household products, building materials, industrial waste, and "other wastes"). The following subsections focus on waste representing suspected high PFAS load or a significant fraction of the waste stream. Fig. 1 presents PFAS concentrations measured in various products and the environment compared to those measured in landfill leachate, compost, and biosolids from WWTPs.

2.1.1. Municipal solid waste

In the US, household waste is among the most significant fractions of MSW. Few studies measured the PFAS concentration of suspected PFAS-containing consumer products in the context of direct exposure during product use (Buck et al., 2011; Favreau et al., 2017; Glüge et al., 2020; Guo et al., 2009; Herzke et al., 2012; ITRC, 2022; Kotthoff et al., 2015; OECD, 2022; US FDA, 2022; Ye et al., 2015). These findings indicate a significant load of PFAS remaining in products at the end of their useful life. Household waste consists of two main categories: the biodegradable fraction and the non-biodegradable fraction. Both types of waste streams contain PFAS, but the fate of their PFAS may differ.

2.1.1.1. Biodegradable fraction. Paper and paperboard are the most

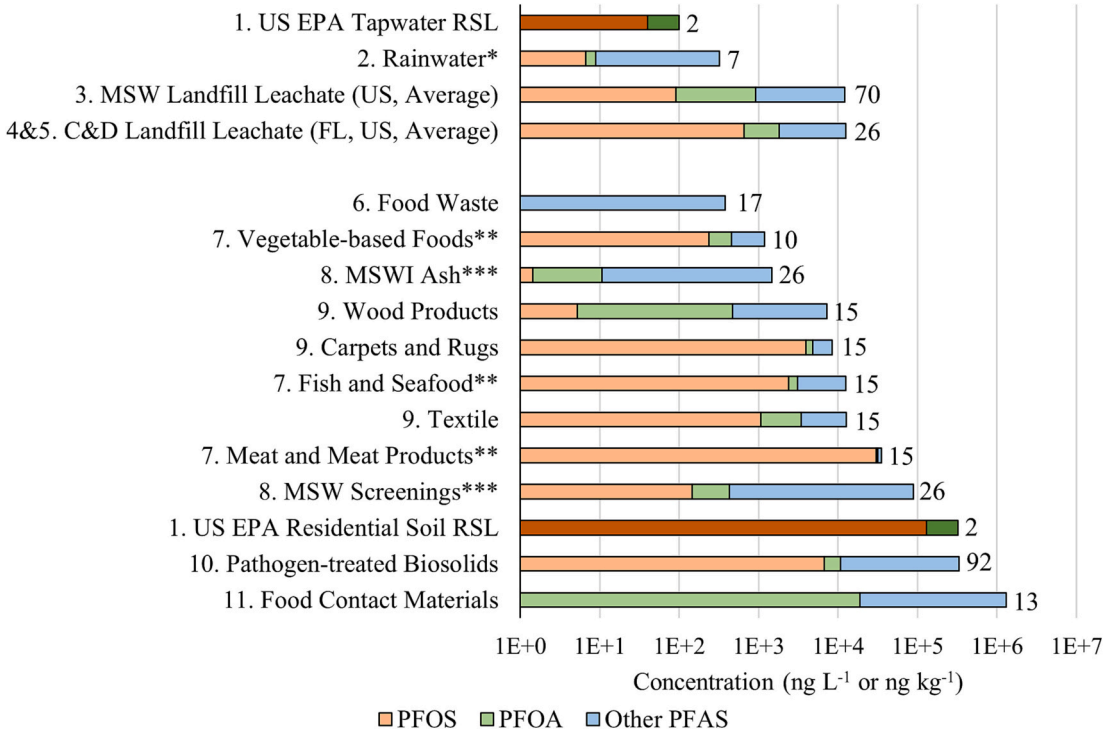


Fig. 1. PFAS concentrations and compositions measured in various products, wastes, and the environment compared to MSW landfill leachate.
* includes ultra-short chain PFAS, TFA.
** upper bound of the mean.
*** minimum total PFAS based on leachable fraction.
Note: numbers prior to matrix type refer to sources. Numbers to the right of the bars are the number of PFAS analytes. RSLs refer to risk-based screening levels, not enforceable regulatory limits. Sources: 1. US EPA (2022d) 2. Pike et al. (2021) 3. Lang et al. (2017) 4. Solo-Gabriele et al. (2020) 5. Chen et al. (2023) 6. Thakali et al. (2022) 7. European Food Safety Authority (2012) 8. Liu et al. (2022b) 9. Bečanová et al. (2016) 10. Thompson et al. (2023a, 2023b) 11. Siao et al. (2022).

abundant components of MSW, representing 23% of the US MSW generation in 2018 (US EPA, 2021a). PFAS are often added to paper products to improve stick and stain resistance, which results in paper products (including food packaging) consistently reported as a significant source of PFAS for human exposure and in the waste stream (Curtzwiler et al., 2021; D'eon et al., 2009; Ramírez Carnero et al., 2021; Robel et al., 2017; Seltenrich, 2020; Yuan et al., 2016; Zabaleta et al., 2016). In a review of studies that measured PFAS in food-contact materials, Siao et al. (2022) reported concentrations of $\sum_{13}$PFAS in food packaging as high as 8500 μg kg^{-1}; at these concentrations, paper and paper products likely contribute significantly to the overall PFAS loading in MSW, as well as contamination of food and food waste. Sapozhnikova et al. (2023) used targeted and total oxidizable precursor (TOP) assays to measure PFAS migration from food packaging into food products among 88 packaged food samples. TOP analysis identified a significant portion of total PFAS in packaging came from unknown precursor PFAS; average $\sum_{8}$PFAA was 28 μg kg^{-1} before oxidation and 380 μg kg^{-1} after oxidation. Migration from the packaging into food was found to increase over the course of the ten-day study. Unfortunately, many new products marketed as environmentally-friendly alternatives to plastic products have been found to contain PFAS (Timshina et al., 2021), and advocacy groups in the US and beyond have moved to revise compostable labeling to preclude PFAS-containing products (BioCycle, 2020). Disubstituted polyfluoroalkyl phosphates (diPAPs) have been found to represent a significant fraction of the PFAS used in paper products. However, most studies do not include diPAP as an analyte (D'eon et al., 2009; Thompson et al., 2023a). These findings suggest the concentration of $\sum$PFAS in paper products may be significantly higher than current estimates.

Another large fraction of biodegradable household waste is food waste, accounting for 22% of the MSW generated in the US in 2018 (US EPA, 2021a, 2021b, 2021c). Unlike paper products, PFAS are not intentionally added to food; contact with PFAS-containing equipment, packaging, water, feed, or soil amendments may result in residual PFAS. Several studies have been published describing the potential migration of PFAS from PFAS-impregnated food packaging (Ramírez Carnero et al., 2021). Up to 33% of extractable PFAS on the surface of food contact materials have been reported to migrate to simulated foods – the migration efficiency depends on the food type and PFAS class (Yuan et al., 2016). Additionally, some PFAS are known to bioaccumulate in the food chain. A European Food Safety Authority (2012) report lists seafood and meat as the food categories most frequently reported containing measurable concentrations of PFAS, with PFOS and PFOA quantified most commonly in 29% and 9% of samples, respectively. The same study estimated mean overall dietary exposure for PFOS and PFOA ranging from 0.07 to 32 ng kg^{-1} body weight per day, with lower exposure rates for 14 additional PFAS. Exposure was highest among toddlers and children due to higher food consumption for body size. Among 25 samples of food waste analyzed for PFAS by Thakali et al. (2022), 17 contained PFAS (mean $\sum_{17}$PFAS = 0.38 μg kg^{-1}); PFOS and PFOA were not detected in any of the samples.

Wood and yard trimmings represent approximately 18% of the US MSW generation (US EPA, 2020b). While natural wood and plant matter are unlikely to contain significant concentrations of PFAS (Thompson et al., 2023b), engineered wood building materials may be coated with PFAS to enhance performance. In a study of PFAS content in consumer and building materials, 100% of oriented strand board and wood products analyzed contained measurable PFAS concentrations, with median and maximum Σ_{15}PFAA of 5 and 18 μg kg^{-1}, respectively (Bečanová et al., 2016).

2.1.1.2. Non-biodegradable fraction. In the non-biodegradable category of household waste, carpets, and textiles have been consistently found to contain intentionally added PFAS that provide stick and stain resistance and waterproof properties (Kallee and Santen, 2012; Kim et al., 2015; Lang et al., 2016; Peaslee et al., 2020; van der Veen et al., 2022). A review of Σ_{15}PFAA in various household and consumer products found textiles, floor covering, and car interior materials represented the three highest maximum concentrations (78, 38, and 36 μg kg^{-1}, respectively); the highest non-biodegradable median PFAS concentration was from insulation (3.6 μg kg^{-1}) (Bečanová et al., 2016). PFAS and fluoropolymers are also used in non-stick cookware (Sajid and Ilyas, 2017) and electronics to provide smudge resistance, insulation, and other properties. An estimated 114 separate PFAS have been identified in electronic production (Garg et al., 2020). PFAS contamination and exposure through e-waste management have been the subject of several studies (Garg et al., 2020; Tansel, 2022; B. Zhang et al., 2020). Notably, the measurement of PFAS in e-waste itself (as opposed to through leachate, environmental contamination, or dust) is limited. A range of 0.07–0.43 μg kg^{-1} PFOS among all electronic products is provided by Garg et al. (2020). Σ_{15}PFAA reported by Bečanová et al. (2016) ranged as high as 11.7 μg kg^{-1} (median: 0.4 μg kg^{-1}) in electronic and electrical equipment (EEE) and as high as 2.2 μg kg^{-1} (median: 1.4 μg kg^{-1}) in waste EEE.

2.1.2. Industrial waste

Industrial processes generate waste and effluent in large volumes; processes that use PFAS, such as the leather tannery, chrome plating, and textile industries, represent a significant contribution of PFAS to the solid waste stream (ITRC, 2022) which are often disposed of in landfills. Other types of industrial processes which generate PFAS-containing waste involve the management of PFAS-contaminated materials, including the separation of wastewater biosolids as part of municipal wastewater treatment, the management of MSW incineration residuals (MSWI ash), and the disposal of PFAS-contaminated soils and other residuals generated as part of environmental cleanup processes.

2.1.2.1. Biosolids. WWTPs manage residential, commercial, and industrial wastewater, including landfill leachate, and have been the subject of many PFAS studies (Lenka et al., 2022). Biosolids account for a significant fraction of WWTP effluent (Fredriksson et al., 2022) and impact PFAS loading to the environment and landfills (Johnson, 2022; Thompson et al., 2023b). Reported PFAS concentrations in biosolids vary with the number of PFAS included in the analytical method. Gallen et al. (2018) reported mean $\sum_{9}$PFAS of 45 μg kg^{-1} of biosolids; Thompson et al. (2023a, 2023b) reported mean $\sum_{92}$PFAS of 500 μg kg (dry)$^{-1}$ in untreated biosludge and 330 μg kg(dry)$^{-1}$ in biosolids (biosludge treated for pathogen removal), indicating that early studies of PFAS in biosolids which measured fewer PFAS, and predominantly PFAAs, did not capture a significant portion of the total PFAS. Over 5.8 million dry metric tons of biosolids were managed in the US in 2018, of which 30% was managed in landfills, 15% was incinerated, and over 50% was used as a soil amendment (NEBRA, 2022).

2.1.2.2. MSW incineration ash. The incineration of MSW for energy recovery (MSWI) produces two solid waste streams – bottom ash, the material that does not burn, and fly ash, fine particulate matter collected in the air pollution control system. Approximately 13% of MSW in the US is managed through incineration (US EPA, 2021a, 2021b, 2021c), resulting in an estimated 7.5 million tons of MSWI ash (Liu et al., 2019). Few studies have measured PFAS in MSWI ash. Liu et al. (2021b) reported $\sum_{21}$PFAS in fly and bottom ash from three facilities in China, with concentrations ranging from 1.5 to 88 μg kg^{-1} in fly ash and from 3.1 to 77 μg kg^{-1} in bottom ash. Based on the concentrations of PFAS in a laboratory leaching study, the average minimum $\sum_{26}$PFAS in MSWI ash from a US facility was 1.5 μg kg^{-1} (Liu et al., 2022b); this represents a conservative estimate of total PFAS. These concentrations are in the same range as MSW. Incineration temperatures may not be sufficiently high to mineralize or destroy PFAS, and operational strategies likely play a significant role in the fate of PFAS during incineration. The impact

of temperatures on PFAS leaching from MSWI is discussed in greater detail in the context of MSWI ash monofill leachates.

2.1.2.3. Manufacturing wastes. There is extensive use of PFAS in some industries, as PFAS is added intentionally to products (i.e., to produce stain-resistant properties in textiles and paper products) and as part of the manufacturing process (i.e., to facilitate demolding). This results in unintentionally contaminated materials through contact. The Interstate Technology Review Committee (ITRC) thoroughly lists PFAS uses in the industrial and manufacturing sectors (ITRC, 2022). PFAS-laden manufacturing waste is often sent to landfills for disposal across industries.

Among specific industries and industrial wastes which have been the subject of PFAS analysis, high-concentration effluents from electronic industries have been described in the literature; photolithographic effluent in Taiwan contained 130,000 ng L^{-1} each of PFHxS and PFOS (Lin et al., 2009); liquid effluent from television and circuit board manufacturing contained 1600 ng L^{-1} of $\sum_{11}$PFAS (Kim et al., 2016); sludge effluent collected from an electronics industry location in South Korea contained 91 μg kg^{-1} of $\sum_{11}$PFAAs (Kim et al., 2016). PFAS are used commonly in paper processing and treatment; a case study in Norway identified PFAS impacts downstream of a landfill used for paper factory waste disposal (Langberg et al., 2021). Chrome plating industry waste sludges are designated hazardous wastes (F006), which contain high concentrations of PFAS (ITRC, 2022) and are therefore managed in Subtitle C hazardous waste landfills. A study of chrome sludge in China identified PFOS as the most predominant PFAS at concentrations as high as 2435 μg kg^{-1} (Qu et al., 2020). The chrome plating industry consumes an estimated 6500 kg of PFOS annually (Garg et al., 2020).

2.1.2.4. PFAS remediation residuals. Sites with high levels of PFAS contamination from the historical use of PFAS-containing aqueous film-forming foams (AFFF) or other releases are frequently remediated, and the contaminated media is commonly disposed of in landfills (either with the waste or used as daily cover). Remediation approaches include mobilization of PFAS and collection of the leachate, sorption of PFAS using activated carbon or other sorbents, or soil excavation for landfill disposal (Bolan et al., 2021; Ross et al., 2018). Brusseau et al. (2020) reviewed PFAS concentrations measured in soils from contaminated sites, reporting median PFOA and PFOS concentrations of 83 and 8700 μg kg^{-1}, respectively, with concentrations as high as 50,000 μg kg^{-1} for PFOA and 460,000 μg kg^{-1} for PFOS.

3. Fate of PFAS in landfills

The fate of solid waste-derived PFAS within landfills is dominated by transformation and partitioning. Many PFAS species are persistent in the environment and PFAS that are degradable can transform into more recalcitrant, typically more environmentally mobile PFAS (Bolan et al., 2021). The partitioning behavior of PFAS are related to the chemical structure of individual species, both according to PFAS class, functional groups, and chain length among homologous species. In turn, the ongoing transformation will impact partitioning behavior (Robey et al., 2020; Zhang et al., 2020a, 2020b; Smallwood et al., 2023). In landfills, PFAS may partition to the liquid phase (leachate) and gaseous phase (landfill gas; LFG), remain sorbed to the waste, and/or interact with the engineering controls of the landfills (e.g., leachate collection systems, gas collection, and control systems). PFAS that are resistant to degradation and minimally soluble or volatile, such as certain polymeric PFAS, have historically been presumed to remain immobile and sequestered in landfills, although more recent studies have called this assumption into question (Lohmann et al., 2020).

3.1. PFAS transformation

Many studies observed the transformation of PFAS precursors into terminal species under abiotic and microbially active aerobic and anaerobic conditions. While this section briefly reviews these processes to provide context to PFAS in landfills, the aim is not to conduct an exhaustive review of the topic, which is available in other reviews (Lu et al., 2023).

3.1.1. Abiotic transformation

PFAS transformation pathways under abiotic conditions include oxidation, photolysis, and thermal degradation (ITRC, 2020; Washington and Jenkins, 2015). While the bulk of PFAS transformations in organic-rich landfills are likely a result of biodegradation, these abiotic processes play an essential role in solid waste management systems. PFAS such as fluorotelomer alcohols (FTOHs) can volatilize under temperatures typical in landfills (35–55 °C). Once in the atmosphere, FTOH can transform via photolysis or other chemical reactions into perfluorocarboxylic acids (PFCAs) which are then deposited on land and waterbodies (Esfahani et al., 2022; Martin et al., 2006). Other abiotic processes include thermal degradation. An increase in the temperature of waste may facilitate PFAS transformation. Wastes within landfills may be exposed to temperatures insufficient to mineralize or defluorinate PFAS but which may cause precursor transformations. Thompson et al. (2023a, 2023b) measured higher concentrations of diPAPs in biosolids that had undergone any form of heat treatment, including heat drying as well as higher temperature vector reduction treatment, indicating the presence and transformation of unidentified precursors.

3.1.2. Aerobic transformation

Aerobic environments exist at the early stages of landfill decomposition. The waste still contains atmospheric oxygen in its void space and likely contributes to the transformation of PFAS in waste. Thompson et al. (2023a, 2023b) observed a proportional increase in PFCAs after aerobic biosolids composting, especially short-chain (perfluoropentanoic acid, PFPeA, and perfluorohexanoic acid, PFHxA). Similarly, Li et al. (2022) found significant increases among short-chain PFAAs (including PFBS and PFOS) in aerobically treated anaerobic digestor sludge. These findings are significant because short-chain PFAS are more mobile in the environment, more likely to be uptaken by plants (Ghisi et al., 2019), and more challenging to treat (Ross et al., 2018). Multiple studies have shown that aerobic decomposition facilitates the transformation of precursor PFAS to shorter-chain terminal PFAS, such as PFOA and PFOS (Hamid et al., 2020; Lee et al., 2010a; Liu et al., 2010; Lott et al., 2023; Rhoads et al., 2008; Schultz et al., 2006; Wang et al., 2009, 2011; Zhao et al., 2013).

3.1.3. Anaerobic transformations

Comparatively, fewer studies have documented PFAS transformation under anaerobic or methanogenic conditions similar to landfills. Liu et al. (2021a) compared 52 PFAS in leachate from waste collection vehicles to anaerobic MSW landfill leachate and concluded the vehicle leachate contained proportionally more precursor PFAS and short-chain PFAAs compared to the landfill leachate as a result of the transformation in the anaerobic landfill environments. Studies of anaerobic precursor transformation identified FTCAs as the predominant by-product of FTOH degradation. Allred et al. (2015) reported increased MeFBSAA and FTCA leaching over abiotic reactors in biologically active landfill microcosm reactors, indicating that methanogenic biological transformation was responsible for the increase. Zhang et al. (2013) observed the accumulation of FTCAs in landfills over time, concluding that FTCAs are indicators of FTOH transformation, while Lang et al. (2016) and Weber et al. (2022) reported PFOA accumulation in leachate as a result of precursor transformation under anaerobic experimental conditions. Lang et al. (2016) attributed this to the longer experimental duration, with PFOA appearing as a significant degradation by-product only 200+

days into the 550-day experiment.

3.2. PFAS partitioning in landfills

3.2.1. PFAS partitioning to the liquid phase

PFAS concentrations in landfill leachate are a function of multiple factors, including the PFAS profile of the incoming waste stream and conditions within the landfill, which, in turn, correspond with waste composition, stage of decomposition, and environmental factors, especially rainfall precipitation. These factors also affect the physical-chemical aspects of the leachate quality, and any discussion of PFAS in leachate should also include matrix contextualization. The number of PFAS that can be detected and quantified in landfill leachate has grown. Early methods were able to quantify 24 PFAS compounds in three classes (Huset et al., 2011), but improvements have been made; more recent studies attempted to measure 92 PFAS and detected 53, as presented in Table 2.

3.2.1.1. PFAS in landfill leachate by type

3.2.1.1.1. MSW landfills. The vast majority of PFAS landfill leachate data are measured from MSW landfills (Allred et al., 2014; California Water Boards, 2023; Chen et al., 2022, 2023; Huset et al., 2011; Lang et al., 2017; Liu et al., 2022a; Masoner et al., 2020; NWRA, 2020; Solo-Gabriele et al., 2020). The ∑PFAS content of MSW landfill leachate in published US studies ranges from BDL - 125,000 ng L^{-1} with an average of 10,500 ng L^{-1} and a weighted average of 12,600 ng L^{-1}. The weighted average is notably similar to the estimated average ∑PFAS concentration reported by Lang et al. (2017) using Monte Carlo simulation. Often, the ∑PFAS content heavily depends on the number of unique PFAS measured in the study, which ranged from two to 70 for MSW landfill leachate (see SI ***Fig. S2***). For comparison among studies, we will focus on PFAS with corresponding US EPA tapwater Regional Screening Levels (RSL) (i.e., PFOA, PFNA, PFBS, PFHxS, PFOS, and Gen-X), as presented in Table 1. Except for Gen-X, which has only been quantified in a single sample of landfill leachate from a North Carolina MSW landfill with a history of accepting PFAS manufacturing wastes (NWRA, 2020), the remaining five PFAS are reliably quantified in all published landfill leachate studies. Other PFAS which reliably contribute significantly to ∑PFAS in landfill leachates, PFHxA and 5:3 FTCA, are also included in Table 1.

PFAS concentrations have also been reported for leachates from MSW landfills in other countries, including Australia (Gallen et al., 2016, 2017), Europe (Ahrens et al., 2011; Busch et al., 2010; Eggen et al., 2010; Fuertes et al., 2017; Kallenborn et al., 2004; Knutsen et al., 2019; Perkola and Sainio, 2013; Woldegiorgis et al., 2005), and Asia (Huang et al., 2022; Liu et al., 2022b; Yan et al., 2015; Yin et al., 2017; Zhang et al., 2014). International differences in waste composition, sample collection, and analytical processes can impact reported PFAS concentrations, making a direct comparison of the overall PFAS content challenging. Concentrations of PFOS and PFOA, which have been reliably measured in most or all studies, are included for eight countries in ***Table S6*** and described by Travar et al. (2020).

Table 2
Number of PFAS measured and ∑PFAS among published landfill leachate studies.

Matrix	Number of samples	Number of PFAS detected (in Method)	Average ∑PFAS (ng L^{-1})	∑PFAS range (ng L^{-1})	Country	Reference
	1	38 (51)	9700	9700	USA	Liu et al. (2021a)
	1	32 (51)	9400	9400	USA	Robey et al. (2020)
	78	25 (26)	12,700	300–58,000	USA	Chen et al. (2023)
	4	10 (11)	17,200	15,000–18,000	USA	Solo-Gabriele et al. (2020)
	6	24 (24)	4700	2700–7400	USA	Huset et al. (2011)
	40	30 (70)	12,200	2000–29,000	USA	Lang et al. (2017)
	11	2 (2)	840	330–2600	USA	Clarke et al. (2015)
	19	28 (28)	5400	230–29,000	USA	Helmer et al. (2022)
	39	2 (2)	1500	47–3400	USA	EGLE (2019)
	9	22 (25)	24,300	1400–125,000	USA	NWRA (2020)
	131	31 (40)	17,500	BDL – 104,000	USA	California Water Boards (2023)
	17	14 (14)	3000	33–15,000	Australia	Gallen et al. (2016)
	94	9 (9)	6100	210–46,000	Australia	Gallen et al. (2017)
	22	15 (15)	7000	Not reported	Australia	Simmons (2019)
MSW LL	6	25 (43)	6100	31–13,000	Germany	Busch et al. (2010)
	11	24 (24)	9800	2500–36,000	Canada	Benskin et al. (2012)
	31	16 (18)	2700	700–6400	Canada	Li (2009)
	10	2 (2)	*	50–2300	Canada	Gewurtz et al. (2013)
	2	16 (27)	4200	2200–6100	Norway	Eggen et al. (2010)
	5	7 (8)	770	200–1500	Norway	Kallenborn et al. (2004)
	2	4 (4)	400	210–610	Finland	Perkola and Sainio (2013)
	48	7 (10)	2400	14–17,500	Ireland	Harrad et al. (2019)
	4	8 (16)	1100	640–1400	Spain	Fuertes et al. (2017)
	12	28 (30)	1700	320–11,000	Norway	Knutsen et al. (2019)
	10	17 (26)	490	0.3–1300	Sweden	Gobelius et al. (2018)
	5	11 (14)	82,100	7300–290,000	China	Yan et al. (2015)
	9	33 (57)	42,900	3040–109,000	China	Liu et al. (2022b)
	6	17 (17)	14,200	1800–43,300	China	Huang et al. (2022)
	12	18 (18)	4060	1270–7660	Singapore	Yin et al. (2017)
	5	8 (9)	6000	4200–11,000	Australia	Gallen et al. (2017)
CDD LL	13	24 (26)	9500	270–30,500	USA	Chen et al. (2023)
	2	11 (11)	15,500	14,000–16,000	USA	Solo-Gabriele et al. (2020)
MSWIA LL	2	9 (11)	3100	2800–3400	USA	Solo-Gabriele et al. (2020)
	31	26 (26)	7300	39–54,500	USA	Chen et al. (2023)
MSW GC	21	26 (26)	12,200	199–80,900	USA	Chen et al. (2023)
	12	53 (92)	19,000	3000–50,000	USA	Smallwood et al. (2023)
HW LL (Primary)	24	17 (28)	68,000	570–377,000	USA	California Water Boards (2023)
HW LL (Secondary)	5	13 (24)	1800	25–3700	USA	California Water Boards (2023)

(LL = landfill leachate; MSW = municipal solid waste; CDD = construction and demolition debris; MSWIA = MSW incineration ash; GC = gas condensate).
* Gewurtz et al. (2013) do not provide detailed data to calculate average ∑PFAS.

3.2.1.1.2. C&D landfills. PFAS were detected in all C&D landfill leachate samples analyzed across three studies with ∑PFAS ranging from 270 to 30,500 ng L^{-1} (weighted average 10,300 ng L^{-1}). Solo-Gabriele et al. (2020) and Chen et al. (2023) found no significant difference in the total measured PFAS between leachate from MSW and C&D landfills. The analytical method used by Chen et al. (2023) included 18 terminal PFAS (PFAAs) and eight precursors (FASAs, FTCAs, and FTSs). The study, however, reported a significant difference in the fraction of ∑Terminal and ∑Precursor species between MSW and C&D landfill leachates. C&D leachate contained, on average, 86% terminal PFAS, while MSW leachate contained 64% terminal PFAS (Chen et al., 2023). This could be attributed to the different types of PFAS present in each waste stream and the type of biological activity prevalent in each landfill type. Because C&D landfills contain proportionally less food waste and more concrete and gypsum drywall, the prevailing landfill conditions result in higher pH leachate and proportionally more sulfate chemical species in the leachate as opposed to ammonia, which is typically at higher concentrations in MSW landfill leachate (Townsend et al., 1999). Further, due to those differences in leachate conditions, microbial differences result from presence of different carbon sources as well as electron donors and acceptors. Generally, sulfur-reducing bacteria are found in higher concentrations at C&D landfills due to higher amounts of sulfate, while methanogens are more prevalent at conventional landfills (Meyer-Dombard et al., 2020).

Fig. 2 includes the range of concentrations for PFAS with RSLs for MSW and C&D landfill leachate; average PFHxS concentrations were higher in C&D landfill leachate than in MSW landfill leachate, and PFBS concentrations were lower in C&D landfill leachate. Waste composition is highly variable between landfills as well as over time at an individual landfill, so, while limited studies may suggest potential sources of select PFAS in C&D debris (e.g., higher concentrations of PFHxS may be attributed to their use in carpeting and other building materials (Beesoon et al., 2012; Jin et al., 2011), generalizations about specific sources may not be appropriate. Gallen et al. (2017) measured nine terminal PFAS in Australian C&D landfill leachates (n = 5), reporting average $\sum_9$PFAS concentrations of 6000 ng L^{-1} (compared to 6100 ng L^{-1} in 94 MSW leachates from the same study).

Unlike MSW landfills, at the US federal level, C&D landfills do not require a bottom liner and leachate collection systems. This contributes to the lower number of studies describing PFAS in C&D relative to MSW landfill leachate and an increase in the probability of groundwater contamination from C&D compared to MSW landfills. Average concentrations of PFOA, PFOS, PFNA, PFBS, and PFHxS, along with corresponding US EPA risk-based thresholds (HALs, MCLs, and RSLs), are included in Table 1. PFOA poses the most significant challenge as its concentration in C&D landfill leachate would have to be diluted by 19 to meet the tapwater RSL or by 287 to meet the US EPA proposed MCL.

3.2.1.1.3. MSWI Ash monofills. Solo-Gabriele et al. (2020) and Chen et al. (2023) found leachate from MSWI ash monofills to have lower ∑PFAS concentrations than leachate from MSW landfills. Solo-Gabriele et al. (2020) reported $\sum_{11}$PFAS in MSWI ash monofill leachates ranging from 2800 to 3400 ng L^{-1} and inversely correlated with incineration temperature. $\sum_{11}$PFAS in leachate from MSWI ash that underwent incineration at 800 °C was almost three times higher than after incineration at 950 °C. The decrease indicates loss of measurable PFAS via mineralization (i.e., destruction), volatilization (i.e., air emission), or transformation to PFAS species which are not measured in standard analytical methods (e.g., products of incomplete combustion or PICs). Leachates from MSWI ash which had undergone incineration at 950 °C, still contained >2000 ng L^{-1} of PFAS, indicating PFAS are not fully mineralized at these operating conditions. Liu et al. (2021b) reported substantially higher $\sum_{21}$PFAS in MSWI ash leachate from three facilities in China, with concentrations ranging from 127,000–450,000 ng L^{-1}. The study did not report incineration temperatures or other operating conditions.

However, when MSWI ash was co-disposed with other wastes, such as MSW or biosolids, ∑PFAS concentration in the leachate was on par with that in MSW landfill leachate (Solo-Gabriele et al., 2020; Liu et al., 2022a). Liu et al. (2022a) found the co-disposal of a small fraction (e.g., 4%) of MSW, including biosolids, with MSWI ash resulted in leachate concentrations that were comparable to MSW landfill leachate, suggesting liquids are preferentially flowing through and leaching PFAS from the non-incinerated waste as opposed to the ash. While MSWI ash-derived leachates have lower concentrations of PFAS, these studies suggest care should be taken to dispose of MSW and MSWI ash separately, and more research is needed to understand the fate of PFAS during MSW incineration.

3.2.1.1.4. Industrial landfills. Unlined industrial landfills that received residuals from manufacturing PFAS and PFAS-containing products have been linked to contamination of local groundwater sources. Notable examples include the House Street landfill in Belmont, Michigan which received tannery waste (US EPA, 2022e); Crown Vantage landfills in Parchment, Michigan (MPART, 2020), that were used to dispose of paper mill waste from the production of laminated paper

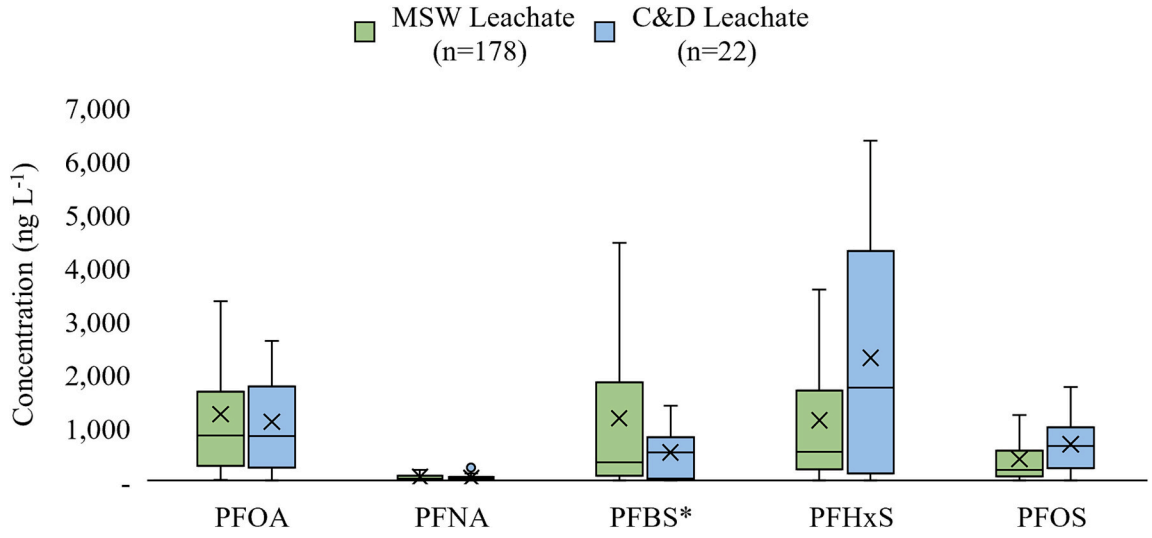


Fig. 2. Average concentrations of five PFAS with US EPA tapwater RSLs.
Data from Gallen et al. (2017), Solo-Gabriele et al. (2020), and Chen et al. (2023).
* Gallen et al. (2017) did not include PFBS analysis.

products; and the 3M Woodbury disposal site in Washington County, Minnesota, that was used to dispose of PFAS production waste. As part of this literature search, no leachate PFAS concentration data from industrial landfills in the US were located. However, Kameoka et al. (2022) measured PFAS in leachate from three industrial landfills in Japan; $\sum_{17}$PFAA concentrations averaged 45,000 ng L^{-1}.

3.2.1.1.5. Hazardous waste landfills. Although PFAS are not federally regulated as listed hazardous wastes, some solid wastes managed in Subtitle C hazardous waste landfills contain PFAS (as discussed in Section 2.1.2, e.g., chrome-plating sludge), while other PFAS-containing wastes may meet hazardous waste characteristic criteria (e.g., flammable, corrosive, etc.). Some hazardous waste landfills have also reported receipt of AFFF waste at their sites. No peer-reviewed studies have evaluated PFAS concentrations in leachate collected from hazardous waste landfills; however, California Water Boards have released PFAS concentrations for landfill leachate, including two hazardous waste landfills in California (California Water Boards, 2023). The data for these sites are included in the SI ***Table S7***. Among 29 samples from the two sites, $\sum_{24}$PFAS and $\sum_{28}$PFAS concentration was as high as 377,000 ng L^{-1} (average 68,000 ng L^{-1}), substantially higher than MSW, C&D debris, or MSWI ash landfill leachates (see Table 2). In the US, hazardous waste landfill disposal requires waste pre-treatment to minimize contaminant mobility – land disposal restrictions for hazardous waste are described in the Code of Federal Regulations (CFR; 40 CFR § 268). Leaching studies have shown minimal PFAS immobilization using traditional solidification techniques (Barth et al., 2021), which may explain elevated PFAS concentrations in the leachate.

US hazardous waste landfills must also use secondary leachate collection systems; California's database includes five samples of secondary hazardous waste landfill leachate from one site, with $\sum_{24}$PFAS averaging 1800 ng L^{-1} (see Table 2). Without exception, for all sampling locations with both primary and secondary leachate PFAS data, concentrations for individual and $\sum_{24}$PFAS were higher in the primary compared to the secondary leachate. While the absence of biological decomposition in hazardous waste landfills may minimize the microbially-mediated precursor transformation to PFAAs, waste treatment methods (e.g., lime treatment) may also impact transformation and partitioning, possibly oxidizing precursor PFAS. Hazardous waste pretreatment standards are designed to minimize traditional hazardous waste constituent leaching (e.g., lime treatment stabilizes metals and neutralizes acidic waste) and have not been optimized for PFAS stabilization; PFAS fate, transport, and transformations under hazardous waste pretreatment processes are not well understood. Because of the strict Subtitle C landfill operation requirements and the pre-treatment of wastes, leachate generation in these landfills is typically minimal, and any leachate which is produced is often managed as hazardous waste (i.e., not discharged to WWTP, as other landfill leachates often are).

3.2.1.2. Other factors impacting PFAS concentrations in leachate

3.2.1.2.1. Waste age. As waste degrades under the anaerobic conditions of biologically active landfills, the overall PFAS concentrations in the leachate and the ratio of the terminal to precursor species have been found to increase. Lang et al. (2017) reported leachate from waste older than ten years had significantly lower concentrations of PFNA, 8:2 FTCA, 5:3 FTCA, PFBS, MeFBSAA, and MeFOSAA than leachate from younger waste. These differences could be attributed to changes in the PFAS formulations in commercial products and/or the conversion of PFAA precursors. Liu et al. (2021a) measured PFAS in leachate from waste collection vehicles alongside leachate from the receiving MSW landfill. The study found significantly higher $\sum_{51}$PFAS concentrations in landfill leachate which had undergone further biological decomposition. Furthermore, Liu et al. (2021a) also reported a difference in PFAS profiles likely caused by the transformation of precursor PFAS in landfill environments.

3.2.1.2.2. Leachate quality. Although most PFAS behavior and solution chemistry studies focus on remediation technologies, generalizations regarding PFAS phase partitioning also apply to landfill leaching (Z. Du et al., 2014). Comparatively, fewer studies have explored PFAS partitioning in the context of leachate chemistry. In a landfill simulator study, Allred et al. (2015) observed increases in longer-chain PFCA and perfluoroalkyl sulfonic acids (PFSA) concentrations when biodegradation reached the methanogenic stage. At this stage, increased methanogenic and secondary fermentation and decreased volatile fatty acid concentrations from the acidogenic stage result In increased pH, more neutral pH, which is theorized to deprotonate waste surfaces, resulting in less sorption of PFAS to the degrading organic matter. This theory is supported by the results described by Solo-Gabriele et al. (2020), where a significant positive correlation was reported between PFAS concentrations and increasing leachate pH. This effect has also been observed in several previous landfill leachate sampling studies (Benskin et al., 2012; Gallen et al., 2017; Hamid et al., 2018; Yan et al., 2015).

In addition to partitioning behavior, the PFAS profile of landfill leachate is a function of PFAA precursor transformation resulting from biodegradation. Biological activity is catalyzed by landfill moisture, resulting in higher landfilled waste temperatures and more PFAS transformation. In a study of WWTP biosolids pathogen removal, precursor transformation and apparent increases in $\sum_{92}$PFAS, driven by increased PFAA content, resulted after aerobic composting and increased diPAP concentrations from heat treatment (Thompson et al., 2023b). Based on a nationwide study of 95 leachate samples collected from 18 landfills, leachate from MSW landfills in US regions with high annual precipitation showed significantly greater $\sum_{19}$PFAS than comparable landfills in arid locations (Lang et al., 2017); see Table 2 for all US-based studies included in this review. Further, leachate generation volume is significantly higher in regions that experience more precipitation. As a result, landfills in arid regions are estimated to contribute <1% of the nationwide landfill leachate PFAS mass load (Lang et al., 2017). When studies have evaluated the short-term impacts of precipitation on PFAS in landfill leachate, however, leachate PFAS concentration decreased within a day of a precipitation event due to dilution (Benskin et al., 2012; Gallen et al., 2017). Normalization of PFAS concentrations to bulk parameters such as chloride or total dissolved solids may be able to account for such dilution.

3.2.2. PFAS partitioning to the gas phase

MSW contains a proportionally more biodegradable organic matter which undergoes anaerobic decomposition in landfill environments compared to other waste streams (e.g., C&D). The decomposition of organic matter produces MSW LFG, which is, on average, about 50% methane (CH_4), and 50% carbon dioxide (CO_2), with a small fraction consisting of other gaseous and volatile constituents (Wang et al., 2021). LFG at MSW landfills is collected and managed according to the requirements of the US EPA New Source Performance Standards (US Clean Air Act, 40 CFR § 60). According to the US EPA's Landfill Methane Outreach Program (LMOP) August 2022 database, 1230 of the 2635 MSW landfills in the US have gas collection systems in place, and 1157 have flares in place (US EPA, 2022a). C&D LFG is rarely collected in the US, as C&D landfills contain less biodegradable organic matter and produce less LFG than MSW landfills. Additionally, C&D LFG contains proportionally more $H_2S_{(g)}$ produced by sulfur-reducing bacteria and the decomposition of gypsum disposed of as drywall.

Gas generation and composition at other landfill types has yet to be the subject of significant research. MSWI ash monofills are not expected to generate LFG because there is minimal biodegradable matter in the ash; however, the co-disposal of WWTP biosolids, MSW, or any degradable organic matter with MSWI ash will produce biogas as a result of decomposition. Gas generation at industrial landfill sites is primarily a function of the type of waste deposited. Organic waste like pulp and paper mill sludges will likely generate gas requiring management. In general, Subtitle C hazardous waste landfills in the US do not contain

putrescible organic waste and do not generate biogas.

3.2.2.1.1. PFAS in MSW landfill gas. PFAS volatilization and release from MSW landfills within the gaseous phase is receiving an increased focus driven by advances in volatile PFAS measurement (Riedel et al., 2019) and an improved understanding of PFAS chemistry. The partitioning coefficients (e.g., Henry's constant) for ionizable PFAS are significantly lower than neutral PFAS (Abusallout et al., 2022), making ionizable PFAS less likely to volatilize under typical MSW landfill conditions. Experimental measurement of PFAS vapor pressures similarly suggests FTOHs (i.e., neutral PFAS) are more readily volatilized than PFCAs (i.e., ionizable PFAS) and that vapor pressure decreases logarithmically with carbon chain length in homologous species (M. Zhang et al., 2020). Measurement and data of PFAS in actual MSW LFG are still minimal.

In a 2007 analysis of landfills that accepted PFAS-containing industrial wastes, the MPCA detected several PFAS (12 PFAAs and perfluorooctane sulfonamide, PFOSA) in MSW LFG with $\sum_{13}$PFAS ranging from 4.1 to 18.7 ng m^{-3} (MPCA, 2010). Titaley et al. (2023) measured neutral PFAS in LFG of three active MSW landfills (n = 12 samples) and reported concentrations of four n:2 FTOHs (n = 6, 8, 10, and 12), one fluorotelomer acrylate (6:2 FTAc), and one fluorotelomer olefins (12:2 FTO). Concentrations for individual PFAS range from 270 to 4900 ng m^{-3}, and the total measured neutral PFAS for each landfill was, on average, between 4600 and 14,000 ng m^{-3} (weighted average across all samples: 10,200 ng m^{-3}). Smallwood et al. (2023) reported FTOH in LFG condensate, which, when normalized to gas volume, was three orders of magnitude lower than the gaseous phase concentrations reported by Titaley et al. (see SI ***Table S8*** for calculations), indicating FTOHs preferentially partition to the gas phase; FTOHs may transform in the atmosphere into PFCAs, such as PFOA, which have known and suspected toxic effects.

3.2.2.1.2. PFAS in C&D landfill gas. While no data exist on the concentration of PFAS in C&D LFG, it can be conservatively assumed, based on data from MSW LFG measurements, that PFAS also leave C&D landfills via gas effluent. As previously described, PFAS-containing wastes are disposed of at C&D landfills, and it is highly likely C&D debris contains volatile PFAS, such as FTOHs, which readily transform into FTCAs and PFCAs as a result of biodegradation and environmental oxidation, respectively. Lower rates of biological activity in C&D landfills may result in slower biodegradation of PFAS like FTOH (and other volatile precursors) may persist longer in C&D compared to MSW landfills and therefore have more opportunity to volatilize and leave the landfill via LFG. This is likely offset by the lower volume of LFG generated overall at C&D landfills compared to MSW. Nonetheless, this read-across should be validated by experimental data.

3.3. Fate of PFAS in traditional landfill leachate and gas management systems

Most landfills compliant with New Source Performance Standards (Clean Air Act) and RCRA must capture gas effluent and leachate to minimize environmental impacts. Leachate is often intercepted using a low-permeability bottom liner made of high-density polyethylene, collected, and may be transported off-site to a WWTP, disposed of using deep well injection, or otherwise managed and treated on-site.

PFAS interactions with low-permeability landfill liners have been the subject of limited studies. Most landfill liners are constructed from polyethylene geomembranes. Laboratory studies of PFAS diffusion through linear low-density polyethylene report below detection diffusion rates (Di Battista et al., 2020). Diffusion through high-density polyethylene has yet to be reported but maybe even lower due to differences in material structure. Landfill liner integrity – the absence of flaws or holes – is the most critical factor in preventing PFAS transmission through geomembrane and composite liners (Di Battista et al., 2020). An analysis of landfill liner performance reported median leakage rates of 44 and 33 L ha^{-1} day^{-1} for geomembrane and composite liners, respectively, with an overall liner collection efficiency of 98% (Jain et al., 2023). Compacted clay liners, which are more common in older landfills and C&D landfills, do not adsorb PFAS, which are reported to pass through bentonite clay at the same rate as other mobile leachate constituents like chloride (Li et al., 2015). PFAS profile, leachate quality, and soil characteristics all play a role in soil interaction, and decisions should be made on a site-specific basis (Li et al., 2019; Gates et al., 2020; Mukhopadhyay et al., 2021).

Management of leachate in the US is dependent on climate – in dry regions, leachate generation is minimal, and many facilities use atmospheric evaporation. In contrast, in wet regions, leachate management presents a significant challenge (US EPA, 2021c). A nationwide survey found approximately 60% of US Subtitle D landfills conveyed their leachate to WWTPs for off-site treatment, 28% recirculated leachate or use other techniques resulting in no necessary leachate treatment, and 12% used on-site treatment (US EPA, 2021c). A breakdown of on-site leachate treatment strategies is included in SI ***Fig. S3***. Traditional leachate treatment typically targets non-PFAS leachate constituents of concern, such as ammonia and chemical oxygen demand (COD). The fate of PFAS in existing leachate treatment systems and wastewater treatment systems that manage leachate have been the subject of several studies and have been reviewed previously (Appleman et al., 2014; Lu et al., 2023; Meegoda et al., 2020; Travar et al., 2020; Zhang et al., 2022). To generalize, the treatment of ammonia and COD relies on chemical or biological oxidation, which do not effectively treat PFAS but often have the unintended effect of transforming precursor PFAS to terminal PFAS (US EPA, 2021b). Furthermore, during treatment, PFAS may partition into solids (e.g., biosolids) to a limited extent, which results in additional management challenges (Thompson et al., 2023b). Studies have recommended PFAS removal prior to such treatment (Lott et al., 2023). The targeted treatment of PFAS via removal or destruction in landfill leachate has been the subject of multiple reviews (Bandala et al., 2021; Berg et al., 2022; Lu et al., 2023; Ross et al., 2018; Travar et al., 2020) which have thoroughly discussed the effectiveness of different technologies and which are, here, summarized in Table 3.

PFAS separation technologies typically rely on adsorption over materials, such as activated carbons and ion exchange resins (US EPA, 2022c; Chow et al., 2022; Crone et al., 2019; Appleman et al., 2013), the use of high-pressure membrane separation (US EPA, 2022c; Lipp et al., 2010; Steinle-Darling and Reinhard, 2008), and newer technologies such as ozo- and foam-fractionation with the aim of concentrating the PFAS into a smaller volume of either a solid phase or concentrated liquid residual to either be disposed or destroyed via a subsequent high-energy destructive treatment method (Du et al., 2021; Labiadh et al., 2016). Several novel technologies are being investigated for the destructive treatment of landfill leachate – most require large amounts of energy in the form of chemical reactions or localized high temperatures to break the C—F bond. MSWI for energy recovery is not currently optimized to target PFAS destruction. Additional research is ongoing to define the conditions needed for PFAS destruction in MSWI and other incineration approaches, such as sewage sludge incineration.

Flaring and combustion are common LFG management techniques. Flaring is typically carried out in an open (candle) or enclosed flare. Combustion processes can generate energy on-site (e.g., a combustion engine) or off-site in a gas-fired power generation system. MSW LFG regulations target the destruction of nonmethane organic compounds (NMOCs), not PFAS. Flares generally operate at ~650 °C to 850 °C and temperatures in combustion engines or boiler systems could be lower (Wade, 2022). PFAS separation treatment has not been applied to LFG, however, laboratory-scale thermal PFAS destruction experiments indicate that temperatures higher than 1000 °C are necessary to achieve the mineralization of PFAS (Winchell et al., 2021). MSW LFG flare temperatures and the time that gaseous PFAS are in the presence of high

Table 3
Summary of treatment methods for PFAS in landfill leachate (Bandala et al., 2021; Berg et al., 2022; Lu et al., 2023; Ross et al., 2018; Travar et al., 2020; Wei et al., 2019).

	Technology	Pros	Cons	Matrix	References
Separation technologies	Activated carbon (GAC, PAC)	• High maturity level • Highly effective for long-chain PFAS	•Generates large quantities of spent sorbent that need additional treatment and disposal	GW	Busch et al. (2010); McCleaf et al. (2017), Pan et al. (2016), Ross et al. (2018); Bao et al. (2014), Pan et al. (2016); Malovanyy et al. (2023)
	Ion exchange resins	• High maturity level • Can remove compounds such as GenX	•Needs secondary treatment and disposal	GW, LL	Gao et al. (2015); Dixit et al. (2021); McCleaf et al. (2017); Ross et al. (2018); Boyer et al. (2021); Park et al. (2020); Ellis et al. (2022); Malovanyy et al. (2023)
	Membranes (RO, UF, NF)	• High maturity level and commonly practiced • 2-stage RO most effective on raw leachate	• Membrane fouling • Secondary stream with high PFAS concentrations and volume requires treatment • UF might not be effective	GW, LL	Das and Ronen (2022); Enzminger et al. (1987); Wei et al. (2019); Ross et al. (2018); Boo et al. (2018); Malovanyy et al. (2023)
	Foam/ ozofractionation	• High maturity level and commercially available pilot-scale technology • Potentially low cost	• Pretreatment of leachate might be required • Secondary treatment of concentrated PFAS required	GW, AFFF, LL	Smith et al. (2022); Robey et al. (2020); Malovanyy et al. (2023)
	Incineration	• Highly effective method • Can be used for regeneration of spent materials	•As a standalone method, not practical for large volumes of leachate		
	Chemical Oxidation	•Controllable by varying pH and temperatures	• Uses additional chemicals for treatment • Low effectiveness of removal • Needs to be paired with other methods such as UV for higher effectiveness	LL	Abu Amr et al. (2013); Lin et al. (2012)
	Electrochemical	• 98–99.7% effectiveness demonstrated • Operates at ambient temperatures • No chemicals required • Lower energy consumption compared to incineration	• Expensive electrode materials • Perchlorates could be formed	LL	Labiadh et al. (2016); Du et al. (2021); Gomez-Ruiz et al. (2017); Witt et al. (2020); Krause et al. (2021)
	Photocatalysis	• 94–99% degradation reported • Can also potentially mineralize PFAS	• Slow kinetics • Lab-scale testing only • Difficult to scale for larger volumes		Esfahani et al. (2022)
Destruction technologies	Sonolysis	• Can destroy short-chain and long-chain molecules • Effective for high concentration samples • Can be combined with chemical oxidation to lower costs • Can be used to regenerate GACs	•High capital costs		Moriwaki et al. (2005); Vecitis et al. (2008); Babu et al. (2016)
	Microwaves	• Catalytic microwave treatment could result in ~65–67% effectiveness	•Expensive for large-scale use		Gagliano et al. (2021); Lee et al. (2010b); Liu et al. (2020)
	Subcritical water oxidation	•Effective for short-chain PFAS	• Additional chemicals (e.g., zero-valent iron) needed for higher effectiveness • Slower kinetics		Hori et al. (2006)
	Supercritical water oxidation	• High maturity and close to commercialization • Low residence times required	• Full fluorine balance needed • High-pressure and temperature processes can be energy intensive	GW, AFF, LL	Pinkard et al. (2021); Hori et al. (2006); Krause et al. (2022)
	Wet Air Oxidation	•No demonstrated benefits for PFAS treatment	Converts FTOH precursors to PFCAs	LL	Travar et al. (2020)
	Biological processes	•Limited aerobic and anaerobic degradation of PFOS by bacteria and fungi reported	• Laboratory demonstrations only and thus low technology readiness level • Slow kinetics • Longer-chain PFAS converted to shorter-chain; no mineralization • Unlikely to be effective		Berhanu et al. (2023); Huang and Jaffé (2019)
	Constructed wetlands	•No demonstrated benefits for PFAS treatment	• Does not result in a concentrated PFAS stream that can be adequately managed • Environmental release of PFAS	LL	Yin et al. (2017, 2019); Awad et al. (2022); Lott et al. (2023)

(GAC = granular activated carbon; PAC = powder activated carbon; RO = reverse osmosis; UF = ultrafiltrations; NF = nanofiltration; GW = groundwater; LL = landfill leachate; AFFF = aqueous film-forming foam).

temperatures are too low to completely mineralize PFAS, but may result in the transformation of volatile PFAS into products of incomplete combustion (PICs). Notably, several PICs have been identified as significant greenhouse gases (Ahmed et al., 2020; Hong et al., 2013; Longendyke et al., 2022).

4. Environmental impact of PFAS emissions from landfills

Waste-derived PFAS may be emitted from landfills through multiple pathways, primarily in leachate or LFG effluent. While most RCRA-compliant landfills are operated to minimize environmental impacts, controls have yet to be designed to manage PFAS, and there is a subclass of small landfills in the US that are not required to install bottom liners as they are exempt from RCRA requirements (40 CFR § 258.1(f)(1)).

PFAS may be released into the atmosphere via fugitive gas emissions or gas flares. No data were found on PFAS concentrations in the ambient air surrounding C&D landfills, hazardous waste landfills, or industrial landfills; however, PFAS concentrations in the ambient air close to MSW landfills have been the subject of studies in the US, Germany, and China. Ahrens et al. (2011) reported average total FTOH concentrations of 2.6 and 26 ng m^{-3} at two US MSW landfills, representing 93% and 98% of total gas phase PFAS, with the remaining fraction consisting of perfluoroalkane sulfonamide (FASAs), perfluoroalkane sulfonamido ethanols (FASEs), and PFAAs. Weinberg et al. (2011) reported average total FTOH concentrations at two German landfill sites of 0.086 and 0.271 ng m^{-3}, representing 80% and 92% of total gas phase PFAS. Tian et al. (2018) measured PFAS in air sampled on-site at two landfills as well as downwind. The PFAS profile of the on-site air samples was more evenly split among classes. Total FTOHs were 0.61 and 2.1 ng m^{-3} at the two sites, representing 42% and 76% of $\sum_6$PFAS, with PFAAs representing the bulk of the remaining fraction. PFAS concentrations downwind of the two landfill sites were lower than on-site but elevated relative to control sites, indicating atmospheric transport of PFAS. Lower concentrations downwind may indicate dilution or deposition of volatile PFAS. Neutral PFAS readily transform in the environment – studies have shown the degradation of FTOHs into PFCAs via photooxidation (Esfahani et al., 2022; Martin et al., 2006). Tian et al. (2018) reported elevated neutral and ionizable PFAS in dry deposition samples on-site and downwind of landfills, driven primarily by PFBA and PFOA. Ahmadireskety et al. (2020) reported PFAS concentrations in landfill cover soils of approximately 8 μg kg^{-1}, similarly driven by PFCAs.

Deposition of PFAS from landfill-impacted air may also contribute to PFAS measured in surface water on landfill sites. Chen et al. (2023) reported $\sum_{26}$PFAS concentrations in stormwater at MSW landfill sites averaging 470 ng L^{-1}, significantly lower than leachate concentrations from the same study but significantly higher than groundwater samples, which averaged 140 ng L^{-1} of $\sum_{26}$PFAS. PFAS may be present in both surface and groundwater due to leachate contamination. At the same time, particulate transport from the working face or atmospheric transport and deposition of PFAS are more likely to impact surface water. The MPCA (2010) reported PFAS contamination in groundwater impacted by landfills accepting PFAS-laden industrial waste. Hepburn et al. (2019) measured PFAS and other landfill leachate indicators in groundwater impacted by legacy landfills in Australia, where PFOA represented >10% of total PFAAs, likely associated with legacy landfills.

Using the landfill liner collection efficiency reported by Jain et al. (2023) and overall leachate leakage rate of 1.9% with the leachate generation rate reported in Lang et al. (2017) (61 billion L $year^{-1}$), approximately 1.2 billion L of MSW landfill leachate enter the groundwater directly as a result of liner imperfections every year (14.3 kg of total PFAS using the average $\sum_{19}$PFAS from Lang et al. (2017)). This represents a conservative estimate, as Lang et al. (2017) note that most but not all landfills contributing to the total estimated leachate generation are lined. Although C&D leachate generation rates are not readily available, using leachate generation rates calculated for 17 MSW landfills in six US states, Jain et al. (2023) reported an average collection rate of 6900 L ha^{-1} day^{-1}. Assuming similar leachate generation rates for C&D landfills, this corresponds to approximately 2.5 million L of C&D leachate entering the groundwater per hectare of C&D landfill annually, representing a $\sum$PFAS mass of 26 g of PFAS per hectare of C&D landfill (see Table S9 in the SI for more calculation information). In 2012, the US EPA inventoried 1504 active C&D landfills (US EPA, 2012).

In the US, most landfill leachate generated from RCRA-permitted landfills is managed off-site (again, many C&D landfills are not required to collect leachate and thus operate without a bottom liner). This represents a significant flux of PFAS leaving the landfill. Multiple studies in the US and Australia have estimated the contribution of PFAS to municipal WWTP from landfill leachate and the environmental impact of PFAS in WWTP effluent. Masoner et al. (2020) estimated the PFAS load in landfill leachates and receiving WWTPs. They reported that landfill leachate while representing, on average, <2% of WWTP influent by volume across three sites, contributed 18% of influent PFAS. Gallen et al. (2017) reported similar contributions of PFAS to WWTPs from landfill leachates. PFAS are not effectively treated with traditional WWTP processes and are released to the environment via WWTP liquid effluent, land-applied biosolids, landfills, and possibly incineration of biosludge (Barisci and Suri, 2021; Coggan et al., 2019; Gallen et al., 2018; Helmer et al., 2022; Tavasoli et al., 2021).

5. Estimate of US MSW landfill PFAS mass balance

Estabrooks and Zemba (2019) evaluated landfill PFAS mass balance at an MSW landfill in Vermont, identifying the PFAS load from targeted waste types suspected to contain PFAS, not including residential MSW, and found that approximately 7% of the PFAS load entering landfills is emitted via leachate annually, and hypothesize the majority of PFAS remain in the waste mass within the landfill. Coffin et al. (2022) propose an estimated extractable $\sum$PFAS load in MSW entering landfills of 50 ng g^{-1} based on the findings in Liu et al. (2022a). This, combined with US EPA estimation of landfilled MSW in 2018 (the most recent year for which MSW generation data is available for the US), corresponds to 6600 kg of extractable PFAS entering MSW landfills in 2018 with MSW (US EPA, 2020b). Biosludge and biosolids also contribute a significant fraction of PFAS loading in MSW landfills. Using $\sum_{92}$PFAS in treated biosolids reported by Thompson et al. (2023b) and biosolids management statistics reported by NEBRA (2022), the 1.74 million dry metric tons of biosolids landfilled each year contribute an additional estimated 850 kg of PFAS to MSW landfills. Based on our calculations, a conservative estimate of 7480 kg of extractable PFAS entered US MSW landfills in 2018. This estimate does not include PFAS polymers.

As described earlier, PFAS can be emitted from landfills via the gaseous and liquid phase. MSW landfills in the US collect approximately 93.5 million m^3 of gas daily according to the US EPA LMOP database. This translates to nearly 1 kg of neutral PFAS emitted via MSW LFG per day (347 kg annually) based on the concentrations reported by Titaley et al. (2023). The US EPA estimates MSW LFG collection efficiency of approximately 75% (US EPA, 2020a), indicating an additional 31.2 million m^3 of LFG are released via fugitive emissions from MSW landfills annually. Leachate generation in the US, estimated by Lang et al. (2017), is 61.1 billion L $year^{-1}$ which corresponds to 750 kg of PFAS emitted from MSW landfills via leachate annually (using the weighted average $\sum$PFAS concentration of 12,300 ng L^{-1} calculated in this study). See Fig. 3 for a flowchart representing PFAS sources, controlled emissions, and uncontrolled emissions to the environment corresponding to MSW landfills, and Fig. 4 for a graphical presentation of the fraction of PFAS entering landfills from MSW and biosolids and corresponding emissions; the majority of PFAS entering landfills remain in the waste (84% annually) and significant a mass of PFAS have likely accumulated since PFAS use in consumer products began. Detailed calculations for Fig. 3 are included in the SI ***Table S10***.

One can estimate the total PFAS released via the gaseous phase per ton of MSW based on the potential methane generation capacity (L_o) of

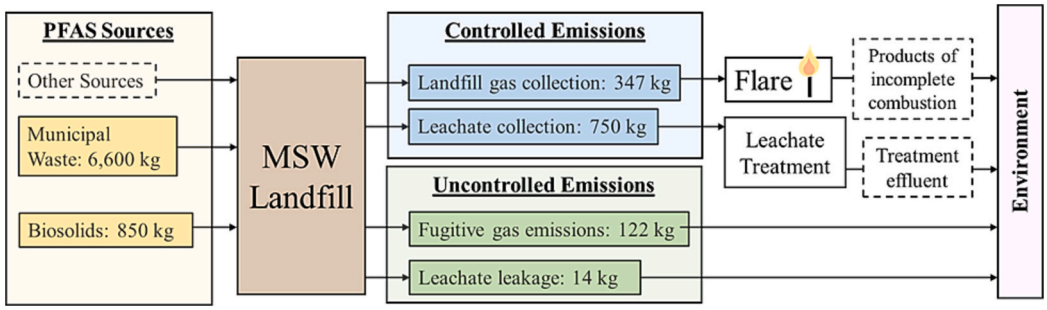


Fig. 3. Flowchart depiction of annual ∑PFAS loading and release at MSW and C&D debris landfills based on current understanding in the literature. Dashed lines represent PFAS streams which have not been quantified to any extent in the literature.

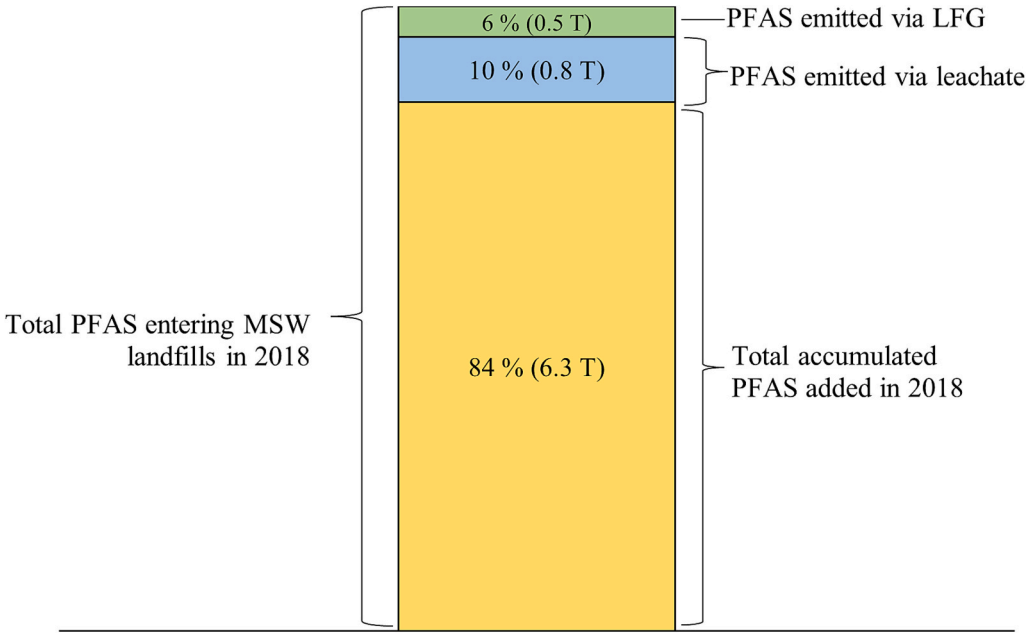


Fig. 4. Estimated PFAS mass balance for US MSW landfills.

MSW. Jain et al. (2021) estimated MSW methane emissions of 68 m^3 of methane per metric ton (Mg) of waste, or approximately 136 m^3 of LFG per Mg of waste; using these values and the Titaley et al. (2023) LFG PFAS concentrations suggest 1.38 mg of PFAS are released, cumulatively, via LFG for every Mg of MSW.

5.1. Limitations

The estimated PFAS mass loading and emissions presented here are based on multiple assumptions and, in some cases, limited data, resulting in significant uncertainty. We have not provided additional data quality assurance in this review process. A small number of studies have explored changes in landfill leachate PFAS profile over time, and no studies have looked for similar relationships in LFG; for this critical review, it was assumed that ∑PFAS reported in leachate and gas are representative of a range of waste ages and stages of decomposition and, overall, are expected to remain consistent over time. Even fewer studies have looked at C&D debris landfills in the US, and those studies are limited to Florida landfills. This critical review of previous analyses provides perspective, not precise values, which should be derived through additional empirical studies.

6. Conclusions and data gaps

The bulk of studies of PFAS in solid waste and landfills focus on MSW landfill leachate, with comparatively fewer studies estimating overall PFAS loading in other types of landfill leachate, in the solid waste itself, or gaseous effluent. Regardless of the type of landfill, in all studies across all locations, PFAS were quantified in all leachate samples. PFAS concentrations in leachates vary across studies, which may be a function of waste type, leachate qualities, climate, and the analytical method.

US MSW and C&D landfill leachates have similar ∑PFAS concentrations. However, C&D leachate contains proportionally more terminal PFAS. This is likely due to the PFAS present and the conditions within each landfill type. Concentrations of the five PFAS which have been the subject of proposed US EPA regulations (i.e., PFBS, PFHxS, PFOS, PFOA, and PFNA) consistently exceed US EPA tapwater RSLs in both MSW and C&D landfill leachates by a factor as high as 20 (PFOA) and in HW landfill leachates by a factor as high as 104 (PFOS); as presented in Table 1 and Fig. 2.

MSWI ash leachates have lower PFAS concentrations than other leachates, however, co-disposal of ash with other wastes results in disproportionately high PFAS concentrations in leachate. To minimize PFAS leaching from MSWI ash landfills, care should be taken to dispose of unburned waste which contains higher concentrations of PFAS separately from MSWI ash. No peer-reiviewed studies have reported

PFAS concentrations in effluent from hazardous waste (Subtitle C) landfills, although hazardous waste management methods are likely to reduce PFAS leaching. Since some hazardous waste landfills likely accept PFAS-laden industrial waste at relatively high levels, it would be helpful to have more information on effluent generated from these facilities.

Traditional leachate treatment methods that use oxidation (e.g., a treatment that targets ammonia, COD) are likely to increase the transformation rate of precursor PFAS to terminal PFAS, such as regulated PFAAs. Treatment that relies on volatilization, such as evaporation, likely contributes significant quantities of PFAS to the atmosphere and surrounding environment, increasing off-site transport. Separating PFAS from leachate prior to additional treatment would avoid these issues. Though there are many aqueous treatment technologies for the targeted removal or destruction of PFAS, few have been tested for effectiveness on landfill leachate. Those tested on leachate and have shown promise include supercritical water oxidation, electrochemical oxidation, reverse osmosis, and foam separation. Assuming treatment efficacy is comparable across PFAAs, reducing PFOA concentration to its limit (e.g., MCL) will reduce all other PFAS to below their respective limits. PFAS treatment of liquid wastes often produces a secondary residual waste requiring additional management.

PFAS are expected to be present in LFG as a product of volatilization and the anaerobic decomposition of biodegradable waste but have been quantified only in MSW LFG. PFAS have not been measured in C&D LFG. However, based on PFAS profiles in C&D landfill leachate, similar PFAS concentrations are likely present in C&D LFG, although LFG generation rates from C&D debris is lower. To reduce gaseous emissions of PFAS, biodegradable waste should be disposed of separately from other PFAS-containing waste. Data do not exist on the effectiveness of PFAS destruction from LFG combustion within flares and internal combustion engines or PFAS removal from LFG to RNG conversion processes. However, the temperatures reached in LFG flares are expected to transform volatile PFAS into terminal PFAS and possible PICs, with minimal mineralization.

Based on our estimate of the PFAS entering and leaving landfills, significant quantities of PFAS are emitted in both LFG and leachate; however, the bulk of PFAS remains within the waste mass on a per-year basis (see Fig. 3). This suggests landfills will be a source of PFAS emissions for the foreseeable future. Studies have demonstrated downgradient impacts on groundwater from landfills. C&D landfills pose the highest risk of environmental contamination since they are not required (at the federal level) to install liners to collect leachate. Even among lined landfills, the average liner collection efficiency is approximately 98%, corresponding to an annual flux of 14.3 kg PFAS entering groundwater via liner imperfections.

Elevated PFAS concentrations were measured in ambient air at landfills across several studies. The highest concentrations were found among FTOHs, which transform into PFAAs in the environment. Atmospheric PFAS may deposit and contribute to soil and surface water concentrations. Even if LFG collection systems were equipped to operate at temperatures and residence times sufficient to destroy PFAS, current MSW LFG collection efficiency is only 75%, and landfills not required to collect LFG will continue to emit PFAS into the atmosphere. The fate of PFAS in LFG that passes through landfill cover soil should be analyzed in future studies.

This review has identified several data gaps for PFAS emissions from US landfills. Data are needed from hazardous waste landfill sites and relevant industrial waste landfills. Furthermore, US C&D landfill leachate data are limited to Florida landfills, and additional efforts should be made to collect information from other states. C&D waste streams may vary due to regional construction requirements. The measurement of PFAS in LFG and other gaseous emissions is an area of emerging study. More research is needed on both controlled and uncontrolled landfill gaseous emissions. A closer evaluation of the fate of PFAS during leachate treatment and LFG management is needed to help decision-makers guide the solid waste community. Geomembrane liners are the most effective tools for the protection from and collection of PFAS-containing liquids, such as landfill leachate. More research is needed to understand long-term interactions between PFAS and liner systems, especially in complex matrices such as landfill leachate. More research is needed to evaluate the long-term implications of PFAS in the landfill environment since the bulk of PFAS remains within the solid waste mass. This review focused on landfilling as a management option for solid waste; evaluation of PFAS fate during other solid waste management processes (e.g., anaerobic digestion, thermal treatment, composting, and recycling) is needed.

CRediT authorship contribution statement

Thabet Tolaymat: conceptualization, approach, methodology, writing-reviewing, editing, funding, **Nicole Robey**: data curation, methodology, calculations, writing-original draft, writing and editing. **Max Krause**: writing and editing, **Judd Larson, Keith Weitz, Sameer Parvathikar**: data curation, original draft preparation, editing, **Lara Phelps, William Linak, Susan Burden, Tom Speth, Jonathan Krug:** writing and editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.167185.

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Air concentrations and particle–gas partitioning of polyfluoroalkyl compounds at a wastewater treatment plant

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Environmental context. Polyfluoroalkyl compounds, widely used chemicals in consumer and industrial products, are global pollutants in the environment. Transport mechanisms and environmental pathways of these compounds, however, are not yet fully understood. We show that a wastewater treatment plant can be an important source for polyfluoroalkyl compounds to the atmosphere where they have the potential to be transported long distances.

Abstract. An air sampling campaign was conducted at a wastewater treatment plant (WWTP) to investigate air concentrations and particle–gas partitioning of polyfluoroalkyl compounds (PFCs). Samples were collected at an aeration tank and a secondary clarifier using both active high volume samplers and passive samplers comprising sorbent-impregnated polyurethane foam (SIP) disks. Water to air transport of PFCs was believed to be enhanced at the aeration tank owing to aerosol-mediated transport caused by surface turbulence induced by aeration. Mean air concentrations of target PFCs at the aeration tank were enriched relative to the secondary clarifier by factors of ~19, ~4 and ~3 for ∑fluorotelomer alcohols (FTOHs) (11 000 *v.* 590 pg m^{-3}), ∑perfluorooctane sulfonamides & perfluorooctane sulfonamidoethanols (FOSAs & FOSEs) (120 *v.* 30 pg m^{-3}) and ∑perfluoroalkyl carboxylates & perfluoroalkyl sulfonates (PFCAs & PFSAs) (4000 *v.* 1300 pg m^{-3}) respectively. The particle associated fraction in the atmosphere increased with increasing chain length for PFCAs (from 60 to 100%) and PFSAs were predominantly bound to particles (~98%). Lower fractions on particles were found for FTOHs (~3%), FOSAs (~30%) and FOSEs (~40%). The comparison of the active and passive air sampling showed good agreement.

Additional keywords: atmosphere, passive air sampler, PFC, PFOA, PFOS, WWTP.

Introduction

Polyfluoroalkyl compounds (PFCs), such as perfluorooalkyl carboxylates (PFCAs) and perfluorooalkyl sulfonates (PFSAs), have been detected in a variety of environmental media and also in remote regions[1]; including rivers,[2] oceans,[3] the atmosphere,[4] wildlife,[1] and in humans.[5] PFCAs and PFSAs are persistent, bioaccumulative and toxic.[6–8] Fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs) and perfluorooctane sulfonamidoethanols (FOSEs) are precursors for PFCAs and PFSAs.[9–11] These precursors are volatile and can be transported in the atmosphere.[12–14]

There is still uncertainty about the origin of PFCs in the environment and the transport pathways of PFCAs and PFSAs are still under discussion. Wastewater treatment plants (WWTPs) are known to be point sources for PFCAs and PFSAs in rivers.[15,16] PFCs can be further transported via ocean currents to remote regions.[3] In terms of atmospheric pathways, the long-range transport of precursors can contribute to the occurrence of PFCs in remote regions.[17,18] However, the amounts from transport of PFCAs and PFSAs in ocean currents or from their precursor compounds in the atmosphere are not sufficient to fully explain the levels detected in remote regions.[13,17] Additionally, atmospheric PFCA and PFSA concentrations in urban areas cannot be explained by only considering the degradation of precursors.[19]

Recently, a laboratory experiment and a model have shown the transport of perfluorooctanoic acid (PFOA) in the gas-phase in its neutral form.[20,21] It was suggested that PFOA originated

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from aerosol-mediated transport from a water body into the atmosphere.[20] PFCAs and PFSAs have been detected in the particle-phase in the atmosphere; however, only a few studies have reported their presence in the gas-phase.[19,22]

The aim of this study was to generate more information on aerosol-mediated sources of PFCs by investigating the air concentrations and particle–gas partitioning of PFCs emitted at two locations in a WWTP – the aeration tank and the secondary clarifier. A secondary aim was to compare measurements conducted using the active high volume air sampler with time-integrated measurements using a sorbent-impregnated polyurethane foam (SIP) disk passive air sampler.

Experimental methods

Chemicals

The target analytes included 10 PFCAs (C_4–C_{12}, C_{14}), 4 PFSAs (C_4, C_6, C_8, C_{10}), 3 FTOHs (6 : 2, 8 : 2, 10 : 2 FTOH), 3 FOSAs, 2 FOSEs, 1 PFOSEA and 19 mass-labelled internal standards (see Tables A1 and A2 in the Accessory publication, available at http://www.publish.csiro.au/?act=view_file&file_id=EN10133_AC.pdf).

Sampling

Sampling took place at a WWTP in Ontario, Canada, during spring 2010. At this sampling site two sampling locations were chosen: one at the aeration tank, where activated sludge is added to the wastewater to remove organic materials; and the other at the secondary clarifier, where the sludge is allowed to settle, to be separated from the water. The main difference between the two sampling sites is that air is blown into the wastewater at the aeration tank, to create an aerobic environment for the microbes. This generates a turbulent and bubbling surface at the aeration tank whereas the surface of the secondary clarifier is relatively calm.

High volume air samples (~140 m^3 per sample) were collected for 24 h, twice per week over a period of 6 weeks at an aeration tank and a secondary clarifier at a WWTP. Glass fibre filters (GFFs) (Pall Corporation, Quebec, QC, Canada, Type A/E Glass 102-mm diameter baked at 250°C before sampling) were used to collect the particle-phase, whereas PUF/XAD/PUF cartridges (precleaned large PUF plug, Supelco, Oakville, ON, Canada, 7.6-cm length, 6-cm diameter, 15 g of XAD-2 (SupelcoTM-2), Supelco) were used for trapping gas-phase compounds. In addition, SIP disks were deployed in duplicate for 37 days during the same time period at both sampling sites to provide a time-integrated sample. To prepare SIP disks, precleaned PUF disks (diameter 14 cm, thickness 1.35 cm, surface area 365 cm^2, mass 4.4 g, volume 207 cm^3, density 0.0231 g cm^{-3}, Tisch Environmental, Cleves, OH, USA) were coated by dipping in a hexane and ground Amberlite XAD-4 slurry (styrene-divenylbenzene, Supelco) and then drying, according to the method described in Shoeib et al.[23]

The effective air volume (V_{air}) for passive samples was calculated using[24]:

$$V_{air} = K_{SIP-air} \times V_{SIP}\left[1 - \exp\left(-\frac{d \times k_a}{K_{SIP-air} \times D_{film}}\right)\right] \quad (1)$$

V_{SIP} is the volume of the SIP disks (2.10×10^{-4} m^3), d the deployment time (37 days), D_{film} the thickness of the SIP disks (5.67×10^{-3} m) and k_a the air-side mass-transfer coefficient (108 m day^{-1}) calculated as the ratio of the sampling rate and the area of the SIP disks (3.7×10^{-2} m^2). The sampling rate was determined during another study ($r = 4$ m^3 day^{-1}).[24] SIP–air partitioning coefficients ($K_{SIP-air}$) and the slope of octanol–air partitioning coefficients (K_{OA}) from the literature[23,25,26] were used for the determination of temperature dependent $K_{SIP-air}$ values (average temperature during sampling period 9°C). The sample volume for FTOHs, FOSAs and FOSEs ranged from 120 to 140 m^3.

For PFCAs and PFSAs, an effective air volume of 150 m^3 was calculated based on the duration of 37 days and a SIP disk sampling rate of 4 m^3 day^{-1} according to Genualdi et al.[24]

Field blank samples for all sample media were collected by exposing them for 1 min at the sampling site and then treated them like real samples. Total suspended particles (TSPs) were determined gravimetrically by weighing the GFFs before and after sampling and dividing the mass by the air sample volumes. Furthermore air temperature was measured at the sampling sites.

Extraction and analysis

The extraction method and analysis was similar to methods used elsewhere.[23,24] All samples were spiked with mass-labelled internal standards before extraction. The PUF/XAD/PUF cartridges and the SIP-disks were extracted using Soxhlet apparatus with petroleum ether (6 h, 240 mL, ~20–40 cycles) for FTOHs, FOSAs and FOSEs and thereafter with methanol (10–14 h, 240 mL, ~50–70 cycles) for PFCAs and PFSAs. The GFFs were extracted by sonication using dichloromethane for FTOHs, FOSAs and FOSEs (three times using 12 mL for 20 min and then combining extracts) and methanol for PFCAs and PFSAs (five times using 12 mL for 20 min and then combining extracts). The two fractions for each sample media were treated separately. All fractions were concentrated by rotary evaporation (Büchi, Flawil, Switzerland) and nitrogen blow down. The methanol fractions were cleaned with Envi-Carb.[27] The petroleum ether and dichloromethane fractions were applied to sodium sulfate columns for removing moisture. After clean up, 80% of the dichloromethane extract was combined with the corresponding methanol extract, because PFCAs and PFSAs were found to be partially extracted into dichloromethane. The methanol fractions were treated by adding 50% water and injections standards $^{13}C_8$-PFOS and $^{13}C_8$-PFOA, whereas Me_2FOSA was added as the injection standard to the other fractions.

Gas chromatography mass spectrometry (GC-MS) in positive chemical ionisation mode (PCI) (Agilent Technologies, Mississauga, ON, Canada, 7890 A GC system) was used for analysis of FTOHs, FOSAs and FOSEs (except for PFOSA). The separation of target compounds was performed on a DB-WAX column (30 m, 0.25-mm inner diameter, 0.25-μm film, J&W Scientific, Folsom, CA, USA). The injection volume was 2 μL and using splitless injection (200°C). The oven temperature program is given in the Accessory publication (Table A3). Helium was used as carrier gas at a flow rate of 1.3 mL min^{-1}. Methane was used as the reaction gas.

Instrumental analysis of PFCAs and PFSAs (including PFOSA) was performed using high pressure liquid chromatography (Agilent 1100 Series) tandem mass spectrometry (HPLC-MS/MS) (Applied Biosystems, Toronto, ON, Canada, 4000 QTRAP) in the electrospray negative ionisation mode at atmospheric pressure. For separation, a pre-column (C_8, 4-mm length, 2-mm diameter, Phenomenex, Torrance, CA, USA) and a Luna column (C_8 (2), 50-mm length, 2-mm

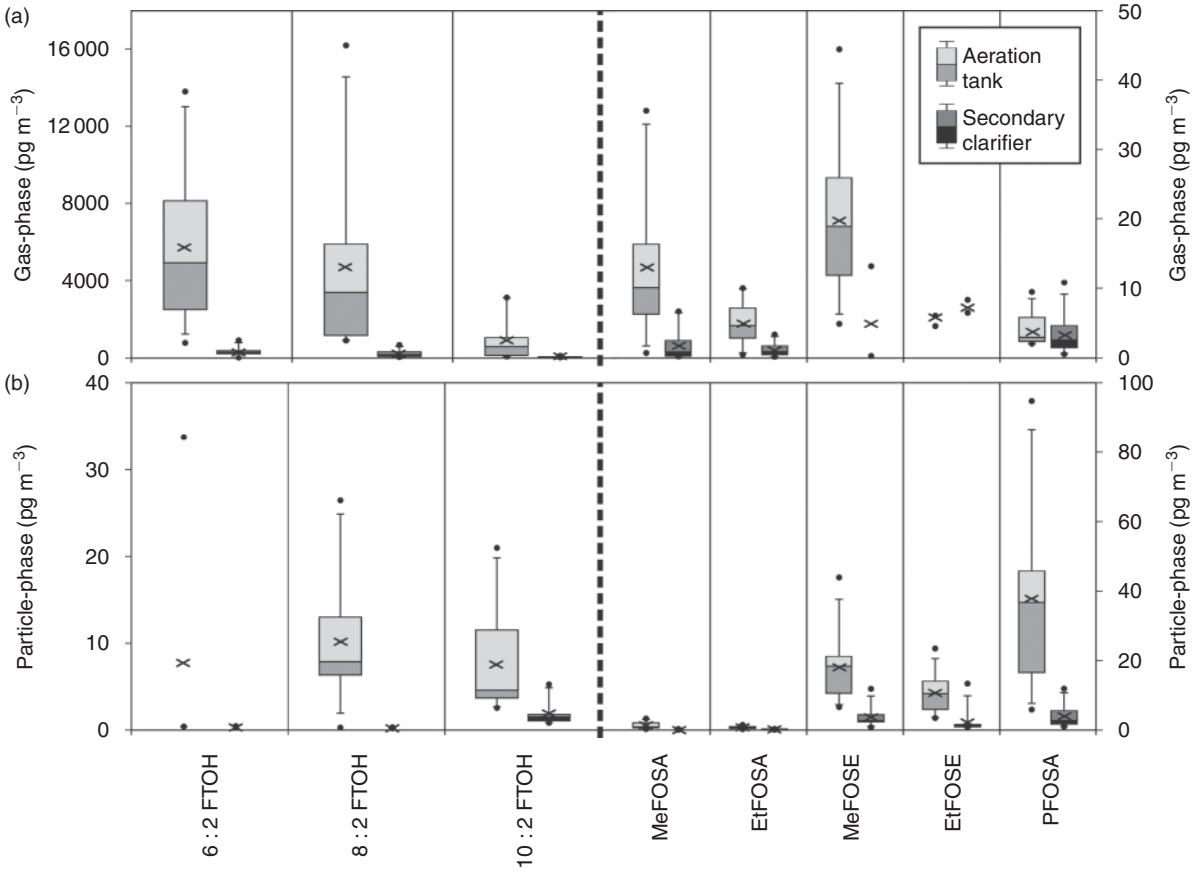


Fig. 1. Box-whisker plots for FTOH, FOSA and FOSE concentrations in the gas (a) and particle-phase (b) at the aeration tank and the secondary clarifier. The boxes show median concentrations and the 25th and 75th percentiles; 10th and 90th percentiles are indicated by the whiskers and the dots represent the minimum and maximum concentrations. The mean concentrations are indicated with an ×. If more then 25% of the data for one compound were below the IDL only minimum, maximum and mean values are shown.

diameter, 3-µm particle size, Phenomenex) was used. Methanol and water, each with 10-mM ammonium acetate, were used as the mobile phase. The flow was set to 0.25 µL min^{-1} and the gradient is given in the Accessory publication (Table A4). The injection volume was 25 µL.

Quantification was performed based on response factors of the target compounds and their corresponding internal standards. The ratio of both response factors was used for recovery correction. The calibration curves included eleven points for FTOHs (0.3–3800 ng mL^{-1}), seven points for FOSAs and FOSEs (0.12–115 ng mL^{-1}) and eight points for PFCAs and PFSAs (0.005–5.0 ng mL^{-1}). Instrument detection limits (IDLs) were calculated by extrapolating instrument response in blank samples to a concentration that would give a S/N value of three. A further limit of detection (LOD) calculated as three times the standard deviation (s.d.) of the blanks was used. Concentrations below the blank levels and below the IDL were set to half of the LOD for statistical analysis. In cases where the substitution for a particular chemical was required for more than 25% of the data set, only the mean value was presented in Figs 1 and 2 as the other statistical parameters are subject to bias by substituting a constant value.[28] Compounds not detected above the IDL in any of the samples were excluded from further investigations.

Prior to extraction, small punches (0.7 cm^2) of seven GFFs from each sampling site were analysed for organic carbon using a Thermal Optical Transmission box (Sunset Laboratory, Tigard, OR, USA). PFC concentrations for the relevant GFFs were corrected based on the punched area.

Results and discussion

Quality control

Concentrations in blank samples ranged from <IDL to 7 pg m^{-3} in PUF/XAD/PUF cartridges and GFFs and from <IDL to 10 pg m^{-3} in SIP disks. All results were corrected for blanks. Details of IDLs and the blank levels for individual compounds are given in Tables A5 and A6 in the Accessory publication.

LODs ranged from 0.4 to 13 pg m^{-3} for FTOHs, FOSAs and FOSEs and from 0.01 to 39 pg m^{-3} for PFCAs and PFSAs (see Table A6 in the Accessory publication).

Recoveries for internal standards of target PFCs in PUF/XAD/PUF cartridges ranged from 5.9 ± 1.8% for ^{13}C-6 : 2 FTOH to 100 ± 18% for ^{13}C-10 : 2 FTOH; from 72 ± 13% for d_3-MeFOSA to 230 ± 37% for d_9-EtFOSE and from 21 ± 11% for $^{13}C_2$-PFDoDA to 180 ± 96% for $^{13}C_2$-PFBA. The low recoveries for ^{13}C-6 : 2 FTOH are associated with the high volatility of this compound and the resulting evaporative losses during Soxhlet extraction and concentration. Signal enhancement caused by solvent or interfering compounds might be responsible for high recoveries, i.e. for d_9-EtFOSE. For GFFs, the recoveries ranged from 9.4 ± 2.8% for ^{13}C-6 : 2 FTOH to 150 ± 25% for d_9-EtFOSE and from 36 ± 8.5% for $^{13}C_2$-PFBA to 67 ± 16% for $^{13}C_2$-PFHxA. For the SIP disks recoveries ranged from 6.4 ± 1.0% for ^{13}C-6 : 2 FTOH to 310 ± 40% for $^{18}O_2$-PFHxS. All samples (including blanks) were recovery corrected using appropriate factors based on recoveries presented above and summarised in Table A7. The poor recoveries

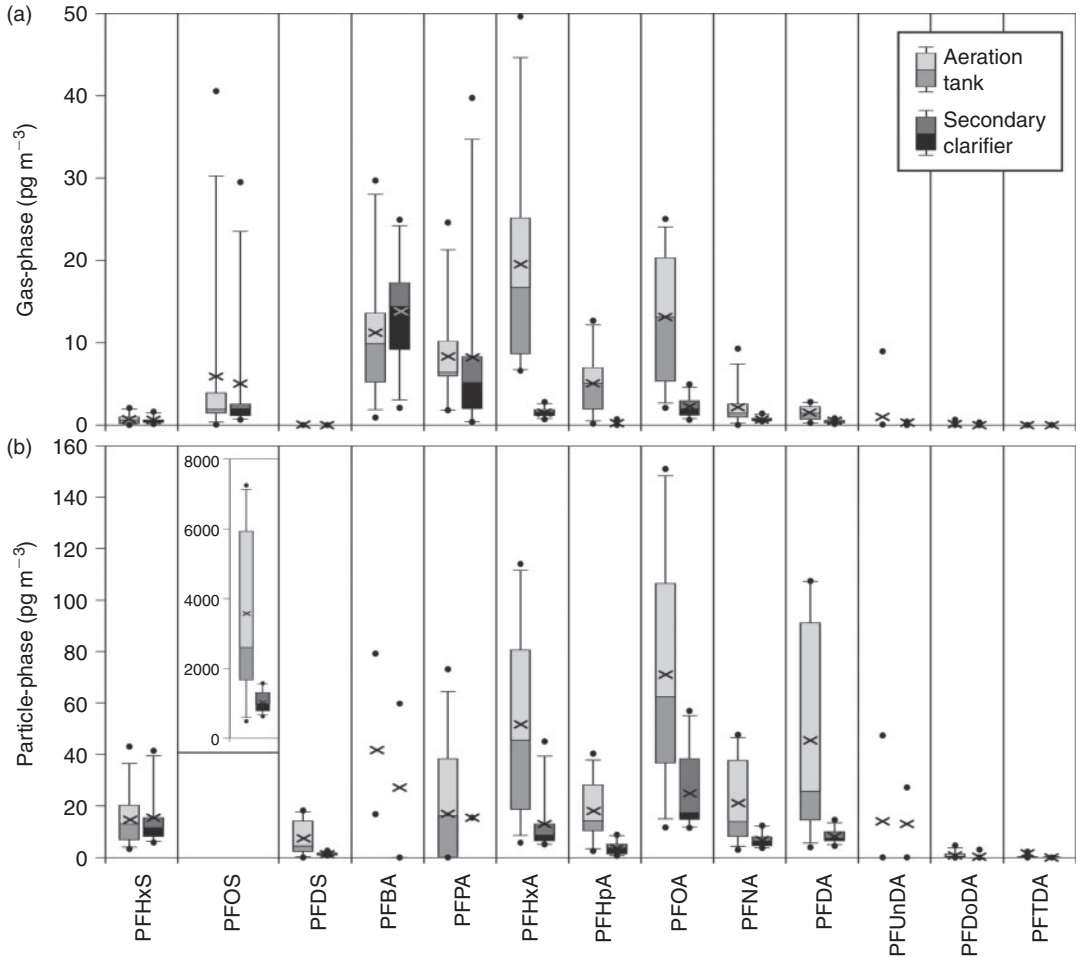


Fig. 2. Box-whisker plots for PFCA and PFSA concentrations in the gas (a) and particle-phase (b) at the aeration tank and the secondary clarifier. The boxes show median concentrations and the 25th and 75th percentiles; 10th and 90th percentiles are indicated by the whiskers and the dots represent the minimum and maximum concentrations. The mean concentrations are indicated with an ×. If more then 25% of the data for one compound were below the IDL only minimum, maximum and mean values are shown.

for 6 : 2 FTOH cause greater uncertainty in the derived air concentration for this compound.

FTOH, FOSA and FOSE air concentrations

Gas- and particle-phase air concentrations for FTOH, FOSA and FOSE are shown in Fig. 1 and are summarised with results from passive samples in Table 1. Detailed results are in Tables A8–A11 in the Accessory publication. PFOSEA was not detected above the IDL in any sample and was therefore excluded from further investigations.

Gas-phase samples were dominated by FTOHs with a mean concentration of 11 000 pg m^{-3} at the aeration tank and 590 pg m^{-3} at the secondary clarifier. Mean ∑FOSA & FOSE concentrations were 43 pg m^{-3} at the aeration tank and 16 pg m^{-3} at the secondary clarifier. Conversely, ∑FTOH exhibited the lowest particle-phase concentrations (25 pg m^{-3} at the aeration tank and 1.9 pg m^{-3} at the secondary clarifier), whereas for ∑FOSA & FOSE particle-phase concentrations were higher at 69 and 11 pg m^{-3} respectively. The mean ∑FTOH concentrations at the aeration tank were 18 times higher for the gas-phase and 13 times higher for the particle-phase compared with the secondary clarifier (*t*-test, $P < 0.001$ and $P < 0.005$ respectively). Mean ∑FOSA & FOSE concentrations were approximately a factor of three to six higher at the aeration tank compared with the secondary clarifier (*t*-test, $P < 0.001$ for gas- and particle-phase respectively). These results point to the important role of the aeration process in emitting high concentrations of PFCs to the atmosphere.

Composition

The composition of FTOHs, FOSAs and FOSEs in each sample is shown in Figs A1 and A2 in the Accessory publication. The profile of FTOHs in the gas-phase was dominated by 6 : 2 FTOH (54%) > 8 : 2 FTOH (38%) > 10 : 2 FTOH (8%) and was similar at both sampling sites. In the particle-phase at the aeration tank, all of the FTOHs were detected (8 : 2 FTOH (47%) > 10 : 2 FTOH (35%) > 6 : 2 FTOH (18%)) whereas at the secondary clarifier only 10 : 2 FTOH was detected above the IDL. For FOSAs and FOSEs the gas-phase profile was different at the two sites. The aeration tank samples were dominated by MeFOSE (47%) and MeFOSA (27%), whereas the secondary clarifier samples were dominated by PFOSA (39%) and MeFOSA (24%). FOSAs and FOSEs in the particle-phase showed a similar pattern at the aeration tank and the secondary

Table 1. Individual PFC concentrations in the gas-phase and particle-phase and from SIP disk passive air samplers at the aeration tank and secondary clarifier in picograms per cubic metre (minimum–maximum and average in parentheses)

	Aeration tank			Secondary clarifier		
	Gas-phase	Particle-phase	SIP disk passive air samples	Gas-phase	Particle-phase	SIP disk passive air samples
6 : 2 FTOH	780–14 000 (5700)	0.36–34 (7.7)	11 000–12 000 (12 000)	0.31–910 (330)	0.36–0.36 (0.36)	670–910 (790)
8 : 2 FTOH	900–16 000 (4700)	0.250–27 (10)	5700–5800 (5800)	27–670 (220)	0.25–0.25 (0.25)	310–350 (330)
10 : 2 FTOH	72–3100 (920)	2.5–21 (7.5)	780–860 (820)	6.2–110 (41)	0.82–5.2 (1.9)	41–48 (45)
∑FTOH	3300–33 000 (11 000)	4.5–79 (25)	18 000–19 000 (18 000)	34–1700 (590)	1.4–5.8 (2.5)	1100–1300 (1200)
MeFOSA	0.71–36 (13)	0.27–3.3 (1.4)	13–14 (14)	0.23–6.7 (1.9)	0.1–0.66 (0.4)	0.79–1.0 (0.90)
EtFOSA	0.46–10 (4.9)	0.25–1.5 (0.8)	5.7–5.9 (5.8)	0.19–3.4 (1.2)	0.1–0.32 (0.23)	1.2–1.6 (1.4)
MeFOSE	4.9–44 (20)	6.6–44 (18)	16–18 (17)	0.54–13 (5.6)	0.77–12 (3.7)	4.5–4.9 (4.7)
EtFOSE	4.1–7.0 (6.5)	3.4–24 (11)	8.5–9.4 (8.9)	<6.96–8.3 (7.1)	0.81–13 (2.2)	1.8–2.3 (2.0)
PFOSA	2.3–9.5 (4.3)	5.9–95 (38)	4.9–10 (7.7)	0.54–11 (3.3)	0.97–12 (4.0)	0.0–0.0 (0.0)
∑FOSA & FOSE	11–100 (43)	23–120 (69)	52–55 (54)	11–31 (16)	4.9–31 (11)	6.9–9.3 (8.1)
PFHxS	0.06–2.1 (0.78)	3.3–43 (15)	0.62–0.87 (0.74)	0.12–1.6 (0.59)	5.8–41 (15)	0.65–0.91 (0.75)
PFOS	1.1–41 (5.8)	480–7200 (3900)	220–260 (240)	0.65–30 (4.7)	620–1600 (1100)	21–38 (30)
PFDS	0.01–0.01 (0.01)	0.04–18 (7.4)	0.01–0.01 (0.01)	0.01–0.01 (0.01)	0.84–2.6 (1.4)	0.01–0.01 (0.01)
PFBA	0.9–30 (11)	9.3–79 (42)	13–15 (14)	2.1–25 (14)	1.4–62 (31)	6.7–13 (9.9)
PFPA	1.7–25 (8.7)	0.99–73 (22)	6.1–6.7 (6.4)	0.42–40 (8.8)	19–19 (19)	0.34–2.4 (1.4)
PFHxA	6.6–50 (20)	5.7–110 (52)	18–20 (19)	0.7–2.8 (1.6)	5.0–45 (13)	1.2–1.7 (1.4)
PFHpA	0.16–13 (5.1)	2.5–40 (18)	5.2–6.0 (5.6)	0.04 –0.81 (0.54)	0.66–8.8 (3.8)	0.85–1.0 (0.94)
PFOA	2.1–25 (13)	12–150 (71)	8.1–11 (9.7)	0.63–4.9 (2.3)	12–57 (25)	2.0–3.1 (2.5)
PFNA	0.69–9.3 (2.1)	3.0–48 (21)	1.1–1.2 (1.1)	0.45–1.4 (0.72)	3.7–12 (6.8)	0.41–0.66 (0.54)
PFDA	0.25–2.8 (1.4)	4.0–110 (46)	2.0–2.2 (2.1)	0.14–0.81 (0.42)	4.5–15 (8.3)	0.28–0.38 (0.33)
PFUnDA	0.03–9.0 (1.2)	0.59–47 (14)	1.2–1.2 (1.2)	0.06–0.41 (0.33)	2.0–27 (15)	012–0.35 (0.24)
PFDoDA	0.09–0.64 (0.24)	0.09–4.7 (1.1)	0.15–0.21 (0.18)	0.06–0.31 (0.11)	0.08–3.1 (1.3)	0.02–0.05 (0.04)
PFTDA	0.004–0.004 (0.004)	0.02–2.2 (0.31)	0.01–0.01 (0.01)	0.0–0.0 (0.0)	0.03–0.36 (0.17)	0.01–0.01 (0.01)
∑PFCA & PFSA	25–120 (69)	849–7600 (3900)	280–320 (300)	17–86 (34)	760–1700 (1100)	35–61 (48)
∑PFC	3300–33 000 (11 000)	29–130 (94)	18 000–19 000 (19 000)	47–1790 (600)	6.0–36 (13)	1100–1300 (1200)

clarifier with dominant compounds being PFOSA (53 and 40% respectively), MeFOSE (27 and 38% respectively) and EtFOSE (~17% at both sites).

Comparisons with other measurements

It is interesting to compare the magnitude of air concentrations for the various PFCs measured at the WWTP to other studies. This comparison will give some sense of the importance of the WWTP as a point source to air. Air concentrations of FTOH in the urban area of Toronto ($\sum$FTOH = 81 pg m^{-3} sum of particle and gas-phase[29]) were two orders of magnitude lower than at the aeration tank and one order of magnitude lower than at the secondary clarifier. Thus WWTPs seem to be an important point source for FTOHs. Differences were less drastic for other PFCs. For instance, FOSA and FOSE concentrations were approximately six times higher at the aeration tank compared with urban areas ($\sum$FOSA & FOSE = 19 pg m^{-3} sum of particle and gas-phase[19,29]) and the FOSA & FOSE concentrations at the secondary clarifier were generally in the same range as in urban areas.[19,29] Ongoing studies at this WWTP are attempting to quantify the emission fluxes to air so that WWTPs as a whole can be assessed in terms of their contribution to the atmospheric burdens of PFCs.

PFCA and PFSA air concentrations

Gas- and particle-phase results for PFCA and PFSA in air are shown in Fig. 2 and further summarised in Table 1 and in Tables A8–A11 in the Accessory publication.

Gas-phase concentrations of PFCAs and PFSAs ($\sum$PFCA & PFSA 70 pg m^{-3} at the aeration tank and 34 pg m^{-3} at the secondary clarifier) were one to three orders of magnitude lower compared with FTOHs; however, they were two times higher than FOSAs and FOSEs. In contrast, $\sum$PFCA & PFSA concentrations in the particle-phase were 500 and 100 times higher than the $\sum$FTOH and $\sum$FOSA & FOSE concentrations respectively. PFOS was the dominant compound in the particle-phase. PFOS concentrations (average 3600 pg m^{-3} at the aeration tank and 1000 pg m^{-3} at the secondary clarifier) were one to three orders of magnitude higher than concentrations of the other PFCs. It is interesting to note that mean $\sum$PFCA & PFSA concentrations were significantly higher at the aeration tank compared with the secondary clarifier (factor of 1–4, *t*-test $P < 0.012$ for the gas-phase, $P < 0.003$ for the particle-phase). In former studies investigating other WWTPs, higher PFC concentrations were reported in treated effluent in comparison to influent wastewater, though mass flow charts from Schultz et al. indicate similar concentrations in the aeration tank and secondary clarifier.[15,30] This indicates that the observed differences in air concentrations are most likely associated with enhanced mass transfer (water to air transfer) of PFCAs and PFSAs owing to the aeration process rather than to differences in wastewater concentrations of PFCAs and PFSAs between the aeration tank and secondary clarifier.

Composition

The composition of PFCAs and PFSAs in each sample is shown in Fig. A3 in the Accessory publication. The profile of PFCAs and PFSAs in the gas-phase was different at the two sampling sites. At the aeration tank, PFHxA was dominant (29%), followed by PFOA and PFBA (both ~19%). The contributions of the remaining compounds were 10% (PFPA)

and lower. Samples from the secondary clarifier were dominated by PFBA (48%), followed by PFPA (15%) and PFOS (11%). The contributions of the remaining compounds were below 9%. These results indicate that the different treatment processes of the wastewater at the WWTP caused different air emission signatures for the PFCAs and PFSAs. However, in general, PFOS and the short chain PFCAs (C_4–C_8) were the dominant compounds in the gas-phase at both the aeration tank and the secondary clarifier, whereas the contribution of the longer chain PFCAs (C_9–C_{14}) was very low (<3%). PFOS was also dominant among the PFCAs and PFSAs in the particle-phase (~91% of ∑PFCA & PFSA) at both sites. The next dominant PFCA and PFSA after PFOS was PFOA (3% at the aeration tank and 5% at the secondary clarifier), followed by PFHxS, PFHxA and PFDA (each >0.5%). The dominance of PFOS and PFOA on atmospheric particles has been reported in the literature[19]; however, the dominance of PFOS as observed in this study was not previously observed or reported. The dominance of PFOS (and PFOA) in particles might reflect the pattern of PFCs used in industrial and consumer products.[31,32]

Comparisons with other measurements

Chemical ratios are sometimes used to compare or differentiate sources. In the current study the ratio of PFOS and PFOA, i.e. PFOS/PFOA, observed at the WWTP could be compared with other locations to gain some sense of whether the WWTP as a point source could be contributing substantially to the broader contamination of the atmosphere. The ratio PFOS/PFOA in the gas-phase from the WWTP (0.4–2.1) was in the same range as the ratio from an urban area (0.5),[19] which suggests a possible contribution of the WWTP to urban air or at least that the source for urban air is similar. However, for the particle-phase, PFOS/PFOA was more than 100 times higher at the WWTP (42–50) compared with an urban area (0.3).[19] This may indicate that the particle-phase signature at the WWTP is a localised or short-lived source.

Most literature reports of PFCAs and PFSAs focus on the particle-phase exclusively. For instance, Dreyer et al. reported ∑PFCA and ∑PFSA concentrations in the particle-phase in Germany of 1.0 and 1.3 pg m^{-3} respectively.[4,33] These concentrations are one to three orders of magnitude lower compared with concentrations at the WWTP in this study. In a study from New York State, PFCAs and PFSAs were measured in the gas and particle-phase.[19] These concentrations (i.e. ∑C_6,C_{10} PFSA & $C_{7–12}$ PFCA 8.0 and PFOS 2.3 pg m^{-3})[19] were also one to three orders of magnitude lower compared with the present study (210 and 3600 pg m^{-3} at the aeration tank and 110 and 1000 pg m^{-3} at the secondary clarifier).

In summary, the measured concentrations of PFSAs and PFCAs at the WWTP were greatly elevated compared with other studies, even for urban areas. This highlights the importance of WWTPs as point-source emitters of these compounds to the atmosphere.

Correlations of atmospheric concentrations with sampling parameters

The influence of various meteorological and particle parameters (e.g. ambient air temperature, TSP and particle OC content) on PFC air concentrations were investigated.

Air temperature, which ranged from −0.2 to 12.5°C during high volume sampling, showed a positive correlation for FOSEs and FOSAs in the gas phase, i.e. MeFOSA and MeFOSE ($P<0.05$). This is likely owing to greater evaporation of these compounds at higher temperatures. However, other PFCs did not exhibit this correlation. It is likely that evaporation from wastewater is governed more by the temperature of the wastewater (versus the air temperature) which is much less subject to variability. A positive correlation of the PFC concentration with the air temperature was found previously[34]; however, owing to a weak correlation, it was assumed that other factors may have also had an influence.[33]

The OC contents of the particles from the two sites were not significantly different (4.0 ± 1.1% OC at the aeration tank, $n=7$, and 3.3 ± 0.9% OC at the secondary clarifier, $n=7$; t-test $P=0.2$) and no correlation with atmospheric PFC concentrations were found. The TSP concentration was significantly higher at the aeration tank (120 ± 29 μg m^{-3}, $n=12$) in comparison to the secondary clarifier (75 ± 20 μg m^{-3}, $n=12$, t-test $P<0.001$) but again no correlation with atmospheric PFC concentrations were found. The higher TSP concentration above the aeration tank is likely the result of aerosol generation and the release of wastewater particulates to air.

Particle–gas partitioning

The percent on particles for the various target PFCs is summarised in Fig. 3. This was calculated as the concentrations in the particle-phase (in picograms per cubic metre) divided by the sum of concentrations in the gas and particle-phase (in picograms per cubic metre) and multiplied by 100. There was no substantial difference in particle–gas partitioning of target compounds collected at the aeration tank versus the secondary clarifier and so average values are represented in Fig. 3.

Of the target PFCs, the FTOHs showed the smallest particle-phase percentages that were typically less than 10%. Particle bound fractions for FTOHs found during ship-based measurements for 8 : 2 FTOH and 10 : 2 FTOH were higher compared with results from the present study (up to 23%,[29] 26% for 8 : 2 FTOH and 15% for 10 : 2 FTOH[35]).

Particle-phase percentages increased for MeFOSA and EtFOSA (~19 and ~15% respectively) and were even higher for MeFOSE, EtFOSE and PFOSA (38–70%). Other studies showed lower particle-phase percentages from land-based measurements (i.e. MeFOSA & EtFOSA <10%, EtFOSE 14%[4]), whereas ship-based measurements were similar to the results for the WWTP (i.e. MeFOSA & EtFOSA ~15%,[4] MeFOSE 30%,[29] EtFOSE 57%[4]).

The PFSAs had the highest particle associated fractions with almost 100% bound on particles. PFCAs were also mainly particle-associated and this increased generally according to chain length as: PFBA (~64%) ≈ PFPA (~68%) < PFHxA (~78%) < PFHpA (~80%) < PFOA (~86%) ≈ PFNA (~88%) < PFDA (~95%) > PFUnDA (~89%) > PFDoDA (~80%) < PFTDA (~100%). This pattern is likely owing to the decrease in vapour pressure (which favours the condensed state) with increasing chain length for the neutral forms of PFCAs.[36,37] Only one study is available for comparison with these results.[19] Particle-phase percentages reported for New York State were 60% for PFHpA, 40% for PFOA and PFNA and 30% for PFDA, PFDoDA and PFOS.[19] Moreover, the shorter chain PFCA, PFHpA, had the highest particle-bound fractions and the longest chain PFCA, PFDA, had the lowest particle-phase fractions.[19] At this time, we have no explanation for these contradictory results.

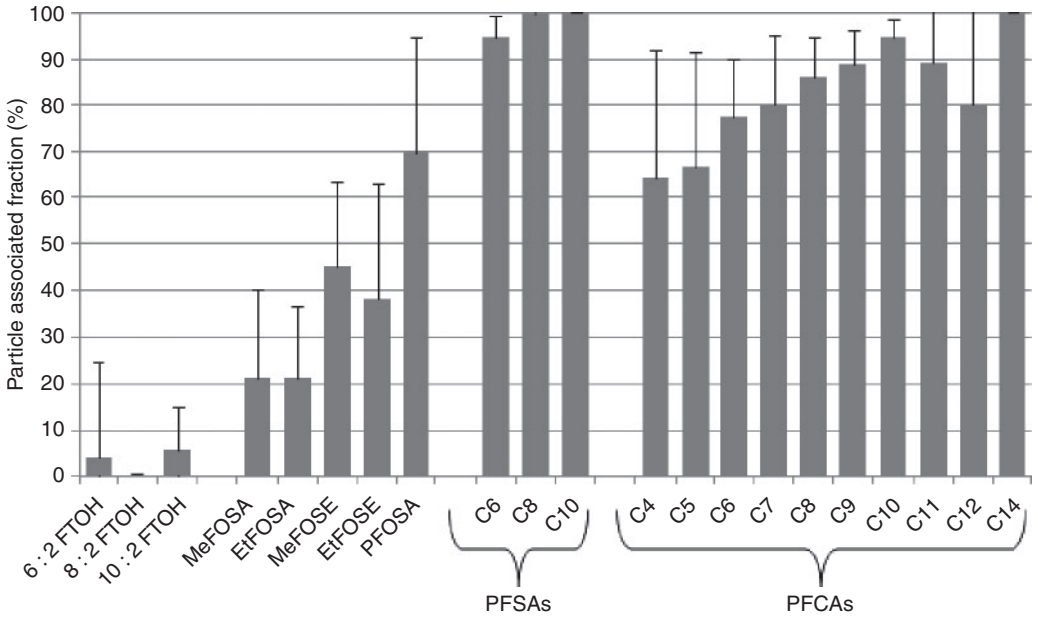


Fig. 3. Particle associated fractions (%) for individual PFCs in air at the aeration tank and secondary clarifier.

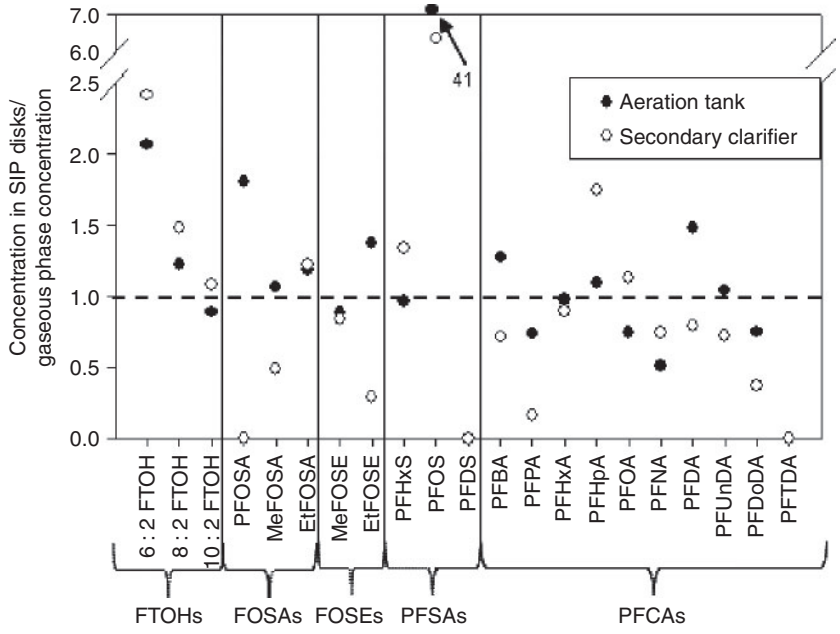


Fig. 4. Ratio between individual PFC concentrations in the SIP disks passive air samples (pg m^{-3}) ($n = 2$) and gas-phase from active air sampling (pg m^{-3}) ($n = 12$). The dashed line represents perfect agreement.

Comparison of active v. *passive sampling techniques*

It is interesting to compare the gas-phase air concentrations from the intermittent high volume samples against the time-integrated concentrations derived using the passive samples. Differences can be expected for several reasons: (i) differences in the sampling time, i.e. the high volume samples were collected on two consecutive days each week and represented ~29% of the time that was sampled by the continuous and time-integrating passive samplers. Thus, high and low air concentration episodes that could offset the true time-integrated air concentrations might not have been captured by this 29% of the time window; (ii) although passive samplers better cover the entire duration of the study, there is greater uncertainty with these derived concentrations owing to uncertainties in the sampling rates; (iii) collection of particles on the SIP disks is known to occur[38] and this may result in an overestimate of the gas-phase concentration for compounds that are particle-associated (this issue is discussed further, below); and (iv) general analytical errors that contribute to uncertainties.

Despite these potential uncertainties and confounding factors, the agreement between gas-phase concentrations derived from high volume samples *v*. SIP disk passive air samples was fairly good as shown in Fig. 4 with detailed results presented in

Table 1. The concentrations differed by a mean factor of 1.5 for FTOHs, 0.96 for FOSAs, 0.85 for FOSEs, 1.1 for PFHxS, 24 for PFOS and 0.8 for PFCAs.

Sampling artefacts

Previous laboratory investigations have shown that PFCAs may adsorb to filters (GFFs and quartz fibre filters (QFFs)) and therefore particle-phase concentrations derived from sampling techniques using GFFs and QFFs could be overestimated.[39] The results of the present study and the comparison of active versus passive samples provides some insight into this issue. PFCAs and PFSAs were found predominantly in the particle-phase. However, the presence of PFCAs in the gas-phase and the good agreement between gas-phase concentrations using high volume sampler and passive air sampler concentrations indicate that this sampling artefact has a relatively minor influence on the gas-phase concentrations. However, we acknowledge that the high concentrations of target compounds at the WWTP may not provide the best conditions for detecting this artefact. It may be more important at lower air concentrations.

Particle-phase sampling by the SIP disks is another 'artefact' that complicates the comparison of results from high volume samples and from SIP disks. It has been shown that the SIP disk sampling chamber allows ~10% of the ambient particles to be sampled and so the SIP disk is not just a gas-phase passive sampler.[38] The net effect is demonstrated well by the results for PFOS (see Fig. 4). In the high volume samples, the PFOS particle-phase air concentrations are more than two orders of magnitude larger than the gas-phase concentration. The air concentration derived from the SIP disk passive air samples, which represents mainly the gas-phase and ~10% of the particle-phase,[38] fall somewhere in between. In this case the 10% of ambient particles that are sampled by the SIP disk outweigh the gas-phase contribution. More studies are required to further elaborate and quantify particle-phase sampling by passive samplers and sorption artefact for filters.

Conclusion

This study demonstrates the importance of WWTPs as point sources of PFCs to the atmosphere. The aeration process in particular is shown to be a key emission process for both gas-phase and particle-associated PFCs. Aerosol-mediated transport is believed to account for the higher amounts of particle-associated PFCs in air near the aeration tank. This pathway is likely also to be important in open water bodies as aerosols are generated and released to air via sea spray and wave action. Passive and active samplers are shown to be complementary and comparable air sampling approaches for PFCs.

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A comprehensive review of landfill leachate treatment technologies

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The management of landfill leachate presents a significant environmental challenge, necessitating a comprehensive and dynamic treatment approach. This comprehensive review delves into the critical issue of landfill leachate treatment, exploring its environmental impact, treatment technologies, regulatory frameworks, and the path towards sustainable management practices. This review explores the complexities of landfill leachate, emphasizing the need for sustainable waste management practices to safeguard environmental health. Our analysis highlights the evolution of conventional and advanced treatment technologies designed to mitigate these risks, focusing on membrane technologies, advanced oxidation processes, and the promising potential of emerging techniques such as adsorption and biological nutrient removal. These technologies are evaluated for their efficiency, cost implications, and sustainability impacts, underscoring the challenges and opportunities within the current landscape of leachate treatment. The review aims to provide insights into designing efficient and effective treatment systems through a detailed analysis of conventional and advanced treatment methods. By examining a case study in Changsha City, the effectiveness of a comprehensive treatment system integrating various technologies is demonstrated. The review underscores the interconnectedness of human activities, environmental health, and waste management, emphasizing the importance of a holistic approach. It stresses the continuous improvement of leachate treatment technologies and the adoption of sustainable practices to reduce the environmental footprint of landfills. Ultimately, it calls for integrating multiple treatment processes, economic considerations, and readiness to address future challenges in landfill leachate treatment, contributing to the advancement of sustainable waste management practices.

KEYWORDS

landfill leachate, treatment technologies, membrane technologies, advanced oxidation processes, waste treatment

1 Introduction

Landfill leachate, a liquid byproduct of the decomposition process in landfills, represents a significant environmental challenge that encapsulates the complexity of modern waste management and the imperative of safeguarding environmental health (Teng et al., 2021). As rainfall or other sources of moisture percolate through the waste material accumulated in landfills, they dissolve and suspend a myriad of substances present

in the waste, creating a potent mixture known as leachate (Mor and Ravindra, 2023). This concoction's composition can vary widely but typically includes dissolved organic matter, inorganic macro-components like salts and metals, and a range of xenobiotic organic compounds, reflecting the diverse nature of disposed materials (Kumar et al., 2023). Organic components, measured in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), indicate the leachate's potential impact on water bodies, while inorganic macro-components, such as ammonia, chlorides, sulfates, and heavy metals like arsenic, cadmium, chromium, lead, and mercury, underline the toxicological concerns associated with leachate (Al-Yaqout and Hamoda, 2020). Furthermore, the presence of xenobiotic compounds, which include pesticides, pharmaceuticals, and industrial chemicals, adds to the complexity of leachate, given their resistance to degradation and potential for bioaccumulation (de Oliveira et al., 2020). The environmental impacts of uncontrolled landfill leachate are profound and far-reaching. Leachate can seep into groundwater and surface water, contaminating aquatic ecosystems, wildlife, and human health (Essien et al., 2022). The infiltration of pollutants into water supplies can disrupt aquatic habitats, harm species diversity, and bioaccumulate the food chain, presenting significant risks to public health through consuming contaminated water and food (Sharma et al., 2023). Moreover, the heavy metals and persistent organic pollutants found in leachate are particularly concerning due to their toxicity, environmental longevity, and potential to cause long-term ecological damage (Hussein et al., 2021).

Recognizing the environmental hazards of landfill leachate, its treatment and management have become critical components of sustainable waste management practices (El-Saadony et al., 2023). Effective leachate treatment aims to neutralize its harmful components, making it safe for discharge or further use (Kumar et al., 2023). This necessitates a multifaceted approach that combines physical, chemical, and biological treatment processes tailored to the specific composition of the leachate and local regulatory requirements (Torretta et al., 2017). Physical treatments, such as sedimentation and filtration, remove suspended solids and particulate matter (Siddiqi et al., 2022). Chemical treatments, including precipitation, coagulation, and advanced oxidation, target dissolved pollutants, reducing their concentration to safer levels (Kurniawan et al., 2006). Biological aerobic and anaerobic treatments further degrade organic substances, transforming them into less harmful compounds (Kurniawan et al., 2010). The importance of landfill leachate treatment extends beyond the immediate goal of pollution control. It embodies the broader principles of environmental protection and sustainable waste management (Mukherjee et al., 2015). By mitigating the adverse impacts of leachate on ecosystems and human health, effective treatment practices contribute to the preservation of water quality, protect biodiversity, and ensure the wellbeing of communities (Senathirajah and Palanisami, 2023). Furthermore, advancements in leachate treatment technologies offer opportunities for resource recovery, such as the extraction of valuable materials or the reuse of treated water, aligning with the principles of the circular economy and resource efficiency (Puyol et al., 2017).

Treating landfill leachate is not just a technical challenge but a fundamental aspect of environmental stewardship and public health protection (Nath and Debnath, 2022). It reflects the evolving understanding of waste not merely as a byproduct to be disposed of but as a potential source of pollution that must be managed with foresight and responsibility. As such, the continuous improvement of leachate treatment technologies, alongside adopting more sustainable waste management practices, is essential to reducing the environmental footprint of landfills. This includes the development of more efficient and cost-effective treatment solutions and the implementation of waste reduction, reuse, and recycling initiatives that can minimize leachate generation in the first place (Kamaruddin et al., 2017).

Ultimately, the comprehensive management and treatment of landfill leachate highlight the interconnectedness of human activities, environmental health, and the need for a holistic approach to waste management (Torretta et al., 2017). This review aims to provides an integrated analysis of both conventional and advanced treatment technologies, emphasizing recent advancements and emerging techniques such as adsorption and biological nutrient removal. Unlike previous reviews that may focus solely on specific technologies or methodologies, this review evaluates a broad spectrum of treatment methods, offering a practical guidance for designing and optimizing treatment systems by evaluating the efficiency, cost implications, and sustainability impacts of various methods. Additionally, we incorporate a detailed case study from Changsha City, demonstrating the practical application and effectiveness of a comprehensive treatment system that integrates various technologies. This real-world example bridges the gap between theoretical discussions and practical implementation, providing actionable insights for practitioners and policymakers. By addressing the interconnectedness of human activities, environmental health, and waste management, our review advocates for a holistic approach that emphasizes continuous improvement of leachate treatment technologies and the adoption of sustainable practices. This comprehensive perspective makes our review an invaluable resource for engineers, environmental scientists, and waste management professionals seeking to implement effective and sustainable treatment solutions in diverse contexts.

2 Characteristics of landfill leachate

2.1 Physical and chemical properties of landfill leachate

Leachate embodies a dynamic concoction of substances, each contributing to its hazardous nature. Landfill leachate's physical, chemical, and biological characteristics delineate a complex and multifaceted environmental challenge that requires a nuanced understanding for effective management and treatment (Table 1) (Andreottola and Cannas, 2024; Castrillón et al., 2010; Naveen et al., 2017; Luo et al., 2020; Subiza-Pérez et al., 2023).

Physically, leachate is primarily a liquid matrix. However, its appearance, viscosity, and other physical properties can vary greatly depending on the landfill's age, the composition of waste, and the amount of precipitation the landfill receives (Anjum et al., 2023). Typically, young leachate is characterized by a high organic load, evident in its dark color and strong odor (Wijekoon et al., 2022). In

TABLE 1 Characteristics of landfill leachate and implications for treatment (Andreottola and Cannas, 2024; Castrillón et al., 2010; Naveen et al., 2017; Luo et al., 2020; Subiza-Pérez et al., 2023).

Aspect	Characteristics	Implications for treatment
Physical	Liquid matrix, varying appearance and viscosity, pH, temperature, conductivity	Influences treatment process selection, affects solubility and treatment effectiveness
Chemical	Dissolved organic/inorganic matter, heavy metals, xenobiotics (e.g., pharmaceuticals, pesticides), COD, BOD, ammonia	Requires targeted removal or neutralization of specific compounds, challenges due to persistence and toxicity of pollutants
Biological	Microbial communities, biodegradation of organic matter, presence of pathogenic organisms	Utilization of microbial activity for degradation, management of pathogenic or harmful microorganisms

TABLE 2 Physical and chemical properties of landfill leachate across different continents (Abunama et al., 2021a).

Parameter		Africa	Asia	Europe	North America	Oceania	South America
Organic	BOD (mg/L)	566.22	1305.85	1281.98	270.11	60.66	875.73
	COD (mg/L)	3026.81	5,983.26	5,890.65	1628.52	1594.5	3117.69
Inorganic	pH	7.72	7.72	8.03	7.95	7.81	8.13
	TKN (mg/L)	26.485	34.55	42.66	26.485	28.33	34.55
	AN (mg/L)	297.89	450.22	525.77	297.89	350.55	450.22
	TDS (mg/L)	10,403.1	11,456.3	15,382.9	3077.1	17,487.5	4364.6
Heavy metals	Cl (mg/L)	84.32	98.72	103.21	72.33	55.66	84.12
	Fe (mg/L)	7.11	25.99	41	22.04	4.88	26.28
	Cu (mg/L)	0.256	0.489	0.323	0.141	0.022	1.131
	Ni (mg/L)	0.45	0.56	0.52	0.32	0.24	0.45
	Zn (mg/L)	0.65	2.738	2.105	0.91	0.159	1.66
	Pb (mg/L)	0.331	0.55	0.54	1.441	0.006	2.524
	Cr (mg/L)	0.49	0.62	0.49	42.585	0.32	1.66
	Hg (mg/L)	0.221	0.33	0.32	0.723	0.0003	3.783
	As (mg/L)	0.0433	0.225	0.0525	33.8	0.1	0.221
	Cy (mg/L)	0.261	0.216	0.075	0.025	0	0.055

contrast, older leachate may appear clearer but contain higher concentrations of dissolved inorganic compounds (Abdel-Shafy et al., 2024). The physical properties of leachate, such as pH, temperature, and conductivity, are critical indicators of its overall composition and the potential challenges it presents for treatment (Abdel-Shafy et al., 2024). For instance, high conductivity in leachate signifies a high concentration of dissolved ions such as chlorides, sulfates, and ammonia, which can affect the efficiency of certain treatment processes. Similarly, pH levels can influence the solubility of metals and the effectiveness of chemical treatments, with acidic or alkaline conditions necessitating specific adjustments in the treatment strategy (Deng et al., 2020).

Chemically, leachate is a cocktail of dissolved organic and inorganic matter, heavy metals, and xenobiotic compounds (Sil and Kumar, 2017). The organic fraction is typically dominated by biodegradable substances like carbohydrates, fats, proteins, and persistent organic pollutants that resist natural degradation processes (Dignac et al., 2000). COD and BOD are key parameters used to quantify the organic strength of leachate, reflecting its potential impact on receiving environments and treatment systems (Naveen et al., 2017). Inorganic components include a range of salts, metals, and nutrients, with ammonia being particularly prevalent due to the nitrogenous decomposition of organic waste (Borah et al., 2020). Heavy metals such as arsenic, cadmium, chromium, lead, and mercury are of significant concern due to their toxicity and propensity to accumulate in ecosystems (Rahman and Singh, 2019). Moreover, the presence of xenobiotics—synthetic chemicals like pharmaceuticals, pesticides, and industrial chemicals—poses a unique challenge, as these compounds often exhibit resistance to degradation and can disrupt biological processes in treatment systems and natural environments (Priya et al., 2024). Table 2 presents a detailed analysis of the physical and chemical properties of landfill leachate from various regions around the world, showing significant variability across different regions (Abunama et al., 2021a). These variations highlight the importance of regional assessments in understanding leachate pollution potential and tailoring appropriate management strategies.

Biologically, leachate is a living, evolving entity, teeming with microorganisms, such as bacteria, fungi and protozoa, which are adapted to its unique chemical milieu. The microbial communities within leachate play a pivotal role in the biodegradation of organic matter, facilitating the natural attenuation of some pollutants (Qi et al., 2023). However, the diversity and activity of these microbial populations can be both a boon and a bane for leachate treatment (Dave et al., 2020). Bacteria such as *Pseudomonas* and *Clostridium* spp., and fungi like Aspergillus and Penicillium spp., are integral to breaking down organic pollutants and transforming hazardous substances. While certain bacteria and fungi are harnessed in biological treatment processes to degrade organic pollutants, the presence of pathogenic organisms or those capable of generating harmful byproducts necessitates careful management to prevent environmental and health risks (Mani et al., 2020). The methanogenic archaea, including Methanobacterium and Methanosarcina spp., also play a crucial role by converting waste into methane, highlighting the importance of microbial activity in both waste reduction and potential energy recovery.

The interplay between the physical, chemical, and biological characteristics of leachate significantly influences the selection and design of treatment processes. Physical attributes like suspended solids and temperature necessitate pre-treatment steps such as sedimentation and filtration to prevent system clogging and optimize subsequent treatment stages. Chemical properties, including pH, organic load, and the presence of toxic compounds, determine the need for neutralization, biological treatment, or advanced oxidation processes to ensure effective contaminant removal. Biological factors, such as microbial content and biodegradability, guide the choice of biological treatment methods, which might require nutrient supplementation for optimal microbial activity. Consequently, tailored and integrated treatment strategies are developed to address the specific challenges presented by leachate's complex composition, ensuring efficient and sustainable management to mitigate its environmental impact.

2.2 Factors on the composition of landfill leachate

The composition of landfill leachate is influenced by a myriad of factors, including the age of the landfill, the types of waste it contains, climatic conditions, and the specific landfill operating technologies employed (Mor and Ravindra, 2023). Each of these factors plays a critical role in determining the leachate's physical, chemical, and biological characteristics, thus influencing its potential environmental impact and the strategies required for its effective management and treatment (Table 2) (Cano et al., 2020; Golwala et al., 2022; Ma et al., 2022; Abdel-Shafy et al., 2024).

The age of a landfill significantly affects the composition of the leachate produced. In the initial stages of landfilling, leachate tends to have a high organic content, characterized by a high BOD and COD, due to the abundance of readily degradable organic matter (Lindamulla et al., 2022). As the landfill matures, the rate of organic matter decomposition decreases, leading to a reduction in BOD levels (Kulikowska and Klimiuk, 2008). However, the concentration of inorganic compounds, such as ammonia, chlorides, and heavy metals, may increase over time due to the continued degradation and leaching processes (Prieto-Espinoza et al., 2022). This temporal evolution in leachate composition necessitates adaptable treatment approaches that effectively address the shifting balance between organic and inorganic constituents (Saxena et al., 2022) (Table 3). In 2022, Liu et al. conducted a study on the molecular differences between young landfill leachate (YL) and mature landfill leachate (ML) (Liu J. et al., 2022). The results indicated that the COD of YL was 74,853 mg/L, while the COD of ML was 3,098 mg/L, suggesting a higher concentration of organic matter in young leachate. Regarding molecular composition, YL contained lower molecular weight organic compounds, primarily consisting of CHO compounds and aliphatic compounds. In contrast, ML predominantly contained CHON compounds and high oxygen highly unsaturated and phenolic compounds. The molecular structure of YL was relatively simple, with higher bioavailability and more straight-chain structures. ML, however, featured more oxygen-containing functional groups and benzene-ring structures, indicating a more complex molecular structure. In terms of chemical properties, YL exhibited lower nominal oxidation state of carbon and modified aromaticity index, indicating that its organic matter was in a more reduced state. Conversely, ML's organic matter had higher oxidation states and aromaticity, reflecting that over time, the organic matter in mature leachate had undergone extensive biochemical reactions, leading to more complex structures (Table 4).

Moreover, the nature of the waste material disposed of in a landfill is another critical determinant of leachate composition. Landfills containing a high proportion of organic waste, such as food scraps and yard waste, tend to produce leachate with high levels of organic pollutants and a greater potential for biological activity (Kjeldsen et al., 2002). Conversely, landfills with significant industrial or hazardous waste may generate leachate with higher concentrations of toxic metals and xenobiotic organic compounds (El-Saadony et al., 2023). The diversity of waste types, including e-waste, pharmaceuticals, and plastics, contributes to the complexity of leachate, requiring targeted treatment solutions capable of addressing a broad spectrum of contaminants (Srivastava et al., 2021).

Also, climatic conditions, including precipitation, temperature, and humidity, play a pivotal role in the generation and composition of leachate. High rainfall areas will likely produce larger volumes of leachate, potentially diluting its contaminant concentrations but increasing the overall load of pollutants that must be managed (Wijekoon et al., 2022). Temperature affects the rate of biochemical reactions within the landfill, with warmer conditions typically accelerating organic matter decomposition and, consequently, influencing the rate of leachate generation and its organic content (Mohammad et al., 2022). Humidity can also impact the moisture content within the landfill, affecting leachate production rates and composition (Abunama et al., 2021b).

Finally, a landfill's design and operational practices can significantly influence leachate composition (Ma et al., 2022). Modern landfills equipped with engineered liners and leachate collection systems are designed to minimize the direct contact of waste with groundwater, thereby reducing leachate generation and its potential contamination (Abdel-Shafy et al., 2024). Additionally, using daily covers can limit rainwater infiltration, further controlling

TABLE 3 Impact of various factors on the composition of landfill leachate (Kulikowska and Klimiuk, 2008; Lindamulla et al., 2022; Prieto-Espinoza et al., 2022; Saxena et al., 2022).

Factors	Options	Leachate composition
Landfill Age	Young Landfill (<10 years)	High in volatile organic compounds, BOD, and COD due to active decomposition of organic matter
	Middle-Aged Landfill (10–20 years)	Reduced levels of BOD and COD as the rate of organic decomposition decreases, increase in inorganic compounds such as ammonia
	Old Landfill (>20 years)	Lower BOD, higher concentrations of inorganic compounds, heavy metals, and stabilized organic compounds
Type of Waste Material	Organic Waste	High levels of BOD, COD, and volatile organic compounds due to decomposition of organic matter
	Industrial and Hazardous Waste	Increased concentrations of toxic metals, xenobiotics, and specific industrial chemicals
	Construction and Demolition Waste	Elevated levels of inorganic compounds, such as salts and heavy metals, lower organic content
	E-Waste	Presence of heavy metals (e.g., lead, mercury, cadmium) and potentially hazardous chemicals from electronic components
Climatic Condition	High Rainfall/High Humidity	Diluted concentrations of contaminants due to increased volume, potential for higher leachate production
	Arid/Dry	Concentrated leachate due to lower precipitation, reduced leachate volume but higher concentration of contaminants
	Cold Temperatures	Slowed decomposition rates leading to lower BOD and COD in the short term, potential for seasonal variation in leachate composition
Design or Operational Practice	Engineered Liners and Leachate Collection Systems	Minimizes the infiltration of external water, reducing leachate volume and potentially concentrating contaminants
	Daily Covers	Reduces rainwater infiltration, controlling leachate production and influencing its composition by limiting dilution
	Landfill Gas Management Systems	Affects the biochemical degradation processes within the landfill, potentially altering the organic content of the leachate

TABLE 4 Comparative Molecular Characteristics of Young and Mature Landfill Leachates in the example landfills in southwest China (Liu J. et al., 2022).

Property		Young landfill leachate	Mature landfill leachate
Age		New Landfill for temporary stockpile	27 years
COD		74,853 mg/L	3098 mg/L
DOM Species Count		1122	5,075
Main Compounds		Aliphatic Compounds, LOHUPC	HOHUPCs
Bioavailability		Higher	Lower
Nominal Oxidation State of Carbon		−0.8010	−0.0692
Aromaticity (AI_{mod})		0.1254	0.2464
Straight-chain Structures		More	Fewer
Benzene-ring Structures		Fewer	More
Proportion of different DOM classes	Low O HUPC	417.96 (23.75%)	2881.86 (27.86%)
	High O HUPC	0%	3863.53 (37.55%)
	Polyphenols and Polycyclic Aromatics	1%	8%
	Aliphatic Compounds	1320.62 (75.03%)	2767.64 (26.76%)

leachate volume and composition (Khasawneh et al., 2022). Landfill gas management systems, which capture and treat or utilize the methane produced during organic decomposition, can also impact the biochemical processes within the landfill, indirectly affecting leachate composition (Japperi et al., 2021).

In sum, the composition of landfill leachate results from complex interactions between the age of the landfill, the types of waste it contains, prevailing climatic conditions, and the technologies employed in landfill operation. Understanding these factors is crucial for the development of effective leachate

management strategies, as they directly influence the environmental impact of landfills and the technical and economic feasibility of leachate treatment solutions.

2.3 Typical values of pollutants in leachate from different regions

To provide a global perspective, typical values for different classes of contaminants in leachate reported from around the world are described below. These values highlight the variability in leachate composition and typical values for different classes of contaminants in leachate from different regions are critical for designing effective treatment strategies.

Organic pollutants like BOD and COD are critical for assessing the pollution levels. For instance, in tropical regions, average BOD values reported were 2435.16 mg/L in Africa, 3455.77 mg/L in America, and 2127.79 mg/L in Asia, while COD values were 7985.1 mg/L in Africa, 6185.17 mg/L in America, and 7504.32 mg/L in Asia (Lindamulla et al., 2022). In China, BOD_5 concentrations varied from 750 to 25,000 mg/L, with an average of 8,500 mg/L, and COD levels ranged from 2,000 to 62,000 mg/L, averaging 19,250 mg/L (Ma et al., 2022).

Inorganic pollutants like Total Dissolved Solids (TDS) and Ammonium Nitrogen (NH_4^+-N) also show significant variability. Polish landfills reported TDS values from 2,225 mg/L to 7,830 mg/L, while NH_4^+-N concentrations in tropical regions varied widely, with higher concentrations in younger leachates (Wdowczyk and Szymańska-Pulikowska, 2021). China reported NH4+-N levels ranging from 100 to 3,100 mg/L, with a mean of 1,300 mg/L (Ma et al., 2022). Brazil's ammonium nitrogen levels ranged between 0.4 and 1,800 mg/L, reflecting the diversity of landfill conditions and waste compositions across the country (Lindamulla et al., 2022).

Heavy metals, another major pollutant category, had varied concentrations with iron ranging from 0.019 mg/L in inactive Polish landfills to 38.73 mg/L in active ones, and zinc reaching up to 2,560 mg/L in Polish active landfills (Wdowczyk and Szymańska-Pulikowska, 2021). In Thailand, heavy metals like cadmium, chromium, copper, nickel, lead, and zinc were generally below 1 mg/L, though still posing potential ecological and health risks (Ma et al., 2022). This highlights the need for careful monitoring and tailored remediation strategies to address potential environmental and health impacts.

The Leachate Pollution Index (LPI) further highlights the pollution potential of leachate, being higher in open dumps compared to engineered landfills (Lindamulla et al., 2022). Young leachates typically show higher LPI values than older leachates, indicating a higher pollution potential in newer landfills. This global variability in leachate composition underscores the importance of site-specific assessments and tailored treatment approaches for effective leachate management.

3 Regulations and standards

Countries around the world are increasingly recognizing the importance of effective landfill leachate treatment as a critical component of waste management and environmental protection. The significant number of research publications on this topic, particularly from nations with large populations, underscores their commitment to addressing the challenges posed by waste and pollutants. Figure 1 shows the research on "landfill leachate treatment" collected from the Scopus database from 2014 to 2023. The top five countries are China (1,675 articles), India (500 articles), the United States (498 articles), Malaysia (418 articles), and Brazil (302 articles). These all reflect a positive stance in mitigating the impact of rapid industrial and urban development on the environment, and countries have also invested heavily in research to develop efficient landfill leachate treatment technologies, further highlighting the global recognition of the need for advanced and sustainable waste management practices. This joint effort is not only aimed at improving public health and environmental quality, but also at promoting global sustainable development.

3.1 Global regulations on landfill leachate management

International and national regulations governing the disposal and treatment of landfill leachate are crucial for protecting the environment and public health from the potential hazards posed by waste management practices (Daniel et al., 2021). These regulations are designed to set minimum standards for leachate management, ensure the safe handling of this potentially toxic byproduct, and encourage sustainable practices in the waste management industry (Table 5) (Oakes and Shank, 1979; Directive, 2003; Protection, 2003; Obradović et al., 2010; Pollutants, 2011; Gas, 2017; Bergesen et al., 2018; Bhawan and Nagar, 2020; Lin et al., 2022; Santana et al., 2022).

At the international level, the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their disposal is one of the most significant treaties (Ahmed, 2019). It impacts leachate management by restricting the international movement of hazardous wastes, which includes leachate, and encouraging proper disposal (Amos et al., 2024). Another important piece of international legislation is the Stockholm Convention on Persistent Organic Pollutants, which addresses the treatment and disposal of leachate due to its potential to carry organic pollutants that can persist in the environment (Omoto, 2014). The European Union (EU) has established stringent directives for waste management, including the Landfill Directive (1999/31/EC), which sets the standards for waste disposal in landfills, including the collection and treatment of leachate (Schiopu and Gavrilescu, 2010). It specifies that landfills must be designed and operated to collect and treat leachate to prevent groundwater and environmental contamination. Furthermore, the EU's Water Framework Directive (2000/60/EC) also affects leachate management by setting out a framework for the protection of inland surface waters, transitional waters, coastal waters, and groundwater, requiring that leachate be treated to prevent the pollution of water bodies (Kyriakopoulos, 2021).

The Resource Conservation and Recovery Act (RCRA) provides the framework for properly managing solid and hazardous waste in the United States (Hinds, 2022). Under Subtitle of RCRA, the Environmental Protection Agency (EPA) has established regulations that require municipal solid waste landfills to use

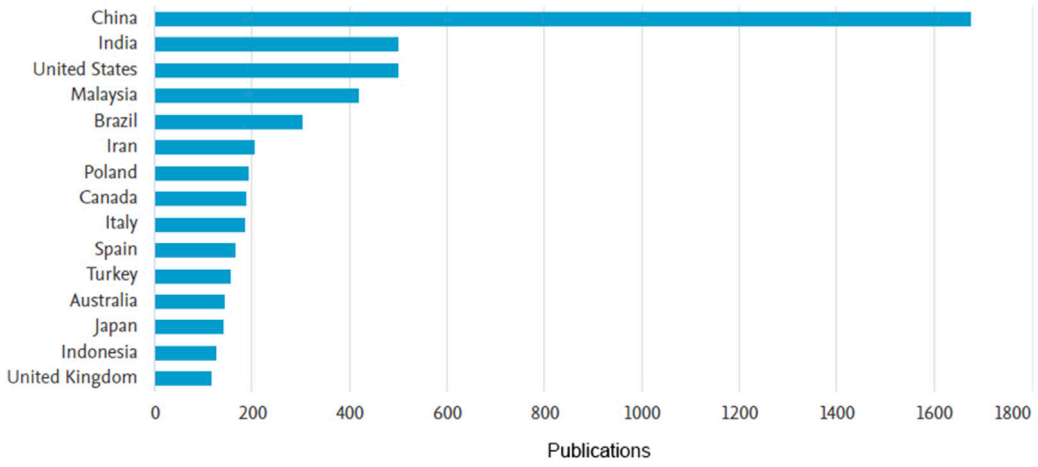


FIGURE 1
Number of publications from the top 15 countries on the topic "Landfill leachate treatment" collected in the Scopus database from 2014 to 2023.

TABLE 5 Global laws and regulations on landfill leachate management (Oakes and Shank, 1979; Directive, 2003; Protection, 2003; Obradović et al., 2010; Pollutants, 2011; Gas, 2017; Bergesen et al., 2018; Bhawan and Nagar, 2020; Lin et al., 2022; Santana et al., 2022).

Country	Regulation/Law	Key provisions
European Union	Landfill Directive (1999/31/EC)	Sets standards for waste disposal in landfills, including leachate treatment to prevent groundwater contamination
United States	Resource Conservation and Recovery Act (RCRA)	Requires municipal solid waste landfills to use liners and leachate collection systems to protect groundwater
China	Standard for Pollution Control on the Landfill Site of Municipal Solid Waste (GB 16889–2008)	Details requirements for leachate collection, treatment, and discharge, including limitations on contaminants
India	Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016	Specifies criteria for handling, treatment, and disposal of hazardous waste, including leachate from landfills
Brazil	National Solid Waste Policy (Política Nacional de Resíduos Sólidos - PNRS, Law No. 12,305/2010)	Emphasizes the treatment and environmentally sound disposal of waste, including leachate management
Canada	Canadian Environmental Protection Act (CEPA)	Provides a framework for the safe management of hazardous waste and substances, including leachate
Australia	National Environment Protection (Assessment of Site Contamination) Measure 1999	Establishes guidelines for the assessment and management of site contamination, including leachate
Germany	Technical Instructions on Municipal Waste (TA Siedlungsabfall)	Specifies technical requirements for waste treatment facilities, including leachate management systems
Japan	Waste Management and Public Cleansing Law	Regulates waste disposal and cleaning operations, ensuring proper leachate control and treatment
South Africa	National Environmental Management: Waste Act, 2008	Lays down waste management measures to protect health and the environment, including leachate standards

composite liners and leachate collection systems to protect groundwater (Bonaparte et al., 2024). The National Pollutant Discharge Elimination System (NPDES), part of the Clean Water Act, regulates the discharge of leachate into surface waters, requiring permits and setting treatment standards (Hudiburgh, 2020). The EPA's treatment standards for hazardous wastes subject to land disposal restrictions include several key parameters that must be monitored under applicable regulations (Agency, 2024). These standards specify regulated hazardous constituents, which are chemicals or compounds that need to be treated to meet specific numerical limits before disposal. For instance, chloroform must be reduced to a concentration of 0.046 mg/L for wastewaters and 6.0 mg/kg for nonwastewaters. Characteristic wastes, such as those exhibiting ignitability, corrosivity, reactivity, or toxicity, require deactivation of these characteristics and treatment of any underlying hazardous constituents (UHCs) to meet universal treatment standards (UTS). Ignitable wastes must be treated by methods such as combustion or deactivation, depending on their total organic carbon content, to remove the ignitability characteristic. Corrosive wastes need deactivation to eliminate corrosivity, with high-level radioactive corrosive wastes requiring vitrification. Reactive wastes are generally treated by deactivation,

with reactive cyanide wastes having specific concentration-based standards, such as 590 mg/kg total cyanide and 30 mg/kg amenable cyanide for nonwastewaters, and 0.86 mg/L amenable cyanide for wastewaters. Toxicity characteristic wastes must be treated to meet numerical standards for metals, pesticides, and organics, as well as the UTS for UHCs. Additionally, alternative treatment standards are available for certain waste types like contaminated soil and debris, allowing for a reduction in hazardous constituent concentration by 90% or to levels not exceeding 10 times the UTS. These parameters ensure that hazardous wastes are adequately treated to minimize their environmental impact before land disposal.

In China, the Environmental Protection Ministry released the "Standard for Pollution Control on the Landfill Site of Municipal Solid Waste" (GB 16889–2008), which sets out leachate collection, treatment, and discharge requirements (Liu Q. et al., 2022). These include specific limitations on contaminants such as BOD, COD, ammonia nitrogen, total phosphorus, and heavy metals in the discharged leachate (Shi et al., 2021). India has enacted the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016, which set forth the criteria for identifying hazardous waste and its handling, treatment, and disposal standards, including leachate from landfills (Sadala et al., 2023). The Central Pollution Control Board (CPCB) of India provides technical guidelines for the secure landfill of hazardous waste, emphasizing the need for a comprehensive leachate management system (Kumar et al., 2007). In Brazil, the National Solid Waste Policy (Política et al. - PNRS) established under Law No. 12,305/2010 requires proper leachate management and emphasizes the treatment and environmentally sound disposal of waste (Galavote et al., 2022).

These examples demonstrate the common goal across different regulatory frameworks: minimizing environmental and health risks associated with leachate from landfills. National regulations often incorporate or build upon international guidelines, tailoring requirements to local conditions and available technologies. However, the effectiveness of these regulations often depends on the robustness of enforcement mechanisms and the commitment of local authorities to uphold standards. The significance of these regulations extends beyond environmental protection. They also have profound economic and social implications. Strict regulatory standards drive innovation in the waste management sector, leading to the development of new treatment technologies and practices that can reduce the volume and toxicity of leachate. Moreover, by requiring the safe disposal of leachate, regulations also prevent the long-term social costs associated with environmental cleanup and healthcare for communities affected by pollution (Fang et al., 2021).

3.2 Regulatory influence on landfill leachate treatment technology selection

Regulatory standards significantly influence the selection of landfill leachate treatment technologies. These regulations protect the environment and public health from the potential hazards posed by untreated or inadequately treated leachate (Tenodi et al., 2020). As such, they set specific benchmarks that leachate must meet before it can be released into the environment or treated further for potential reuse.

The impact of regulatory standards on the choice of treatment technology is multifaceted. Initially, these standards determine the permissible levels of various pollutants, such as organic matter, heavy metals, and nitrogen compounds, that can be present in the treated leachate (Salem et al., 2008). This directly affects the technology selection, as different processes vary in their ability to remove or neutralize specific contaminants (Ahmed et al., 2017). For instance, high BOD and COD levels might necessitate biological treatment processes, such as activated sludge systems (Haydar et al., 2007). At the same time, the presence of heavy metals may require chemical precipitation or ion exchange technologies (Saleh et al., 2022). Furthermore, regulations often specify the methods that must be used for testing and monitoring leachate quality (Brennan et al., 2016). These requirements can influence the choice of technology by necessitating systems that treat leachate effectively and allow for easy sampling and monitoring. Technologies that offer more control and predictability in their operation, such as membrane bioreactors, can become preferred options under stringent monitoring requirements (Galinha et al., 2018). Advanced treatment technologies like reverse osmosis, nanofiltration, and advanced oxidation processes become more prevalent in jurisdictions with strict environmental standards (Valdés et al., 2021). These technologies can achieve the low contaminant levels required for discharge into sensitive environments or for meeting the high-quality standards necessary for leachate reuse in irrigation or industrial processes (Torretta et al., 2017).

Moreover, regulations also impact the economic aspects of technology choice. Compliance with stringent standards often comes with higher operational and maintenance costs (Siddiqi et al., 2022). As a result, regulatory frameworks can indirectly incentivize the development and adoption of more cost-effective and energy-efficient technologies (Pan et al., 2015). For example, the push to meet low nitrogen limits could encourage the adoption of innovative nitrogen removal processes that consume less energy than traditional methods (Nourmohammadi et al., 2013). Regulatory standards also influence the long-term planning and scalability of treatment solutions. Facilities must consider current regulations and potential future tightening of standards (Bunce et al., 2018). This foresight leads to the selection of technologies that are compliant now and adaptable to future regulatory changes, thereby protecting the investment in treatment infrastructure over time. Environmental policies and regulatory standards can also foster the integration of multiple treatment technologies. To meet comprehensive standards that cover a wide range of contaminants, treatment plants may combine physical, chemical, and biological processes in a tiered treatment strategy. Such integration can achieve higher levels of purification than standalone systems.

In addition to these factors, regulations may promote sustainable practices by advocating for treatment technologies that minimize waste generation or allow for resource recovery (Capodaglio, 2017). Techniques that enable the recovery of byproducts, such as biogas production or the retrieval of precious metals, might be preferred in regions where sustainability is a regulatory goal (Chrispim et al., 2021).

In conclusion, the impact of regulatory standards on the choice of landfill leachate treatment technology is profound, driving innovation and influencing every aspect from the design phase to operational strategy. By setting the bar for environmental

TABLE 6 Conventional landfill leachate treatment technologies (Torretta et al., 2017; Dogaris et al., 2020; Ahmed et al., 2021; Younas et al., 2021; Siddiqi et al., 2022).

Treatment	Brief overview	Advantages	Limitations	Applicability	Representative technologies	Typical target pollutants	Removal efficiency
Physical	Involves the separation of substances without a chemical reaction, such as screening, sedimentation, and flotation	— Low energy requirement — Simple operations	— Often requires subsequent treatment — Limited effectiveness for dissolved contaminants	— Preliminary treatment — Suitable for large suspended solids	— Screening — Sedimentation — Flotation	— Suspended solids — Particulate matter — Colloidal particles	— Sedimentation: 50%–70% suspended solids — Filtration techniques: 85%–95% COD, 80%–90% BOD
Chemical	Uses chemical reactions to remove pollutants, including precipitation, oxidation, and ion exchange	— Effective for specific contaminants — Can achieve high levels of purification	— Can produce secondary waste — Chemicals used can be hazardous	— Versatile, can treat a range of leachate types — Used for heavy metals	— Precipitation — Oxidation — Ion Exchange	— Heavy metals — Dissolved organics — Inorganic compounds	— Coagulation-flocculation: 60%–90% suspended solids and 50%–70% COD — Precipitation:80%–95% heavy metals — Oxidation-reduction: 80%–90% color and 70%–85% COD — Fenton's reagent:75%–90% COD and 80%–95% organic pollutants
Biological	Employs microorganisms to degrade organic pollutants, categorized into aerobic and anaerobic processes	— Cost-effective — Environmentally friendly	— Sensitive to toxic compounds — May require long treatment times	— Ideal for organic-rich leachate — Commonly used in municipal wastewater	— Aerobic and Anaerobic Digestion — Membrane Bioreactors	— Organic matter (BOD, COD) — Nitrogen — Phosphorus	— Activated sludge: 70%–90% BOD and 60%–80% COD — Digesters: 80%–90% BOD and 70%–85% COD — Constructed wetlands: 60%–80% BOD, 50%–70% COD, and 40%–60% ammonia

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compliance, regulations ensure that the selected technologies not only mitigate the potential impact of leachate on the environment but also align with the broader goals of sustainability and public health protection.

4 Conventional landfill leachate treatment technologies

Landfill leachate treatment is a crucial component of modern waste management systems, aiming to mitigate the environmental impact of leachate discharge from landfills. As leachate comprises a complex mixture of dissolved and suspended contaminants, its treatment requires a multifaceted approach involving various conventional technologies. These include physical, chemical, and biological methods, each with principles, advantages, limitations, and practical considerations (Table 6) (Torretta et al., 2017; Dogaris et al., 2020; Ahmed et al., 2021; Younas et al., 2021; Siddiqi et al., 2022).

4.1 Physical methods

Physical methods for landfill leachate treatment involve processes that primarily rely on physical separation or filtration mechanisms to remove suspended solids and particulate matter (Renou et al., 2008). These methods typically include sedimentation, filtration, and membrane technologies (Bashir et al., 2016). Sedimentation involves allowing suspended solids to settle out of the leachate under the influence of gravity, facilitating their removal from the liquid phase (Wang et al., 2021). Filtration techniques, such as sand or activated carbon filtration, employ porous media to trap suspended solids and organic compounds as the leachate passes through the filter bed (Loh et al., 2021). Membrane technologies, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, utilize semi-permeable membranes to remove contaminants based on their molecular size and charge selectively (Rai and Shrivastav, 2022). Air stripping is a physical treatment process that removes volatile contaminants, such as VOCs and ammonia, from landfill leachate by passing air through the liquid (De et al., 2019a; 2022). The process relies on Henry's Law to transfer contaminants from the liquid to the gas phase, using packed towers or aeration tanks to maximize contact surface area. Air stripping is effective, simple to operate, and can achieve high removal efficiencies (up to 90% for ammonia). However, it produces off-gas that requires further treatment to prevent air pollution and can be energy-intensive. Despite these challenges, air stripping is an essential part of leachate treatment, often used alongside other technologies to improve overall performance.

In terms of efficiency, sedimentation can remove 50%–70% of suspended solids. Filtration techniques, such as activated carbon filtration, can achieve removal efficiencies of 85%–95% for COD and 80%–90% for BOD (De et al., 2019b; Mojiri et al., 2019). Membrane technologies, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, utilize semi-permeable membranes to selectively remove contaminants based on their molecular size and charge. Microfiltration and ultrafiltration can remove 90%–99% of suspended solids and bacteria, while nanofiltration is effective in removing 70%–90% of divalent ions and 50%–70% of monovalent ions (Peng, 2017). Reverse osmosis offers the highest removal efficiencies, capable of removing 95%–99% of dissolved solids, heavy metals, and organics (Peng, 2017).

The principal advantage of physical treatment methods lies in their ability to achieve high levels of contaminant removal, particularly for suspended solids and larger organic molecules (Saravanan et al., 2021). These methods are often effective in reducing turbidity and removing colloidal particles, thereby improving the treated leachate's visual clarity and overall quality (Zakaria et al., 2023). Additionally, physical treatment processes are generally straightforward to implement and operate, requiring minimal chemical additives and relatively low energy inputs compared to some chemical and biological methods (Nyabadza et al., 2023). However, physical treatment methods also have certain limitations and practical considerations. The potential for membrane fouling or clogging, particularly in membrane-based processes, can reduce treatment efficiency and increase operational costs (Asif and Zhang, 2021). Moreover, physical methods may not effectively remove dissolved contaminants such as heavy metals or organic compounds, which may require additional treatment steps (Saleh et al., 2022). Furthermore, membrane technologies' high capital and operational costs can limit their widespread adoption, particularly in regions with limited financial resources (Othman et al., 2022).

4.2 Chemical methods

Chemical methods for landfill leachate treatment involve the addition of chemical reagents or agents to facilitate the precipitation, coagulation, flocculation, oxidation, or neutralization of contaminants present in the leachate (Aziz et al., 2022). These methods aim to enhance the removal of dissolved metals, organic compounds, and other pollutants through chemical reactions that transform them into insoluble precipitates or aggregates that can be separated from the liquid phase (El-Saadony et al., 2023; Chen et al., 2024). Common chemical treatment processes include coagulation-flocculation, precipitation, oxidation-reduction, and advanced oxidation processes (AOPs) (Sengupta and Pal, 2021).

Coagulation-flocculation involves the addition of coagulants, such as ferric chloride or aluminum sulfate, followed by the addition of flocculants, such as polymers, to promote the aggregation of suspended solids and colloidal particles into larger flocs that can be easily separated from the leachate (Abujazar et al., 2022). Precipitation methods rely on adding chemicals that react with dissolved contaminants to form insoluble precipitates, which can then be removed by sedimentation or filtration (Pohl, 2020). Oxidation-reduction processes, such as ozonation or chlorination, involve adding oxidizing agents to degrade organic pollutants or reduce the concentration of toxic compounds (Wang and Chen, 2020). AOPs utilize powerful oxidants such as hydrogen peroxide or ozone, combined with UV radiation or catalysts, to generate highly reactive hydroxyl radicals that can mineralize organic contaminants into simpler, less harmful compounds (Pandis et al., 2022).

Regarding removal efficiency, coagulation-flocculation can remove 60%–90% of suspended solids and 50%–70% of COD (Teh et al., 2016). Precipitation is highly effective in removing

heavy metals, achieving removal efficiencies of 80%–95% for metals such as lead, cadmium, and chromium (Fu and Wang, 2011). Oxidation-reduction processes like ozonation can remove 80%–90% of color and 70%–85% of COD (Miklos et al., 2018). Advanced oxidation processes, such as the use of Fenton's reagent, can remove 75%–90% of COD and 80%–95% of organic pollutants (Babuponnusami and Muthukumar, 2014).

The primary advantage of chemical treatment methods lies in their versatility and effectiveness in targeting a wide range of contaminants present in leachate (Pisharody et al., 2022). Chemical processes can achieve high removal efficiencies for dissolved metals, organic compounds, and recalcitrant pollutants that may not be effectively treated by physical or biological methods alone (Nidheesh et al., 2022). Additionally, chemical treatment processes can often be tailored to specific leachate compositions and treatment objectives by adjusting the type and dosage of chemical additives used (Khoo et al., 2020). One of the common disadvantages of chemical treatment methods, particularly coagulation-flocculation and precipitation, is the generation of sludge. This sludge, a byproduct of the treatment process, consists of the aggregated contaminants and excess chemical reagents, posing a significant disposal challenge (Sharma et al., 2022). Using chemical reagents can also increase operational costs and pose health and safety risks to operators if improperly handled. The management of this sludge is crucial as it requires appropriate handling, treatment, and disposal to avoid secondary pollution. Chemical sludge typically needs to be dewatered and may require further stabilization or treatment before disposal in landfills or use in other applications. The disposal costs and environmental impacts associated with sludge management must be considered when evaluating the overall feasibility and sustainability of chemical treatment methods (Hou et al., 2023).

4.3 Biological methods

Biological methods for landfill leachate treatment harness the metabolic activity of microorganisms to degrade organic pollutants and remove nutrients from the leachate (Wu D. et al., 2015). These methods typically involve aerobic treatment, anaerobic treatment, and constructed wetlands, which utilize different microbial communities and environmental conditions to facilitate the leachate's biodegradation and transformation of contaminants (Kurniawan et al., 2010). Aerobic treatment involves exposing the leachate to oxygen-rich conditions, allowing aerobic bacteria to metabolize organic compounds and oxidize them into simpler, less harmful substances (Bhambore and Suresh Kumar, 2022). On the other hand, anaerobic treatment processes operate under oxygen-free conditions and rely on anaerobic bacteria to degrade organic matter through fermentation and methanogenesis, producing methane gas as a byproduct (Zamri et al., 2021). Constructed wetlands are engineered systems that mimic natural wetland ecosystems and utilize wetland vegetation, soil, and microbial communities to remove contaminants from the leachate through physical, chemical, and biological processes (Hassan et al., 2021). These systems provide an ideal habitat for the growth of wetland plants and microorganisms, which can absorb, adsorb, and metabolize pollutants in the leachate, improving its quality (Bakhshoodeh et al., 2020). Additionally, constructed wetlands can enhance nutrient removal and promote groundwater recharge by facilitating water infiltration and retention in the soil (Chand et al., 2022).

When it comes to biological methods for landfill leachate treatment, aerobic treatment processes, such as activated sludge, can remove 70%–90% of BOD and 60%–80% of COD (Peng, 2017). Anaerobic treatment using digesters can achieve removal efficiencies of 80%–90% of BOD and 70%–85% of COD, with the added benefit of producing biogas as a byproduct (Mukherjee et al., 2015). Constructed wetlands offer another effective solution, capable of removing 60%–80% of BOD, 50%–70% of COD, and 40%–60% of ammonia (Wu S. et al., 2015).

Here we need to mention a mature biological treatment technology that has been widely used in the field of wastewater treatment for many years, biological nutrient removal (BNR). BNR harnesses the metabolism of microorganisms to remove nutrients, notably nitrogen and phosphorus, from wastewater (Deng et al., 2023). BNR is crucial for preventing eutrophication in aquatic environments caused by nutrient overloads (Kabuba et al., 2022). BNR operates through various biological mechanisms, including nitrification, denitrification, and phosphorus uptake by specific bacteria, under different operational conditions to remove these nutrients (Rout et al., 2021a). Factors influencing the efficiency of BNR include biomass concentration, hydraulic retention time, temperature, and pH, which need to be optimized to enhance microorganism activity and nutrient removal (Mishra et al., 2022). The complexity of BNR systems, which can include multiple tanks and stages for different phases of nutrient removal, requires careful design and operation to achieve the desired outcomes (Al-Hazmi et al., 2022). BNR offers a cost-effective and environmentally friendly approach to nutrient removal, avoiding using chemicals and leveraging natural biological processes (Al-Hazmi et al., 2024). This technology requires for a large footprint due to the extensive infrastructure needed and the complexity of operation and maintenance, which demands skilled personnel and continuous monitoring (Abyar and Nowrouzi, 2023).

Biological treatment methods can achieve sustainable and cost-effective leachate treatment through natural processes (Chand et al., 2022). Biological processes are highly efficient in removing organic pollutants and nutrients from the leachate, often achieving high removal efficiencies under favorable environmental conditions (Li et al., 2021). Moreover, biological treatment methods are generally environmentally friendly and produce minimal secondary waste or harmful byproducts compared to chemical or physical methods (Sathya et al., 2023). Nevertheless, compared with chemical or physical methods, the required processing time is longer because the microbial degradation process can be relatively slow, especially under certain environmental conditions (Sharma, 2020). Additionally, biological treatment systems may be sensitive to fluctuations in temperature, pH, and other environmental parameters, which can affect treatment performance and reliability (Sundui et al., 2021). Moreover, toxic or inhibitory substances in the leachate, such as heavy metals or recalcitrant organic compounds, may limit the effectiveness of biological treatment processes and require additional pre-treatment or post-treatment steps to achieve desired treatment objectives (Ilmasari et al., 2022).

TABLE 7 Membrane technology in landfill leachate treatment (de Almeida et al., 2020; Magalhães et al., 2020; Yusuf et al., 2020; El Batouti et al., 2022).

Process	Introduction	Mechanism	Target pollutants	Removal efficiency	Factors affecting removal efficiency	Advantages	Limitations
RO	RO is a high-efficiency filtration process that removes contaminants by applying pressure to push water through a semi-permeable membrane	Solution/ diffusion; Size exclusion	Dissolved salts, metals, organics, and some microorganisms	Remove exceeding 99% for various contaminants	Membrane fouling level, feed water quality, operating pressure	High removal efficiencies for a wide range of contaminants; Produces high-quality effluent	High energy consumption; Generates concentrated waste stream
NF	NF is a selective filtration technology that removes specific ions and small molecules from water	Size exclusion; Electrostatic exclusion	Hardness ions (e.g., Ca, Mg), heavy metals, certain organic compounds	Up to 99.62% removal of PFAS.	Membrane fouling level, feed composition, operating pressure	Lower pressure and energy requirements than RO; Can selectively remove contaminants	Less effective for monovalent ions; Still produces a waste concentrate
UF	UF uses a semi-permeable membrane to remove suspended solids, bacteria, viruses, and large molecules	Size exclusion	Suspended solids, bacteria, viruses, macromolecules	Remove 90%–99% of suspended solids and bacteria	Membrane fouling level, pore size of the membrane, feed water turbidity	Low energy requirement; Effective pre-treatment for RO/ NF; High removal of particulates and microorganisms	Limited in removing dissolved ions and small molecules
MBR	MBR combines biological treatment with membrane filtration to degrade organic pollutants and remove solids	Biological degradation; Size exclusion	Organic pollutants, nutrients (N, P), suspended solids	High removal rates for BOD (85%–95%) and COD (70%–85%)	Biomass concentration, membrane fouling level, hydraulic retention time	High-quality effluent; Compact design; High organic and nutrient removal efficiency	Higher operational and maintenance costs due to fouling; Energy-intensive

In conclusion, conventional landfill leachate treatment technologies encompass diverse physical, chemical, and biological methods, each offering unique advantages, limitations, and practical considerations. Physical methods rely on separation or filtration mechanisms to remove suspended solids and colloidal particles from the leachate. In contrast, chemical methods involve the addition of chemical reagents to facilitate the precipitation, coagulation, or oxidation of contaminants. Biological methods harness the metabolic activity of microorganisms to degrade organic pollutants and remove nutrients from the leachate through natural processes. While each treatment method has its strengths and weaknesses, selecting an appropriate treatment technology depends on factors such as leachate composition, treatment objectives, regulatory requirements, and site-specific considerations. By understanding each treatment method's principles, advantages, limitations, and practicality, stakeholders can make informed decisions to design and implement effective leachate treatment systems that meet environmental standards and protect human health and the environment.

5 Advanced landfill leachate treatment technologies

5.1 Common technology

5.1.1 Membrane technology

Membrane technology has emerged as a pivotal solution in treating landfill leachate (Chen et al., 2021). This technology offers a versatile and efficient approach to removing contaminants, including dissolved salts, heavy metals, organic compounds, and particulates (El Batouti et al., 2021). The application of membrane technology in leachate treatment primarily involves reverse osmosis, nanofiltration, ultrafiltration, and membrane bioreactors, each serving unique roles in the purification process (Table 7) (de Almeida et al., 2020; Magalhães et al., 2020; Yusuf et al., 2020; El Batouti et al., 2022).

5.1.2 Reverse osmosis (RO)

Reverse osmosis is a cornerstone of membrane technology for leachate treatment, renowned for its ability to remove a wide array of contaminants, including dissolved salts and organic molecules (Feria-Díaz et al., 2021). The principle of RO involves applying pressure to the leachate across a semi-permeable membrane, which allows water molecules to pass while retaining the majority of dissolved solids (Mengesha and Sahu, 2022). This process is particularly effective in reducing leachate conductivity, making it a critical step in compliance with stringent discharge regulations (Keyikoglu et al., 2021). RO systems can achieve removal efficiencies exceeding 99% for various contaminants, rendering them indispensable in scenarios requiring high-quality effluent (Srivastava et al., 2022). However, the performance of RO systems is significantly influenced by factors such as membrane fouling, feed water quality, and operating pressure (Odabaşı et al., 2022). Membrane fouling, caused by the accumulation of particles and microorganisms on the membrane surface, can lead to decreased efficiency and increased operational costs (Sengar and Vijayanandan, 2022). To mitigate these effects, pre-treatment processes and regular maintenance are crucial. Additionally, generates a concentrated brine that requires further management

or treatment, presenting an environmental and operational challenge (Sengar and Vijayanandan, 2022). RO is particularly suitable for final polishing of treated leachate to meet discharge standards.

5.1.3 Nanofiltration (NF)

Nanofiltration occupies a niche between reverse osmosis and ultrafiltration, with a pore size that allows it to selectively remove divalent and multivalent ions, some monovalent ions, and organic molecules (Zhao et al., 2021). NF is particularly valued for its ability to soften water by removing hardness ions, such as calcium and magnesium, alongside a significant reduction in organic content and color (Patel et al., 2023). NF's selectivity allows it to target pollutants with lower pressure and energy requirements than RO, making it a cost-effective option for many treatment scenarios (Yadav et al., 2022). The process is well-suited for pre-treatment in RO systems or as a standalone treatment for leachates with moderate contamination levels (Ali, 2021). Like RO, NF also produces concentrate streams that require careful disposal or further treatment (Song et al., 2020). The efficiency of NF is contingent upon membrane fouling, feed composition, and operating pressure (Yang et al., 2024). Similar to RO, the presence of pre-treatment processes is vital to prevent fouling and ensure consistent performance. While NF offers the advantage of selective contaminant removal with reduced energy consumption, its limitations include less effectiveness for monovalent ions and the production of a waste concentrate that requires further treatment (Tian et al., 2021).

5.1.4 Ultrafiltration (UF)

Ultrafiltration is a membrane filtration process employing larger pore sizes than NF and RO, making it ideal for removing suspended solids, bacteria, viruses, and high molecular weight solutes (Urošević and Trivunac, 2020). Factors like membrane fouling, pore size, and feed water turbidity can impact UF's removal efficiency (Peters et al., 2021). Nonetheless, UF systems require lower energy to operate and serve as an excellent pre-treatment step for RO and NF processes by reducing the load of suspended solids and microbial content, thereby extending the lifespan of downstream membranes (El Batouti et al., 2022). UF is often used as a pre-treatment step to protect downstream RO or NF systems from fouling. It can typically remove 90%–99% of suspended solids and bacteria. The primary advantage of UF lies in its ability to operate at lower pressures, thereby reducing energy costs (Fan et al., 2020). It is also less susceptible to chemical damage, allowing for a broader range of chemical cleaning agents. Although UF is highly effective in removing particulates and microorganisms, its limitations lie in its inability to address dissolved ions and small molecules, underscoring the need for a comprehensive treatment approach that may include subsequent NF or RO stages (Castro-Muñoz, 2020).

5.1.5 Membrane bioreactors (MBR)

The membrane bioreactor technology integrates biological treatment processes with membrane filtration, offering a compact and efficient solution for degrading organic pollutants and removing solids (Neoh et al., 2016). In an MBR system, a bioreactor degrades organic pollutants through microbial activity, while a membrane filtration unit separates treated water from biomass and suspended solids (Deng et al., 2022). MBRs can achieve high levels of organic and nutrient removal, with the added benefit of producing a clarified, disinfected effluent (Hai et al., 2014). Integrating biological treatment and membrane separation enhances system stability and reduces the footprint compared to conventional treatment setups (Waqas et al., 2020). MBRs are suitable for leachate with high organic loads and in locations where space is limited. They can achieve high removal rates for BOD (85%–95%) and COD (70%–85%), along with effective solids separation. The performance of MBRs is influenced by factors such as biomass concentration, membrane fouling, and hydraulic retention time. Despite the challenges of operational and maintenance costs associated with fouling and energy consumption, MBRs provide significant advantages, including high-quality effluent, compact design, and efficient removal of organic matter and nutrients (Meng et al., 2007).

5.2 Advanced oxidation processes

The treatment of landfill leachate using AOPs has garnered significant attention due to the complexity and variability of leachate composition (Fang et al., 2021). AOPs are characterized by their ability to generate highly reactive species, particularly hydroxyl radicals, which can non-selectively degrade a wide range of pollutants (Anandan et al., 2020). Usually there are four primary AOPs: the Fenton process, ozonation, photocatalysis, and electrochemical oxidation (Table 8) (Rekhate and Srivastava, 2020; Wang and Zhuan, 2020; Pandis et al., 2022).

5.2.1 Fenton process

The Fenton process is a chemical treatment method that involves the reaction of hydrogen peroxide (H_2O_2) with ferrous iron (Fe^{2+}) to produce hydroxyl radicals (·OH·) (Benassi et al., 2021). These radicals are extremely reactive and can break down various organic pollutants, including dyes, pharmaceuticals, and other complex organic compounds in landfill leachate (Ateş and Argun, 2021). The mechanism of action in the Fenton process is homogeneous catalysis, where the reaction occurs in solution, allowing for the widespread generation of hydroxyl radicals (Liu et al., 2021). This process is particularly effective for treating organic-rich leachate, offering several advantages, such as high efficiency in degrading organic pollutants and operating under ambient conditions (Soltani et al., 2022). The Fenton process is effective for treating leachate with high concentrations of refractory organic compounds. It can remove 75%–90% of COD and 80%–95% of organic pollutants. However, the process is highly sensitive to operational conditions such as pH, temperature, and the ratios of Fe to H_2O_2 and reaction time (O'Dowd and Pillai, 2020). A major limitation of the Fenton process is sludge production from iron salts, necessitating further treatment steps (Ziembowicz and Kida, 2022). Additionally, precise control over the reaction conditions is crucial to prevent the consumption of hydrogen peroxide by excessive iron, which would otherwise reduce the efficiency of pollutant degradation (Liu et al., 2024).

TABLE 8 AOPs in landfill leachate treatment (Rekhate and Srivastava, 2020; Wang and Zhuan, 2020; Pandis et al., 2022).

Process	Introduction	Mechanism of action	Target pollutants	Removal efficiency	Factors affecting removal efficiency	Advantages	Limitations
Fenton Process	A chemical process using hydrogen peroxide (H_2O_2) and iron (Fe) catalysts to produce hydroxyl radicals for the oxidation of pollutants	Homogeneous catalysis	Organic pollutants, dyes, pharmaceuticals	Remove 35%–90% of COD and 80%–95% of organic pollutants	pH, temperature, Fe and H_2O_2 ratio, reaction time	Highly efficient in degrading organic pollutants; Can operate at ambient conditions	Production of sludge; Requires post-treatment to remove iron; Sensitive to operational conditions
Ozonation	The application of ozone (O_3), a strong oxidizing agent, to break down organic and inorganic materials	Direct oxidation	Color, odor, microorganisms, some organic compounds	Remove 80%–90% of color and 70%–85% COD.	Ozone dosage, contact time, water quality	Effective for color and odor removal; Can disinfect; No sludge production	High energy consumption for ozone generation; May form by-products
Photocatalysis	Uses light to activate a catalyst (typically TiO_2), generating reactive species that degrade contaminants	Heterogeneous catalysis	Organic pollutants, bacteria, viruses	achieved up to 86.14% removal of endosulfan, 96.2% of methylene blue, 97.3% of rhodamine B, and 84.67% of crystal violet dye	Light intensity, catalyst type and concentration, pH	Can be powered by solar energy; Low energy cost; No sludge	Catalyst recovery and reuse; May require UV light
Electrochemical Oxidation	An electrochemical reaction where pollutants are oxidized at the anode surface or in the bulk solution	Direct and indirect oxidation	Dyes, pharmaceuticals, complex organic molecules	Remove 75%–95% of COD and up to 90% of ammonia	Electrode material, current density, conductivity, pH	No chemical addition needed; Precise control over process	High energy consumption; Electrode degradation; Sludge generation; Management

5.2.2 Ozonation

Ozonation employs ozone (O_3), a potent oxidizing agent, to oxidize pollutants directly (Tripathi and Hussain, 2022). This process is highly effective for removing color, odor, and microorganisms from landfill leachate and degrading some organic compounds (Yang C. et al., 2021). The direct oxidation mechanism of ozonation allows for rapid reaction rates, making it a valuable option for enhancing the biodegradability of recalcitrant organic compounds in leachate (Yang Y. et al., 2021). Ozonation can remove 80%–90% of color and 70%–85% of COD. The efficiency of ozonation is influenced by ozone dosage, contact time, and the quality of water being treated. Its advantages include effective color and odor removal, disinfection capabilities, and the absence of sludge production (Hussain et al., 2022). However, ozonation requires significant energy to generate ozone gas, and the potential formation of by-products during the oxidation of certain pollutants can be a concern (Wang and Chen, 2020). Despite these limitations, ozonation remains a favored choice for specific applications within leachate treatment, particularly when targeting pollutants susceptible to oxidation by ozone.

5.2.3 Photocatalysis

Photocatalysis involves using light (typically UV) and a catalyst (commonly titanium dioxide, TiO_2) to produce reactive species capable of degrading pollutants (Gopinath et al., 2020). This process is governed by heterogeneous catalysis, where the catalyst remains in a solid phase, distinct from the liquid phase in which the pollutants are dissolved (Iervolino et al., 2020). Photocatalysis is effective against many contaminants, including organic pollutants, bacteria, and viruses, making it an attractive option for treating landfill leachate (Han et al., 2020). Factors affecting the efficiency of photocatalysis include light intensity, catalyst type and concentration, and the pH of the solution (Gusain et al., 2020). Photocatalysis offers the potential for low energy costs, especially when powered by solar energy, and the absence of sludge production (Ahmad et al., 2020). Catalyst recovery and reuse and dependence on UV light for optimal performance limit its widespread application (Kefeni and Mamba, 2020). Despite these challenges, photocatalysis presents a sustainable option for leachate treatment, especially in sunny climates where solar radiation can be effectively harnessed.

5.2.4 Electrochemical oxidation

Electrochemical oxidation utilizes an electrical current to facilitate the oxidation of pollutants at an electrode surface or within the bulk solution (Fitch et al., 2022). Through direct and indirect oxidation mechanisms, this method can target a broad spectrum of pollutants, including dyes, pharmaceuticals, and complex organic molecules (da Silva et al., 2021). This process is effective for treating leachate with a high load of organic pollutants and ammonia. Electrochemical oxidation can remove 75%–95% of COD and up to 90% of ammonia. One of the primary advantages of electrochemical oxidation is the absence of chemical additives coupled with precise control over the treatment process (Yang L. et al., 2021). This method offers an environmentally friendly approach to leachate treatment, albeit with considerations for

TABLE 9 Emerging technologies in landfill leachate treatment (Bhambri and Karn, 2020; Deng et al., 2020; Hasan et al., 2021; Rajesh Banu et al., 2021).

Technology	Introduction	Mechanism of action	Target pollutants	Removal efficiency	Factors affecting removal efficiency	Advantages	Limitations
Adsorption	A process where pollutants are captured on the surface of a material	Surface adsorption; Physical and chemical adsorption	Organic compounds, metals, dyes	Achieve up to 99% removal of emerging contaminants and 95.1% for strontium	Adsorbent material, contact time, concentration of pollutants, temperature	Low cost; Simplicity of design; No harmful by-products	Limited capacity; Requires regeneration or disposal of adsorbents
Ion Exchange	Involves the exchange of ions between a solid phase and a liquid phase to remove dissolved ions	Electrostatic exclusion	Heavy metals, hardness, radionuclides	Remove nutrients up to 98% for ammonium, 91.38% for arsenic, and over 99% colorants	Ion exchange capacity, flow rate, water chemistry	High specificity; Efficient for targeted contaminants	Regeneration of resins needed; Sensitive to competing ions
Simultaneous Partial Nitrification, Anammox, and Denitrification	An innovative biological process integrating partial nitrification, anammox, and denitrification to treat high-strength nitrogenous leachate efficiently	Partial Nitrification, Anammox, and Denitrification	Ammonia (NH^{4+}) Nitrite (NO^{2-}) Nitrate (NO^{3-})	SNAD achieves nitrogen removal efficiencies of 80%–94.56% for total inorganic nitrogen and over 90% for total nitrogen	Dissolved Oxygen Levels, Temperature, pH, Organic Carbon Availability, ammonia and Nitrite Concentrations	Cost-effective; High Efficiency; Low Sludge Production; Sustainable	Complex Control; Environmental Sensitivity; Startup Time; Monitoring Needs

high energy consumption and potential electrode degradation over time (Deng et al., 2020).

5.3 Other technologies

As environmental standards become increasingly stringent, adopting innovative and efficient treatment technologies is essential. Emerging technologies for treating landfill leachate are pivotal in addressing the environmental challenges posed by the complex and variable composition. These technologies, including adsorption, ion exchange, and biological nutrient removal (BNR), offer innovative solutions to remove many pollutants, from organic compounds and heavy metals to nitrogen and phosphorus (Table 9) (Bhambri and Karn, 2020; Deng et al., 2020; Hasan et al., 2021; Rajesh Banu et al., 2021).

5.3.1 Adsorption

Adsorption is a versatile and widely implemented method for contaminant removal, characterized by the adherence of pollutants onto the surface of an adsorbent material (Shen et al., 2023). This process can occur through physical adsorption, driven by weak van der Waals forces, or chemical adsorption, involving stronger covalent bonds (Rathi and Kumar, 2021). The mechanism is influenced by the surface area, porosity, and chemical nature of the adsorbent, as well as the properties of the pollutants (Ambaye et al., 2021). Adsorption is particularly effective for removing organic compounds, heavy metals, and dyes from leachate, making it a valuable tool for improving water quality (Saravanan et al., 2021). The adsorption efficiency is determined by factors such as the type and concentration of pollutants, contact time, adsorbent material, and environmental conditions like temperature (Rathi and Kumar, 2021). Activated carbon is among the most commonly used adsorbents due to its high surface area and porosity, although other materials like biochar, zeolites, and engineered nanomaterials are also employed (Sharma et al., 2022). The primary advantages of adsorption include its simplicity, cost-effectiveness, and the absence of harmful by-products. The finite adsorption capacity of materials, which necessitates their periodic regeneration or replacement (Sharma et al., 2024). Similar to coagulation-flocculation, the adsorption method also generates sludge, which consists of spent adsorbent materials saturated with contaminants (Kurniawan et al., 2021a). The management of this adsorption sludge is a critical issue, as it involves the disposal or regeneration of spent adsorbents. Regeneration can often be achieved through thermal, chemical, or biological methods to restore the adsorbent's capacity for reuse. However, these processes can be energy-intensive and costly, and not all adsorbents can be regenerated effectively. Disposal of non-regenerable adsorbents must be conducted in an environmentally safe manner, often requiring landfilling or incineration, which introduces additional costs and environmental concerns. The environmental impact and cost of managing adsorption sludge are important factors in assessing the overall sustainability of the adsorption process.

5.3.2 Ion exchange

Ion exchange is a specialized technique designed for removing dissolved ions from wastewater, functioning through the reversible exchange of ions between a liquid and a solid phase (Liu et al., 2023). Ion exchange relies on electrostatic interactions between charged particles, making it particularly suitable for targeting specific ionic contaminants such as heavy metals, hardness-causing ions (e.g., calcium and magnesium), and radionuclides (Liu et al., 2023). The performance of ion exchange systems is influenced by the resin or medium's ion exchange capacity, the leachate's flow rate, and the water's chemical composition, including the presence of competing

ions (Xu et al., 2024). Factors such as resin specificity, regeneration requirements, and operational parameters must be carefully managed to optimize performance (Clark et al., 2024). Ion exchange resins, synthetic or natural, are chosen based on their selectivity for certain ions, offering high specificity and efficiency in contaminant removal (Wang et al., 2024). Ion exchange offers the advantage of high specificity and efficiency for targeted contaminants, providing a tailored approach to leachate treatment (Aziz et al., 2023). The need for regular resin regeneration with chemicals like brine, which can generate secondary waste streams (Sahu, 2021). It is sensitive to competing ions, which can reduce the efficiency of targeted ion removal, requiring careful water chemistry management (Chen et al., 2023).

5.3.3 Simultaneous partial nitrification, anammox, and denitrification (SNAD)

SNAD is an emerging biological treatment technology that integrates partial nitritation, anaerobic ammonium oxidation (anammox), and denitrification processes within a single reactor (Singh et al., 2022). This integrated approach shows great potential for treating landfill leachate with high ammonia concentrations. The SNAD process involves three main steps: partial nitritation, which converts part of the ammonia into nitrite; anammox, which utilizes the remaining ammonia and the produced nitrite to generate nitrogen gas; and denitrification, which reduces any remaining nitrate to nitrogen gas. These processes occur simultaneously in the same reactor, achieving efficient nitrogen removal. SNAD achieves nitrogen removal efficiencies of 80%–94.56% for total inorganic nitrogen and over 90% for total nitrogen, while also reducing oxygen demand and sludge production compared to conventional methods (Zheng et al., 2016). SNAD technology offers several advantages for landfill leachate treatment, including high nitrogen removal efficiency, energy savings due to lower oxygen and organic carbon requirements compared to traditional nitrification-denitrification processes, reduced operational costs, smaller footprint due to the integration of three processes in one reactor, and less sludge production, which lowers sludge handling costs (Su et al., 2022). Despite its promising prospects, SNAD technology faces challenges such as the need for precise control of parameters like dissolved oxygen and pH, long startup times due to the slow growth of anammox bacteria, and sensitivity to temperature. Future research will focus on optimizing operational parameters, enhancing system stability, and exploring innovative reactor designs to further improve the application of SNAD technology in landfill leachate treatment.

In summary, when selecting an appropriate landfill leachate treatment technology, it is essential to consider the balance between efficiency, cost, and sustainability (Özdemir et al., 2020; Cherni et al., 2021; Dereli et al., 2021; Saadatlu et al., 2023). Membrane technologies are highly effective, capable of removing up to 99% of dissolved salts and other specific pollutants. However, their application involves significant capital and operational costs, particularly with RO, due to the expenses associated with energy use, membrane replacement, and maintenance. Despite these costs, advancements in technology are gradually improving the sustainability of membrane processes, although energy use and membrane disposal remain concerns. AOPs offer another robust solution, particularly for degrading resistant organic compounds and pathogens. Nevertheless, they come with high operational costs, mainly due to the chemical inputs and energy demands, such as for ozone generation or UV lamps. These factors also contribute to moderate sustainability concerns, especially regarding potential secondary pollution. Emerging technologies provide a more cost-effective and sustainable approach. While their efficiency varies depending on the materials and infrastructure used, they excel in targeting specific contaminants like heavy metals and nutrients. These technologies emphasize the use of recyclable materials and natural processes, thereby enhancing environmental friendliness. The choice of leachate treatment technology should be guided by specific treatment goals, regulatory requirements, and sustainability objectives, balancing efficiency with environmental and economic considerations to achieve effective and responsible leachate management.

6 Comprehensive treatment system

The cornerstone of addressing the leachate challenge lies in implementing a comprehensive treatment system that synergistically combines various treatment methodologies to remove contaminants effectively and meet or exceed regulatory discharge standards (Abdelfattah and El-Shamy, 2024). These systems are designed not only to mitigate the adverse environmental impacts of leachate but also to contribute to the sustainability of landfill operations by enabling the possibility of resource recovery and reuse of treated water (Mojiri et al., 2020).

6.1 Comprehensive treatment system

A comprehensive landfill leachate treatment system is a multi-faceted and dynamic approach that mitigates leachate contaminants' environmental impacts through a well-orchestrated sequence of processes (Figure 2) (Britz, 2020; Babaei et al., 2021; Fang et al., 2021; Righetto et al., 2021; Teng et al., 2021; Nath and Debnath, 2022). Initiating with pretreatment, the system begins by addressing the more tangible aspects of leachate—easily separable solids are removed, and the pH is carefully adjusted. This foundational step is about preparing the leachate for the complex journey ahead and safeguarding the intricate mechanisms of downstream processes from potential abrasion, blockages, and harmful chemical interactions. As the leachate advances, it encounters the primary treatment phase, a sophisticated interplay between biology and chemistry. Here, living microbes engage in a digestive ballet, utilizing both aerobic and anaerobic pathways to metabolize organic pollutants, thereby reducing the load of substances that demand oxygen in the water. Concurrently, a suite of physical-chemical treatments, each a targeted strike—coagulation, flocculation, and flotation—work in concert to clear out suspended solids, strip away color, and separate particulate organic matter. This systematic approach continues into the secondary treatment, where a more refined attack is launched on dissolved organic compounds that have eluded the grasp of biological processes. This stage employs the precision of AOPs, the fine sieve of membrane filtration technologies like reverse

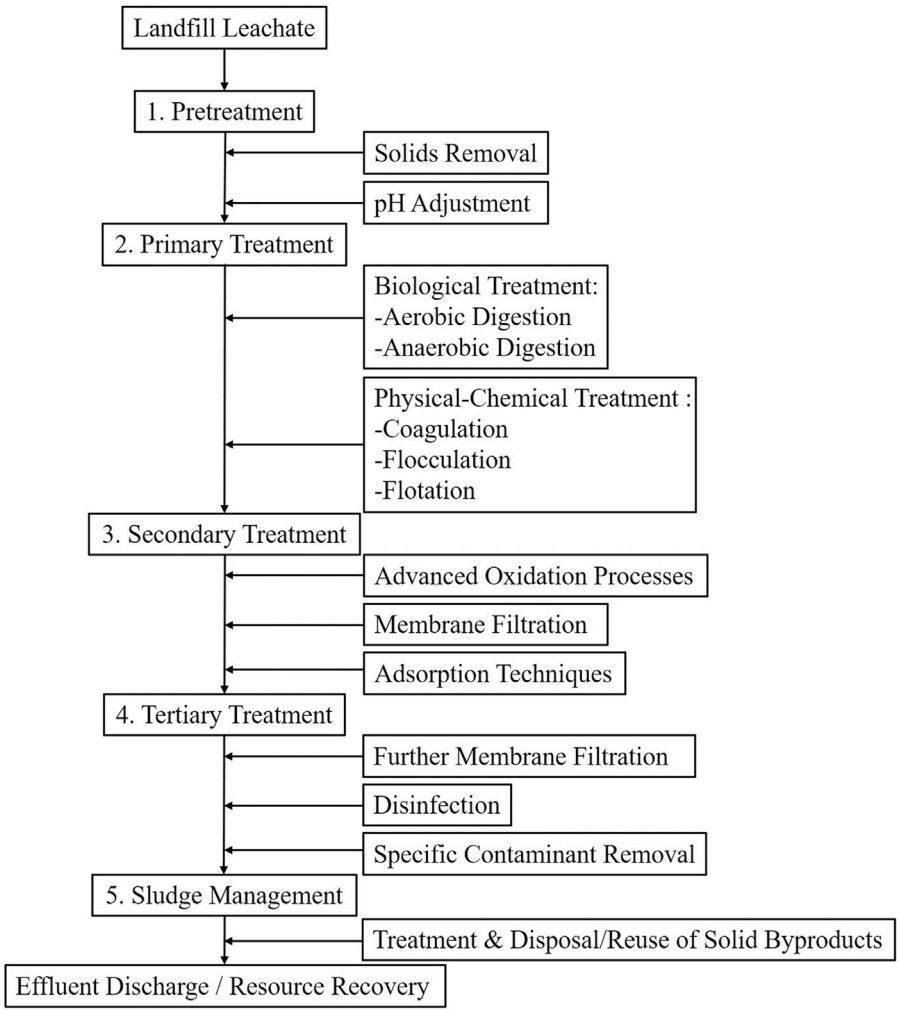


FIGURE 2
Components of a comprehensive treatment system.

osmosis, and the binding affinities of adsorption techniques, each method meticulously selected to ensure no contaminant is left unchallenged. Nearing the end, the leachate undergoes tertiary treatment—an exemplary display of purification, where the effluent is polished to meet stringent quality standards. Further, membrane filtration stands sentinel against the minutest of pollutants, disinfection processes wage war on pathogenic microorganisms, and additional specific treatments meticulously remove any lingering traces of heavy metals or nitrogen compounds.

The comprehensive landfill leachate treatment system's responsibility does not end with the effluent; sludge management remains a testament to the ethos of sustainability that underpins the entire operation (Torretta et al., 2017). This critical phase manages the solid byproducts of the leachate's treatment to minimize further environmental impact, reclaim valuable resources, and embody the cyclic nature of waste transformed into worth (Remmas et al., 2023). Implementing a comprehensive landfill leachate treatment system is a paragon of environmental responsibility and technological ingenuity, offering multifarious benefits that resonate far beyond the confines of waste management. Such systems are critical in preventing the percolation of hazardous contaminants into the groundwater and surface waters, safeguarding the aquatic ecosystems and public health against the potential onslaught of toxic substances (Ravindiran et al., 2023). By utilizing progressively targeted treatments that include biological degradation, chemical transformation, and physical separation, these systems adeptly reduce the concentrations of organic and inorganic pollutants, heavy metals, and pathogens to meet stringent regulatory standards (Rathod et al., 2024). Beyond the immediate environmental benefits, these systems embrace the principles of a circular economy, often allowing for the recovery of resources such as biogas, which can be converted to energy, and treated water, which can be repurposed for industrial or agricultural use (Zarei, 2020). This contributes to the conservation of natural resources and offers economic advantages by offsetting operational costs and generating revenue (Ekins and Zenghelis, 2021). Comprehensive treatment systems are committed to sustainable development as they adapt to the ever-changing waste composition and emerging contaminants, ensuring resilience against future environmental challenges. Thus, these systems' significance lies in their immediate efficacy in pollution control and their strategic contribution to long-term environmental sustainability and economic viability (Mojiri et al., 2020).

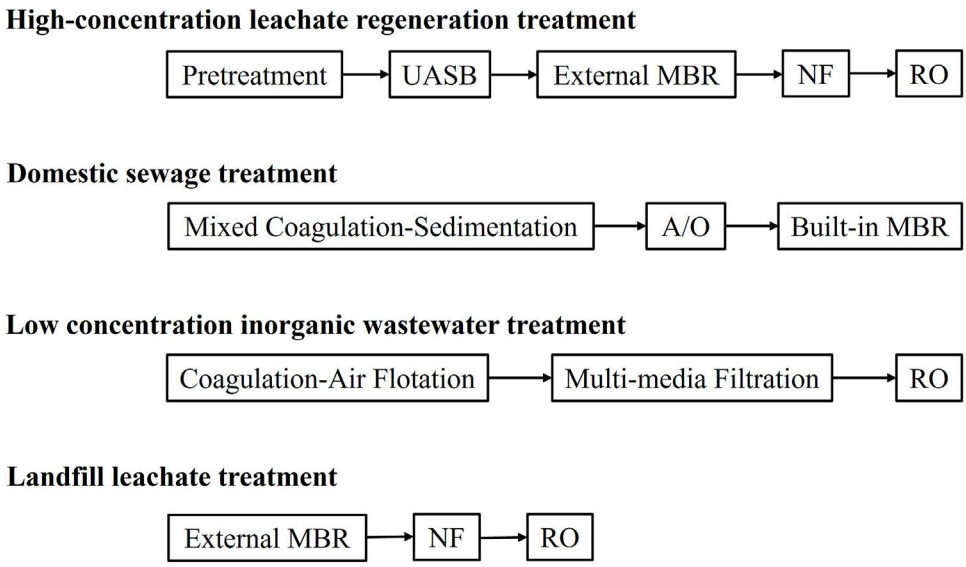


FIGURE 3
Comprehensive wastewater treatment system by Welle Group Co., Ltd, addressing high-concentration landfill leachate and domestic/low-concentration sewage through advanced multi-stage processes for effective contaminant removal and safe discharge or reuse.

6.2 Example of comprehensive treatment system for landfill leachate

In the bustling urban environment of Changsha City, the capital of Hunan Province, China (28.2282°N, 112.9388°E), located 35 km north in Qiaoyi Town, Wangcheng District, the Changsha Municipal Solid Waste Treatment Site stands as a pivotal solution to the city's waste management challenges. Operated by Welle Environmental Protection Technology Group Co., Ltd., this project exemplifies a cutting-edge approach to handling landfill leachate treatment (Welle Environmental Protection Technology Group Co.L, 2024). As the sole comprehensive co-processing site for municipal solid waste in Changsha, it is responsible for managing domestic waste from the city's expansive area, municipal sludge from 13 sewage treatment plants, and all leachate in the reservoir area. The facility is ingeniously divided into two functional units: landfill and incineration plant, with 80% of domestic waste processed through incineration for electricity generation and the remaining 20% allocated for landfilling. The core challenge in managing landfill leachate stems from its highly concentrated and variable composition, which can severely impact local water sources and the broader environment.

To tackle this, Welle Group Co., Ltd has designed a comprehensive leachate treatment system addressing both landfill leachate and domestic/low-concentration sewage (Figure 3). The process for high-concentration leachate regeneration is a testament to engineering excellence, employing a sophisticated combination of "pretreatment + up-flow anaerobic sludge blanket (UASB) + external membrane bioreactors (MBR) + nanofiltration (NF) + reverse osmosis (RO). This multi-stage approach ensures the thorough removal of contaminants, making the leachate safe for discharge or reuse. In addition to the high-concentration leachate treatment, the facility also addresses the treatment of domestic and low-concentration inorganic sewage. The domestic sewage treatment follows a "mixed coagulation and sedimentation + anaerobic-aerobic (A/O) + built-in MBR" process. In contrast, the low-concentration inorganic sewage is treated through "coagulation and air flotation + multi-media filtration + RO." These processes are designed to efficiently handle the varied waste streams entering the facility, ensuring that all forms of wastewater are effectively managed. The landfill leachate treatment, in particular, employs an "external MBR + NF + RO" process. This specific treatment path is crucial for dealing with the highly contaminated leachate from the landfill, effectively reducing its pollutant load before release or reuse. The concentrated liquid produced from these treatment processes undergoes advanced oxidation/reduction treatment, showcasing the facility's commitment to minimizing environmental impact. This liquid is then cleverly returned to the factory for consumption, embodying the principles of sustainability and resource recovery. The achievements of this project are both tangible and impactful. After undergoing the comprehensive treatment processes, the landfill leachate meets the stringent emission standards outlined in Table 2 of the "Pollution Control Standards for Domestic Waste Landfills" (GB16889-2008) (Table 10). Similarly, the effluent from the three sewage systems at the incineration plant complies with the "Water Quality for Industrial Water for Recycling of Urban Wastewater" (GB/T19923-2005), which sets the water quality standards for supplementary water in open circulating water systems. The project addresses the immediate need for waste and leachate treatment and contributes to resource conservation and pollution reduction goals. It stands as a testament to the power of technology and strategic planning in solving the complex environmental challenges of our time.

6.3 Optimizing integrated landfill leachate treatment systems

In environmental management, optimizing and modeling an integrated system for landfill leachate treatment serve as

TABLE 10 Emission standards in Table 2 of the 'pollution control standards for municipal solid waste landfills' (GB16889-2008).

Pollutant control item	Emission concentration limit
Color (Dilution times)	40
Chemical Oxygen Demand (COD_Cr) (mg/L)	100
Biochemical Oxygen Demand (BOD_5) (mg/L)	30
Suspended Solids (SS) (mg/L)	30
Total Nitrogen (TN) (mg/L)	30
Ammonia Nitrogen (NH_3-N) (mg/L)	25
Total Phosphorus (TP) (mg/L)	3
Fecal Coliform Group (CFU/L)	10,000
Total Mercury (Hg) (mg/L)	0.001
Total Cadmium (Cd) (mg/L)	0.01
Total Chromium (Cr) (mg/L)	0.1
Hexavalent Chromium (Cr^{6+}) (mg/L)	0.05
Total Arsenic (As) (mg/L)	0.1
Total Lead (Pb) (mg/L)	0.1

cornerstones for enhancing system efficiency, curbing expenditures, and adhering to environmental norms (Awewomom et al., 2024). The essence of this optimization lies in crafting a flexible treatment architecture that proficiently manages the intricate and diverse makeup of leachate while remaining nimble to fluctuations in waste inputs and legislative edicts. A synergy of suitable treatment modalities—such as UASB, MBR, NF, and RO—complements the specific leachate profile, ensuring that downstream processing is primed for optimal treatment (Huang et al., 2024). Operational parameters like retention time, aeration rate, and chemical dosing are meticulously fine-tuned to bolster the removal of pollutants, and real-time monitoring systems are deployed for on-the-fly adjustments. The model's sophistication extends to embodying resource recovery, advocating for repurposing byproducts like biogas into energy and advocating for the reuse of treated water.

The modeling facet delves into the assimilation of comprehensive data, which informs the simulation of the system's multifaceted treatment dynamics through advanced mathematical constructs (Ergene et al., 2022). These models are enriched with predictive analytics and scenario simulations, courtesy of machine learning algorithms, paving the way for a thorough understanding of potential operational outcomes. Validation through empirical data ensures the model's fidelity, while optimization algorithms distill the operational sweet spot that marries environmental efficacy with economic prudence (Podlasek, 2023). This ongoing, iterative process is honed by real-world performance feedback and shifting regulatory frameworks, propelling landfill leachate treatment toward unparalleled operational finesse.

7 Challenges and future

In addressing the complex challenges of landfill leachate treatment, it is crucial to consider the economic, operational, and emerging contaminant-related hurdles that impede the efficacy of current systems. This section delves into the multifaceted issues faced by waste management facilities, highlighting the significant financial burdens, operational difficulties due to leachate variability, and the rising threat of emerging contaminants like pharmaceuticals and microplastics. These challenges necessitate innovative solutions and strategic approaches to ensure effective, sustainable leachate management in the future.

7.1 Comprehensive challenges in landfill leachate treatment: Economic, operational, and emerging contaminant

The foremost economic challenge in landfill leachate treatment lies in the high capital and operational costs associated with advanced treatment systems (El-Saadony et al., 2023). Technologies such as RO, NF, and MBRs are effective in removing a wide range of contaminants but require substantial financial investment. These systems are not only expensive to install but also incur ongoing costs related to energy consumption, maintenance, and the need for skilled personnel to operate and monitor the processes. The financial burden is further amplified by the variability in leachate composition, which demands adaptable systems capable of handling fluctuations in pollutant concentrations. This variability necessitates continuous system optimization, leading to additional costs associated with adaptive management and process upgrades (Yadav et al., 2021). Table 11, which outlines the costs of various representative leachate treatment technologies, underscores the financial strain on waste management facilities (Gerald et al., 1998; Randall and Ubay Cokgor, 2000; Mahamuni and Adewuyi, 2010; Ju-Chang Huang, 2017; Ighalo et al., 2022; Pérez et al., 2022; Kurniawan et al., 2023). Moreover, the costs are not merely limited to initial capital outlays but extend to operational expenses that accumulate over the system's lifecycle (Abdelfattah and El-Shamy, 2024). As such, the economic challenges of landfill leachate treatment call for innovative approaches to reduce costs while maintaining treatment efficacy.

Operationally, the treatment of landfill leachate is fraught with difficulties due to the high variability of leachate quality. This variability is influenced by factors such as seasonal changes, waste composition, and the age of the landfill, all of which affect the concentration and types of pollutants present in the leachate. The dynamic nature of leachate composition requires continuous monitoring and adjustment of treatment processes to ensure consistent performance (Upadhyay et al., 2023). Operators must continuously monitor and adjust treatment processes, requiring skilled personnel and sophisticated control systems. The potential for system failure or suboptimal performance poses significant environmental risks, including groundwater contamination and non-compliance with discharge regulations, leading to potential fines and reputational damage. Addressing these operational challenges requires a holistic approach that integrates cost-effective treatment technologies with operational efficiency and

TABLE 11 Costs of representative leachate treatment technologies (Gerald et al., 1998; Randall and Ubay Cokgor, 2000; Mahamuni and Adewuyi, 2010; Huang, 2017; Ighalo et al., 2022; Pérez et al., 2022; Kurniawan et al., 2023).

Treatment method	Approximate cost (/m^3 of treated wastewater)
Adsorption	0.038–51,120 USD The main cost is depended on the adsorbent Adsorbent Cost Performance: - Very cheap: <1 $/mol chemical species - Most adsorbents: 1–200 $/mol chemical species - Very expensive: >200 $/mol chemical species
Air-stripping	0.0134 USD
Reverse osmosis	0.5 USD
Biological nutrient removal	0.615USD
Ultrafiltration	0.69 USD
Advanced oxidation processes	US/UV/O_3: 23.717 USDUS/UV/H_2O_2: 17.216 USDUS/UV: 6.821 USD

environmental stewardship (Kundariya et al., 2021). The development of more energy-efficient membrane technologies or the adoption of natural treatment solutions, such as constructed wetlands, offers promising avenues for reducing operational difficulties and associated costs (Kataki et al., 2021). For instance, the development of more energy-efficient membrane technologies or the adoption of natural treatment solutions, such as constructed wetlands, offers promising avenues for reducing operational difficulties and associated costs. Moreover, embracing circular economy principles, where treated leachate is reused for industrial or agricultural purposes, can help mitigate operational challenges while contributing to sustainability goals. (Bakan et al., 2022; Das et al., 2023).

The emergence of new contaminants, such as pharmaceuticals, personal care products, microplastics, and other micropollutants, presents a significant challenge to traditional wastewater and landfill leachate treatment systems (Kumar et al., 2023). These substances, often called emerging contaminants (ECs), have become a focal point for environmental scientists and engineers due to their potential to bypass conventional treatment processes and enter the aquatic environment, posing risks to wildlife and human health (Ahmed et al., 2021; Morin-Crini et al., 2021). Traditional wastewater and landfill leachate treatment systems were designed to remove organic matter, nutrients, and major pollutants (Lindamulla et al., 2022). However, these systems often lack the specificity to capture and degrade ECs effectively, many of which are designed to be biologically active and resistant to degradation (Teng and Chen, 2023). Pharmaceuticals, for example, are engineered to resist metabolic breakdown to ensure their efficacy, making them persistent in the environment (González-González et al., 2022). Microplastics, conversely, are resistant to biodegradation due to their synthetic polymer composition, accumulating in water bodies and potentially entering the food chain (Huang et al., 2021). The presence of ECs in water and leachate streams can significantly reduce the treatment efficiency of these systems (Rout et al., 2021b). Certain contaminants can inhibit microbial activity in biological treatment processes, reducing the degradation rate of organic pollutants and altering the microbial community structure (Aragaw, 2021). For example, antibiotics in wastewater can inhibit the growth of bacteria critical to the biological treatment processes, leading to a decrease in overall treatment efficiency (Zhu et al., 2021). Moreover, some ECs can form complex compounds with other elements in the wastewater, making them more difficult to remove and requiring additional treatment stages or more advanced treatment technologies (Shahid et al., 2021). Notably, based on the environmental risks and regulatory status of chemicals, and following technical feasibility and socioeconomic assessments, the Ministry of Ecology and Environment of China published the latest list of key controlled emerging contaminants in 2023 (Table 12) (China, 2022). The newly listed contaminants are now subject to environmental risk management measures, including those related to their manufacture, use, import, or export. Some contaminants have transition periods or exemptions. This initiative highlights the government's commitment to addressing emerging contaminants and urges relevant departments to take action to prevent environmental and public health risks. For landfill leachate treatment, the presence of these new pollutants complicates the process, often requiring upgrades or advanced technologies to effectively manage them. Proactively addressing these contaminants can improve treatment efficiency and reduce environmental contamination risks. It is worth mentioning that, Per- and polyfluoroalkyl substances (PFAS) are synthetic chemicals widely used for their water- and grease-resistant properties, found in various consumer products and industrial applications (Venkatesh Reddy et al., 2024). Their strong carbon-fluorine bonds make them highly persistent and resistant to conventional water treatment methods, posing significant challenges for removal (Jin et al., 2021). Traditional processes like coagulation, sedimentation, and standard filtration are largely ineffective against PFAS, necessitating the use of advanced technologies (Nguyen and Le Tran, 2024). Methods such as granular activated carbon adsorption, ion exchange, and high-pressure membrane filtration (nanofiltration and reverse osmosis) show varying degrees of success but often involve high operational costs and complex waste management (Lee et al., 2022). Emerging technologies like electrochemical treatment, plasma-based processes, and combined treatment approaches offer potential but require further development and investment (Blotevogel et al., 2023). The inclusion of PFAS-specific treatments increases operational complexity and costs for water treatment facilities, which must adapt to stringent regulatory standards. Research continues to focus on more efficient and cost-effective removal technologies to address the persistent nature of PFAS and protect public health and the environment.

The impact of emerging contaminants on the efficiency of wastewater and landfill leachate treatment systems presents a complex challenge that requires immediate and sustained attention. While these contaminants pose significant environmental and public health risks, they also provide an impetus for innovation in treatment technologies and strategies. Addressing this challenge will require a combination of technological advancement, regulatory action, public education, and international cooperation to ensure the safety and

TABLE 12 2023 List of Key Controlled New Pollutants posted by Ministry of Ecology and Environment of the People's Republic of China (China, 2022).

No.	New pollutant name	CAS no.	Main environmental risk control measures
1	Perfluorooctane sulfonic acid (PFOS) and its salts and perfluorooctane sulfonyl fluoride	1763–23–1 307–35–7 2795–39–3 29,457–72–5 29,081–56–9 70,225–14–8 56,773–42–3 251,099–16–8	1. Prohibit production. 2. Prohibit processing and use (except for certain uses such as firefighting foam until 31 Dec 2023). 3. Conduct mandatory clean production audits for companies using PFOS for firefighting foam. 4. Require environmental management clearance for import/export until 1 Jan 2024. 5. Manage as hazardous waste if no longer in use or declared as waste 6. Establish soil pollution prevention measures for enterprises involving PFOS.
2	Perfluorooctanoic acid (PFOA) and its salts and related compounds	—	1. Prohibit new production facilities. 2. Prohibit production and use (except for certain uses in semiconductor manufacturing, photography coatings, protective textiles, invasive medical devices, and other specified uses). 3. Conduct mandatory clean production audits for companies using PFOA. 4. Require environmental management clearance for import/export. 5. Manage as hazardous waste if no longer in use or declared as waste 6. Establish soil pollution prevention measures for enterprises involving PFOA.
3	Decabromodiphenyl ether	1163–19–5	1. Prohibit production and use (except for certain uses in textiles, plastic casings, polyurethane foam until 31 Dec 2023). 2. Conduct mandatory clean production audits for companies using decabromodiphenyl ether. 3. Require environmental management clearance for import/export until 1 Jan 2024. 4. Manage as hazardous waste if no longer in use or declared as waste 5. Establish soil pollution prevention measures for enterprises involving decabromodiphenyl ether
4	Short-chain chlorinated paraffins	85,535–84–8 68,920–70–7 71,011–12–6 85,536–22–7 85,681–73–8 108,171–26–2	1. Prohibit production and use (except for certain uses in rubber, leather, lubricants, decorative lights, paints, adhesives, metal processing, and flexible PVC until 31 Dec 2023). 2. Conduct mandatory clean production audits for companies using short-chain chlorinated paraffins. 3. Require environmental management clearance for import/export until 1 Jan 2024. 4. Manage as hazardous waste if no longer in use or declared as waste 5. Establish soil pollution prevention measures for enterprises involving short-chain chlorinated paraffins
5	Hexachlorobutadiene	87–68–3	1. Prohibit production, use, and import/export. 2. Ensure compliance with emission standards for related enterprises. 3. Manage as hazardous waste if no longer in use or declared as waste 4. Establish soil pollution prevention measures for enterprises involving hexachlorobutadiene
6	Pentachlorophenol and its salts and esters	87–86–5 131–52–2 27,735–64–4 3772–94–9 1825–21–4	1. Prohibit production, use, and import/export 2. Manage as hazardous waste if no longer in use or declared as waste 3. Establish soil pollution prevention measures for enterprises involving pentachlorophenol
7	Trifluralin	115–32–2 10,606–46–9	1. Prohibit production, use, and import/export. 2. Manage as hazardous waste if no longer in use or declared as waste
8	Perfluorohexane sulfonic acid (PFHxS) and its salts and related compounds	—	1. Prohibit production, use, and import/export. 2. Manage as hazardous waste if no longer in use or declared as waste
9	Dechlorane Plus and its isomers	13,560–89–9 135,821–03–3 135,821–74–8	1. Prohibit production, use, and import/export from 1 Jan 2024 2. Manage as hazardous waste if no longer in use or declared as waste
10	Dichloromethane	75–09–2	1. Prohibit production of paint removers containing dichloromethane 2. Prohibit use in cosmetics 3. Ensure compliance with volatile organic compounds content limits and emission standards. 4. Conduct regular environmental risk assessments. 5. Establish soil pollution prevention measures for enterprises involving dichloromethane. 6. Strictly control soil pollution risks

(Continued on following page)

TABLE 12 (*Continued*) 2023 List of Key Controlled New Pollutants posted by Ministry of Ecology and Environment of the People's Republic of China (China, 2022).

No.	New pollutant name	CAS no.	Main environmental risk control measures
11	Chloroform	67–66–3	1. Prohibit production of paint removers containing chloroform 2. Ensure compliance with volatile organic compounds content limits and emission standards. 3. Conduct regular environmental risk assessments. 4. Establish soil pollution prevention measures for enterprises involving chloroform. 5. Strictly control soil pollution risks
12	Nonylphenol	25,154–52–3 84,852–15–3	1. Prohibit use as pesticide adjuvants. 2. Prohibit use in the production of nonylphenol ethoxylates. 3. Prohibit use in cosmetics
13	Antibiotics	—	1. Strictly enforce prescription requirements for antibacterial drugs. 2. Manage antibiotic residues as hazardous waste. 3. Ensure compliance with emission standards for pharmaceutical industries
14	Phased-out group (hexabromocyclododecane, chlordane, mirex, hexachlorobenzene, DDT, α-hexachlorocyclohexane, β-hexachlorocyclohexane, lindane, endosulfan as a raw material and its isomers, and polychlorinated biphenyls)	—	1. Prohibit production, use, and import/export. 2. Manage as hazardous waste if no longer in use or declared as waste. 3. Strictly control soil pollution risks according to soil pollution risk management standards

sustainability of water resources in the face of emerging environmental threats.

7.2 Future research

Embracing the future of landfill leachate treatment demands a multi-faceted approach: pioneering new materials for adsorption and catalysis, harnessing microbial genetic engineering for targeted bioremediation, and committing to process intensification for enhanced efficiency. These innovative pathways herald a new era of sustainability and effectiveness in managing complex waste challenges.

7.2.1 New materials for adsorption and catalysis

Future research in landfill leachate treatment increasingly focuses on developing new materials for adsorption and catalysis, driven by the need for more efficient, cost-effective, and sustainable treatment solutions. These materials are at the forefront of addressing complex pollutants, including emerging contaminants that traditional treatment methods struggle to remove. Advanced adsorbents, such as modified biochars, nanocomposites, and metal-organic frameworks (MOFs), are being explored for their high surface area, porosity, and tunable surface chemistry, which can significantly enhance the adsorption of pollutants (Zango et al., 2020). For instance, biochars produced from agricultural waste can be engineered at the nano-scale to improve their adsorption capacity for specific contaminants like pharmaceuticals and heavy metals (Bhandari et al., 2023). Catalytic materials are equally crucial for breaking down pollutants through AOPs. New photocatalysts, including quantum dots and graphitic carbon nitride (g-C_3N_4), offer the potential for more efficient light absorption and utilization, enabling the degradation of contaminants under visible light and thus reducing energy consumption (Wang et al., 2020). The development of these materials aims to enhance the efficiency and specificity of contaminant removal and minimize secondary pollution and the use of harsh chemicals in the treatment process (Ahmed et al., 2021). Research also focuses on the regeneration and reuse of these materials to ensure the sustainability of the treatment processes (Baskar et al., 2022). Innovative approaches to regenerate spent adsorbents and catalysts, such as thermal, chemical, and ultrasonic methods, are being studied to extend their life and reduce operational costs (Ferella, 2020). Overall, exploring new materials for adsorption and catalysis represents a dynamic and promising area of landfill leachate treatment, offering potential breakthroughs in efficiency, sustainability, and tackling a broader spectrum of pollutants.

7.2.2 Microbial genetic engineering

Microbial genetic engineering stands at the forefront of biotechnological innovations in landfill leachate treatment (Saeed et al., 2022). The natural biodegradation processes employed by microorganisms offer a sustainable and efficient means of removing organic pollutants from leachate (Pisharody et al., 2022). However, leachate's complex and toxic nature often limits the effectiveness of native microbial communities (Nimonkar et al., 2022). Genetic engineering presents an opportunity to overcome these limitations by enhancing the metabolic capabilities of microorganisms, enabling them to degrade a wider array of contaminants, including recalcitrant and emerging pollutants (Haripriyan et al., 2022). The manipulation of microbial genomes involves introducing genes responsible for producing specific enzymes that can break down complex molecules or modifying existing metabolic pathways to increase their efficiency and specificity (Michalska et al., 2020). This can lead to the creation of microbial strains capable of rapid pollutant degradation, reduced biomass production, and enhanced tolerance to high pollutant concentrations and toxic substances (Maqsood et al., 2023). Ongoing research focuses on identifying key enzymatic pathways for the degradation of specific contaminants, developing genetic tools for efficient genome editing, and integrating genetically engineered microbes into existing treatment processes (Saravanan et al., 2022). Additionally, the ecological safety of releasing genetically modified organisms into environmental treatment

systems is a critical consideration, necessitating rigorous containment strategies and risk assessments.

7.2.3 Process enhancement

Process intensification in landfill leachate treatment aims to enhance the efficiency and effectiveness of treatment processes by integrating and optimizing physical, chemical, and biological methods. The goal is to achieve more with less—reducing the footprint, energy consumption, and operational costs of treatment systems while maximizing pollutant removal efficiency (Cardoso et al., 2021). This can involve the development of novel reactor designs that facilitate enhanced contact between the leachate and treatment agents, using AOPs to break down complex organic molecules, and integrating membrane technologies for selective pollutant removal and water recovery (Titchou et al., 2021). Process intensification can leverage the synergies between different treatment modalities, such as combining adsorption processes with biodegradation to handle a broader range of contaminants more effectively.

Future research directions include exploring hybrid treatment systems that integrate emerging materials for adsorption and catalysis with genetically engineered microbial processes, developing energy-efficient AOPs, and optimizing process parameters through advanced modeling and control strategies. The aim is to develop compact, modular treatment systems that can be easily adapted to varying leachate compositions and volumes, ensuring robust and sustainable leachate management strategies for the future.

7.2.4 Circular economy and sustainability in future landfill leachate treatment

The circular economy and sustainability principles are increasingly influencing the development and adoption of future landfill leachate treatment technologies, steering them towards more environmentally friendly and resource-efficient solutions (Bandala et al., 2021). This shift is a response to the growing awareness of the environmental impacts of waste management practices and the urgent need to transition towards more sustainable models of production and consumption. The role of circular economy concepts in shaping future leachate treatment technologies is profound, focusing on waste minimization, resource recovery, and the closed-loop reuse of materials and water (Yusuf et al., 2020).

At the heart of the circular economy is reducing waste and preventing pollution (Dincă et al., 2022). Future landfill leachate treatment technologies are being designed with a preventative approach, aiming to minimize the generation of leachate and its associated contaminants at the source (Bandala et al., 2021). This can be achieved through better landfill design, including impermeable liners and covers and waste pre-treatment to reduce its leachate-generating potential. By addressing the problem at its source, these technologies contribute to a more sustainable and less resource-intensive waste management system. Another cornerstone of the circular economy is the recovery and reuse of resources, which plays a significant role in shaping leachate treatment technologies (Puntillo et al., 2021). Emerging technologies are not only aimed at treating leachate to meet environmental discharge standards but also at recovering valuable resources from it (Li and Liu, 2021). Nutrient recovery, for example, can transform leachate into a source of nitrogen and phosphorus for agricultural use (Kurniawan et al., 2021b). Similarly, advanced treatment processes can recover water for irrigation or industrial applications, contributing to water conservation and reducing the demand for freshwater resources (Meese et al., 2022). The recovery of energy in the form of biogas from the anaerobic treatment of leachate further underscores the potential of these technologies to contribute to a more sustainable and energy-efficient waste management system (An et al., 2023). The circular economy encourages a systemic view of waste management, promoting the integration of leachate treatment technologies within broader waste and water management systems (Smol et al., 2020). Future technologies will likely be characterized by their ability to integrate with other treatment and recovery processes, creating synergies that enhance overall efficiency and sustainability (Kehrein et al., 2020). For example, integrating leachate treatment with solid waste management processes can facilitate the co-treatment of organic waste and leachate, optimizing resource recovery and minimizing environmental impacts (Mishra et al., 2023).

Collectively, the influence of circular economy and sustainability principles on the future of landfill leachate treatment technologies is transformative, driving innovation towards solutions that are effective in treating leachate and minimizing waste, recovering resources, and integrating seamlessly into a circular and sustainable waste management framework. As these principles continue to gain traction, they will undoubtedly shape the development of more sustainable, efficient, and integrated leachate treatment technologies, aligning waste management practices with the broader goals of environmental sustainability and resource conservation.

8 Conclusion

The environmental impact of untreated leachate is significant, with potential contamination of groundwater, surface water, and overall ecosystem health, necessitating robust and dynamic treatment solutions.

This comprehensive review of landfill leachate treatment technologies presents a global perspective, focusing on the physicochemical properties of leachate, regulatory frameworks, and specific country examples. The study highlights the complex composition of landfill leachate, which includes a mix of organic and inorganic pollutants, heavy metals, and xenobiotic compounds. The review also underscores the importance of global regulatory frameworks in shaping landfill leachate management practices. International agreements, such as the Basel Convention and the Stockholm Convention, along with national regulations from countries like the United States, China, India, and Brazil, are setting standards and encouraging the adoption of advanced treatment technologies.

Key findings emphasize the evolution of conventional and advanced treatment technologies. Traditional methods such as physical, chemical, and biological treatments remain fundamental. Physical methods, including sedimentation and membrane filtration, effectively remove suspended solids and larger organic molecules. Chemical treatments like coagulation-flocculation and advanced oxidation processes are crucial for targeting dissolved pollutants and heavy metals. Biological treatments utilize microbial processes to degrade organic pollutants and are particularly effective for nutrient removal.

Advanced treatment technologies, including MBRs, NF, RO, and AOPs), provide higher efficiency and are essential for meeting stringent regulatory standards. These technologies can remove a broader range of contaminants, including emerging pollutants such as pharmaceuticals and microplastics, which traditional methods may not adequately address. Economic considerations are also crucial in the treatment process. The high capital and operational costs of advanced leachate treatment systems pose significant challenges. Technologies such as RO, NF, and MBR are effective but require substantial investment in equipment, maintenance, and energy consumption. Addressing these economic challenges necessitates the development of cost-effective, energy-efficient solutions and the integrating of resource recovery practices, such as biogas production and water reuse, to offset operational costs. A case study from Changsha City illustrates the practical application and effectiveness of a comprehensive treatment system that integrates various technologies. This example provides valuable insights into designing integrated systems capable of meeting diverse regulatory requirements and addressing complex environmental challenges.

In conclusion, the continuous improvement of landfill leachate treatment technologies is vital. Adopting innovative and sustainable practices is essential to reduce the environmental footprint of landfills. Future research should focus on developing cost-effective, energy-efficient solutions and exploring emerging technologies for better pollutant removal. By emphasizing a global perspective and integrating multiple treatment processes, this review significantly contributes to advancing sustainable waste management practices and protecting environmental health.

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JW: Conceptualization, Data curation, Formal Analysis, Resources, Software, Writing–original draft, Writing–review and editing. ZQ: Conceptualization, Project administration, Supervision, Writing–original draft, Writing–review and editing.

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