Review of the fate and transformation of per- and polyfluoroalkyl substances (PFASs) in landfills

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ARTICLE INFO
Article history:
Received 21 March 2017
Revised in revised form 2 August 2017
Accepted 8 December 2017
Available online 21 December 2017

Keywords:
Landfill
Polyfluoroalkyl
Perfluoroalkyl
Leachate
Degradation

ABSTRACT
A critical review of existing publications is presented i) to summarize the occurrence of various classes of per- and polyfluoroalkyl substances (PFASs) and their sources in landfills, ii) to identify temporal and geographical trends of PFASs in landfills; iii) to delineate the factors affecting PFASs in landfills; and iv) to identify research gaps and future research directions. Studies have shown that perfluoroalkyl acids (PFAs) are routinely detected in landfill leachate, with short chain (C4-C7) PFAs being most abundant, possibly indicating their greater mobility, and reflecting the industrial shift towards shorter-chain compounds. Despite its restricted use, perfluorooctanoic acid (PFOA) remains one of the most abundant PFAs in landfill leachates. Recent studies have also documented the presence of PFAA-precursors (e.g., saturated and unsaturated fluorotelomer carboxylic acids) in landfill leachates at concentrations comparable to, or higher than, the most frequently detected PFAs. Landfill ambient air also contains elevated concentrations of PFASs, primarily semi-volatile precursors (e.g., fluorotelomer alcohols) compared to upwind control sites, suggesting that landfills are potential sources of atmospheric PFASs.

The fate of PFASs inside landfills is controlled by a combination of biological and abiotic processes, with biodegradation releasing most of the PFASs from landfilled waste to leachate. Biodegradation in simulated anaerobic reactors has been found to be closely related to the methanogenic phase. The methane-yielding stage also results in higher pH (>7) of leachates, correlated with higher mobility of PFAs. Little information exists regarding PFAA-precursors in landfills. To avoid significant underestimation of the total PFAS released from landfills, PFAA-precursors and their degradation products should be determined in future studies. Owing to the semi-volatile nature of some precursor compounds and their degradation products, future studies also need to include landfill gas to clarify degradation pathways and the overall fate of PFASs.

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Allred et al., 2015; Eggen et al., 2010). Given that solid wastes (Fig. 1). Most often, leachate from lined landfills are collected and (e.g., desorption) (Allred et al., 2015), as shown in Fig. 1.

As more and more studies are published regarding environmental occurrence, fate and degradation of PFASs, it is important to systematically review the published literature to critically evaluate the state of knowledge and identify research gaps. Recent reviews of PFASs have addressed environmental biodegradation (Liu and Avendano, 2013), fate and removal of PFASs in drinking water treatment plants (Rahman et al., 2014), and WWTPs (Merino et al., 2016; Arvaniti and Stasinakis, 2015). A comprehensive review on the fate and transformation of PFASs in landfills is needed. This study critically reviews existing publications i) to summarize the occurrence of various classes of per- and polyfluoroalkyl substances (PFASs) and their sources in landfills, ii) to identify temporal and geographical trends of PFASs in landfills; iii) to delineate factors affecting PFASs in landfill; and iv) to identify research gaps and key future research directions.

2. Methodology

Based on an online database search (Web of Science, Science-Direct and Google Scholar) of peer-reviewed articles, 14 journal articles were identified that reported PFAS concentrations in landfill leachate. Two studies reporting PFAS concentrations in ambient landfill air, three investigating degradation and leaching of PFAS inside landfills and one reporting leaching of PFASs through sodium bentonite (landfill barrier material) were also uncovered. While the subsequent sections in this paper are heavily based on these 18 articles (published between 2004 and 2017), additional citations from peer-reviewed journals are also cited to contextualize and explain the observations of the selected articles. The reported concentrations of PFASs are compiled in Table S1 (PFAs) and S2 (perfluoroalkane sulfonamide derivatives and polyfluoroalkyl compounds) of SI. Concentration ranges and, where possible, median and other statistical values were calculated for studies reporting concentrations from multiple samples (from one or more landfills). During data analysis, below-quantification-limit values were assumed to be zero.

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>PFAS Per- and polyfluoroalkyl substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIPAP</td>
<td>Disubstituted fluoroelomer phosphate esters</td>
</tr>
<tr>
<td>EtFOSA</td>
<td>Ethyl-perfluoroctane sulfonamide acetic acid</td>
</tr>
<tr>
<td>EtFOSA</td>
<td>Ethyl-perfluorooctane sulfonylamine acetic acid</td>
</tr>
<tr>
<td>FASA</td>
<td>Perfluoroalkane and N-alkyl perfluoroalkane sulfonylamine acetic acid</td>
</tr>
<tr>
<td>FOSA</td>
<td>Perfluoroalkane and N-alkyl perfluoroalkane sulfonylamine</td>
</tr>
<tr>
<td>FOSE</td>
<td>Perfluoroalkane and N-alkyl perfluoroalkane sulfonylamidoethanols</td>
</tr>
<tr>
<td>FTCA</td>
<td>Fluorotelomer saturated carboxylic acid</td>
</tr>
<tr>
<td>FIT</td>
<td>Fluorotelomer iodide</td>
</tr>
<tr>
<td>FTOH</td>
<td>Fluorotelomer alcohol</td>
</tr>
<tr>
<td>FTP</td>
<td>Fluorotelomer polymer</td>
</tr>
<tr>
<td>FTSA</td>
<td>Fluorotelomer sulfonate</td>
</tr>
<tr>
<td>FTOCA</td>
<td>Fluorotelomer unsaturated carboxylic acid</td>
</tr>
<tr>
<td>MeFOSA</td>
<td>Methyl-perfluorobutane sulfonamide acetic acid</td>
</tr>
<tr>
<td>MSW</td>
<td>Municipal solid waste</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>PAP</td>
<td>Polyfluorinated phosphate ester</td>
</tr>
<tr>
<td>PEPE</td>
<td>Perfluoropolyether</td>
</tr>
<tr>
<td>PFAN</td>
<td>Perfluorooctyl acid</td>
</tr>
<tr>
<td>PFIRO</td>
<td>Perfluorooctane sulfonyl fluoride</td>
</tr>
<tr>
<td>PPIA</td>
<td>Perfluorooctyl phosphonic acids</td>
</tr>
<tr>
<td>PEM</td>
<td>Perfluorooctane sulfonyl amide</td>
</tr>
<tr>
<td>POE</td>
<td>Perfluorooctane sulfonyl amide</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent organic pollutant</td>
</tr>
<tr>
<td>POSF</td>
<td>Perfluorooctane sulfonamide acetic acid</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse osmosis</td>
</tr>
<tr>
<td>SI</td>
<td>Supplemental Information</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
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</table>

Photography (Arvaniti et al., 2014; Kissa, 2001). A variety of consumer products (e.g., paper, textiles, carpets) and packaging containing PFASs and their precursors are sent to municipal landfills at the end of their useful lives. In many municipalities, biosolids containing PFASs are also landfilled (Guerra et al., 2014; Arvaniti et al., 2012). Following disposal, PFASs are released from the waste through biological and abiotic leaching (e.g., desorption) (Alfred et al., 2015), as shown in Fig. 1. Depending on their physio-chemical properties, some anionic, water soluble PFASs (e.g., PFAs) can be released with the landfill leachate (Yan et al., 2015; Benskin et al., 2012); on the other hand, neutral PFASs with low water solubilities and relatively high vapor pressures (e.g., fluorotelomer alcohols (FTOHs)) partition with landfill gas and are subsequently released to the atmosphere, if not captured efficiently by a gas collection system (Fig. 1). Most often, leachate from lined landfills are collected and sent to wastewater treatment plants (WWTPs) for treatment before their final disposal in surface water bodies. However, WWTPs, already burdened with PFAS from wastewater, are not equipped to remove these classes of contaminants, instead are acting as secondary sources of PFASs in the aquatic environment (Alfred et al., 2015; Eggen et al., 2010). Given that solid wastes have been, and will continue to be, landfilled, it is critical to investigate landfills as long-term point sources of PFASs in the environment.
3. Per- and polyfluoroalkyl substances (PFASs) in landfills

3.1. Occurrence and sources of PFASs in leachate

3.1.1. Perfluoroalkyl acids (PFAAs)

Perfluoralkyl carboxylic acids (PFCAs) and Perfluoralkyl sulfonic acids (PFSA), together known as PFAAs, are the most commonly studied PFASs in landfills. PFCAs with 4–14 carbon chain length and PFSA of mostly even chain length from C4-C10 have been reported in landfill leachate in the ng/L to µg/L range. Concentration ranges of PFAAs (C4-C10) in various countries are plotted in Fig. 2(a). Possible sources of PFAAs include consumer products (e.g., paper, textile, packaging, food contact paper, carpet) (Bečanová et al., 2016; Kotthoff et al., 2015; Ye et al., 2015), building materials (Bečanová et al., 2016), electronics (Bečanová et al., 2016) resulting from intentional addition of PFAAs during production and/or product use, and contamination with by-products impurities during production (Bečanová et al., 2016). Furthermore, PFAA precursors (e.g., FTOH, n:2 fluorotelomer carboxylic acids (n:2 FTCA) and n:2 unsaturated fluorotelomer carboxylic acids (n:2 FTUCAs) present in the consumer products (Kotthoff et al., 2015; Ye et al., 2015) can degrade to PFAAs during product use and/or after disposal in the landfill (Allred et al., 2015; Lang et al., 2016).

3.1.2. Fluorotelomer-based compounds

Fluorotelomer based compounds such as, n:2 FTCAs, n:2 FTUCAs, n:3 fluorotelomer carboxylic acids (n:3 FTCA), fluorotelomer sulfonates (n:2 FTSAs) have been detected in landfill leachate (Lang et al., 2017; Allred et al., 2014; Benskin et al., 2012; Huset et al., 2011) and lab-scale landfill reactors (Lang et al., 2016; Allred et al., 2015) ranging from a few ng/L to µg/L (Fig. 2(b)). The FTCAs and FTUCAs are known degradation products of FTOHs (Buck et al., 2011), a major raw material of fluorotelomer polymers (FTPs), commonly used in textiles, upholstery, paper and carpets as surface protection agent (Rao and Baker, 1994). In addition to FTOH monomer released through biological (Washington et al., 2015; Rankin et al., 2014) and abiotic hydrolysis (Washington and Jenkins, 2015), residual FTOH present in FTPs (Dinglasan-Panilio and Mabury, 2006) can biodegrade to FTCAs and FTUCAs, and subsequently to PFCAs in soil and activated sludge from WWTPs under both aerobic and anaerobic conditions (Liu and Avendano, 2013). The n:2 FTSAs can be released from consumer products applied with FTSAs-containing surface protectors (Lang et al., 2016; Allred et al., 2015; Yang et al., 2014a), and by the degradation of complex fluorotelomer-based substances used in food packaging applications (Buck et al., 2011).

3.1.3. Perfluoroalkyl sulfonamide derivatives

Several unsubstituted, methyl- and ethyl-perfluorooctane sulfonamide acetic acids (FASAs) with C4-C8 carbon chain length have been reported in landfill leachates (Lang et al., 2017; Allred et al., 2014; Benskin et al., 2012; Huset et al., 2011) as shown in Fig. 2(b). Biodegradation of ethyl-perfluorooctane sulfonamide ethanol (EtFOSA), a major raw material of paper and packaging products (Buck et al., 2011), is said to form C8-based ethyl-perfluorooctane sulfonamide acetic acid (EtFOSAA) (Rhoads et al., 2008). Similar biodegradation pathways could be responsible for the shorter FASAA, MeFASAA and EtFASAA homologues resulting from methyl- and ethyl-perfluorooctyl sulfonamidoethanols (FOSE) (Allred et al., 2014).

3.1.4. Polyfluoralkyl phosphate esters (PAPs)

Detection of a few classes of polyfluoralkyl phosphate esters (PAPs) (e.g., Di-substituted fluorotelomer phosphate esters (6:2–10:2 DiPAPs) and EtFOSA-based polyfluoralkyl phosphate diester (DiSAmPAP)) have been reported in leachate (Allred et al., 2014, 2015, Lang et al., 2017) (see Table S2, in SI). PAPs are used in papers and synthetic fibers to impart oil and water repellency, in semiconductor materials and in personal care products (Liu and Liu, 2016). Microbial degradation of PAPs resulting in a mixture of FTOCs and PFCAs has been reported in activated sludge (Lee et al., 2010), and in aerobic soil (Liu and Liu, 2016; Lee et al., 2013), accounting for the infrequent detection of PAPs in leachate, despite their widespread use and high production volume (De Silva et al., 2012).

3.2. General observations and geographical trends of PFASs in leachate

Despite the high variabilities in PFAAs profiles and concentrations in landfill leachate reported in North America, Europe, China and Australia (Yan et al., 2015; Clarke et al., 2015; Allred et al., 2014; Bossi et al., 2008; Kallenborn et al., 2004), a few general trends emerge. For example, PFCAs are generally found to be the dominant
PFASs (Fuertes et al., 2017; Allred et al., 2014; Li et al., 2012; Huset et al., 2011). Also, C4-C7 chain length PFASs are more abundant than their longer-chain (>C8) homologues (Fuertes et al., 2017; Li et al., 2012; Busch et al., 2010; Bossi et al., 2008; Kallenborn et al., 2004). Short-chain PFASs are prone to preferential release and leaching from municipal solid waste (MSW), consistent with their higher aqueous solubilities and lower organic carbon-water partition coefficients relative to longer-chain PFASs (Yan et al., 2015). In addition, the dominance of C4-C7 PFASs could be related to the shift towards production of shorter-chain perfluorinated compounds since the early 2000’s (Fig. 3). For example, 3M has commercialized surface treatment products containing C4-based side-chain fluorinated polymers since 2003 (Wang et al., 2013); 6:2 perfluorotelomer-based side-chain fluorinated polymers have been registered in the Inventory of Effective Food Contact Substances Notifications of the United States Food and Drug...
Administration since 2008 (Wang et al., 2013). Most of the landfill studies discussed here, involving sampling after 2010, likely reflect a product shift resulting from disposal of PFAS-containing consumer products with short residence life (e.g., food contact paper, packaging, other paper). For consumer products with longer residence times (e.g., carpet, upholstery, textiles), a time lag is expected before fluorinated alternatives used in these products reach measurable levels in leachate. The high frequency of PFOA detection in consumer products (Vester gren et al., 2015; Liu et al., 2014), together with its historical use in surface treatment agents of leather, textiles, paper and electronics (Wang et al., 2014a) explain the observed high detection frequencies and concentrations (often comparable to those of C4-C8 PFCA s) of PFOA in leachate. Studies have also reported that ∑PFAs from landfill leachate (for a facility closed 2-4 decades ago), ranges from hundreds to a few thousands of ng/L (Gallen et al., 2016; Allred et al., 2014; Huset et al., 2011).

An increasing number of studies showing degradation of polyfluorinated compounds to PFAs in the environment (Liu and Liu, 2016), along with increasing availability of chemical standards and improved analytical techniques, have led to recent studies (summarized in the next section) to investigate PFAA-precursors and their degradation products, as well as other classes of perfluorinated compounds (e.g., perfluorooalkyl sulfonamide derivatives) in landfill leachate. Some of the fluorotelomer-based (e.g., n:2 FTCA, FTUCAs) and N-alkyl FASAAs are frequently detected (Table S2) with concentration ranges (shown in Fig. 2(b)) that are comparable to and/or higher than those of PFCA s (>µg/L).

3.2.1. Concentration and trends in the USA and Canada

PFAs in landfill leachate in the USA have been studied by Huset et al. (2011), Allred et al. (2014) and Lang et al. (2017) (Table S1, in SI). PFCA contributed 20–90% of ∑PFAs (molar concentration basis), with concentrations from 10 to 8900 ng/L (Allred et al., 2014; Huset et al., 2011). While the median concentration reported by Allred et al. (2014) exceeded 1000 ng/L for all C4-C8 PFCA s, Huset et al. (2011) observed smaller concentrations (100–600 ng/L) for the same compounds. The difference in concentrations could result from variation in waste composition, climatic condition, age of the landfill and/or leachate management system (i.e., leachate recirculation vs flow-through), as indicated in Table 1 (see also section 3.5). PFSA concentrations in leachate have varied from 50 to 3200 ng/L in the USA, with median concentrations of a few hundred ng/L for perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS) and PFOS (Allred et al., 2014; Huset et al., 2011), as shown in Fig. 2(a). While PFOS was detected in all leachate samples, its concentration was generally lower than that of PFBS and PFHxS (Allred et al., 2014; Huset et al., 2011). This dominance of shorter-chain PFASs over historically used PFOS could be indicative of the transition towards C4-based chemistry after 2002, as shown in Fig. 3 (Vester gren et al., 2015; Huset et al., 2011; Lindstrom et al., 2011). Leachates from waste cells closed in 1993 or earlier also shows dominance of PFBS and PFHxS, indicating the role of C4-based chemistry even prior to 2002 (Wang et al., 2014b; Huset et al., 2011), in addition to the higher mobility of shorter chain PFASs, leading to their release in aqueous phase (Higgins and Luthy, 2006).

PFCA concentrations in leachates collected from Canadian landfills have been in the range of tens to few thousands of ng/L (Li et al., 2012; Benskin et al., 2012). PFASs, namely PFBS, PFHxS and PFOS, also varied within the same range, with median PFHxS concentration of 200 ng/L higher than for PFOS and PFBS in a cross-Canada study (Li et al., 2012). Landfill gas condensate was reported to contain C4-C8 PFCA s, with PFBS being the dominant compound at a concentration of 1000 ng/L (Li, 2011).

3.2.2. Concentration and trends in European Countries

PFAs have been reported in several European countries, including Spain (Fuertes et al., 2017), Finland (Perkola and Sainio, 2010: Miteni concludes global action warranted for PFOA and related compounds

![Timeline of PFCAs](image_url)
<table>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Location (Country)</td>
<td>Strandmossen, Djupdalen (Sweden)</td>
<td>Gulf Coast, Pacific Northwest, west coast, Mid-Atlantic states, Southeast (USA)</td>
<td>Pacific Northwest (Canada)</td>
<td>Espoo (Finland)</td>
<td>(USA)</td>
<td>Changzhou, Guangzhou, Nanjing, Shanghai, Suzhou (China)</td>
<td>(Australia)</td>
<td>(Australia)</td>
<td>18 active</td>
<td>2 active, 2 closed between 2015 and 2015</td>
<td></td>
</tr>
<tr>
<td>PFAS Analytes</td>
<td>13 not available</td>
<td>43 flow-through</td>
<td>24 recirculation, except one flow through system 2006</td>
<td>24 flow-through and recirculated</td>
<td>4 not available</td>
<td>70 not available</td>
<td>14 flow through</td>
<td>14 flow through except one recirculated</td>
<td>9 recirculation and flow through system August 2013 - December 2014</td>
<td>March, 2015</td>
<td>16 flow through</td>
</tr>
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<td>Leachate System</td>
<td>not available</td>
<td>municipal and commercial</td>
<td>primarily municipal</td>
<td>primarily municipal</td>
<td>municipal</td>
<td>municipal</td>
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</tr>
<tr>
<td>Waste Type</td>
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<td>primarily municipal</td>
<td>primarily municipal</td>
<td>municipal</td>
<td>municipal</td>
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<tr>
<td>Sampling Method</td>
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<td>grab samples</td>
</tr>
<tr>
<td>Leachate Treatment System</td>
<td>aerobic pond</td>
<td>biological and physical</td>
<td>not available</td>
<td>off-site at WWTP</td>
<td>not available</td>
<td>not available</td>
<td>off-site with two-stage process (MBR/RO or NF)</td>
<td>off-site at WWTP, evaporation pond</td>
<td>Off-site WWTP</td>
<td>Off-site WWTP</td>
<td>Off-site WWTP</td>
</tr>
<tr>
<td>Estimated PFAS loading in leachate</td>
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<td>not available</td>
<td>not available</td>
<td>8-25 kg/y/landfill</td>
<td>not available</td>
<td>not available</td>
<td>3100 - 4000 kg/(nationwide)</td>
<td>not available</td>
<td>not available</td>
<td>563 - 638 kg in 2013 (nationwide)</td>
<td>563 - 638 kg in 2013 (nationwide)</td>
</tr>
</tbody>
</table>

*WWTP: wastewater treatment plant; MBR: membrane bioreactor; RO: reverse osmosis; UF: ultrafiltration; NF: nanofiltration; PFAS: per- and polyfluoralkyl substance.*
3.3. Estimating PFAS mass discharged with landfill leachate

The mass of PFASs discharged with landfill leachate is a function of PFAS concentrations in leachate and leachate volume. As discussed in section 3.2, the total PFAS concentration in leachate is determined by the number/classes of PFAS analyzed and can be highly variable, depending on landfill- and waste-related factors (discussed in section 3.5 below). Similarly, leachate volume is highly dependent on climate (in particular, rainfall and subsequent infiltration into landfill), and may vary substantially from month to month, and from year to year (Gallen et al., 2017). A recent survey (Lang et al., 2017) of PFASs in landfill leachates in the USA (70 PFASs in 95 samples) estimated national release of 19 PFASs, with >50% of samples having quantifiable concentrations. A mass estimate was obtained by coupling waste age and climate-specific PFAS concentration estimates with climate-specific estimates of annual leachate volumes using Monte Carlo analysis. The estimates for the 19 PFASs ranged from 563 to 638 kg for the sampling year, 2013. PFAs accounted for the majority of mass estimated (291 kg/yr), closely followed by FCAs (285 kg/yr), with lower releases of PFAs and their precursors (84 kg/yr) (Lang et al., 2017). This indicates that the estimated mass budget of PFASs, often based on measured PFASs concentration only (Fuertes et al., 2017; Yan et al., 2015; Benskin et al., 2012; Busch et al., 2010; Olael et al., 2006), (<1–25 kg/yr per landfill as shown in Table 1) could grossly underestimate the total release of PFASs from landfills.

3.4. Occurrence of PFASs in landfill ambient air

While many of the PFAS-precursors and their degradation products (e.g., FTOHs, fluorotelomer iodides (FTIs), FOSAs) are semi-volatile in nature, the role of landfills as sources of PFAS gaseous emissions to the atmosphere has received little attention. Two studies (Ahrens et al., 2011; Weinberg et al., 2011) reported higher (2–30 times) PFAS concentrations in landfill ambient air compared to control sites that were presumably not contaminated with landfill emissions. Ambient landfill air predominantly contained FTOHs, with concentrations being >90% of total precursor compounds measured (see Table 2). While FOSAs and FOSEs were also detected, their concentrations were orders of magnitude lower than for the FTOHs (Ahrens et al., 2011; Weinberg et al., 2011). 8:2 FTOH was found to be the highest sole contributor (50–65% of the ∑FTOHs, FOSAs, FOSEs), followed by 6:2 FTOH (15–40%) FTOHs (Ahrens et al., 2011; Weinberg et al., 2011). Higher abundance of 8:2 FTOH compared with 6:2 FTOH has been reported (Jahneke et al., 2007; Shoeib et al., 2006) to be typical of urban air. This is also supported by a recent survey (Vestergren et al., 2015) of PFASs in consumer products in Norway imported from China, which showed that 6:2 and 8:2 FTOHs were the most abundant extractable PFASs measured.

PFAs were also detected in the particulate phase (Weinberg et al., 2011) and gas phase (Ahrens et al., 2011) of ambient landfill air. PFBA, PFHxAs, PFOA were detected most frequently and at higher concentrations compared to other PFASs in the gas phase (Ahrens et al., 2011). This might indicate abundance of PFOA and shorter-chain PFASs in landfill waste, or reduced availability of longer-chain PFASs in air due to their higher affinity for solid particles (Arvaniti et al., 2012). This dominance of short and even chain length PFASs is also consistent with the PFCA distribution in landfill leachates from 22 sites in Germany (Busch et al., 2010), indicating that this pattern is typical for landfill emissions. Although PFOS is frequently detected in landfill leachate, it exhibited very low air concentrations at the landfill sites (<5 pg/m³), likely due to strong sorption of PFOS to landfill solids, efficient trapping of PFOS in landfill gas collection, and partitioning of PFOS to landfill leachate (Ahrens et al., 2011).

3.5. Factors affecting per- and polyfluoroalkyl substances (PFASs) in landfill

Following landfilling, PFASs undergo long-term leaching, as well
as degradation of precursor compounds, processes that are affected by the physio-chemical properties of the PFASs, as well as the landfill leachate (Yan et al., 2015). As the landfilled waste passes through successive stages of aerobic, acetogenic, and methanogenic stabilization stages, significant changes occur in the physio-chemical properties, such as pH and organic and inorganic constituents (Table S3 in SI) of the leachate (Renou et al., 2008), likely affecting the mobility and degradation of PFASs. In most cases leachate from various waste cells undergoing varying stages of decomposition are collected together and subsequently sampled for PFAS analysis. This, along with the uncertainty surrounding waste input in various cells, makes it challenging to conduct any mass balance to better understand the PFAS release and transformation inside landfills. In addition, climatic factors (e.g., precipitation) affecting the moisture content inside landfills, and operating conditions (e.g., compaction of the waste, waste filling procedure, leachate recirculation) could also play an important role in determining the fate and transformation of PFASs in landfills.

3.5.1. Effect of leachate physiochemical properties

Several studies have reported increased mobility of PFASs with increasing pH (Gallen et al., 2017; Yan et al., 2015; Benskin et al., 2012), possibly due to the altered electrostatic behavior of the sorbents (Higgins and Luthy, 2006). This observation is consistent with sorption studies of PFOS and PFOA to diverse adsorbents, which indicated decreased sorption with increasing solution pH due to protonation of the adsorbent surface, leading to fewer positive sites on the sorbent (Wang and Shih, 2011; Yu et al., 2009). Total organic carbon (TOC) has been weakly correlated with the PFAS concentration in leachate (Gallen et al., 2017; Benskin et al., 2012), possibly due to hydrophobic partitioning of the perfluorinated chain with organic matter. Electrical conductivity (a measure of ion concentration in solution) has been both positively (Benskin et al., 2012) and negatively (Yan et al., 2015) correlated with PFAS concentration in leachate. While earlier studies (You et al., 2010; Higgins and Luthy, 2006) indicated decreased mobility of PFASs with increasing ionic strength, more recent work suggests that the effect of ionic strength of PFAS adsorption is quite complex and often ion-type and concentration specific. For example, multivalent cations can increase sorption by acting as bridges between anionic PFASs and negatively charged surfaces (Kim et al., 2015), whereas anions (e.g., Cl-, SO42- or Cr2O72-) have been reported to compete with anionic PFASs for adsorption sites. (in boehmite, chitosan and resins) leading to increased solubility of anionic PFASs (Du et al., 2014). This suggests that the observed seasonal variation of macro-constituents (e.g., Cl-, Ca2+, Mg2+, SO42-) in leachate (Kukliowska and Klimiuk, 2008) likely contributes to the observed variability and patterns of PFASs concentration in leachates. Sorption behavior is also affected by carbon chain length and the functional head group of the PFASs (Higgins and Luthy, 2006).

3.5.2. Biological processes inside landfills

Biodegradation is arguably one of the most important factors determining the fate of PFASs in landfills. Allred et al. (2015) and Lang et al. (2016) studied the evolution of PFASs into leachate using anaerobic landfill reactors (fed with MSW, carpets and clothing). While PFASs were released through a combination of biological (e.g., biodegradation) and abiotic (e.g., desorption) processes, the leachates from live bioreactors (producing methane) had on average 5 to 10 times higher ΣPFAS than the average for biologically inactive reactors (Lang et al., 2016; Allred et al., 2015). Following the onset of methanogenic conditions, concentrations of known biodegradation intermediates of PFAA precursors (i.e., methyl-perfluorobutane sulfonamide acetic acid (MeFBSMA), n:2 and n:3 FTCAs) increased steadily, with 5:3 FTCA becoming the single most concentrated PFAS (Allred et al., 2015). While the aforementioned studies have provided some valuable insights into the release of PFASs in landfills, further research including measurement of semi-volatile PFASs is needed to fully comprehend the transformation process.

Landfill operating conditions, such as leachate recirculation, could be important factors affecting biodegradation. For example, Benskin et al. (2012) reported order of magnitude lower ΣPFAS concentrations, (consisting entirely of PFASs) in recirculated leachate, compared with flow-through leachate containing both PFASs and their precursors (31–71% PFAS and 29–69% PFAA-precursors). While it is possible that the PFAS profile observed in the single recirculated leachate sample was not representative of leachate from this site over the long term, another explanation could be that recirculating leachate back to the landfill facilitated more biodegradation of PFAA-precursors (Benskin et al., 2012). While Huset et al. (2011) observed slightly higher ΣPFAS-precursors in flow-through leachate, the few other studies which measured PFAS-precursors (Lang et al., 2017; Allred et al., 2014) did not identify the recirculated leachate sample. Therefore the observations of Benskin et al. (2012) need to be substantiated by other studies.

3.5.3. Effect of climate

Precipitation can dilute leachate, resulting in decreased PFAS concentration within a time frame of a single day (Gallen et al., 2017; Benskin et al., 2012). On the other hand, changes in the moisture content of wastes resulting from rainfall can affect hydrolysis reactions and bioactivity (through bacterial growth, mixing of leachate resulting in PFAS concentration change, etc.) inside landfill over longer periods (e.g., 2 weeks) (Benskin et al., 2012). However, Benskin et al. (2012) did not observe any significant correlations between any PFAS congenor and cumulative 2-week precipitation for temporal leachate samples collected from a landfill. A more recent study (Lang et al., 2017) of 18 landfills located in different climatic conditions (wet, temperate and arid) observed that several PFAS compounds (perfluorononanoic acid (PFNA), perfluorooleic acid (PFDA), PFBS, PFOS, 6:2 FTSA, and...
methyl-perfluorooctane sulfonamide acetic acid (MeFOSAA)) had significantly higher concentrations in leachates from wet climates, suggesting that leaching governed release of these compounds.

3.5.4. Effect of waste age and waste composition

Statistically significant decreases in the concentrations of several PFASs with increasing landfill age have been observed in studies of multiple landfills (both active and closed) (Gallen et al., 2017; Lang et al., 2017; Busch et al., 2010). This trend could result from industrial significant shift of PFASs used in consumer products (Gallen et al., 2017; Lang et al., 2017). For example, Lang et al. (2017) observed higher PFAS and PFNA concentration in leachate from young waste, possibly due to increasing manufacture of PFBS- and PFNA-based products as alternatives to PFOS- and PFOA-based products. Decreases in the concentrations of PFASs in wastes (e.g., due to biodegradation) could account for the observed decreasing trend of PFAS degradation intermediates (e.g., 8:2 FTCA, 5:3 FTCA, MePBSAA and MeFOSA) with landfill age (Lang et al., 2017). PFASs with similar concentrations in old and young wastes, will likely continue to be released for many years (Lang et al., 2017). Collected leachate samples often contained mixtures of leachate which have undergone various stages of degradation from various waste cells. As a result, it is impossible to comment on the effect of any specific stabilization stage on the PFAS concentration. The above-mentioned studies considered the total period of operation (final year minus opening year) to calculate the average age of the waste.

Lab-scale anaerobic reactors treating various types of refuse, such as MSW (Allred et al., 2015), carpets and clothing (Lang et al., 2016), have demonstrated the abundance of various classes of PFAS, indicating the importance of waste type in determining the PFAS concentration. For example, Lang et al. (2017) observed that short carbon-chain (≤6) PFAS were dominant in reactors treating waste carpets, whereas reactors treating clothing accumulated short-chain PFCA, PFOA, and 8:2 FTSA. High variability in total PFAS release was observed, even for reactors receiving similar types of waste (i.e., clothing) (Lang et al. 2016). Gallen et al. (2017) also observed that leachate from operating landfills accepting >50% construction and demolition waste generally had higher PFAS concentrations compared to landfills accepting >50% MSW. Understanding PFAS trends due to variation in waste type could be challenging considering the variation in PFAS contents in similar categories of waste (Lang et al., 2016), the heterogenous nature of the solid waste and uncertainties surrounding the input of solid wastes to landfills.

4. Fate of PFAS in leachate treatment systems

One of the most common waste management practices is to send leachate to an off-site domestic WWTP. The fate and occurrence of PFASs in WWTPs have recently been thoroughly reviewed by Arvaniti and Stasinakis (2015), and are outside the scope of this paper. Other leachate management options include on-site pre-treatment, followed by off-site discharge at a WWTP, and complete treatment and discharge on-site (Townsend et al., 2015). Leachate treatment options can be broadly categorized as either physio-chemical treatment (e.g., coagulation-floculation, chemical precipitation, membrane filtration, activated carbon adsorption, chemical oxidation) or biological treatment (e.g., activated sludge system, aerated lagoon) (Foo and Hameed, 2009; Renou et al., 2008). Similar technologies are also used for groundwater and drinking water treatment, and their effectiveness in groundwater PFAS has been reviewed elsewhere (Merino et al., 2016; Rahman et al., 2014). Therefore, the focus of this section is to discuss removal/fate of PFASs specifically resulting from landfill leachate treatment.

Several studies (Fuertes et al., 2017; Yan et al., 2015; Busch et al., 2010) reported an overall increase in PFAA concentrations following on-site biological leachate treatment, which is consistent with their persistent nature and possible formation from PFAS-precursors. The extent of formation observed was analyte- and site-specific, ranging between 10 and 250% for individual PFAAs (Yan et al., 2015). A wet air oxidation process contacting with ozone to create OH-radicals to degrade contaminants, also showed slightly higher (≤5%) ∑PFAA concentrations in the effluent leachate, but the increase was less than for biological treatment (Busch et al., 2010). An adsorption technique using activated carbon was reported to be somewhat effective (removal efficiency ranges between 70 and 99%) in removing PFAAs from leachate (Busch et al., 2010). High-pressure membrane filtration techniques such as reverse osmosis (RO) and nanofiltration (NF) removed >95% PFAAs directly from leachate (Busch et al., 2010) and from biologically-treated leachate (e.g., membrane bioreactor; followed by RO or NF) (Yan et al., 2015). On the other hand, Fuertes et al. (2017) found that ultrafiltration (UF) integrated with membrane bioreactors showed little or no removal of PFAAs. Despite the success of high-pressure filtration systems, disposal of PFAS-rich concentrate remains a challenging issue in need of careful consideration (Rahman et al., 2014).

5. Future research directions

While the presence of various classes of PFASs in landfill leachate is well documented in North America, several Northern European countries, Australia and China, no data exist for South and Southeast Asia, Southern Europe and Africa. Considering the lack of regulations limiting the manufacture and use of C8-based PFASs and the lack of pollution abatement measures such as leachate collection systems and lining materials (Ismail and Manaf, 2013), landfills in these countries could be a significant source of PFASs in the environment. This could undermine regulatory initiatives in some parts of the world, due to the long-range transport and persistence of some PFASs (such as PFAAs).

Widespread application of FTPs to consumer products (e.g., paper, textiles, leather) (Rao and Baker, 1994) imply that most FTP products will ultimately be landfilled (Washington and Jenkins, 2015). Despite the decade-long debate on their stability, recent studies show that FTPs can undergo abiotic (Washington and Jenkins, 2015) and biological hydrolysis releasing FTOHs, which then biodegrade to PFCS with an estimated half-life range of 8–100 years (Washington et al., 2015; Rankin et al., 2014). Therefore, degradation of FTPs under landfill conditions (e.g., anaerobic, pH>7) needs to be studied, including the measurement of semi-volatile compounds (e.g., FTOHs). As indicated by Washington et al. (2014), concentrations of volatile degradation products of FTP measured by GC-MS could be much more than an order of magnitude higher compared to non-volatile PFASs measured by LC-MS/MS.

To avoid significant underestimation of the total PFAS released with landfill leachate, PFAS-precursors and their degradations products (e.g., n:3 FTCA, PSAA) should be included in monitoring studies. Phillips et al. (2007) reported a 100-times smaller toxicity threshold of FTCA compared to PFCS for freshwater microorganisms. PFAS-precursor concentrations in leachate would provide valuable information from a water quality perspective as well. Owing to the semi-volatile nature of some precursor compounds and their degradation products, studies need to include landfill gas to understand degradation pathways and the overall fate of PFASs. This would also enable more realistic assessments of the release of PFASs to the environment with landfill gas.
More than 3000 PFAs are available on the market, and the identity of many are unknown (Wang et al., 2017). In addition to the maximum number (70 compounds) of PFAs studied in landfills, there must be more PFAs present in landfill leachates. Application of non-targeted methods (e.g., total oxidable precursor assay, total fluoride analysis) could provide valuable information regarding the unknown PFASs in leachates. New analytical techniques including PFAS classes never studied in leachate could provide useful information. For example, among the legacy PFASs, mixtures of C6–C12 perfluoralkyl phosphonic and phosphoric acids (PFPPAs and PFOPAs) used as wetting agents in consumer products (Wang et al., 2016); FTI, fluorotelomer acrylate and fluorotelomer methacrylate (FTMAC) used in impregnating agents (and their degradation products) (Favreau et al., 2017) should be included in landfill studies. Emerging PFAS like perfluoropolyethers (PFPEs), used as fluorinated alternatives of PFOS and PFOA in fluoropolymer manufacture (e.g., ADAOA from 3M/Dyneon (CF3OCF2CF2OCO(NH4)), GenX from DuPont (CF3OCF2OC(F3)COO-NH4)), surface treatment food contact material (Wang et al., 2013), are now being increasingly detected in various environmental media, as outlined in a recent review (Xiao, 2017). Research gaps regarding fate and transport of the emerging PFAs (e.g., PFEPs) in the environment (including landfills) need to be addressed.

While the fate and release of PFASs in landfill have been studied to some extent, very limited research exists on the performance of common containment practices (e.g., landfill liners). Leaching cell tests with sand/bentonite mixture barriers showed partial retention of PFASs (10 PFCAs, 4 PFSAs, 1FOSA and 3 rMCA), decreasing over time, indicating limited effectiveness of sodium bentonite liners in landfills in containing PFASs (Li et al., 2015). Therefore, more research is needed to evaluate the effectiveness of current containment practices and how they can be improved to reduce PFAS emissions from landfills.

6. Conclusions

This study reviews publications which have reported the occurrence and sources of PFASs in landfills, to identify temporal and geographical trends of PFASs in landfill leachate and to identify and discuss factors affecting PFASs in landfills. The need for further research has been discussed. Research over the past decade has shown that PFASs are routinely detected in landfill leachate, with short chain (C4–C7) PFASs being more abundant than longer-chain ones, possibly reflecting greater mobility and increasing application of shorter-chain compounds. Despite its restricted use, PFOA remains one of the most frequently detected and abundant PFASs in landfill leachate. This indicates that, if not managed properly, landfills could act as secondary sources of PFOS in the environment.

Recent studies also document the presence of PFAS-precursors and their degradation products in landfill leachate, at concentrations comparable to, or higher than, the most frequently detected PFASs (e.g., PFBA, PFOA, PFOs). Landfill ambient air also contains elevated concentrations of PFASs, primarily semi-volatile precursor compounds (such as FTOHs), compared to upwind control sites, suggesting that landfills likely act as emission sources of atmospheric PFASs. The fate and transformation of PFASs inside landfills are complex, affected by combinations of external (e.g., climate, waste input) and internal (e.g., biodegradation, sorption) factors. Release of most of the PFASs from waste to leachate occurs as a result of biodegradation, closely associated with onset of the methanogenic phase. The methane yielding stage also results in higher pH (7–7) of leachate, correlated with greater mobility of PFASs.

Acknowledgment

The authors gratefully acknowledge scholarship assistance to Hanna Hamid from the Natural Science and Engineering Research Council of Canada (NSERC) (CGSD3-475849-2015) and The Schlumberger Foundation, Faculty for the Future fellowship program, as well as funding from an NSERC Discovery Grant (RGPIN 185040-13).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.12.030.

References


