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DOI:

[10.1016/j.scitotenv.2019.133810](https://doi.org/10.1016/j.scitotenv.2019.133810)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Harrad, S, Drage, D, Sharkey, M & Berresheim, H 2019, 'Brominated flame retardants and perfluoroalkyl substances in landfill leachate from Ireland', *Science of the Total Environment*, vol. 695, 133810, pp. 1-7. <https://doi.org/10.1016/j.scitotenv.2019.133810>

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**Brominated Flame Retardants and Perfluoroalkyl Substances in
Landfill Leachate from Ireland**

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12 **ABSTRACT**

13 Between June and November 2017, leachate samples were collected from 40 landfills
14 across the Republic of Ireland. Concentrations of perfluoroalkyl substances (PFASs),
15 polybrominated diphenyl ethers (PBDEs), and hexabromocyclodecane (HBCDD)
16 determined in these samples were within the range previously reported in other
17 countries. Average concentrations of PFASs exceeded those of PBDEs and HBCDD;
18 likely due to the higher water solubility of PFASs. Log-transformed concentrations of
19 BDEs-47, 100, 153, and 183, as well as perfluorooctanoic acid (PFOA),
20 perfluorononanoic acid (PFNA) and perfluorobutane sulfonate (PFBS) were
21 significantly ($p<0.05$) higher in leachate from newer, lined landfills than in samples
22 from unlined landfills. These higher concentrations in lined landfills are likely related
23 to the fact that lined landfills are found to retain organic matter leading to a higher
24 organic content of leachate from such landfills. This is evidenced by the significant
25 ($p<0.05$) correlation between log-transformed concentrations in leachate of most of the
26 same contaminants and those of chemical oxygen demand (COD). Concentrations of
27 the less water-soluble, higher molecular weight BDE-209 were not correlated with
28 leachate COD, nor landfill age or the presence of a landfill liner. This suggests that the
29 presence of BDE-209 in landfill leachate is driven more by physical abrasion of
30 particles and fibres from waste articles, than dissolution into the aqueous phase. The
31 higher concentrations of some PFASs and PBDEs in leachate from lined landfills
32 present a challenge with respect to leachate disposal, when leachate is sent to
33 wastewater treatment plants that do not necessarily have mechanisms in place to
34 remove or destroy these chemicals prior to discharge into the environment. Moreover,
35 the presence of these persistent organic chemicals in leachate from unlined landfills

raises concerns about releases to the environment including groundwater over the lifetime of such landfills and beyond.

HIGHLIGHTS

- PFASs, PBDEs, and HBCDD detected in leachate from Irish landfills
- Average concentrations of PFASs exceed those of BFRs
- Concentrations of most PFASs and PBDEs higher in lined than in unlined landfills
- Concentrations of some PFASs and PBDEs correlated with leachate COD
- BDE-209 in leachate likely associated with abraded particles from waste articles

INTRODUCTION

Brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) have found widespread application in goods and materials such as electrical and electronic equipment, as well as soft furnishings and fabrics (BiPRO, 2011). Likewise, perfluoroalkyl substances (PFASs) are widely applied to *inter alia* impart stain repellency to fabrics in both domestic and office environments (BiPRO, 2011, Miralles-Marco and Harrad, 2015). As articles containing such contaminants come to the end of their useful life, they enter the waste stream. One commonly-favoured waste disposal method has historically been landfill. While landfilling of waste electrical and electronic equipment (WEEE) has been severely restricted within the European Union (EU) since promulgation of the WEEE directive in 2003 (EC, 2003); no restrictions on landfilling of waste soft furnishings and fabrics exist, and landfills open before 2003 may contain WEEE received before this date. The presence of such material in landfill is of interest given much contains elevated

concentrations of PBDEs, HBCDD, and PFASs (Drage et al, 2018; Gallen et al, 2017). Concern about potential leaching of such contaminants from landfilled waste has been raised by a number of laboratory studies reporting on the magnitude and mechanisms of leaching of PFOS, PBDEs and HBCDDs under laboratory conditions (Allred et al., 2015, Choi et al., 2009, Danon-Schaffer et al., 2013, Kajiwara et al., 2014, Lang et al, 2016; Stubbings et al., 2016a,b). While such studies illustrate the potential for leaching under real-world conditions, the number of studies of leaching of BFRs and PFASs from landfill sites is limited (Allred et al, 2014, Busch et al, 2010; Daso et al., 2013, Gallen et al., 2016, 2017, Huset et al, 2011, Kwan et al., 2013, Odusanya et al., 2009, Osako et al., 2004, Weber et al., 2011; Yan et al, 2015). Consistent with EU policy (EC, 2011), Ireland is committed to phasing out landfill as a waste disposal option. In particular, by 2020 the objective is to ensure that landfilling is limited to residual (i.e. non recyclable and non recoverable) waste. As a consequence of this, there remain in 2019, only 5 active landfills operating in Ireland. However, there will likely have been substantial past disposal in Ireland of waste containing BFRs and PFASs in a much greater number of landfills. This study tests the hypothesis that disposal of such waste to landfill will have led to significant contamination of landfill leachate in Ireland consistent with observations elsewhere (mentioned above). To do so, we report concentrations of PBDEs, HBCDD, and PFASs in samples of leachate from landfills in the Republic of Ireland.

MATERIALS AND METHODS

Sampling - Leachate was collected between June and November 2017 from 40 municipal solid waste (MSW) landfill sites across the Republic of Ireland (Figure 1). Samples from sites without high density polyethylene (HDPE) liners (i.e. unlined sites)

were pumped from “boreholes” (pipes inserted into the landfill body for collection and sampling of leachate), while samples from newer state of the art sites (i.e. mixed and lined sites) were collected from on-site leachate storage tanks. At least 1 sample of leachate was collected from each landfill studied with 48 samples collected in total. Each sample consisted of 1 L leachate collected in polystyrene bottles that were pre-rinsed, in triplicate, with distilled water followed by a small aliquot of the sample to be collected. Following transfer to the laboratory, each sample was split, with one half analysed for BFRs and the other for PFASs.

Target analytes – The following BFRs and PFASs were targeted in this study: PBDEs 28, 47, 99, 100, 153, 154, 183, and 209; α -, β - and γ -HBCDD, and perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluoro-1-octanesulfonamide (FOSA), N-methylperfluoro-1-octanesulfonamide (MeFOSA), N-ethylperfluoro-1-octanesulfonamide (EtFOSA), 2-(N-methylperfluoro-1-octanesulfonamido)-ethanol (MeFOSE), and 2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol (EtFOSE).

Sample Extraction and Purification - For BFRs, 500 mL aliquots of each sample were subjected to gravity filtration through pre-cleaned polyurethane foam (PUF) plugs and a glass fibre filter (GFF) using similar methods to those reported previously (Yang et al. 2014). Following this filtration, the PUF disks and GFFs for each aliquot were allowed to dry under a fume hood. PUFs and filters were loaded into a 66 mL extraction cell and spiked with known masses of internal standards (BDE-77, BDE-128, $^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD, $^{13}\text{C}_{12}$ - β -HBCDD and $^{13}\text{C}_{12}$ - γ -HBCDD (Wellington

Laboratories)). Samples were then subjected to pressurised liquid extraction on an ASE 350 (Dionex) using hexane:acetone (1:1, v/v ratio) with a rinse volume of 40 %; at a temperature of 90 °C heated over 5 min; and purged over 90 sec. Extracts were concentrated under a gentle stream of nitrogen to ca. 0.5 mL in hexane and loaded onto an ENVI-florisil (3 mL/500 mg, Sigma Aldrich) SPE cartridge. Fraction 1 was eluted with 8 mL hexane. Fraction 2 was eluted with 10 mL acetone. Fraction 1 was further cleaned up by concentrating to 1 mL and washing with 1 mL >95% concentrated sulfuric acid. Fraction 2 was concentrated to 1 mL and transferred onto an ENVI-carb (3 mL/250 mg, Sigma Aldrich) SPE cartridge. Target compounds were eluted 20 mL acetone. Eluents were concentrated to 200 µL in toluene and transferred to autosampler vials. Both fractions were recombined, concentrated to 200 µL in toluene containing known quantities of PCB-129 (Greyhound Chromatography) and d₁₈-γ-HBCDD (Wellington Laboratories) as recovery determination standards.

For PFASs, 50 mL aliquots were loaded onto Oasis WAX cartridges (6 mL/150 mg, Waters) at 1 drop/second. Samples were spiked with known quantities of internal standards (M8PFOS, M8PFOA, M8FOSA, MPFHxS, MPFNA, d-N-MeFOSA, d-N-EtFOSA (Wellington Laboratories)). The cartridges were dried under vacuum for 30 minutes, and eluted with 4 mL methanol, followed by 5 mL methanol (0.1% NH₄OH). Eluents were concentrated at 35 °C under a gentle stream of nitrogen to ca. 0.5 mL and loaded onto an ENVI-carb (3 mL/250 mg, Sigma Aldrich) SPE cartridge. PFAS were eluted with 2 mL methanol (0.1% NH₄OH) and concentrated to 200 µL containing 10 ng of MPFOS (Wellington Laboratories) and transferred to inserted LC vials.

Instrumental Analysis

PBDEs (BDEs -28, -47, -99, -100, -153, -154, -183 and -209) were analysed on a Thermo TRACE 1310 GC coupled to a Thermo ISQ MS as described in Abdallah et al. 2017). HBCDDs (α -, β - and γ -) were analysed on an LC-MS/MS system composed of a Shimadzu LC-20AB Prominence liquid chromatograph coupled to a ABS Sciex API 2000 triple quadrupole mass spectrometer operated in negative ion mode. Full details are provided elsewhere (Abdallah et al. 2008)

PFASs (PFOA, PFOS, PFNA, PFHxS, PFBS, FOSA, EtFOSA, MeFOSA, EtFOSE, MeFOSE) were analysed on a Sciex Exion HPLC coupled to a Sciex 5600+ triple TOF MS. Ten microliters of extract was injected onto a Raptor C18 column (1.8 μ m particle size, 50 mm length, 2.1 mm internal diameter, Restek). Full details of the method including acquisition parameters and HPLC conditions are provided in the supporting information.

Quality Control

All samples were processed using procedures that have been previously validated (Harrad et al., 2010, Gallen et al. 2016). For ongoing accuracy of analysis of BFRs an aliquot of SRM-2585 (NIST) was analysed with every batch of samples (n=4). For PFAS, a MilliQ sample spiked with target compounds was also analysed with each batch of samples (n=4). All target analytes were found to be within 80-120 % of their certified or spiked values, with less than 15% relative standard deviation. Further information can be found in the Supporting Information. Four field blanks comprising distilled deionised water sampled from the same polystyrene leachate collection bottles were analysed in identical fashion to leachate samples. Concentrations of most target compounds were below detection limits in all blanks. Low concentrations of PFOA, PFHxS, PFNA, and PFBS were detected in 2, 1, 3, and 1 blanks at average

159 concentrations of 1.9, 1.0, 0.6, and 1.4 ng L⁻¹ respectively. In the majority of cases
160 blank concentrations were less than 5% of the sample concentrations, and were
161 therefore not corrected. In a small number of samples for PFNA (2 out of 48) and PFBS
162 (2 out of 48), the blank concentrations were between 15-20% of the sample
163 concentration. In these cases, the blank concentration from that particular batch of
164 samples was subtracted from the measured concentration. Therefore, method limits of
165 quantification were estimated based on a signal to noise (S/N) ratio of 10:1.

166

167 **Figure 1: Locations of landfills from which samples of leachate were taken in this**
 168 **Study (Map sourced and adapted from [https://www.ezilon.com/maps/europe/ireland-](https://www.ezilon.com/maps/europe/ireland-road-maps.html)**
 169 **[road-maps.html](https://www.ezilon.com/maps/europe/ireland-road-maps.html))**

RESULTS AND DISCUSSION

Concentrations of PBDEs, HBCDDs, and PFASs in Landfill Leachate from the Republic of Ireland

Table 1 summarises concentrations of selected PBDEs, Σ HBCDDs, and PFASs detected in leachate from Irish landfill in our study, and those from other studies. Data were acquired for PFASs, PBDEs, and HBCDDs in 48, 46, and 43 samples respectively – the numbers of samples analysed for the different compound groups varies slightly because of sample losses at different points of the extraction and purification process. A full list of concentrations of all target PBDEs, HBCDDs, and PFASs in each individual sample is provided in supporting information (Tables S1 and S2).

As evidenced by the wide range of concentrations detected, our data reveal substantial inter-landfill variation in concentrations of our target BFRs and PFASs detected in leachate from Irish landfills.

Concentrations detected in this study of leachate from Irish landfills are at the low end of the range of those reported elsewhere in the world for PBDEs and are within the range of those reported previously for PFASs (Table 1). To our knowledge, our study is only the fourth report of HBCDD in landfill leachate worldwide and the first in Europe. Concentrations in our study are similar to those reported previously in Australia (Gallen et al, 2016), Japan (Suzuki and Hasegawa, 2006), and South Africa (Olunkunle and Okonkwo, 2015).

Predominant BFRs and PFASs in Irish Landfill Leachate

Likely due to their greater aqueous solubility, concentrations of PFASs generally exceed those of PBDEs and HBCDD, with the median Σ PFAS: Σ BFR ratio being 300 (in samples where all compounds were measured). The predominant PBDEs in our samples were as follows: BDE-209 (arithmetic mean expressed as a percentage of the arithmetic mean of Σ PBDEs = 51 %), BDE-47 (22 % Σ PBDEs), and BDE-99 (14 % Σ PBDEs).

With respect to PFASs, the predominant compounds were: PFBS (arithmetic mean = 1100 ng L⁻¹) > PFOA (790 ng L⁻¹) > PFOS (270 ng L⁻¹) > PFHxS (200 ng L⁻¹) > PFNA (30 ng L⁻¹). Other target PFASs i.e. FOSA, MeFOSA, EtFOSA, MeFOSE, and EtFOSE were detected rarely if at all.

For HBCDDs, while the arithmetic mean concentrations of α - and γ -HBCDD were similar (1.9 and 2.0 ng/L), γ -HBCDD was detected more frequently (detection frequency of 58% c.f. 23% for α -HBCDD). The generally higher abundance of the γ -diastereomer likely reflects the presence in our studied landfills of HBCDD-treated waste such as expanded polystyrene (EPS) building insulation foam, as the γ -diastereomer predominates (α : γ ratio <0.14) in the commercial HBCDD formulation used to flame retard such foam (Peled et al, 1995), and also predominates in Irish polystyrene packaging and building insulation foam (Abdallah et al, 2018).

Factors influencing concentrations of PBDEs, HBCDD, and PFASs in landfill leachate.

The presence or absence of a landfill liner

To prevent landfill leachate contaminating the surrounding environment including groundwater; modern landfills are constructed with an impervious HDPE liner. This contrasts with older landfills that are unlined. Moreover, some landfills operational

before the use of such liners continued operations but were required to retrospectively fit new waste cells with HDPE liners; such landfills are categorised here as “mixed”. While other factors, such as the mass of BFRs and PFASs present in a landfill, will exert an important influence on concentrations of these contaminants in leachate; we hypothesised that concentrations of BFRs and PFASs in leachate from lined landfills would exceed those in leachate from unlined landfills – as the liners are designed to retain such contaminants within the landfill, and prevent their leaching into the environment. To test this hypothesis, we compared log-transformed concentrations of individual contaminants in unlined landfills with those in lined landfills using a t-test. This (see Table 2) revealed concentrations of the following contaminants to be significantly higher ($p < 0.05$) in leachate from lined than unlined landfills: PFOA, PFNA, PFBS, BDE-47, BDE-100, BDE-153, BDE-183, and Σ PBDEs. While we hypothesised that concentrations in “mixed” landfills would be intermediate to those in their lined and unlined counterparts; the data on the lined or unlined status of our landfills was only considered fully reliable for those landfills categorised here as either lined ($n=15$) or unlined ($n=17$). As we could not definitively categorise the remaining 16 landfills, we did not include these in our statistical evaluation of the influence of landfill lining. However, as Table 2 shows, for many contaminants (specifically: PFOA, PFHxS, PFNA, PFBS, and BDE-47) our data showed leachate from these “mixed” landfills to contain median concentrations that were lower than in leachate from lined and greater than those in leachate from unlined landfills.

Period during which landfill was operational

We examined possible linear correlations between log-transformed concentrations of PFASs and BFRs in landfill leachate and the year the landfill opened and closed

(assumed as 2019 for landfills still open), as well as the number of years for which the landfill was open. There were no significant correlations between concentrations and the length of time the landfill was open. However, the year of landfill closure displayed a significant ($p<0.05$) positive linear correlation with concentrations in leachate of: PFOA ($R=0.38$), PFNA ($R=0.57$), PFBS ($R=0.56$), BDE-47 ($R=0.38$), BDE-100 ($R=0.33$), BDE-99 ($R=0.33$), BDE-153 ($R=0.40$), and BDE-183 ($R=0.36$). These correlations are likely to be due to the increase in use of these chemicals between 1980-2000 (Gallen et al. 2016, Gallen et al. 2017). Given that products containing these chemicals, would have a lifetime in-use of anywhere from 5-20 years, it is likely that those landfills closing later are likely to receive greater quantities of waste containing these particular chemicals. Similar significant ($p<0.05$) positive linear correlations were also detected between leachate concentrations and the year of landfill opening for: PFNA ($R=0.30$) and PFBS ($R=0.31$). PFNA and PFBS have mostly been used as replacements for PFOA and PFOS respectively since their restrictions, meaning that they have been used more intensively in recent years (Loughran & Managahas, 2019). This potentially explains why they also display positive correlations with landfills that have opened more recently as such landfills are likely to have received greater quantities of waste containing PFNA and PFBS. Our finding that newer leachate from newer landfills contains higher concentrations of some PFASs and BFRs, is consistent with that of Gallen et al (2017), who reported leachate from operating landfills in Australia to contain higher concentrations of PFASs than leachate from closed landfills.

Leachate pH and Chemical Oxygen Demand (COD)

While we did not measure parameters other than BFR and PFAS concentrations in leachate in this study, we were able to access from an on-line repository managed by

the Environmental Protection Agency of Ireland (EPA), data obtained during routine leachate monitoring by the landfill operators of both pH and COD (EPA, 2019). A minimum of one measurement per landfill was obtained and where more than one measurement was available, the average value was used. In most instances these measurements were made during 2018, but in a few cases they were taken earlier than this, with the exact dates provided in supporting information (Table S3). Using these data, we examined linear correlations between log-transformed concentrations of individual BFRs and PFASs and both pH and COD.

Gallen et al (2017) reported that log-transformed concentrations of PFASs (including PFOA, PFNA, PFOS, and PFHxS) in Australian landfill leachate were associated with increased pH. Similar analysis of our data, revealed a significant ($p < 0.05$) positive linear relationship between leachate pH and log-transformed concentrations of PFOA ($R = 0.38$) and PFNA ($R = 0.40$), but no such correlations with any of our target BFRs. The reason why some PFASs have a positive linear relationship with pH but not PBDEs, is likely a result of repulsive electrostatic interactions with the anionic functional group head on some PFASs (Gallen et al, 2017), which is absent for PBDEs and HBCDDs. Gallen et al (2017) also reported that higher concentrations of PFASs in leachate were associated with higher concentrations of total organic carbon. In our study, significant ($p < 0.05$) positive linear correlations were detected between COD and concentrations of the following compounds: PFNA ($R = 0.33$), PFBS ($R = 0.37$), BDE-47 ($R = 0.53$), BDE-99 ($R = 0.51$), BDE-100 ($R = 0.52$), BDE-153 ($R = 0.46$), BDE-154 ($R = 0.37$) and Σ PBDEs ($R = 0.44$). As discussed below, COD is significantly higher in leachate from newer, lined landfills, which as discussed earlier also display significantly elevated concentrations of many of our target contaminants. It is noticeable that COD does not correlate with leachate concentrations of the higher

molecular weight BDEs -183, and -209. This may be due to their lower water solubility (World Health Organization & International Programme on Chemical Safety, 1994; Tittlemeier et al. 2002), which means their migration to leachate may occur to a greater extent via physical abrasion of polymer/fabric particles and fibres - which has been shown to occur under laboratory conditions for HBCDD-containing insulation foam (Stubbings and Harrad, 2019) and - which would not be related to the organic matter content of the leachate and thus its COD concentration. For the PFASs, association with dissolved organic matter is less likely than for BFRs, and thus the correlation between COD and PFBS may suggest more recent use of PFBS than the other PFASs targeted here (Loughran & Managahas, 2019). This is because as discussed below, COD is significantly higher in leachate from newer, lined landfills, which also display significantly elevated concentrations of PFBS. Moreover, close inspection of our data for PFBS, shows the correlation is driven largely by a single sample in which PFBS was detected at 17,000 ng L⁻¹, ~15 times the arithmetic mean for all samples. Removal of this sample as an outlier, renders the correlation insignificant (R=0.28; p>0.05).

CONCLUSIONS

Our data represent an important contribution to the international database on the presence of PFASs and BFRs in landfill leachate. We reveal that leachate from newer landfills fitted with impervious liners contain significantly higher concentrations of some PFASs and BFRs. Consistent with previous observations for landfill leachate from the Republic of Ireland (Brennan et al, 2016), t-test comparison of COD in lined and unlined landfills showed COD to be significantly greater in leachate from newer, lined landfills. Given COD was significantly positively correlated with log-transformed

leachate concentrations of 6 of our target contaminants, it appears that such higher concentrations of COD in lined landfill leachate (presumably due to less dilution than in unlined landfills), provides a plausible at least partial explanation for the higher concentrations of some PBDEs and PFASs in leachate from newer, lined landfills. Finally, it is important to note that while the higher contaminant levels on leachate from lined landfills presents a challenge in treatment and disposal of the leachate (note that in Ireland all lined and mixed landfills are required to send their leachate off-site for treatment), our data also raises concern about the environmental fate of PFASs and BFRs present in leachate from those unlined landfills that do not send their leachate for treatment.

Acknowledgement

This project (FUEL, reference 2015-HW-MS-4) is funded under the EPA Research Programme 2014-2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Communications, Climate Action and Environment.

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457 **Table 1: Summary of Concentrations (ng L⁻¹) of Selected BFRs and PFAS in Landfill Leachate from Ireland and Comparison with**
458 **Arithmetic Mean Concentrations in Selected Other Studies**

	BDE-47	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣBDEs	α-HBCDD	γ-HBCDD	ΣHBCDD	PFOA	PFOS	PFNA	PFBS	FOSA	PFHxS
Minimum (This Study)	<0.1	<0.3	<0.4	<0.4	<0.4	<1.0	<1.0	<0.2	<0.2	<0.2	9.0	<0.1	0.61	<0.1	<0.2	<0.1
Median (This Study)	<0.1	<0.3	<0.4	<0.4	<0.4	3.4	6.5	<0.2	0.69	1.0	230	83	7.6	79	<0.2	34
Arithmetic Mean (This Study)	9.6	6.0	0.93	1.3	0.89	22	43	1.9	2.0	4.1	790	270	30	1100	2.3	200
Maximum (This Study)	140	58	14	22	11	220	400	37	16	43	11000	7400	250	17000	65	2600
Detection Frequency (%)^a	57	20	24	33	37	59	85	23	58	65	100	94	100	85	23	79
Australia (Gallen at al, 2016)	43	54	9.1	15	12	18	170	0.7	0.6	1.8	450	310	17	250	-	380
Japan (Suzuki and	-	-	-	-	-	-	-	<2	4.2	6.2	-	-	-	-	-	-

Hasegawa, 2006)																
South Africa (Olokunle and Okonkwo, 2015)	-	-	-	-	-	-	-	-	-	0.024	-	-	-	-	-	-
South Africa (Daso et al, 2013)	230	220	62	880	480	950	2600	-	-	-	-	-	-	-	-	-
Canada (Li et al, 2012)	16	33	-	-	3	85	170	-	-	-	440	280	-	-	8.0	-
USA (Huset et al, 2011)	-	-	-	-	-	-	-	-	-	-	660	110	23	570	1.7	340
Germany (Busch et al, 2010)	-	-	-	-	-	-	-	-	-	-	150	31	7.3	220	2.8	22
China (Yan et al, 2015)	-	-	-	-	-	-	-	-	-	-	49000	2700	150	15000	-	130

459 ^aonly those BFRs/PFAS with detection frequency ≥ 20 % shown

460 ^bfor the purposes of calculating descriptive statistics, “not detects” replaced by $df \times LOD$, where df = the fractional detection frequency and LOD

461 = the detection limit

462

463 **Table 2: Comparison of Concentrations (ng L⁻¹) of Selected BFRs and PFAS in Leachate from Lined, Unlined, and “Mixed” Irish Landfills**

Landfill Type		BDE -47	BDE -99	BDE -154	BDE -153	BDE -183	BDE -209	ΣBDEs	α-HBCD	γ-HBCD	ΣHBCD	PFOA	PFOA	PFNA	PFBS	FOSA	PFHxS
Unlined (PBDE n=17, HBCD n=16, PFAS n=18)	Median	<0.1	<0.3	<0.4	<0.4	<0.4	<1.0	2.2	<0.2	0.21	0.97	92	84	3.4	11	<0.2	12
	Arithmetic Mean	1.2	1.1	0.97	0.19	0.22	22	28	0.48	2.1	2.7	860	97	6.7	20	0.35	32
	Standard Deviation	3.0	2.7	3.4	0.13	0.14	57	66	1.0	4.2	4.3	2700	93	8.3	30	0.86	39
Mixed (PBDE n=15, HBCD n=12, PFAS n=15)	Median	<0.1	<0.3	<0.4	<0.4	<0.4	15	22	<0.2	<0.2	<0.2	180	44	7.1	110	<0.2	37
	Arithmetic Mean	0.03	2.0	0.35	0.6	0.42	20	25	1.4	0.89	2.5	380	510	27	740	1.6	270
	Standard Deviation	0.06	4.7	0.52	0.8	0.52	26	27	3.4	1.8	6.2	400	1800	43	1800	3.6	690
Lined (PBDE n=14,	Median	2.5	<0.3	<0.4	<0.4	0.4	3.9	26	<0.2	1.3	1.9	590	140	26	500	<0.2	89
	Arithmetic Mean	28	16	1.5	3.2	2.2	21	80	1.6	2.2	4.0	1200	200	60	2600	5.4	330

HBCD D n= 14, PFAS n=15)	Standard Deviation	46	23	3.0	6.1	3.7	34	120	3.7	2.9	6.6	1400	270	69	4500	17	610
	P value*	0.015	0.092	0.383	0.03	0.013	0.343	0.05	0.667	0.182	0.231	0.004	0.502	<0.00 1	<0.00 1	0.179	0.19

464 *p value for t-test comparison of concentrations in leachate from unlined and lined landfills