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Furthering Understanding of Emissions from Landfilled Waste Containing POP-BFRs and PFASs (FUEL)

Authors: Stuart Harrad, Daniel Drage, Martin Sharkey and Harald Berresheim

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Rialtas na hÉireann
Government of Ireland

ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

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- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

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Furthering Understanding of Emissions from Landfilled Waste Containing POP-BFRs and PFASs (FUEL)

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by

University of Birmingham

and

National University of Ireland Galway

Authors:

Stuart Harrad, Daniel Drage, Martin Sharkey and Harald Berresheim

ENVIRONMENTAL PROTECTION AGENCY
An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

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The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Project Partners

Stuart Harrad
School of Geography, Earth and Environmental Sciences
University of Birmingham
Birmingham
B15 2TT
UK
Tel.: +44 (0) 121 414 7298
Email: s.j.harrad@bham.ac.uk

Daniel Drage
School of Geography, Earth and Environmental Sciences
University of Birmingham
Birmingham
B15 2TT
UK
Tel.: +44 (0) 121 414 7243
Email: d.s.drage@bham.ac.uk

Martin Sharkey
School of Physics and Centre for Climate Studies
National University of Ireland Galway
Galway
Ireland
H91 CF50
Tel.: +353 (0) 87 642 3705
Email: martin.sharkey@nuigalway.ie

Harald Berresheim
School of Physics and Centre for Climate Studies
National University of Ireland Galway
Galway
Ireland
H91 CF50
Tel.: +353 (0) 91 49 5705
Email: harald.berresheim@nuigalway.ie

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Executive Summary

Brominated flame retardants (BFRs) and perfluoroalkyl substances (PFASs) have found extensive use in electrical and electronic goods, soft furnishings and building insulation foam to impart flame retardancy and stain resistance. Following concerns about their persistence and their ability to bioaccumulate and cause adverse health effects in humans and wildlife, some BFRs and PFASs have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), an international treaty designed to eliminate POPs from the environment. While such actions have severely restricted the manufacture and new use of such contaminants, there remains a substantial reservoir that has entered the waste stream and will continue to do so for some years. Moreover, despite Irish national and EU policies severely limiting use of landfill, many items treated with BFRs and PFASs are likely to be present in Irish landfills. This is concerning, as reports from other countries show that landfill leachate contains such chemicals. In this study, we measured PFASs, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDDs) in leachate from 40 landfills within Ireland. Levels detected were within the range previously reported elsewhere. Average concentrations of PFASs exceeded those of PBDEs and HBCDDs. Concentrations of some PBDEs and PFASs were significantly ($p < 0.05$) higher in leachate from newer, lined landfills than in samples from unlined landfills. This is probably because lined landfills retain organic matter, leading to a higher organic content of leachate in such landfills; this is supported by the significant ($p < 0.05$) correlation between concentrations in leachate of most of the same contaminants and those of chemical oxygen demand (COD) – an indicator of organic matter content.

In a second phase of the study, air and soil samples were collected from locations downwind and upwind of 10 Irish landfills. Groundwater was also collected from locations with links traceable to the landfills studied. Concentrations of PFASs, PBDEs, HBCDDs and decabromodiphenyl ethane (DBDPE) in air and soil samples were not significantly different ($p > 0.05$) between downwind and upwind locations. The arithmetic mean concentration of perfluorooctanoic acid (PFOA) in groundwater from landfills that were not fully lined ($n = 4$; 69 ng/L) exceeded that in groundwater sourced from lined landfills ($n = 6$; 4.1 ng/L), although this was not statistically significant ($p > 0.1$). A positive correlation ($p = 0.014$) was observed between concentrations of PFOA in groundwater and those in leachate from the same landfills. However, this was driven substantially by one landfill that displayed the highest concentrations in both groundwater and leachate. DBDPE was detected in groundwater for the first time anywhere, in all samples at concentrations (median = 9.4 ng/L; arithmetic mean = 78 ng/L) that exceeded those of any of the other BFRs or PFASs measured. This probably reflects its use as a “drop-in” replacement for the recently restricted decabromodiphenyl ether (BDE-209).

Laboratory experiments were conducted to examine leaching of BDE-209 and HBCDDs from fabrics. Concentrations in leachate were markedly higher in the first 24 hours, diminishing by an order of magnitude after 1 week. The influence of the waste-to-leachate ratio was examined, with leaching of both BDE-209 and HBCDDs significantly greater ($p < 0.05$) at a waste-to-leachate ratio of 0.005 g/mL than at one of 0.05 g/mL. Using dissolved humic matter (DHM) solutions as proxies for organic landfill leachates, leaching of both BDE-209 and HBCDDs was significantly greater at higher DHM concentrations. Agitation of waste-to-leachate mixtures significantly enhanced leaching. While leaching of HBCDDs decreased significantly as leachate pH increased from 5.8 to 6.5 and to 8.5, no significant impact of pH on leaching of BDE-209 was detected. Concentrations of both BDE-209 and HBCDDs in leachate decreased significantly on increasing leachate temperature from 20°C to 60°C and then 80°C. This is considered most likely to be due to volatilisation of these contaminants into the headspace of the leaching vessel at higher temperatures.

Finally, a desktop study suggests that even over the estimated 75-year aftercare timeline of most landfills, the quantities of PBDEs, HBCDDs and PFASs associated with landfill leachate represent only a very small fraction of those present overall in the Irish waste stream.

The following recommendations are made:

- Concentrations of PFASs in groundwater potentially affected by unlined or partially lined landfills should be monitored closely.
- Leaching of BFRs and PFASs may be minimised by reducing the organic matter content of leachate.
- Further monitoring in landfill leachate and groundwater of concentrations of DBDPE and other chemicals designed as replacements for restricted BFRs and PFASs is recommended.
- Restrictions on the landfilling of textiles would reduce the quantity of BFRs and PFASs entering landfill.
- Further research should be conducted into methods for treating collected leachate to remove PFASs.

1 Introduction

1.1 Sources and Applications of PBDEs, HBCDDs and PFASs

Brominated flame retardants (BFRs) such as hexabromocyclododecanes (HBCDDs) and polybrominated diphenyl ethers (PBDEs) have found extensive use worldwide as flame retardants (FRs) in a wide variety of commercial, domestic and industrial applications. Applications of PBDEs include electrical and electronic equipment (EEE – e.g. televisions, personal computers, small domestic appliances) and soft furnishings (e.g. sofas, mattresses, curtains, pillows). In the former case, PBDEs were added both to the polymer casing for electronics [e.g. high impact polystyrene (HIPS) or acrylonitrile butadiene styrene (ABS)] and to internal circuit boards. In addition, they were added both to the foam fillings and to the fabric covers of soft furnishings such as sofas and chairs in domestic, office or vehicular environments. With respect to HBCDDs, the most important application (96% of all uses in the EU) was its widespread use as an FR in expanded polystyrene (EPS) and extruded polystyrene (XPS) used in building insulation foam in the construction industry (ECHA, 2009), with some minor application to plastic housing for electronics (Weil and Levchik, 2007). As of 2001 (the last reliable figures publicly available), Europe accounted for 2%, 16%, 14% and 57% of the annual global demand for penta-BDE, octa-BDE, deca-BDE and HBCDDs, respectively (BSEF, 2003).

Perfluoroalkyl substances (PFASs) are an important family of synthetic compounds characterised by a fully fluorinated hydrophobic linear carbon chain, to which are attached different hydrophilic functional groups (Fromme *et al*., 2009). These chemicals have been manufactured by the 3M Company (3M, 1999) as well as by other companies such as Dupont, and have been produced and used in commercial products and industrial processes for many years (Lindstrom *et al*., 2011). PFASs possess low molecular polarisability, short carbon–fluorine (C-F) bond length and large C-F bond binding energy. Such characteristics govern the oil and water repellency, physical and chemical stability, and surfactant properties of PFASs (Zushi *et al*., 2012). These properties mean that PFASs have found wide use in a variety of applications, with historical production peaking at the end of the 20th century in North America and Europe (Paul *et al*., 2009). The history of PFAS production is difficult to portray accurately owing to the proprietary nature of this information (Lindstrom *et al*., 2011), but the 3M Company was the first main producer of perfluorooctane sulfonyl fluoride (POSF) [an intermediate product for the synthesis of perfluorooctane sulfonate (PFOS)], with the total cumulative production estimated to be approximately 96,000 tonnes in the peak years between 1970 and 2002 (Paul *et al*., 2009). In 2002, the 3M Company discontinued production of POSF; however, other companies commenced manufacture at this point to meet existing market demands, with an estimated 1000 tonnes being produced annually since 2002 (Paul *et al*., 2009). The major applications of POSF derivatives have been (1) in carpets and other fabrics (including vehicle seat covers) to impart stain and dirt repellence, (2) in clothing to provide water repellence, (3) in paper and packaging to afford oil and grease repellence, (4) in performance chemicals such as hydraulic fluids for aviation, and (5) in aqueous fire-fighting foams (AFFFs). Prior to the widespread restrictions on PFOS from the early 21st century onwards, AFFFs were perhaps the most prominent method of widespread environmental dispersal from their use in oil drilling and military fire-fighting practice (Paul *et al*., 2009).

1.2 Toxicity of POP-BFRs and PFASs

Animal studies have shown PBDEs to pose potential health risks, including endocrine disruption, neurodevelopmental and behavioural outcomes, hepatic abnormality and possibly cancer (Birnbaum and Staskal, 2004; Darnerud, 2003; Hakk, 2010; Wikoff and Birnbaum, 2011). The few data available from human epidemiological studies imply effects on male reproductive hormones (Palace *et al*., 2010; Johnson *et al*., 2013), semen quality (Akutsu *et al*., 2008), thyroid hormone homeostasis (Turyk *et al*., 2008), cryptorchidism (Crump *et al*., 2010), behavioural factors in pregnant women (Buttke *et* *al.*, 2013), and have been suggested to have a link to lower birth weight and length (Chao *et al.*, 2007; Lignell *et al.*, 2013). The Dutch National Institute for Public Health and the Environment (RIVM) suggested a health-based limit value (HBLV) of 7 ng/kg body weight/day (bw/day) for human exposure to BDE-47 [neurodevelopmental toxicity and thyroid toxicity were identified as the critical endpoints (Bokkers *et al.*, 2011)] and a range of 0.23–0.30 ng/kg bw/day for exposure to BDE-99 [impaired spermatogenesis as the critical endpoint (Bakker *et al.*, 2008)]. The United States Environmental Protection Agency (US EPA) reported reference doses (RfD) of 100, 100, 200 and 7000 ng/kg bw/day for overall human exposure to BDE-47, -99, -153 and -209, respectively. It is noteworthy that these HBLVs and RfDs were exceeded in some high-end exposure scenarios of UK and US children and toddlers (Harrad *et al.*, 2010; Lorber, 2008). They were also exceeded occupationally for Thai workers in e-waste recycling facilities (Muenhor *et al.*, 2010). At a pan-European level, the European Food Safety Authority (EFSA) (2011a) delivered a scientific opinion that recommended a benchmark dose (BMD) for a number of PBDEs, concluding that, while dietary exposure in the EU to BDE -47, -153 and -209 was not of concern, the lower BMD for BDE-99 (12 µg/kg bw/day) was potentially so. An important caveat is that additional exposure to PBDEs via house dust was not explicitly considered by EFSA.

Oral exposure to HBCDDs was reported to induce hepatic cytochrome P450 enzymes and alter the normal uptake of neurotransmitters in rat brain. It can cause disruption of thyroid function, the reproductive system, nerve function and development in various classes of vertebrates (Marvin *et al.*, 2011). Overall daily intakes as high as 6000 ng/kg bw/day were estimated for some UK toddlers under worst-case exposure scenarios (Abdallah *et al.*, 2008). Moreover, as with PBDEs, EFSA (2011b) has published a scientific opinion recommending a BMD for HBCDDs, concluding that dietary and house dust exposure in the EU to HBCDDs was not of concern.

Several human health concerns exist over exposure to PFOS. These include hepatotoxicity, carcinogenicity, immunotoxicity and developmental toxicity (Andersen *et al.*, 2008), with associations between elevated blood levels of PFOS and elevated cholesterol levels also reported (Nelson *et al.*, 2010). More recent concerns about the potential adverse human health impacts of some PFASs are exemplified by the reports of the European Environment Agency (EEA, 2019) and Fidra (2020). Based on the toxicological evidence available to date, in mid-2018, EFSA proposed provisional tolerable weekly intakes (TWIs) for both PFOS and PFOA. At 13 ng/kg bw/week and 6 ng/kg bw/week for PFOS and PFOA, respectively (EFSA, 2018), these are substantially lower than those mentioned above. For PFOA, EFSA identified the key toxicological endpoint to be increased serum cholesterol in adults. By comparison, the critical toxicological endpoint identified by EFSA for PFOS was decreased antibody response post vaccination in children. EFSA is currently evaluating the evidence for human health effects arising from exposure to a range of other PFASs such as perfluorononanoic acid (PFNA) and perfluorohexane sulfonate (PFHxS). In February 2020, this EFSA opinion underwent public consultation (closing on 20 April 2020). If adopted, it will supersede these provisional TWIs. A single group TWI of 8 ng/kg bw/wk for PFOA, PFNA, PFHxS and PFOS, based on effects on the immune system observed in humans, is proposed (EFSA, 2020). In addition to this, some stringent guideline values have emerged recently in relation to the presence of PFASs in drinking water. These include that promulgated by Swedish authorities that specifies a limit of 90 ng/L for ∑PFASs (Livsmedelsverket, 2016), a US EPA HBLV of 70 ng/L for the sum of PFOS and PFOA concentrations (US EPA, 2016a,b), as well as a screening level of 40 ng/L (PFOA/PFOS) that in groundwater would “warrant further attention” (US EPA, 2019). Moreover, the same 2019 US EPA guidance lists drinking water standards of 14 ng/L, 13 ng/L and 13 ng/L for PFOA, PFOS and PFNA, respectively. Furthermore, a proposal to revise the Drinking Water Directive (Directive 98/83/EC) was recently agreed (Council of the European Union, 2020). This specifies a limit in drinking water of 100 ng/L based on the sum of a range of PFASs that include some but not all of those targeted in our study.

1.3 International Action to Limit Environmental Health Impacts

As highlighted above, the widespread use of PBDEs and HBCDDs has been the subject of concern, owing to their documented presence in the environment, including human tissues, coupled with evidence of their toxicity. At a global level, this concern is exemplified by the listing of HBCDDs and the penta-, octa- and deca-BDE commercial formulations under the United Nations Environment Programme Stockholm Convention on Persistent Organic Pollutants. Within the EU, the manufacture and new use of penta- and octa-BDE has been banned since the mid-2000s, and that of deca-BDE has been restricted severely since 2008. Since the 2013 listing under the Stockholm Convention of HBCDDs, use of this BFR has also been restricted, although there was a time-limited derogation that, up to the end of 2018, permitted its use within the EU in EPS and XPS for building insulation.

Likewise, the strong C-F bond means that PFASs are resistant to thermal, chemical and biological degradation (Kissa, 2001) and are capable of bioaccumulation and long-range environmental transport, exemplified by their detection in the Arctic (Chaemfa *et al*., 2010). As a result, PFOS and its salts, as well as POSF, were in 2009 listed as persistent organic pollutants (POPs) under the Stockholm Convention. More recently, in early 2019, PFOA was also listed under this Convention, with PFHxS recommended in October 2019 for further consideration for inclusion. Moreover, a potential proposal exists at the EU level to consider for listing under the Stockholm Convention C_{10}–C_{14} analogues of PFOA (including PFNA and its salts), which (along with PFOA and PFHxS) have also been listed under REACH (Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals) as substances of very high concern recommended for restriction (ECHA, 2019).

1.4 Environmental Hazard Presented by POP-containing Waste

Despite these recent restrictions, many items/products containing these PBDEs, HBCDDs and PFASs remain in use. Moreover, in view of the turnover times of such articles, it is further apparent that there is a growing inventory of materials containing restricted chemicals that have or will shortly be entering the waste stream. In 2011, more than 25,000 tonnes of waste electrical and electronic equipment (WEEE) were collected and 20,079 tonnes of hazardous waste were disposed of in landfills in Ireland (EPA, national hazardous waste management plan 2014–2020). In 2015 ≈3,313,858 tonnes of construction and demolition (C&D) waste was produced in Ireland (EPA, 2017). There are no specific data for the proportion of C&D waste in Ireland that is insulation material. However, in the UK it has been estimated that 2.8% of C&D waste is insulation material, 5% of which is EPS and XPS (Defra, 2010). This is of potential concern as waste EPS and XPS is often treated at percent concentrations with HBCDDs (Drage *et al.*, 2018). Assuming the same proportions for Ireland generates an estimate of 4639 tonnes/year of waste EPS/XPS generated in Ireland. Moreover, in 2018, more than 162,500 end-of-life vehicles (ELVs) were generated in Ireland (EPA, 2020). Such ELVs contain a variety of potentially POP-containing items such as electronics, plastics (ABS and HIPS), upholstery foams (polyurethane) and fabrics. With respect to waste arisings of soft furnishings, we are not aware of data specific to Ireland. However, if we assume such arisings to be identical per capita to those in the UK in 2010/11 (WRAP, 2012), ≈51,000 tonnes of waste furniture and ≈24,000 tonnes of waste textiles will be generated per annum in Ireland. The massive scale on which waste that may contain these regulated environmental contaminants (PBDEs, HBCDDs and PFASs) has already entered and is expected to enter the waste stream over the next 5 years and beyond requires detailed research studies to generate the knowledge base needed to allow regulatory bodies to formulate effective policies to address this important issue.

One commonly favoured waste disposal method has historically been landfill. While it is important to stress that the quantities of ELV waste and waste C&D EPS/XPS insulation foam that may have reached landfill in the past are likely to be low, and that landfilling of WEEE has been severely restricted within the EU since the promulgation of the WEEE Directive (Directive 2002/96/EC) in 2003 (EC, 2003), it should also be noted that no restrictions on landfilling of waste soft furnishings and fabrics exist, and landfills open before 2003 may contain WEEE received before this date. EU policies (EC, 2011; EEA, 2013) aim to virtually eliminate landfill as a waste disposal option by 2020, and, consistent with this, 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, there remain in 2020 only three active landfills operating in Ireland. The intake of these three landfills is limited to non-hazardous wastes, specifically, municipal solid waste (MSW), biodegradable solid waste, non-hazardous industrial waste and inert C&D waste.

Despite this, the possible existence must be acknowledged of illegal or unauthorised landfills in Ireland (and elsewhere within the EU) that may also contain waste contaminated with POPs, alongside possibly uncontrolled generation of leachate. In addition, it is likely that a substantial reservoir of waste items and associated PBDEs, HBCDDs and PFASs have already been disposed of in landfill (Drage *et al.*, 2018; Gallen *et al.*, 2017). This reservoir represents a long-term potential emission source of BFRs and PFASs to the environment given that, even under effective management, aftercare timelines for landfills are of the order of 75 years (Wang, 2013). The potential for such emissions from POP-containing soft furnishings has been summarised (Stubbings and Harrad, 2014) and projections made of long-term emissions of PBDEs from landfilled e-waste (Danon-Schaffer *et al.*, 2013b). Despite the magnitude of potentially POP-containing waste currently present in and projected to reach landfill in Ireland, little is known about the extent to which and over what timeframe this inventory may be emitted to the environment and its impacts.

Concern about the 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.*, 2013a; Kajiwara *et al.*, 2014; Lang *et al.*, 2016; Stubbings and Harrad, 2016; Stubbings *et al.*, 2016). 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). Such leaching is a particular concern for human exposure if leachate has an impact on groundwater used either for drinking water or for agriculture. Moreover, additional concerns have been voiced that volatilisation of PBDEs and PFASs from landfilled waste may lead to elevated concentrations in air in the vicinity of landfills (St-Amand *et al.*, 2008; Weinberg *et al.*, 2011). Following atmospheric deposition, such airborne emissions can also have an impact on soil in the vicinity of landfills, with concomitant impacts on wildlife and agriculture.

1.5 What Factors Influence Leaching of POP-BFRs and PFASs from Landfilled Waste?

As highlighted above, both POP-BFRs and PFASs have been detected in several studies of landfill leachate. The findings of these studies, combined with those involving controlled laboratory experiments, have highlighted a number of potential factors that are likely to control the magnitude to which these contaminants may enter landfill leachate. Aside from the influence of the contaminant concentration in landfilled waste, other factors include the aqueous solubility of the contaminant and the agitation of the waste (i.e. when waste first enters landfill), as well as the pH, organic matter content and temperature of the leachate. Another possible influence on leaching is the waste matrix in which contaminants are present, with laboratory studies examining leaching of PBDEs from waste cathode ray tube (CRT) plastic housing (Stubbings and Harrad, 2016), as well as HBCDDs from polystyrene building insulation foam (Stubbings and Harrad, 2019) and polyester curtain fabrics (Stubbings *et al.*, 2016). Moreover, other researchers such as Choi *et al.* (2009) and Danon-Schaffer *et al.* (2013a,b) have undertaken laboratory studies of PBDE leaching from WEEE. A final variable of interest is the waste-to-leachate ratio, as this might plausibly influence the extent of contact between the leachate and the surface of the POP-containing waste.

1.6 Objectives of the FUEL Project

The overriding objectives of the FUEL (Furthering Understanding of Emissions from Landfilled Waste Containing POP-BFRs and PFASs) project were:

- To measure concentrations of PBDEs, HBCDDs and PFASs in leachate from active and recently closed landfills in Ireland.
- For the 10 most contaminated landfills identified in the above study, to measure concentrations of PBDEs, HBCDDs and PFASs in samples of air, soil and groundwater.

- To conduct controlled laboratory studies to enhance understanding of the processes governing leaching of PBDEs, HBCDDs and PFASs from materials treated with such contaminants.
- To carry out a preliminary desktop evaluation of potential long-term emissions of target POPs from landfills.

2 Methods

2.1 BFRs and PFASs Measured in This Project and Methods for Determining Their Concentrations

The following BFRs and PFASs were measured in this study: PBDEs 28, 47, 99, 100, 153, 154, 183, and 209; α-, β- and γ-HBCDD; and PFOS, perfluorobutane sulfonate (PFBS), PFHxS, PFOA, 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). Full details of the methods deployed to measure concentrations of these BFRs and PFASs are provided in the peer-reviewed papers that have arisen from this project (see Appendix 1).

2.2 Method for Determining Total Organic Carbon in Soil Samples

Total organic carbon (TOC) was determined in the soil gravimetrically by measuring the loss on ignition after heating the dried samples at 500°C for 4 hours. A clean crucible was accurately weighed and the weight recorded ($W1$). One gram of the soil sample was added to the crucible before being placed in an oven at 105°C for 24 hours to remove all moisture and the weight recorded again ($W2$). The crucible was then placed in an oven at 500°C for 4 hours and left to cool before the weight of the crucible was recorded a final time ($W3$). TOC was then determined using equation 2.1:

$$\text{TOC (\%)} = [(W2 - W3)/(W2 - W1)] \times 100 \tag{2.1}$$

2.3 Collection of Samples from Irish Landfills

2.3.1 *Collection of landfill leachate*

Leachate was collected between June and November 2017 from 40 MSW landfill sites across Ireland (Figure 2.1). Samples from sites without an engineered lining system as per the requirements of the Landfill Directive (Directive 1999/31/EC) (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 one sample of leachate was collected from each landfill studied, with 48 samples collected in total. Each sample consisted of 1 L of 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.

2.3.2 *Collection of air and soil samples*

Air and soil samples were collected between 6 November 2018 and 31 January 2019 from 10 MSW landfill sites across Ireland (Figure 2.1). A summary of the methods employed is provided here, with further information about the sampling locations and factors such as the passive air sampling rates used to calculate concentrations in air samples provided in the corresponding peer-reviewed paper based on this work listed in Appendix 1 (paper 2).

Each passive air sampler deployed consisted of a polyurethane foam (PUF) disc (140 × 140 × 12 mm) mounted between two stainless steel bowls lined with hexane-rinsed aluminium foil. Each PUF disc was coated with pre-cleaned Amberlite XAD powder by submerging each disc in a solution of the powder crushed to a particle size of 0.75 µm suspended in hexane. Once dried, the discs were loaded into the passive air samplers, two of which were placed at locations upwind and downwind, respectively, of each landfill site. The locations of sampling sites were based on wind direction data taken from the Irish Meteorological Service (Met Éireann), with slight modification where necessary based on local information from the site operators and ease of access. Sampling points were located between 150 and 500 m from the waste body.

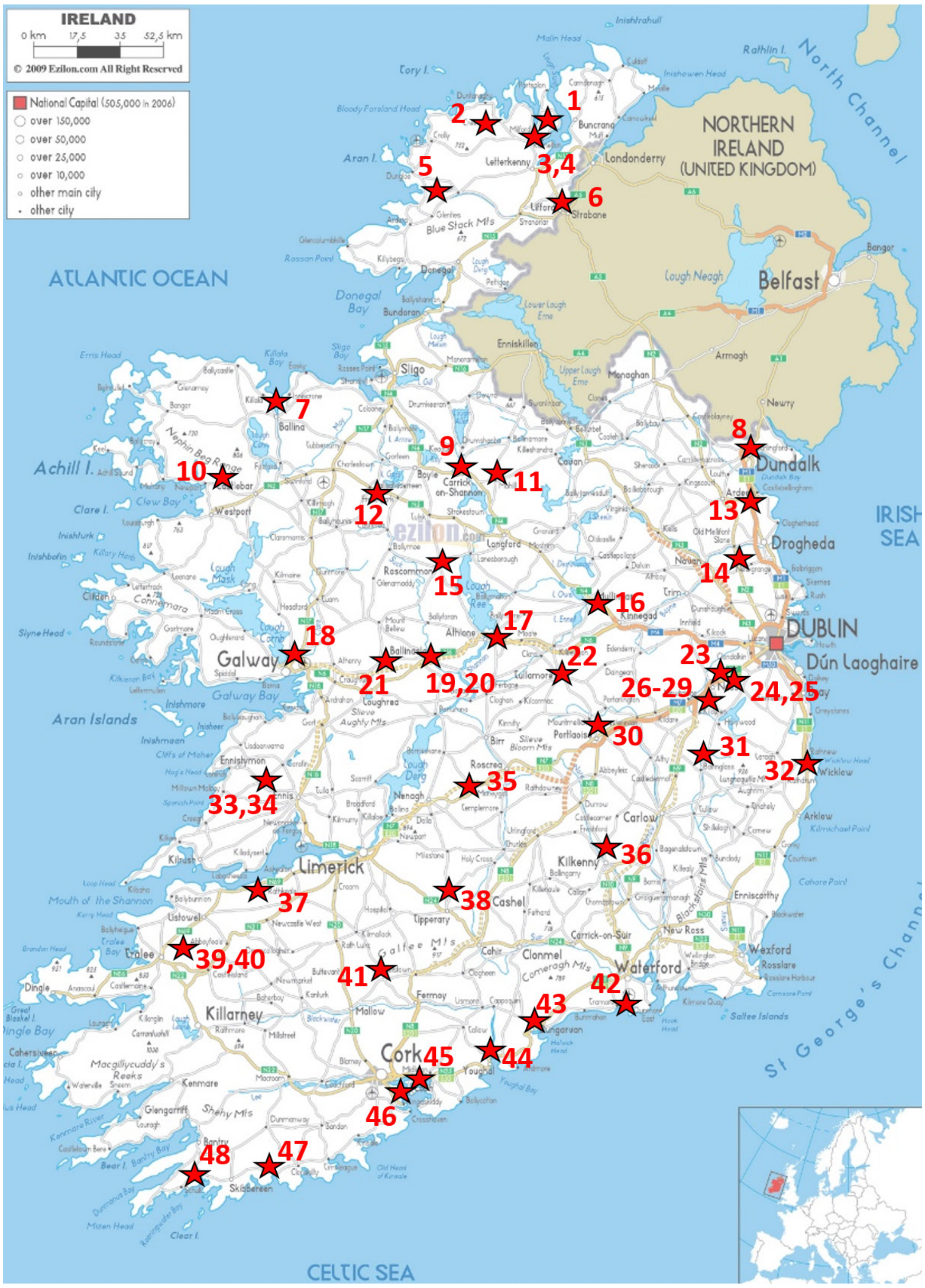

Figure 2.1. Locations of landfills ($n = 40$) from which samples of leachate were taken in this study (numbers refer to leachate samples as more than one leachate sample was taken from some landfills). Air, soil and groundwater samples were taken from landfills corresponding to leachate samples 7, 14, 21, 22, 24–25, 26–29, 32, 33–34, 44 and 45. (Map sourced and adapted from https://www.ezilon.com/maps/europe/ireland-road-maps.html.)

To maximise the effective air volume collected from each location for analysis, two samplers were placed at each sampling point, hung either side of a fence post at a height of 1.2 m above the ground, and left in place for approximately 2 months. At the end of this period, the PUF discs were collected, sealed in a piece of hexane-rinsed aluminium foil and placed in resealable plastic bags for transport to the University of Birmingham for analysis.

Soil samples were also collected both upwind and downwind of the main landfill body, in the same area from which the air samples were taken. These samples were taken within the boundaries of the landfill operational facility, but with care taken to avoid sampling soil used as capping on landfill cells to ensure (1) that soil samples were not collected from soil placed *after* landfill operations ceased, and (2) that farming activities would not influence concentrations of target compounds found.

Nine sub-samples of soil (100 g each) were taken from each downwind and upwind sampling location, in a “W” formation, with each sub-sample 10 m apart, using a small pre-cleaned stainless-steel shovel. For each 100-g sub-sample, the overlaying foliage was removed from a circular area with a diameter of 10–15 cm. A cylinder of soil 10–15-cm wide and ≈5 cm deep was loosened and homogenised, and a ≈100-g sub-sample of soil was removed. This was repeated for each of the nine sub-sampling points before each sub-sample was homogenised into a single sample in an amber glass jar, sealed and then transported to the University of Birmingham. On receipt in Birmingham, samples were air-dried in a fume hood at ambient temperature and homogenised further before an aliquot was removed for analysis.

2.3.3 Collection of groundwater samples

Groundwater samples were collected from each of the 10 sites from two sampling points down-gradient from the main body of the landfills (per landfill zoning maps information). All groundwater samples were taken down-gradient from the main landfill bodies, from dedicated boreholes that are also used by the EPA for routine groundwater monitoring of other parameters (ammonia, pH, TOCs, heavy metals, etc.) These boreholes align with EPA guidelines on landfill monitoring (EPA, 2003); therefore, all samples were taken from the saturated zone underneath the landfills and met the requirements to allow for purging for a representative groundwater sample.

Each sampling point consisted of a ≈5-cm-wide borehole leading down to water reservoirs at a minimum depth of 5 m below ground level. A number of such sampling points are present at every Irish landfill to facilitate monitoring of water quality by the site operator and the EPA. Samples were manually pumped and collected using clean polyethylene tubes and a foot-valve (allowing for the one-way flow of water through the tube). Approximately 25 L of water was purged from each of the two sampling points per landfill, before a 500-mL sample was collected in a pre-cleaned polystyrene bottle. The two samples taken per landfill were then combined into a single 1-L pre-cleaned polystyrene bottle, with this combined sample used for analysis. Following transfer to the laboratory, each combined sample was split, with one half analysed for BFRs (passed through a glass fibre filter and PUF before extraction) and the other for PFASs (subjected to solid phase extraction).

2.4 Laboratory Leaching Experiment Protocols

2.4.1 Preparing homogeneous mixtures of material treated with PBDEs and HBCDDs for use in leaching experiments

A “waste” fabric mixture was created by homogenising aliquots of three polyester fabrics determined to contain elevated concentrations of either HBCDDs or decabromodiphenyl ether (BDE-209). Although two of the fabrics originated from Japan and the other from the UK, we have shown previously that HBCDDs and BDE-209 are the BFRs present at highest concentrations in waste furniture fabrics in Ireland (Drage *et al.*, 2018). Three aliquots (60 mg) of the fabric mix were analysed for BDE-209, as well as for α-, β- and γ-HBCDD, to evaluate its homogeneity.

2.4.2 Leaching experiment protocols

Leaching experiments were carried out in 250-mL high-density polyethylene (HDPE) bottles (Thermo Fisher Scientific). To an accurately weighed mass of fabric mix (either 5 g or 0.5 g depending on the waste-to-leachate ratio examined) was added 100 mL of leaching fluid. The resultant mixture was sealed within the leaching vessel and left for 24 hours, after which the leaching fluid was removed and filtered for analysis. The fabric mix was returned to the leaching container and replaced with a further 100 mL of fresh fluid of identical composition to the initial leaching fluid. The vessel was again sealed and the fabric and leaching fluid left in contact for a further 24 hours before removal of the leachate for analysis. This process of leaching fluid removal for analysis at the end of the contact time, and its replenishment with fresh fluid, was conducted on a total of five occasions, thereby generating samples where the fabric mix had been leached for 24, 48, 72, 96 and 168 hours.

As well as examining the effect of waste-to-leachate contact time, we also examined the impact on leaching of the following parameters: (1) leaching fluid temperature (20°C, 60°C and 80°C), (2) dissolved humic matter (DHM) content [0 mg/L (i.e. distilled deionised water), 100 mg/L and 1000 mg/L], (3) pH (5.8, 6.5 and 8.5), (4) agitation of the waste-to-leaching fluid mix and (5) waste-to-leachate ratio (0.005 and 0.05 g/mL). Overall, a total of nine unique leaching experiments (each conducted in duplicate) were conducted.

2.4.3 Calculating BDE-209 and HBCDDs leached fractions

The percentage of PBDEs present in the test textiles that was leached into each leachate sample (PL) was calculated as in equation 2.2:

$$PL = [(C_{\text{leachate}} \times V)/C_{\text{waste}} \times W)] \times 100\% \qquad (2.2)$$

where PL is the percentage leached (%), C_{leachate} is the concentration of PBDEs collected in leachate (mg/L), V is the volume of leachate (L), C_{waste} is the concentration of PBDEs in the waste sample (mg/kg) and W is the total weight of the waste sample (kg).

The cumulative percentage leached (CPL) represents the sum of PL values recorded for each sample taken within a given time period during each experiment – e.g. CPL at 48-hour contact time equals the sum of the PL values for the 0- to 24-hour and 24- to 48-hour samples.

2.5 Approach Taken to Estimate Emissions of BFRs and PFASs Associated with Landfill Leachate in Ireland

Our approach first estimated the annual mass of PBDEs, HBCDDs and PFASs associated with leachate from Irish landfills. To do so, the estimated total volume of leachate generated by Irish landfills was multiplied by the arithmetic mean concentration of a given contaminant in landfill leachate. The considerable uncertainties associated with this approach are acknowledged in section 4.4, but we believe it provides a reasonable indication of the magnitude of such emissions.

3 Results

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

Table 3.1 summarises concentrations of selected PBDEs, ∑HBCDDs and PFASs detected in leachate from Irish landfills 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. 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 3.1). To our knowledge, our study is only the fourth report of HBCDDs 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).

3.2 Concentrations of PBDEs, HBCDDs and PFASs in Air Samples from the Vicinity of Selected Irish landfills

Table 3.2 summarises concentrations of BDE-47, BDE-209, ∑HBCDDs and selected PFASs detected in samples of air from locations both downwind and upwind of the landfills in this study, alongside those from other relevant studies. Decabromodiphenyl ethane (DBDPE) was detected above its limit of quantification (LOQ) of 0.9 pg/m^3 in only one air sample taken downwind of a landfill (2 pg/m^3). To our knowledge, these are the first reported data on concentrations of PFASs in Irish outdoor air and represent a very substantial addition to the measurements of PBDEs and HBCDDs made at the background Malin Head site as part of another project (Lee *et al.*, 2016; Rauert *et al.*, 2018). Comparison of our data with those for Malin Head suggests that concentrations of BDE-209 and HBCDDs around the landfills studied here slightly exceed those at Malin Head. Concentrations of PBDEs, DBDPE and HBCDDs in the vicinity of Irish landfills are well below those reported recently for indoor air in Ireland (Wemken *et al.*, 2019). For BDE-47, concentrations in the current study are lower than those reported previously in the UK, Sweden, Germany and the USA (Drage *et al.*, 2016; Hoh and Hites, 2005; Newton *et al.*, 2015; Weinberg *et al.*, 2011). With respect to BDE-209, our concentrations exceed those reported for Sweden (Newton *et al.*, 2015) but are markedly lower than those detected in the UK and the USA (Drage *et al.*, 2016; Hoh and Hites, 2005). Meanwhile, concentrations of HBCDDs in this study are lower than in the UK (Drage *et al.*, 2016), Sweden (Newton *et al.*, 2015) and the USA (Hoh *et al.*, 2005).

Concentrations of all our target PFASs in this study are substantially lower than those reported recently for indoor air in Ireland (Harrad *et al.*, 2019). PFOA was detected at higher concentrations in this study than in the UK (Goosey and Harrad, 2012), at both landfill and reference (i.e. non-landfill-impacted) locations in Germany (Weinberg *et al.*, 2011) and in Canada (Shoeib *et al.*, 2011). This is consistent with our recent report that concentrations of PFOA in Irish indoor air exceed those reported elsewhere (Harrad *et al.*, 2019) and, combined, these observations suggest extensive use of PFOA in Ireland. In contrast, concentrations of PFOS and PFHxS in this study are lower than those reported in outdoor air at a number of UK locations (Goosey and Harrad, 2012). Moreover, concentrations of PFOS, PFNA, PFBS and PFHxS in this study are all within a similar range to those reported at landfill and reference locations in Germany (Weinberg *et al.*, 2011).

3.3 Concentrations of PBDEs, HBCDDs and PFASs in Soil Samples from the Vicinity of Selected Irish Landfills

Concentrations of HBCDDs, selected PBDEs and PFASs in soil from locations both downwind and

Table 3.1. Summary[a,b] of concentrations (ng/L) of selected BFRs and PFASs in landfill leachate from Ireland (n = 48) and comparison with arithmetic mean concentrations in selected other studies

Parameter (source)	BDE-47	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣBDEs	α-HBCDD	γ-HBCDD	ΣHBCDDs	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	11,000	7400	250	17,000	65	2600
Detection frequency (%)	57	20	24	33	37	59	85	23	58	65	100	94	100	85	23	79
Australia (Gallen *et al*., 2016)	43	54	9.1	15	12	18	170	0.7	0.6	1.8	450	310	17	250	–	380
Japan (Suzuki and Hasegawa, 2006)	–	–	–	–	–	–	–	<2	4.2	6.2	–	–	–	–	–	–
South Africa (Olukunle 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)	–	–	–	–	–	–	–	–	–	–	49,000	2700	150	15,000	–	130

[a] Only those BFRs/PFASs with a detection frequency ≥20% are shown.

[b] For the purposes of calculating descriptive statistics, "not detects" replaced by df × LOD, where df = the fractional detection frequency and LOD = the detection limit.

Table 3.2. Summary[a,b] of concentrations (pg/m^3) of selected BFRs and PFASs in air from locations downwind and upwind of Irish landfills and comparison with concentrations reported in selected other studies

Parameter (source)	BDE-47	BDE-209	ΣHBCDDs	PFOA	PFOS	PFNA	PFBS	PFHxS
Range (downwind, this study)	< 0.1–0.32	< 0.5–9.2	< 0.05–3.6	4.4–97	0.23–4.3	0.08–0.52	< 0.15–1.4	< 0.15–0.79
Median (downwind, this study)	0.22	6.0	< 0.05	23	1.6	0.17	0.35	0.23
Arithmetic mean (downwind, this study)	0.20	6.6	0.62	33	1.7	0.23	0.50	0.34
Range (upwind, this study)	< 0.1–0.4	< 0.5–8.3	< 0.05–6.1	2.7–59	< 0.2–2.7	< 0.08–0.31	< 0.15–1.2	< 0.15–0.81
Median (upwind, this study)	0.20	5.5	0.07	16	0.60	0.13	0.26	0.08
Arithmetic mean (upwind, this study)	0.20	5.9	1.2	21	0.91	0.15	0.34	0.23
Range (indoor air, homes, Ireland, Wemken *et al.*, 2019; Harrad *et al.*, 2019)	< 0.43–28	< 7.5–5500	0.9–2500	< 0.3–390	< 0.4–210	< 0.3–13	< 0.4–270	< 0.4–4.6
Range ($n = 4$, Malin Head, Ireland, 2005–06, Lee *et al.*, 2016)	–	–	< 0.1–4.6	–	–	–	–	–
Range ($n = 4$, Malin Head, Ireland, 2014, Rauert *et al.*, 2018)	< 2	< 1	< 0.09	–	–	–	–	–
Range of arithmetic means (UK West Midlands, Drage *et al.*, 2016)	1.6–7.9	92–370	64–130	–	–	–	–	–
Range (Birmingham, UK, Goosey and Harrad, 2012)	–	–	–	< 1.9–20	< 1.0–6.1	–	–	< 1.1–30
Range (Stockholm, Sweden, Newton *et al.*, 2015)	0.19–2.4	0.03–0.55	< 0.03–0.58	–	–	–	–	–
Range (Germany, landfill locations, Weinberg *et al.*, 2011)	< LOQ	–	–	0.2–1.2	0.23–1.3	< LOQ to 0.7	< LOQ to 0.46	<LOQ to 0.4
Range (Germany, reference locations, Weinberg *et al.*, 2011)	< LOQ to 20	–	–	0.2–1.8	< LOQ to 1.1	< LOQ to 0.3	< LOQ to 0.5	< LOQ to 0.6
Range (Canada, Shoeib *et al.*, 2011)	–	–	–	<0.47–9.2	< 0.02	–	–	–
Arithmetic mean (Germany, Dreyer *et al.*, 2009)	–	–	–	0.3	1.3	–	–	–
Range (USA, Hoh and Hites, 2005; Hoh *et al.*, 2005)	2.7–41	0.2–65	0.2–9.6	–	–	–	–	–

[a] Only those BFRs/PFASs with a detection frequency ≥20% are shown.

[b] For the purposes of calculating descriptive statistics, "not detects" replaced by 0.5 × LOD, where LOD = the detection limit.

upwind of Irish landfills are summarised in Table 3.3. Similarly to air samples, DBDPE was detected above its LOQ of 250 pg/g (dry weight) in only one sample taken downwind of a landfill (540 pg/g dry weight). To the best of our knowledge, our study is the first to report concentrations of our target contaminants in Irish soil and may be the first report of concentrations in soil anywhere for PFBS. To aid comparison with relevant previous studies for PBDEs and HBCDDs, data are provided both on a soil dry weight basis as well as normalised to soil organic matter content. Compared with landfill-impacted locations in northern Canada (Danon-Schaffer, 2010), dry weight concentrations in the current study of BDE-47, -99, -153, -183 and -209 are approximately one to two orders of magnitude lower. Instead, concentrations in this study resemble more closely those reported by Danon-Schaffer (2010) for soil from reference (non-landfill-impacted) locations in northern Canada. Other pertinent comparisons for PBDEs and HBCDDs are with organic matter-normalised concentrations reported for various locations along rural–urban transects in both the UK (Drage *et al.*, 2016) and Sweden (Newton *et al.*, 2015). Overall, concentrations in our study are broadly consistent with those in these earlier surveys.

Table 3.3. Summary[a] of concentrations (pg/g dry weight) of selected BFRs (pg/g organic matter in parentheses) and PFASs in soil from locations downwind ($n = 9$[b]) and upwind ($n = 7$[b]) of Irish landfills and comparison with concentrations reported in selected other studies

Parameter (source)	BDE-47	BDE-99	BDE-153	BDE-183	BDE-209	ΣHBCDDs	PFOA	PFOS	PFNA	PFBS	PFHxS
Range (downwind, this study)	6.33–320 (38–4100)	7.4–440 (16–5700)	<13–480 (<26–1700)	<13–750 (<26–5300)	430–63,000 (1100–640,000)	80–6200 (780–44,000)	150–5800	2.4–140	<1.0–7.7	<0.6–44	<1.0–2.9
Median (downwind, this study)	77 (260)	61 (400)	13 (180)	48 (330)	5000 (18,000)	560 (4500)	470	6.6	4.3	0.60	<1.0
Arithmetic mean (downwind, this study)	100 (840)	180 (1300)	81 (380)	150 (950)	12,000 (100,000)	1700 (13,000)	1100	26	4.5	5.9	0.77
Range (upwind, this study)	3.8–52 (20–420)	10–26 (32–260)	<13–940 (<60–13,000)	<13–7300 (<78–38,000)	<130–5700 (<340–53,000)	<15–1500 (<90–10,000)	130–7800	3.7–2000	2.9–33	<0.6–2.9	<1.0–3.7
Median (upwind, this study)	14 (140)	14 (96)	<13 (<60)	<13 (<78)	240 (1000)	180 (1200)	610	9.3	6.0	1.2	2.3
Arithmetic mean (upwind, this study)	20 (170)	15 (140)	140 (1900)	1100 (5400)	1000 (10,000)	520 (4400)	1600	300	14	1.1	1.8
Range (UK West Midlands, Drage *et al.*, 2016)[c]	580–2100	550–1600	<43–440	<56–1600	940–45,000	–	–	–	–	–	–
Range (Stockholm, Sweden, Newton *et al.*, 2015)[c]	240–1700	200–1100	<33–190	–	310–31,000	380–12,000	–	–	–	–	–
Arithmetic mean (Canada, landfill impacted sites, Danon-Schaffer, 2010)	8300	12,000	5000	16,000	62,000	–	–	–	–	–	–
Arithmetic mean (Canada, reference sites, Danon-Schaffer, 2010)	100	54	5	15	1600	–	–	–	–	–	–
Arithmetic mean (UK, Goosey and Harrad, 2012)	–	–	–	–	–	–	1100	560	–	–	14
Range of arithmetic means (Belgium, Groffen *et al.*, 2019)	–	–	–	–	–	–	<130–1500	<670–8900	–	–	–
Range (North America, Rankin *et al.*, 2016)	–	–	–	–	–	–	22–1800	30–2000	15–1100	–	2.0–37
Range (Europe, Rankin *et al.*, 2016)	–	–	–	–	–	–	15–2700	7.1–3100	9.1–220	–	3.3–100
Range (near fluorochemical industrial park, China, Bao *et al.*, 2019)	–	–	–	–	–	–	1200–6300	<200–1400	<200–1100	<200–42,000	<200–950

[a] For the purposes of calculating descriptive statistics, “not detects” replaced by 0.5 × LOD, where LOD = the detection limit.

[b] Soil samples from three upwind and one downwind locations destroyed in transit from field to laboratory.

[c] Concentrations expressed as pg/g normalised to soil organic matter content.

With respect to PFASs, consistent with our observations for air, dry weight concentrations in soil of PFOA in our study are at the high end of the range previously reported for various locations in Europe and North America (Goosey, 2010; Groffen *et al.*, 2019; Rankin *et al.*, 2016). In contrast, concentrations of PFOS, PFNA and PFHxS in our soils are at the low end of the range of concentrations previously reported. While our data appear to be the first report of PFBS in soil from non-industrial locations, our concentrations are around three orders of magnitude below those reported in the vicinity of a fluorochemical industrial park in China (Bao *et al.*, 2019).

3.4 Concentrations of PBDEs, HBCDDs and PFASs in Groundwater Samples from the Vicinity of Selected Irish Landfills

Table 3.4 summarises the concentrations of HBCDDs, selected PBDEs and PFASs detected in samples of groundwater in this study, with data from comparable studies elsewhere provided for reference. As far as we can ascertain, our data are the first anywhere to report concentrations of both HBCDDs and DBDPE in groundwater. We detected DBDPE in all 10 groundwater samples that were sampled down-gradient from the main landfill bodies analysed at median and arithmetic mean concentrations that exceeded those of any of the other contaminants measured in this study. While we did not measure DBDPE in a previous study of leachate from Irish landfills (including some of those monitored here), our observations in groundwater are consistent with our recent report of elevated concentrations of DBDPE in indoor air and dust in Ireland (Wemken *et al.*, 2019). This suggests strongly that use of DBDPE is more substantial than thought hitherto, probably as a "drop-in" replacement for the deca-BDE formulation.

As expected, PBDE concentrations in our groundwater samples were lower than those reported previously to be present in leachate from Irish landfills (Table 3.1). Moreover, our concentrations of PBDEs are lower than those reported previously for groundwater from Canada and Taiwan (Levison *et al.*, 2012; Trinh *et al.*, 2019). Turning to PFASs, our concentrations in groundwater are well below those reported in Irish landfill leachate (Table 3.1) but fall within a similar range to that reported for Irish tap water (Harrad *et al.*, 2019). Consistent with the predominance of PFOA in air and soil observed in this study, PFOA is the dominant PFAS of those targeted here, being the only PFAS detected in all samples and at concentrations exceeding those of other PFASs. Compared with other studies of PFASs in groundwater, the concentrations of PFOS, PFBS and PFHxS reported here for Ireland are all at the low end of previous reports for Japan and various European locations (Atkinson *et al.*, 2008; Loos *et al.*, 2010; Murakami *et al.*, 2009; Weiss *et al.*, 2012). In contrast, while concentrations in Irish groundwater of PFOA are within the range reported for Japan, Germany and the UK (Atkinson *et al.*, 2008; Murakami *et al.*, 2009; Weiss *et al.*, 2012), they appear higher than those measured in well water from the Netherlands (Eschauzier *et al.*, 2013) and those reported in a survey of various EU locations (Loos *et al.*, 2010). While we are unaware of previous reports of FOSA in European groundwater, the concentrations we report here are consistent with those measured previously in Japan (Murakami *et al.*, 2009).

To place the concentrations reported here for PFASs in a human health context, it is instructive to compare them with the maximum contaminant levels adopted by the state of New Jersey, which highlight that a screening level of 40 ng/L (PFOA/PFOS) observed in groundwater would "warrant further attention" (US EPA, 2019). Moreover, the same guidance lists drinking water standards of contaminants as follows: PFOA 14 ng/L; PFOS 13 ng/L; and PFNA 13 ng/L. Most recently, a proposal to revise the Drinking Water Directive was agreed (Council of the European Union, 2020). This specifies a limit in drinking water of 100 ng/L based on the sum of a range of PFASs that include some but not all of those targeted in our study. While it is important to highlight that the groundwater samples analysed in this study are not drinking water, the maximum concentration (96 ng/L) of PFOA reported here would be deemed to "warrant further attention" in New Jersey.

3.5 Leaching of BDE-209 and HBCDDs from Fabrics under Simulated Landfill Conditions

Table 3.5 summarises the concentrations detected in the three aliquots of the fabric mix used in all leaching experiments, along with their average and relative standard deviation (RSD). This reveals

Table 3.4. Summary[a,b] concentrations (ng/L) of selected BFRs and PFASs in groundwater samples linked to Irish landfills and comparison with concentrations reported in selected other studies

Parameter (source)	BDE-47	BDE-99	BDE-209	DBDPE	ΣHBCDDs	PFOA	PFOS	PFBS	PFHxS	FOSA
Range (this study)	0.17–0.57	<0.1–1.4	5.8–26	1.3–630	<0.1–2.4	1.6–96	<0.1–1.3	<0.1–0.22	<0.1–0.28	<0.1–1.0
Median (this study)	0.28	<0.1	9.0	9.4	0.81	3.7	<0.1	<0.1	<0.1	0.11
Arithmetic mean (this study)	0.31	0.31	12	78	0.91	30	0.21	<0.1	<0.1	0.22
Detection frequency (%)	100	50	100	100	80	100	20	20	20	70
Range (landfill leachate, Ireland, this study, Table 3.1)	<0.1–140	<0.3–58	<1.0–220	–	<0.2–43	9.0–11,000	<0.1–7400	<0.1–1700	<0.1–2600	<0.2–65
Range (tap water, Ireland, Harrad *et al.*, 2019)	–	–	–	–	–	0.04–18	<0.15–0.76	<0.2–15	–	–
Range (Tokyo, Murakami *et al.*, 2009)	–	–	–	–	–	0.47–60	0.3–130	–	–	<0.1–0.49
Range (UK, Atkinson *et al.*, 2008)	–	–	–	–	–	<24–260	<11–160	–	–	–
Range (Germany, Weiss *et al.*, 2012)	–	–	–	–	–	<LOQ-160	0.02–8400	<LOQ-100	<LOQ-2400	–
Arithmetic mean (EU, Loos *et al.*, 2010)	–	–	–	–	–	3.0	4.0	<0.3	1.0	–
Range (pumping well water, the Netherlands, Eschauzier *et al.*, 2013)	–	–	–	–	–	0.5–1.3	<0.01	<0.01	<0.22	–
Range (Taiwan, Trinh *et al.*, 2019)	1.1–390	0.2–77	6.9–3100	–	–	–	–	–	–	–
Range (Canada, Levison *et al.*, 2012)	<2–10	<1–7.2	<2–92	–	–	–	–	–	–	–

[a] Only those BFRs/PFASs with detection frequency ≥20% are shown.

[b] For the purposes of calculating descriptive statistics, "not detects" replaced by 0.5 × LOD, where LOD = the detection limit.

Table 3.5. Concentrations (mg/kg) of BDE-209 and HBCDDs in fabric mix used in leaching experiments

Result	BDE-209	α-HBCDD	β-HBCDD	γ-HBCDD	ΣHBCDDs
Replicate 1	1600	2700	1100	1700	5500
Replicate 2	1500	2700	890	1600	5200
Replicate 3	1600	3400	960	2000	6900
Arithmetic mean	1600	2900	980	1800	5700
Relative standard deviation (%)	3.6	14	11	12	16

acceptable reproducibility, with RSD in the range of 11–14% for individual HBCDDs and 3.6% for BDE-209. Concentrations in the fabric mix (i.e. in the low percentage range) are consistent with those reported to be used to impart flame retardancy to fabrics as well as those reported in some samples of waste fabrics in a recent survey of waste furniture fabrics in Ireland (Drage *et al.*, 2018). The fabric mix used is thus considered a realistic representation of BFR-treated fabrics present in landfills.

Tables 3.6–3.8 report the concentrations and CPL values of BDE-209 and ΣHBCDDs in leaching experiments examining the effect of waste agitation and waste-to-leachate ratio, as well as the pH, DHM content and temperature of the leaching fluid.

Table 3.6. Results of leaching experiments[a] examining impact of waste agitation and waste-to-leachate ratio

Waste-to-leachate ratio (g/mL)	Agitated (Y/N)	BFR	Parameter/contact time	24 h	48 h	72 h	96 h	168 h
0.05	Y	BDE-209	Leachate concentration[b] (ng/mL)	260	160	92	25	23
			CPL[b,c] (%)	0.33	0.53	0.65	0.68	0.71
		∑HBCDDs	Leachate concentration (ng/mL)	130	130	44	36	13
			CPL (%)	0.16	0.33	0.39	0.43	0.45
0.05	N	BDE-209	Leachate concentration (ng/mL)	76	37	23	4.7	4.9
			CPL (%)	0.093	0.14	0.17	0.17	0.18
		∑HBCDDs	Leachate concentration (ng/mL)	140	57	24	1.2	5.3
			CPL (%)	0.18	0.25	0.28	0.28	0.29
0.005	N	BDE-209	Leachate concentration (ng/mL)	37	30	18	20	4.1
			CPL (%)	0.47	0.84	1.1	1.3	1.4
		∑HBCDDs	Leachate concentration (ng/mL)	53	36	14	15	18
			CPL (%)	0.66	1.1	1.3	1.5	1.7

[a] Other parameters identical in these experiments, namely leaching fluid pH, temperature and DHM content of 6.5, 20°C, and 0 mg/L, respectively.

[b] All concentrations and CPL values are the average of duplicate measurements.

[c] Cumulative percentage leached.

Table 3.7. Results of leaching experiments[a] examining impact of pH and DHM content of leaching fluid

DHM content (mg/L)	pH	BFR	Parameter/contact time	24 h	48 h	72h	96 h	168 h
0	5.8	BDE-209	Leachate concentration[b] (ng/mL)	54	63	22	20	3.4
			CPL[b,c] (%)	0.067	0.15	0.17	0.20	0.20
		∑HBCDDs	Leachate concentration (ng/mL)	200	40	27	50	23
			CPL (%)	0.24	0.29	0.33	0.39	0.42
0	8.5	BDE-209	Leachate concentration (ng/mL)	35	19	55	11	15
			CPL (%)	0.045	0.068	0.14	0.15	0.17
		∑HBCDDs	Leachate concentration (ng/mL)	34	57	3.6	18	13
			CPL (%)	0.043	0.11	0.12	0.14	0.17
0	6.5	BDE-209	Leachate concentration (ng/mL)	76	37	23	4.7	4.9
			CPL (%)	0.093	0.14	0.17	0.17	0.18
		∑HBCDDs	Leachate concentration (ng/mL)	140	57	24	1.2	5.3
			CPL (%)	0.18	0.25	0.28	0.28	0.29
100	6.5	BDE-209	Leachate concentration (ng/mL)	110	35	19	8.2	9.8
			CPL (%)	0.14	0.18	0.20	0.21	0.23
		∑HBCDDs	Leachate concentration (ng/mL)	210	62	43	26	26
			CPL (%)	0.26	0.34	0.39	0.42	0.45
1000	6.5	BDE-209	Leachate concentration (ng/mL)	140	52	52	15	8.7
			CPL (%)	0.18	0.24	0.31	0.32	0.33
		∑HBCDDs	Leachate concentration (ng/mL)	220	140	84	71	33
			CPL (%)	0.27	0.45	0.55	0.64	0.69

[a] Other parameters identical in these experiments, namely leaching fluid temperature of 20°C, no agitation and waste-to-leachate ratio of 0.05 g/mL.

[b] All concentrations and CPL values are the average of duplicate measurements.

[c] Cumulative percentage leached.

Table 3.8. Results of leaching experiments[a] examining impact of leaching fluid temperature

Leaching fluid temperature (°C)	BFR	Parameter/contact time	24 h	48 h	72 h	96 h	168 h
20	BDE-209	Leachate concentration (ng/mL)	76	37	23	4.7	4.9
		CPL[b] (%)	0.093	0.14	0.17	0.17	0.18
	∑HBCDDs	Leachate concentration (ng/mL)	140	57	24	1.2	5.3
		CPL (%)	0.18	0.25	0.28	0.28	0.29
60	BDE-209	Leachate concentration (ng/mL)	57	34	21	14	9.2
		CPL (%)	0.071	0.11	0.14	0.16	0.17
	∑HBCDDs	Leachate concentration (ng/mL)	100	29	17	15	4.7
		CPL (%)	0.12	0.16	0.18	0.20	0.21
80	BDE-209	Leachate concentration (ng/mL)	19	5.5	2.5	2.6	1.0
		CPL (%)	0.024	0.031	0.034	0.037	0.039
	∑HBCDDs	Leachate concentration (ng/mL)	45	11	3.8	3.6	1.7
		CPL (%)	0.056	0.070	0.075	0.079	0.082

[a]Other parameters identical in these experiments, namely leaching fluid pH and DHM content of 6.5 and 0 mg/L, respectively, no agitation and waste-to-leachate ratio of 0.05 g/mL.

[b]Cumulative percentage leached.

Table 3.9. Estimated annual and total masses of PBDEs, HBCDDs and PFASs associated with leachate generated by Irish landfills

Contaminant	Mass per year (g/year)	Total mass generated over landfill lifetime[a] (kg)
PFOA	1100	85
PFOS	390	29
PFNA	43	3.2
PFBS	1600	120
FOSA	3.3	0.25
PFHxS	290	21
BDE-47	14	1.0
BDE-99	8.6	0.64
BDE-154	1.3	0.10
BDE-153	1.9	0.14
BDE-183	1.3	0.10
BDE-209	31	2.4
∑PBDEs	61	4.6
∑HBCDDs	5.9	0.44

[a]Estimated 75-year aftercare timeline for landfill (Wang, 2013).

3.6 Estimation of emissions of BFRs and PFASs from Irish landfills

To estimate the mass of BFRs and PFASs associated with leachate generated by Irish landfills annually, we multiplied the arithmetic mean concentrations of our target contaminants detected in leachate in this study (Table 3.1) by 1.4 million m^3, which is the estimated volume of leachate collected from Irish landfills in 2008 (McCarthy *et al.*, 2010), corrected for the fact that the same source states that an additional 2% of leachate is not collected. This approach yielded the estimates of annual contaminant masses associated with Irish landfill leachate shown in Table 3.9.

4 Discussion

4.1 BFRs and PFASs in Irish Landfill Leachate

4.1.1 Predominant BFRs and PFASs in Irish landfill leachate

As evident from Table 3.1, probably due to their greater aqueous solubility, concentrations of PFASs generally exceed those of PBDEs and HBCDDs, with the median ∑PFAS:∑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 ∑PBDEs = 51%), BDE-47 (22% ∑PBDEs) and BDE-99 (14% ∑PBDEs).

With respect to PFASs, the predominant compounds were PFBS (arithmetic mean = 1100 ng/L) > PFOA (790 ng/L) > PFOS (270 ng/L) > PFHxS (200 ng/L) > PFNA (30 ng/L). Other target PFASs, i.e. FOSA, MeFOSA, EtFOSA, MeFOSE and EtFOSE, were detected rarely, if at all. The relative abundance of individual PFASs will be a complex integral of the aqueous solubility of a PFAS, combined with the quantity present in a given landfill.

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% compared with 23% for α-HBCDD). The generally higher abundance of the γ-diastereomer probably reflects the presence in our studied landfills of HBCDD-treated waste such as EPS building insulation foam, as the γ-diastereomer predominates (α:γ ratio < 0.14) in the commercial HBCDDs 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).

4.1.2 Factors influencing concentrations of PBDEs, HBCDDs and PFASs in landfill leachate

4.1.2.1 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, which 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 (Table 4.1) 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-153, BDE-183 and ∑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 were considered fully reliable only 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 3.10 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 those in leachate from lined and greater than those in leachate from unlined landfills.

4.1.2.2 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

Table 4.1. Comparison of concentrations (ng/L) of selected BFRs and PFASs in leachate from lined, unlined and “mixed” Irish landfills

Landfill type	Parameter	BDE-47	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209	ΣBDEs	α-HBCDD	γ-HBCDD	ΣHBCDDs	PFOA	PFOS	PFNA	PFBS	FOSA	PFHxS
Unlined (PBDEs $n = 17$, HBCDDs $n = 16$, PFASs $n = 18$)	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 (PBDEs $n = 15$, HBCDDs $n = 12$, PFASs $n = 15$)	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 (PBDEs $n = 14$, HBCDDs $n = 14$, PFASs $n = 15$)	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
	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[a]	0.015	0.092	0.383	0.03	0.013	0.343	0.05	0.667	0.182	0.231	0.004	0.502	< 0.001	< 0.001	0.179	0.19

[a] *p*-value for *t*-test comparison of concentrations in leachate from unlined and lined landfills.

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 and 2000 (Gallen *et al*., 2016, 2017). Given that products containing these chemicals would have a lifetime in use of anywhere from 5 to 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 and 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.

4.1.2.3 Leachate pH and chemical oxygen demand

While we did not measure parameters other than BFR and PFAS concentrations in leachate in this study, we were able to access from an online repository data obtained during routine leachate monitoring by the landfill operators of both pH and chemical oxygen demand (COD) (EPA, 2019b). 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. 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 to be 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 TOC. 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 ∑PBDEs ($R = 0.44$). Consistent with observations from 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 that COD was significantly positively correlated with log-transformed leachate concentrations of some 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. 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 (Tittlemeier *et al*. 2002; WHO and IPCS, 1994), 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 and 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 that the correlation is driven largely by a single sample in which PFBS was detected at 17,000 ng/L, ≈15 times the arithmetic mean for all samples. Removal of this sample as an outlier renders the correlation insignificant ($R = 0.28$; $p > 0.05$)

4.2 PFASs and BFRs in Landfill-related Air, Soil and Groundwater from Ireland

This section discusses the results of the second phase of the project, in which concentrations of BFRs and PFASs were measured in samples of air, soil and groundwater associated with 10 of the 40 landfills for which leachate samples were collected and analysed.

All 10 landfills included in this second phase of the study primarily accepted MSW, along with some non-hazardous industrial and C&D waste. None of the 10 landfills is located near any potential sources (such as airfields and chemical production facilities) of our target compounds. It is important to acknowledge that all samples were collected over the late autumn/winter period during which temperatures are lower. It is plausible that sampling in warmer periods of the year would lead to higher concentrations in air owing to enhanced volatilisation of our target compounds. Further monitoring in spring and summer months would thus be advisable to verify whether this is the case.

4.2.1 Downwind and upwind concentrations of HBCDDs, PBDEs and PFASs in air and soil in the vicinity of Irish landfills

4.2.1.1 Air

Table 3.2 shows that, with the exception of HBCDDs, arithmetic mean and median concentrations of all target compounds were higher at downwind than upwind locations. To evaluate whether there was a statistically significant increment at sites downwind of the landfills in this study, we compared downwind and upwind concentrations of HBCDDs, PBDEs and PFASs at our 10 landfills using a non-parametric Wilcoxon signed-rank test. This revealed that downwind and upwind concentrations were statistically indistinguishable ($p > 0.1$).

4.2.1.2 Soil

To evaluate whether there was any statistically significant difference between concentrations (expressed as both dry and organic carbon-normalised weight) of our target contaminants in soil from the six landfills for which we had samples from both downwind and upwind locations, we employed a non-parametric Wilcoxon signed-rank test. This showed no significant difference between downwind and upwind locations ($p > 0.1$).

Overall, our findings suggest no discernible impact of the landfills studied here on concentrations of HBCDDs, PBDEs, DBDPE and PFASs in the air and soil surrounding these facilities. This is consistent with the data on concentrations of a similar range of contaminants measured in air in the vicinity of landfills in Germany (Weinberg *et al.*, 2011) but appears to be in contrast with the data of Danon-Schaffer (2010) who detected markedly higher concentrations of PBDEs in soil around landfills in northern Canada than in reference locations.

4.2.2 Influence of landfill lining status on concentrations of HBCDDs, PBDEs and PFASs levels in groundwater

In section 4.1.2.1, we reported that concentrations of some BFRs and PFASs in leachate from lined landfills exceeded those in leachate from unlined landfills. We therefore hypothesised that groundwater impacted by unlined landfills may contain relatively higher concentrations of BFRs and PFASs. To test this hypothesis, we used a *t*-test to compare concentrations of our target contaminants in groundwater sampled near the six lined landfills with those in groundwater obtained close to the one unlined and three mixed landfills in phase 2 of this study. This revealed no significant difference ($p > 0.1$) in concentrations between groundwater from lined and mixed/unlined landfills. However, we note our small sample size, the fact that for PFOA the *p*-value is 0.12, and that arithmetic mean concentrations of PFOA in groundwater from lined and mixed/unlined landfills were 4.1 and 69 ng/L, respectively.

4.2.3 Relationship between concentrations of HBCDDs, PBDEs and PFASs in groundwater and landfill leachate

We examined our data on BFR and PFAS concentrations in groundwater in this study for any correlation with those we recorded in leachate from the same 10 landfills. Note that DBDPE was not measured in leachate. We observed only one significant correlation, that between concentrations of PFOA in groundwater and leachate ($R = 0.74$; $p = 0.014$). However, this positive correlation was driven substantially by samples obtained from/near one landfill, which displayed the highest concentrations of PFOA in both leachate (11,400 ng/L) and groundwater (140 ng/L). Thus, when the correlation was examined for log-transformed concentrations, it was no longer significant ($R = 0.54$; $p > 0.1$).

4.3 Laboratory Experiments Investigating Leaching of BFRs from Fabrics

A series of laboratory experiments were conducted to examine the influence of a number of factors on the leaching of BFRs from fabrics. These were waste-to-leachate ratio, waste-to-leachate contact time and waste agitation, as well as leachate temperature, DHM concentration and pH. It is important to acknowledge that these represent only some of the factors that might influence BFR leaching under real landfill scenarios, such as pressure and whether landfill conditions are aerobic or anaerobic.

4.3.1 Concentrations of BDE-209 and HBCDDs in leaching fluid

Overall, concentrations in leaching fluid in this study (Tables 3.6–3.8) ranged between 0.58 and 270 ng/mL for BDE-209 and between 1.1 and 260 ng/mL for ∑HBCDDs. As expected, these exceed substantially the concentrations in leachate from Irish landfills of <0.001–0.22 and <0.002–0.043 ng/mL for BDE-209 and ∑HBCDDs, respectively (Table 3.1). However, we note that the maximum concentrations of BDE-209 in Irish landfill leachate were close to the minimum value observed in our experiments, and that BDE-209 was reported to be present at an arithmetic mean of 0.95 ng/mL in South African landfill leachate (Daso *et al.*, 2013).

4.3.2 Impact of waste-to-leachate ratio

Table 3.6 shows the average values of CPL and concentrations in leaching fluid for the two sets of duplicate experiments that compared the impact of varying the waste-to-leachate ratio from 0.005 to 0.05. In both sets of experiments, other parameters were identical, namely temperature of 20°C, pH of 6.5, DHM of 0 mg/L and no agitation. To our knowledge, this is the first study of how the waste-to-leachate ratio influences the leaching of BFRs from treated materials. A *t*-test comparison of values of CPL obtained for each experiment at different waste-to-leachate ratios revealed significantly higher ($p < 0.05$) leaching for both BDE-209 and ∑HBCDDs leaching at the lower waste-to-leachate ratio. The average cumulative percentages leached over 1 week at the lower ratio are 1.4% for BDE-209 and 1.7% for ∑HBCDDs, compared with 0.18% and 0.29%, respectively, at the higher ratio. This finding may reflect the lower fabric surface area to leaching fluid volume ratio at the higher waste-to-leachate ratio. More specifically, at the higher waste-to-leachate ratio, the pieces of fabric comprising the mix used will be more prone to overlaying each other, thereby restricting contact between the fabric surface and the leaching fluid.

4.3.3 The influence of waste agitation on leaching

It has been shown previously that agitation of waste/leachate mixtures under laboratory conditions significantly enhances leaching of HBCDDs from both EPS and XPS building insulation foam (Stubbings and Harrad, 2019) and from fabrics (Stubbings *et al.*, 2016), and of PBDEs (including BDE-209) from CRT housing plastic (Stubbings and Harrad, 2016). Here we compared the extent of leaching of BDE-209 and HBCDDs during two sets of experiments where all parameters were held constant, with one set agitated but the other not. In line with previous observations, we observed (Table 3.6) higher average values of ∑CPL in the agitated experiments (0.71% and 0.45% for BDE-209 and ∑HBCDDs, respectively) than in the experiments without agitation (0.18% and 0.29% for BDE-209 and ∑HBCDDs, respectively). A *t*-test comparison of CPL values at each contact time obtained in agitated relative to those observed for non-agitated experiments revealed leaching of both BDE-209 and ∑HBCDDs during agitated experiments to exceed significantly ($p < 0.05$) those that were not agitated.

4.3.4 Influence of dissolved humic matter content of leaching fluid

To examine the impact of the DHM concentration of the leaching fluid, we compared the extent of leaching of BDE-209 and HBCDDs during three sets of experiments where the DHM content of the leaching fluid varied between 0, 100 and 1000 mg/L, while all other parameters were held constant (pH 6.5, temperature 20°C, no agitation, waste-to-leachate ratio 0.05). The resulting concentrations and CPL values are shown in Table 3.7. Values of ∑CPL increase with increasing DHM content, specifically from an average of 0.18% at 0 mg/L, to 0.23% at 100 mg/L and 0.33% at 1000 mg/L for BDE-209, with the corresponding values for ∑HBCDDs being 0.29%, 0.45% and 0.69%. The significance of these increases in leaching was evaluated using analysis of variance (ANOVA) to compare CPL values for each duplicate experiment at each contact time obtained using leaching fluids of different DHM content. This revealed significantly greater ($p < 0.05$) leaching of both BDE-209 and ∑HBCDDs at 1000 mg/L DHM than at either 100 or 0 mg/L. There was no significant difference, however, between CPL values at 100 and 0 mg/L. As highlighted above, the influence of the DHM content of leachate on leaching has not to our knowledge previously been studied for HBCDDs. We have previously examined the influence of DHM on leaching of PBDEs including BDE-209 from waste CRT plastics but detected no significant impact (Stubbings and Harrad, 2016). Our observation here of increased leaching of BDE-209 and HBCDDs is, however, consistent with previous reports of a positive correlation between concentrations of PFASs in landfill leachate from Australia and the TOC content of the leachate (Gallen *et al.*, 2017). It is also in line with our data showing that concentrations of some PFASs and PBDEs (but not BDE-209) in Irish landfill leachate are significantly higher at higher levels of COD (section 4.1.2.3).

4.3.5 Influence of pH of leaching fluid

The average ∑CPL values for three sets of experiments where only the pH of the leaching fluid was varied between 5.8, 6.5 and 8.5 were 0.20%, 0.18% and 0.17% for BDE-209 and 0.42%, 0.29% and 0.17% for ∑HBCDDs. Statistical analysis (ANOVA) of CPL values in these experiments – which along with concentrations in leachate are provided in Table 3.7 – revealed that leaching of BDE-209 was not significantly influenced by pH ($p > 0.05$). In contrast, CPL values of ∑HBCDDs were significantly greater ($p < 0.05$) at pH 5.8 than at either pH 6.5 or 8.5. Moreover, leaching of ∑HBCDDs at pH 6.5 exceeded significantly ($p < 0.05$) that measured at pH 8.5. The absence of any discernible influence of pH on the leaching of BDE-209 is consistent with the lack of correlation between leachate pH and concentrations of PBDEs and HBCDDs in Irish landfill leachate (section 4.1.2.3). Likewise, no influence of leaching fluid pH was detected in a laboratory study of PBDE leaching from CRT plastics (Stubbings and Harrad, 2016). In contrast, Danon-Schaffer *et al.* (2013a) reported more facile leaching of PBDEs (especially lower brominated congeners) from WEEE at pH values of 4–5 than at pH 7 and 9. With respect to HBCDDs, the enhanced leaching at pH 5.8 (which is observed for each individual diastereomer) contrasts with a report that leaching of α-HBCDD from EPS building insulation foam was greatest at pH 8.5 (Stubbings and Harrad, 2019). The same study did not detect any influence of pH on leaching of either β- or γ-HBCDD from EPS, or of any of the three diastereomers from XPS building insulation (Stubbings and Harrad, 2019). Our findings for HBCDDs leaching from fabrics are more in line with those of Danon-Schaffer *et al.* (2013a) for PBDEs. It is possible that the contrasting findings of Stubbings and Harrad (2019) for building insulation may be matrix-related. Specifically, Stubbings and Harrad agitated their experiments with EPS and XPS insulation foam, leading to abrasion of small particles of friable foam. Such abrasion elevated the HBCDDs concentrations in leachate above the aqueous solubility of HBCDDs and thus may have masked any impact of pH.

4.3.6 Influence of leaching fluid temperature

Three sets of experiments were conducted to examine the impact of leaching fluid temperature on leaching. Heat released during aerobic degradation of waste can raise internal landfill temperatures to as high as 80–90°C (Kjeldsen *et al.*, 2002). Average ∑CPL values for BDE-209 were 0.18%, 0.17% and 0.039% at 20°C, 60°C and 80°C, respectively, while those for ∑HBCDDs were 0.29%, 0.21% and 0.082% at 20°C, 60°C and 80°C, respectively. These data – see Table

3.8 – imply reduced leaching at higher temperatures and are confirmed by ANOVA analysis of CPL values for these experiments, which show significantly ($p < 0.05$) reduced CPL values for both BDE-209 and ∑HBCDDs as leaching fluid temperature increases. This differs from a previous study where leaching of PBDEs (including BDE-209) increased as the leaching fluid temperature was raised from 20°C to 50°C and 80°C (Stubbings and Harrad, 2016). Moreover, leaching of HBCDDs from curtain fabrics was enhanced at 80°C compared with 20°C (Stubbings *et al.*, 2016). This temperature-related enhancement of leaching was noticeably greater for γ- than α-HBCDD and was attributed to either isomerisation or isomer-specific changes in aqueous solubility at higher temperatures (Stubbings *et al.*, 2016). By comparison, while leaching of HBCDDs from EPS building insulation foam increased with temperature, this effect was greatest for α-HBCDD (Stubbings and Harrad, 2019). In contrast, some support for our finding in the current study that leaching was reduced at higher temperatures is provided by a study examining the leaching of tris(1-chloro-2-propyl) phosphate (TCIPP) from PUF, in which, although increasing temperature from 20°C to 50°C enhanced leaching, leaching was markedly reduced at 80°C to levels either equivalent to or below that observed at 20°C (Stubbings and Harrad, 2018). This was attributed to enhanced volatilisation of TCIPP at 80°C, with concomitant losses on opening the leaching vessel to remove leaching fluid for analysis. We also considered the possibility of temperature-related degradation of BDE-209 and HBCDDs, as well as HBCDDs isomerisation. However, examination of mass chromatograms for other PBDEs did not reveal convincing evidence of degradation such as enhanced abundance of lower brominated PBDEs in the leaching fluids at 80°C. Moreover, we detected no evidence of any meaningful temperature-related differences in HBCDDs diastereomer pattern. We therefore believe that the difference between our findings and those of the studies of Stubbings and Harrad (2016, 2019) may be explained as follows. While, in the current study, heated experiments were cooled for only as long as it took for the vessels to be no longer too hot to touch before opening the leaching vessel to remove the fluid for analysis, the heated experiments of Stubbings and Harrad were cooled to room temperature before opening. Combined, the evidence suggests that enhanced leaching of PBDEs and HBCDDs occurs at higher leaching fluid temperatures, with the leached BFRs either returning to solution when the leachate cools (as observed by Stubbings and Harrad), or volatilising at the higher temperatures, as observed here.

4.3.7 *Influence of waste-to-leachate contact time*

Consistent with previous studies (Stubbings *et al.*, 2016; Stubbings and Harrad, 2016, 2019), CPL values increase with increasing duration of contact between waste and leaching fluid. However, it is also apparent that BFR concentrations in leachate diminish substantially as contact time increases. Although we have insufficient measurements (five contact time points) for each experiment to permit reliable calculation of leaching rate kinetics, they are consistent with previous data that suggest leaching of both PBDEs and HBCDDs from treated materials is a second-order process (Stubbings *et al.*, 2016; Stubbings and Harrad, 2016, 2019). Specifically, concentrations in leachate are markedly higher during the first 24 hours of fabric-to-leachate contact time (probably due to more facile leaching of BFRs present on the surface of materials and thus more loosely bound) than in leachate samples taken at subsequent contact times.

4.4 Estimated Emissions of BFRs and PFASs from Irish Landfills

In this section, we provide some preliminary estimates of the extent to which such leaching emits PBDEs, HBCDDs and PFASs to the environment. While we recognise that emissions from landfills to the atmosphere via volatilisation will also occur, this study could not detect a discernible influence on concentrations of our target contaminants in either air or soil. Thus, we are unable to provide a meaningful estimate of such emissions.

Inspection of Table 3.9 reveals that landfill leachate represents a minor reservoir of PBDEs and HBCDDs, with only 61 g of ∑PBDEs and 5.9 g of HBCDDs associated with landfill leachate per annum. This increases somewhat for our target PFASs, with a total of ≈3.5 kg of our target PFASs associated with landfill leachate each year. Clearly, for both BFRs and PFASs, these masses – which represent the worst case for emissions to the environment via leaching from landfill – are only a small fraction of the mass of these chemicals produced and used. Of course, landfill leachate is generated over long timescales, with an estimate of 75 years cited as a typical aftercare timeline for even well-managed landfills (Wang, 2013). Using this figure of 75 years, Table 3.9 also provides the estimated mass of our target contaminants associated with leachate over the lifetime of the landfills in Ireland. The following caveats apply to these estimates:

- Our data on contaminant concentrations in leachate provide a snapshot in time and space of the concentrations in leachate generated by Irish landfills. First, we studied only a subset (*n* = 40) of the landfills either currently or historically operational in Ireland and – while we believe that we have analysed leachate from a representative proportion of landfills – we cannot exclude the possibility that analysis of leachate from landfills not studied here would alter our estimates to a substantial degree. Furthermore, we were not able to examine any seasonal variation in concentrations. Data from previous studies involving laboratory experiments suggest that higher internal landfill temperatures (up to 60–80°C achieved during aerobic degradation) may generate higher concentrations of BFRs in leachate, but the data presented in this project suggest that, under real landfill conditions, the BFRs thus released into leachate at higher temperatures may actually volatilise. However, the extent to which any such volatilisation may be attenuated by landfill capping and daily/intermediate covering is not clear.
- It is important to note that our estimate of contaminant mass associated with leachate generated by Irish landfills does not necessarily equate to the mass that will be emitted to the environment. This is because not all leachate is released directly to the environment. Specifically, while at least a proportion of leachate from unlined or partially lined landfills will be released to soil or groundwater, the EPA estimates that 98% of leachate is collected and sent to wastewater treatment facilities (McCarthy *et al.*, 2010). Subsequent releases of BFRs (and PFASs) via effluent from such facilities will depend on the efficiency with which such contaminants are removed during wastewater treatment. Any contaminants not destroyed during treatment may then potentially be released via aqueous effluent to the aquatic environment, or via waste solids that may be applied to agricultural land.

While we do not have estimates of the masses of PFASs associated with waste items generated annually in Ireland, we did generate such estimates previously for PBDEs and HBCDDs (Drage *et al.*, 2018). Specifically, a total of 32,643 kg/year of PBDEs and HBCDDs combined are estimated to enter the Irish waste stream. Of this, 17,004 kg are HBCDDs, 15,518 kg are BDE-209 and the remaining 121 kg are other PBDEs. Evidently, the estimates listed in Table 3.9 constitute only a very small fraction of the total inventory of these chemicals in the Irish waste stream.

A further cautionary note is struck by an alternative approach to estimating emissions of BDE-209 and HBCDDs via landfill leachate. This approach assumes that all BDE-209 and HBCDDs associated with soft furnishings [totalling 10,204 kg/year and 11,319 kg/year for BDE-209 and HBCDDs, respectively; see Drage *et al.* (2018)] are landfilled. This mass is then multiplied by the CPL values for these contaminants obtained from our laboratory experiments (Tables 3.6–3.8) over 1 week. We have used CPL values of 0.18% and 0.29% obtained at a waste-to-leachate ratio of 0.05, using leachate of pH 6.5, 0 g/mL DHM and at 20°C. As our data are consistent with those reported previously suggesting that leaching slows dramatically after an initial period of rapid dissolution, we believe the CPL values for 1 week are not a gross underestimate of leaching over 1 year. In addition to extrapolating CPL values for 1 week to predict leaching over 1 year, we also acknowledge that only a proportion of waste soft furnishings are sent to landfill. Notwithstanding these caveats, using these figures puts the estimated annual mass of BDE-209 and HBCDDs leached at 18.4 kg and 32.8 kg, respectively. These values exceed substantially by three orders of magnitude those reported in Table 3.9 (31 g for BDE-209 and 5.9 g for HBCDDs). The discrepancy between the two sets of figures is likely to be due to a range of factors and suggests that laboratory experiments like those conducted in this project overestimate the extent to which BFRs are emitted from landfill via leaching. It is plausible that following dissolution of BFRs into leachate, under real landfill conditions, BFRs will be sorbed onto organic-rich surfaces present on other waste materials – which will form the majority of waste mass in most landfills. Another factor mitigating contaminant emissions via leaching from landfill is potential degradation. While all our target contaminants are by definition persistent, PBDEs and HBCDDs in particular are known to degrade in the environment. Such degradation will probably reduce the mass of such contaminants present in landfill and thus available for leaching.

5 Conclusions and Recommendations

Concentrations of PFASs, PBDEs and HBCDDs determined in samples of leachate collected from 40 landfills in Ireland were within the range previously reported in other countries. Average concentrations of PFASs exceeded those of PBDEs and HBCDDs; this is likely to be due to the higher water solubility of PFASs. Log-transformed concentrations of BDE-47, -100, -153 and -183, as well as PFOA, PFNA and PFBS, were significantly ($p < 0.05$) higher in leachate from newer, lined landfills than in samples from unlined landfills. These higher concentrations in lined landfills are likely to be related to the fact that lined landfills are found to retain organic matter, leading to a higher organic content of leachate from such landfills. This is evidenced by the significant ($p < 0.05$) correlation between log-transformed concentrations in leachate of most of the same contaminants and those of COD. Concentrations of the less water-soluble, higher molecular weight BDE-209 were not correlated with leachate COD, landfill age or the presence of a landfill liner. This suggests that the presence of BDE-209 in landfill leachate is driven more by physical abrasion of particles and fibres from waste articles than dissolution into the aqueous phase. The higher concentrations of some PFASs and PBDEs in leachate from lined landfills present a challenge with respect to leachate disposal, when leachate is sent to wastewater treatment plants that do not necessarily have mechanisms in place to remove or destroy these chemicals prior to discharge into the environment. Moreover, 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.

Samples of air and soil were collected from locations downwind and upwind of 10 of the same Irish landfills. Samples of groundwater ($n = 10$) were also collected from locations with links traceable to the studied landfills. Concentrations of PFASs, PBDEs, HBCDDs and DBDPE determined in air and soil samples were not significantly different ($p > 0.05$) between downwind and upwind locations. The arithmetic mean concentration of PFOA in groundwater sourced from landfills ($n = 4$) that were not fully lined (69 ng/L) exceeded that in groundwater samples sourced from lined landfills ($n = 6$; 4.1 ng/L), with the difference, however, not statistically significant ($p > 0.1$). A positive correlation ($p = 0.014$) was observed between concentrations of PFOA in groundwater and those reported in leachate from the same landfills. However, this correlation was driven substantially by one landfill, which displayed the highest concentrations in both groundwater and leachate, and no significant correlation ($p > 0.1$) was observed between log-transformed concentrations of PFOA in groundwater and leachate. DBDPE was detected in groundwater for the first time anywhere, in all samples at concentrations (median = 9.4 ng/L; arithmetic mean = 78 ng/L) that exceeded those of any other BFRs or PFASs targeted in this study. This is likely to reflect its recent use as a “drop-in” replacement for the recently restricted BDE-209 product. Overall, our data suggest that the 10 landfills studied do not exert a discernible influence on local air and soil concentrations of BFRs and PFASs.

A series of laboratory experiments were conducted to examine the leaching of BDE-209 and HBCDDs from a mix of three fabrics. Consistent with previous reports that such leaching is governed by second-order kinetics, concentrations in leachate were markedly higher in the first 24 hours of leaching, and diminished by an order of magnitude after 1 week. The influence of the waste-to-leachate ratio was examined for the first time, with leaching of both BDE-209 and HBCDDs significantly greater ($p < 0.05$) at a waste-to-leachate ratio of 0.005 g/mL than at 0.05 g/mL. Using DHM solutions as proxy for simulating organic landfill leachates, we found that leaching of both BDE-209 and HBCDDs was also significantly greater at a DHM concentration of 1000 mg/L in leachate than that observed at DHM values of 100 and 0 mg/L. Agitation of waste-to-leachate mixtures significantly enhanced leaching. While leaching of HBCDDs decreased significantly as leachate pH increased from 5.8 to 6.5 and then to 8.5, no significant impact of pH on leaching of BDE-209 was detected. Concentrations in leachate of both BDE-209 and HBCDDs decreased significantly on increasing leachate temperature from 20°C to 60°C and 80°C. This is considered most likely to be due to volatilisation of these contaminants into the headspace of the leaching vessel at higher temperatures.

Overall, our data suggest that leaching is more facile while waste is agitated (e.g. during waste disposal) before compressing over time with subsequent reduction in the waste-to-leachate ratio. Our findings also imply potential for emissions of BFRs via volatilisation, during periods of active waste decomposition when internal landfill temperatures are elevated.

Finally, a desktop study suggests that even over the estimated 75-year aftercare timeline of most landfills, emissions via leaching represent only a very small fraction of PBDEs, HBCDDs and PFASs present in the Irish waste stream.

Based on our findings, the following recommendations are made:

- Although concentrations of PBDEs, HBCDDs and PFASs in Irish landfill leachate are consistent with those reported elsewhere and do not appear to be of immediate concern, the indication in this study that, in groundwater linked to a small number of landfills that are not fully lined, concentrations of PFOA exceed those in groundwater surrounding lined landfills, suggests that concentrations of PFASs in groundwater potentially affected by unlined or partially lined landfills should be monitored closely.
- Data from both measurements in landfill leachate and controlled laboratory experiments measuring leaching from fabrics suggest that leaching of BFRs and PFASs is greater at higher concentrations of organic matter in leachate and at higher pH. This suggests that leaching of these contaminants may be minimised by reducing the organic matter content of leachate, while making it more alkaline.
- While putative sources of BFRs and PFASs such as WEEE are already prohibited from disposal to landfill, data from related work (Drage *et al.*, 2018) show that waste textiles can contain substantial quantities of BFRs. Moreover, PFASs were widely used to e.g. stainproof textiles. Restrictions on the landfilling of textiles would thus reduce the quantity of BFRs and PFASs entering landfill.
- Given concerns about the health impacts of PFASs and the concentrations reported here in landfill leachate, further research into methods for treating collected leachate to remove PFASs is recommended.
- While DBDPE was not measured in landfill leachate, it was detected in groundwater samples at concentrations that exceeded those of any of the PBDEs, HBCDDs or PFASs in the same samples. Further monitoring of this emerging BFR in landfill leachate and in groundwater is recommended. Moreover, as chemicals intended as replacements for restricted BFRs and PFASs potentially enter landfill, monitoring of their presence in landfill leachate would appear prudent. While challenging, this could potentially be achieved by screening a small number of leachate samples collected for other purposes such as monitoring for regulated PFASs.

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Abbreviations

BDE-209	Decabromodiphenyl ether
BFR	Brominated flame retardant
C&D	Construction and demolition
COD	Chemical oxygen demand
CPL	Cumulative percentage leached
CRT	Cathode ray tube
DBDPE	Decabromodiphenyl ethane
DHM	Dissolved humic matter
EC	European Commission
ECHA	European Chemicals Agency
EEA	European Environment Agency
EEE	Electrical and electronic equipment
EFSA	European Food Safety Authority
ELV	End-of-life vehicle
EPA	Environmental Protection Agency
EPS	Expanded polystyrene
EU	European Union
HBCDD	Hexabromocyclododecane
HBLV	Health-based limit value
HDPE	High-density polyethylene
LOQ	Limit of quantification
MSW	Municipal solid waste
PBDE	Polybrominated diphenyl ether
PFAS	Perfluoroalkyl substance
PFBS	Perfluorobutane sulfonate
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POP	Persistent organic pollutant
POSF	Perfluorooctane sulfonyl fluoride
PUF	Polyurethane foam
TOC	Total organic carbon
WEEE	Waste electrical and electronic equipment
XPS	Extruded polystyrene

Appendix 1 List of peer-reviewed publications emerging from the research described in this report

Harrad, S., Drage, D.S., Sharkey, M. and Berresheim, H., 2019. Brominated flame retardants and perfluoroalkyl substances in landfill leachate from Ireland. *Science of the Total Environment* 695: 133810.

Harrad, S., Drage, D.S., Sharkey, M. and Berresheim, H., 2020. Perfluoroalkyl substances and brominated flame retardants in landfill-related air, soil, and groundwater from Ireland. *Science of the Total Environment* 705: 135834.

Harrad, S., Drage, D.S., Sharkey, M. and Berresheim, H., 2020. Leaching of decabromodiphenyl ether and hexabromocyclododecane from fabrics under simulated landfill conditions. *Emerging Contaminants* 6: 33–38.

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú

Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:

- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce

- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol

- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn

- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil

- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta

- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch

- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas

- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta

- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:

- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

EPA Research Report 345

Furthering Understanding of Emissions from Landfilled Waste Containing POP-BFRs and PFASs (FUEL)

Climate - Water - Sustainability
Identifying pressures • Informing policy • Developing solutions

Authors: Stuart Harrad, Daniel Drage, Martin Sharkey and Harald Berresheim

Identifying Pressures

Brominated flame retardants (BFRs) and perfluoroalkyl substances (PFASs) have found extensive use in applications such as electrical goods, soft furnishings and building insulation foam. Given their environmental persistence, ability to bioaccumulate and adverse health effects, some BFRs and PFASs are listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), an international treaty designed to eliminate POPs and to which Ireland is a Party. Although the manufacture and use of such substances has been severely restricted, there remains a substantial mass of materials that has entered the waste stream and will continue to do so for some years. Moreover, despite national and European Union policies limiting landfill use, many waste materials containing BFRs and PFASs are likely to be present in Irish landfills. This is concerning, as reports from other countries show that landfill leachate contains such substances. The FUEL study measured PFASs, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) in leachate from 40 landfills within Ireland. In a second phase of the study, air and soil samples were collected from locations downwind and upwind of 10 Irish landfills. Groundwater was also collected from locations traceable to these landfills.

Informing Policy

Concentrations of BFRs and PFASs in leachate from Irish landfills were within the range reported elsewhere. Average concentrations of PFASs exceeded those of PBDEs and HBCDD. Concentrations of some PBDEs and PFASs were significantly higher in leachate from newer, lined landfills than in samples from unlined landfills, implying that lined landfills are less likely to release leachate to the environment. Consistent with this, the average concentration of perfluorooctanoic acid (PFOA) in groundwater from landfills that were not fully lined ($n = 4$; 69 ng/L) exceeded that in groundwater sourced from lined landfills ($n = 6$; 4.1 ng/L). Concentrations of PFASs and BFRs in air and soil samples were not significantly different between downwind and upwind locations, suggesting that the landfills studied are not a significant source of these substances in the surrounding air and soil. The BFR decabromodiphenyl ethane (DBDPE) was detected in groundwater for the first time anywhere, in all samples at concentrations (median = 9.4 ng/L) that exceeded those of any of the other BFRs or PFASs measured. This probably reflects the use of DBDPE as a replacement for the recently restricted BFR POP, decabromodiphenyl ether.

Developing Solutions

The findings of the FUEL study suggest that concentrations of PFASs in groundwater potentially impacted by unlined or partially lined landfills should be monitored closely. Moreover, as concentrations in leachate of many BFRs and PFASs correlated significantly with those of chemical oxygen demand – an indicator of organic matter content – leaching of BFRs and PFASs may be minimised by reducing the organic matter content of leachate. Further monitoring in landfill leachate and groundwater of concentrations of DBDPE and other chemicals designed as replacements for restricted BFRs and PFASs is recommended. Given the widespread application of BFRs and PFASs to textiles, restrictions on the landfilling of such material would reduce the quantity of such substances in waste materials entering landfill. Moreover, as leachate from modern landfills is collected and subjected to treatment, further research should be conducted into methods for removing PFASs from landfill leachate.

EPA Research: McCumiskey House,
Richiew, Clonskeagh, Dublin 14.

Phone: 01 268 0100
Twitter: @EPAResearchNews
Email: research@epa.ie

www.epa.ie

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