PERSISTENT ORGANIC POLUTANTS IN OCCUPATIONAL AND PRIVATE ENVIRONMENTS

Measuring different pathways of human exposure to persistent organic pollutants in aerosol form

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Abstract

Air pollution is a complex issue with a variety of sources. Anthropogenic aerosols, such as persistent organic pollutants (POPs), can be harmful to the environment and humans due to their chemical properties: low water solubility, high lipid solubility and persistence. Brominated flame retardants (BFRs) such as hexabromocyclododecane (HBCDD) and polybrominated diphenyl ethers (PBDEs) were used as flame retardants in a variety of soft furnishings, building insulation foams and electrical goods; while PFOS has been used as a water and stain repellent in waterproof apparel, in textiles such as carpets, and in firefighting foams. The exposure to POPs has been linked to several severe health issues such as the formation of cancerous cells, impaired thyroid function, and fertility problems. The routes of exposure play a vital part in exposure assessment, often via the inhalation of aerosols and also through surface transfer via deposited dust. There is a lack of information on concentrations of BFRs and PFOS in indoor air, dust, and water in different occupational and private environments, information which is required to understand both the overall magnitude of exposure and the relative contributions of the different exposure pathways. The objective of this study is to assess the overall exposure and relative contributions of different routes of exposure of POPs to the Irish population. Air, water and deposited dust samples will be collected and analysed for brominated flame retardants (BFRs) and perfluorooctane sulfonate (PFOS). In order to assess the effect of semi-volatile organic compounds (SVOCs), like BFRs, it is essential to understand their levels and partitioning between various indoor matrices and the indoor environment as a significant route for human exposure.
TABLE of CONTENTS

1 INTRODUCTION ................................................. 4
1.1 WHY ARE WE INTERESTED IN POPs? .................. 4

2 ROUTES OF POP EXPOSURE .................................... 7

3 HEALTH EFFECTS OF POP EXPOSURE ...................... 9

4 POPS OF PARTICULAR INTEREST .......................... 10
4.1 EXPOSURE PATHWAYS ...................................... 11

5 OBJECTIVES OF THIS PROJECT .............................. 12

6 PROVISIONAL RESULTS ...................................... 12

7 CONCLUSION ..................................................... 14

8 ACKNOWLEDGEMENTS ........................................ 14

9 REFERENCES ....................................................... 15

List of Tables

Table 1.1-1. The 12 Initial POPs. .............................. 5
Table 1.1-2. Additional added chemicals. .................. 6

List of Figures

Figure 2-1. Release and Dispersion of POPs. ............... 7
Figure 2-2. Biomagnification of POPs. ....................... 7
Figure 2-3. The human respiratory system and aerosol deposition. 8
Figure 6-1. Boxplot of BFRs. ................................ 13
1 Introduction

An air pollutant is defined as a gaseous substance distributed as independent molecules or tiny condensed-phase liquid droplets or solid particles. Particulate matter (PM) or aerosol is the commonly used term for the condensed airborne material (NRC, 2009). Hinds describes an aerosol as “a collection of solid or liquid particles suspended in gas” (Hinds, 1982). Aerosols permit us to understand the development of cloud formation in the atmosphere. Its particles impact the production, transportation, and outcome of atmospheric particulate pollutants. Atmospheric aerosols can be natural or anthropogenic. Anthropogenic aerosols, such as persistent organic pollutants (POPs), can be harmful for the environment and humans due to their chemical properties.

Over the last 50 years it became increasingly apparent that emissions of air pollutants and related secondary pollution may have hazardous consequences impacting, not only the local area, but affecting air quality, public health, and ecosystem sustainability on areas hundreds to thousands of kilometres downwind from sources. Atmospheric pollution has often far-reaching effects, affecting the environment on regional and continental levels (particulate matter climate impact, persistent toxic organic pollutant contamination etc.) and also on hemispheric and global levels (mercury contamination, greenhouse gas warming etc.) (NRC, 1998). At the beginning of the 21st century it became more apparent that climate change and global air quality are tightly connected, thus the risks posed by intercontinental air pollution and its worrying consequences on the air quality of local and regional residents is now more universally acknowledged. Air pollution is now treated as a complex issue that can have regional, hemispheric, and even global impacts; therefore, transboundary international pollution is a new area of concern.

1.1 Why are we interested in POPs?

Over the last century, the chemical industry experienced a great boom and the general public profited greatly from this chemical revolution. However, not only good came from these newly produced chemicals; shortly thereafter, problems storing, using and disposing of these chemicals arose, resulting in environmental and health issues. Greater public awareness into the environmental impacts and health effects of pollution now exists. Nevertheless, producing reliable scientific evidence about these adverse effects was a lengthy process, requiring the development of novel analytical technologies which were desperately needed to investigate how these adverse effects may impact on our wellbeing and surroundings. In 1962 Rachel Carson linked the use of pesticides and its adverse effects in the “Silent spring” (Carson, 1962) but it took a further 10 years until different governments initiated national and international actions. Public awareness rose notably following catastrophes such as the Seveso Incident in 1976, when an explosion at a chemical plant resulted in the
unintentional release of large quantities of tetrachlorodibenzo-p-dioxin (TCDD) (Umberto Fortunati, 1985). This accident polluted 1800 hectares of land and injured 220,000 people, many of whom were consequently scarred for life from the onset of chloracne (Baccarelli et al., 2005). Consequently, the term persistent organic pollutant (POP) became increasingly prevalent among environmental scientists as an area of interest and concern. POPs represent a group of toxic chemicals that are not easily degraded or metabolised leading to their bioaccumulation and persistence in the environment for long periods of time. Some POPs were produced for industrial use or were generated as by-products of industrial activities. Their stable nature makes them particularly susceptible to long range transportation via ocean and air currents and can therefore be found in even the remotest parts of the world, such as the Arctic. Additionally, their lipophilic tendencies give them the predisposition to accumulate in fat-rich tissue. Therefore POPs have the potential to reach toxic concentrations, with continuous exposure even at a low doses (Ritter et al., 1996; US EPA, 2009; Harrad and Abdallah, 2014; IPEN, 2017).

Only in the late 90s was the POPs International Negotiating Committee (INC) was formed by the United Nation Environmental Programme (UNEP) to address global action on persistent organic pollution, but it was not until May of 2001 that the international breakthrough regarding awareness came about by the formation of the Stockholm Convention on POPs. The Stockholm Convention came into force on the 17th of May 2004 and is a global treaty ratified by the international community which calls for the elimination and/or phasing out of 12 chemicals, colloquially known as the “dirty dozen”, scientifically recognised as POPs (Table 1.1-1) (UNEP, 2008; Harrad and Abdallah, 2014). The following characteristics are essential for a chemical to be listed under the convention:

- persistence;
- bioaccumulation;
- potential for long range transport;
- and adverse effects.

<table>
<thead>
<tr>
<th>Table 1.1-1. The 12 Initial POPs.</th>
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<tbody>
<tr>
<td><strong>Pesticides</strong></td>
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<tr>
<td>Aldrin</td>
</tr>
<tr>
<td>Chlordane</td>
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<tr>
<td>Dieldrin</td>
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<tr>
<td>Endrin</td>
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<tr>
<td>Heptachlor</td>
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<tr>
<td>Mirex</td>
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<tr>
<td>Toxaphene</td>
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<tr>
<td>Hexachlorobenzene (HCB)</td>
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<tr>
<td>Polychlorinated byphenyl (PCBs)</td>
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<tr>
<td>Chlorinated dioxins</td>
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<td>Chlorinated furans</td>
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</tbody>
</table>

To date, 152 signatures have signed the treaty, 181 parties are taking part in the global fight against persistent organic pollutants, and another 14 chemicals have been listed for restriction and/or elimination (Table 1.1-2). Participating parties are obliged to take actions “to protect human health and the environment from persistent organic pollutants” requiring each to create suitable legislation and restrictions regarding any production and use of the 26 currently-listed POPs and any additional POPs recognised in the future (UNEP, 2008).

### Table 1.1-2. Additional added chemicals.

<table>
<thead>
<tr>
<th></th>
<th>Pesticides</th>
<th>Industrial chemicals</th>
<th>By-products</th>
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<tbody>
<tr>
<td>α-hexachlorocyclohexane</td>
<td>X</td>
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<tr>
<td>β-hexachlorocyclohexane</td>
<td>X</td>
<td></td>
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<tr>
<td>γ-hexachlorocyclohexane (lindane)</td>
<td>X</td>
<td></td>
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<tr>
<td>Chlordecone</td>
<td>X</td>
<td></td>
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<tr>
<td>Hexabromodiphenyl</td>
<td></td>
<td></td>
<td>X</td>
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<tr>
<td>Commercial pentabromodiphenyl ether (Penta-BDE)</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Commercial octabromodiphenyl ether (Octa-BDE)</td>
<td></td>
<td></td>
<td>X</td>
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<tr>
<td>Hexachlorobutadiene</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Hexabromocyclododecane</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>X</td>
<td></td>
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<tr>
<td>Technical endosulfan</td>
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<tr>
<td>Perfluorooctane sulfonate (PFOS)</td>
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<tr>
<td>Pentachlorobenzene</td>
<td>XX</td>
<td>XX</td>
<td>XX</td>
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<tr>
<td>Polychlorinated naphthalenes</td>
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**Annex A** Intentionally produced chemicals that need to be eliminated. **Annex B** Intentionally produced chemicals with restrictions. **Annex C** Unintentionally produced chemicals (UNEP, 2008).
2 Routes of POP exposure

Due to the combination of several factors, humans are exposed to POPs via diet, air and deposited airborne dust. They are released from anthropogenic origins into the air and oceans; from there, they are distributed globally through atmospheric processes, air-exchange and cycles including dry particles, rain, soil, atmospheric aerosols and snow (Figure 2-1). POPs can undergo long range atmospheric transport if their gas-phase reaction half-lives are greater than two days and are absorbed onto fine particulate matter. POPs found in water, soil and sediment have a longer reaction half-live and are sustained for longer in the atmosphere. POPs can be found in both atmospheric removal mechanism phases – the aerosol-phase and gas-phase – depending on their volatility. These involve gas exchange, wet and dry deposition, as well as direct and indirect photolysis. The ability to undergo long range transport of POPs adsorbed onto fine particles is increased if the photochemical degradation rate declines and atmospheric half-life inclines (NRC, 2009). These progressions lead to the contact of POPs in distant regions to humans and wildlife that are contingent upon aquatic foods, resulting in an increase in concentration in the food chain (biomagnification) (AMAP, 1998). With every step in the food chain, the concentration of POPs increases as more are ingested and stored. The bioaccumulation is higher in food chains with more stages to the top predator (Figure 2-2).

Another important route of exposure is inhalation of aerosolized POPs, which occurs when the POPS are bound to other smaller particles, such as dust. Several POPs are particularly prevalent in indoor air concentrations making inhalation a major exposure pathway; for example, PBDEs have a high molecular weight and a lower vapour pressure, and can therefore bind to indoor dust on floors and other areas (Harrad and Abdallah, 2014).
In order to assess the effect of semi-volatile organic compounds (SVOCs), like BFRs, it is essential to understand their levels and partitioning between various indoor matrices and the indoor environment as a significant route for human exposure (Venier et al., 2016).

Dust is commonly present in private and occupational environments, it’s a complex heterogeneous combination of SVOCs and particle-bound matter, which originates from biological matter such as human and animal hair, fungal spores, skin cells, textile fibres, plant pollens and others. Thus dust represents a perfect matrix to analyse pollutants due to its existence in the environment, basic traits, and especially its impact to human exposure via dermal absorption, ingestion and inhalation (Cunha et al., 2010).

POPs can be absorbed by fine particulate matter (PM) (NRC, 2009). Liquid droplets and small particles are formed by a large range of elements such as dust, soil particles, organic chemicals, or acids, and are the make-up of PM. They are typically measured in micrometres (µm) (1.0x10⁻⁶ metres) and the range of their diameter lies between 100-0.001µm (EPA, 2016).

The size of the particles is directly related to their health effects. Particles greater that 100 µm are too large to be taken up via inhalation. At sizes between 10-100 µm, particles can be inhaled but are generally blocked by the mucus membranes in the respiratory system (Figure 2-3). Particles between 2.5-10 µm (PM₁₀-Coarse particles) can be taken up into the superior airways and can travel to the nose, pharynx and larynx. Fine particles smaller than 2.5µm (PM₂.₅) can enter deep into the inferior airways and are often found in the trachea, bronchioles and alveoli. The lattermost is the most vulnerable area, as gaseous exchange occurs and the small particles are inhaled through the mechanisms of settling and diffusion (CAICE, 2014). From this area they can even reach the blood stream and circulate around the body (EPA, 2016).
3 Health effects of POP exposure

The WHO links 7 million premature deaths every year to air pollution (WHO, 2014). Inhalation of aerosols is causing serious harm to the human body and contribute to a number of health issues such as cardiovascular and respiratory diseases, along with many other adverse effects (Cohen et al., 2004; EPA, 2004, 2006; WHO, 2006; NRC, 2008). The World Health Organisation (WHO) estimates that 41,200 US citizens die prematurely each year as a result of elevated PM$_{10}$ concentrations (less than 10 µm) (WHO, 2002). Due to their low water solubility, high lipid solubility and persistence in the environment, aerosolized POPs are highly likely to accumulate in adipose tissue. The different POPs have varying toxicological characteristics which result in numerous health issues on humans, fish and wildlife, and extensive adverse effects have been linked with POP exposure (Harrad and Abdallah, 2014). Possible human health consequences of exposure include damage of the nervous, hormonal and immune systems, as well as reproductive functionality. The route(s), concentration and duration of exposure are important factors when assessing the ramifications of POP exposure in humans (NRC, 2009).
4 POPs of particular interest

Polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) are flame retardants developed to delay or prevent the burning of a variety of soft furnishings, building insulation foams, electronic and electrical goods. In the middle of 1970s, brominated flame retardants (BFRs) were initiated as flame retardants (Daso et al., 2010). An estimated 25% of all flame retardants include bromine (Andersson, Öberg and Örn, 2006). In 2001, Europe was responsible for 2%, 16%, 14% and 57% of the yearly worldwide demand of penta-BDE, octa-BDE, deca-BDE, and HBCDD respectively (BSEF, 2003). PBDEs in the manufacturing process but are also included in the polymer casing for electronics (e.g. acrylonitrile butadiene styrene- ABS or high impact polystyrene-HIPS). The restrictions have created a market demand for replacement flame retardants, such as decabromodiphenyl ethane (DBDPE), which has been marketed since the early 1990’s as a replacement for BDE-209. HBCDD has primarily been used as a flame retardant in expanded and extruded polystyrene (EPS/XPS), which is used mainly in building insulation foam, in addition to some applications in textiles.

Perfluorooctane sulfonate (PFOS) belong to the perfluorinated compounds (PFCs). PFOS and related chemicals have been used to impart stain and dirt repellence in carpets, paper and packaging, to provide water repellence in clothing and apparel, as well as being used in firefighting foams. Historically, companies such as 3M and Dupont were the leading manufacturers of these chemicals for industrial and commercial products (Lindstrom, Strynar and Libelo, 2011).

PBDE exposure in animal studies showed neurodevelopmental and behavioural outcomes such as hepatic abnormality, endocrine disruption and possibly cancer (Birnbaum and Staskal, 2004; Darnerud, 2008; Hakk, 2010; Wikoff and Birnbaum, 2011). Exposure of HBCDDs in animals induced hepatic cytochrome P450 enzymes and altered the normal uptake of neurotransmitters; in humans it has been found to trigger cancer through a non-mutagenic mechanisms and disruption of the thyroid hormone system (Law et al., 2005; Covaci et al., 2006; Darnerud, 2008). PFOS exposure in rodents showed an increase in liver weight, a decrease in overall body weight, and a steep dose-response curve for mortality (Seacat et al., 2003). The results of these toxicology studies caused the ban or restriction under the UNEP Stockholm Convention on POPs (UNEP, 2008). Octa- and penta-BDE were banned in 2009, the use of deca-BDE was restricted in 2009 and later banned in 2017. HBCDD was banned in 2013 with a restricted use in Europe in EPS and XPS for building insulation. In 2009 the convention added PFOS and its salts due to strong evidence of these chemicals being able to undergo long –range environmental transport and bioaccumulation (Chaemfa et al., 2010).
4.1 Exposure Pathways

To be used as BFRs or PFCs, the compound must not interfere with the polymers appearance and physical properties and be constant during the lifespan of the product (Wilkie and Morgan, 2010). Polymers are hydrophobic and most of them originate from petroleum material, hence hydrophobic compounds are predisposed to bioaccumulation in the food chain (Alaee and Wenning, 2002; Darnerud, 2003). PBDE are easily integrated into polymers during the manufacturing process. However, as a result of the deficiency of binding sites on polymers surface are not chemically bonded to the material. All of them can be easily released into the environment by volatilisation or dust formation during the handling of treated products (Mcdonald, no date; Alaee et al., 2003; Darnerud, 2003; Covaci et al., 2007; Law et al., 2008; Muenhor et al., 2010). A consequence of a BFR’s and PFCs ability to function throughout the whole lifespan of the product is its persistence in the environment which extends beyond the life cycle of the product (WHO, 1994, 1997; de Boer, de Boer and Boon, 2000; Darnerud, 2003; Watanabe, 2003).

PBDEs, HBCDDs, and PFOS has been detected in a variety of different human tissues such as adipose tissues, blood serum, liver, placenta and breast milk (Tao et al., 2008; Frederiksen et al., 2010; Abdallah and Harrad, 2011, 2014; Pratt et al., 2013). Different external exposure pathways (i.e. dermal exposure, inhalation, diet, ingestion of dust and water) can cause human body burdens of the specified POPs, as shown in the direct measurements of these previous biomonitoring studies. A combination of factors, e.g. diet, air and indoor dust (by dermal contact or ingestion), causes occupational and non-occupational human exposure to PBDEs and HBCDDs (Lorber, 2008; Abdallah and Harrad, 2011, 2014; Trudel et al., 2011).

Human body burdens of PFOS occur in a similar manner, with the most prominent exposure pathways being identified as ingestion of drinking water (Ericson et al., 2008; Thompson, Eaglesham and Mueller, 2011) and indirect exposure via metabolism of the “PFOS-precursors” which produce PFOS as end product (Miralles-Marco and Harrad, 2015). Ambient air particulates have recently risen some awareness, as they hold a significant responsibility in several environmental processes. SVOCs can accumulate in street dust and be transported by the runoff into water. Some POPs, like BFRs, are insoluble in water and therefore would not affect the water quality. However, PFCs hold the ability to dissolve in water and can affect waste as well as drinking water. Studies have looked at PFCs in ambient air particulates (PM$_{2.5}$, PM$_{10}$ and total suspended particles (TSP)). The outcome of a Chinese study indicated presence of PFCs in TSP, PM$_{10}$ and PM$_{2.5}$ (Zhang et al., 2016). Consequently, these harmful compounds are able to enter the airways and circulate throughout the human body.

Up to date there have been no correlations between external and internal exposure metrics established. This is most likely due to inadequate sample quantities in conjunction with the element of long human...
residence times of POPs, which implies that body burdens must be evaluated as a complex integral of different pathways of exposures and over long periods of time; subsequently, body burdens of a given pathway may not relate to recent eternal exposure (Harrad et al., 2010). Comprehension of the origins of current body burdens of these contaminants will only be possible if exposure via different pathways are characterized.

5 Objectives of this project

The ELEVATE project will conduct the first study of levels of BFRs (tri- through deca-PBDEs, and α-,β- and γ-HBCDD) and perfluorooctane sulfonate (PFOS) in indoor air, dust and water in Irish private microenvironments (homes and cars), as well as occupational environments (offices and primary schools). Data will be combined with existing data on concentrations in the Irish diet to evaluate the relative contribution of the different exposure pathways. A human biomonitoring study will also be carried out (by analysing human milk samples) to provide information on body burdens in the Irish population. Comparison with a previous such study will facilitate assessment of the impact on body burdens of restrictions on the manufacture and use of these chemicals. Specific project objectives are to:

- Evaluate the relative contributions of different exposure pathways (diet, indoor air and dust) to POP-BFRs and PFOS in Ireland.
- Establish the current body burdens of POP-BFRs and PFOS in the Irish population and by comparison with previous biomonitoring data in Ireland, assess the impact of recent restrictions on the manufacture and use of these contaminants.
- Evaluate the relationships between external and internal exposure of the Irish population to POP-BFRs and PFOS using simple one compartment pharmacokinetic models.

6 Provisional Results

Approximately 32 samples each of air, dust and tap water were collected from Irish microenvironments such as homes, cars, primary schools and offices between August 2016 and January 2017. Air samples were collected using a sorbent (XAD-3) impregnated polyurethane foam disk (PUF). Dust samples were collected by vacuuming a measured area of the floor surface (1 m² of carpet floor and 4 m² for tiles/wood) in each home and office for 4 minutes. Air samples were extracted via pressurised liquid extraction (PLE) using an ASE-350, with hexane and dichloromethane (3:2, v/v ratio). Dust samples were extracted via a combination of vortexing and
ultrasonication in hexane:acetone (1:1, v/v ratio). Extracts (air and dust) were further purified on a SPE cartridge (silica (dust) or florisil (air)). Clean extracts were concentrated and analysed via GC-EI/MS (PBDEs and DBDPE) or LC-MS/MS (HBCDDs).

Dust samples collected from Irish offices and schools contained relatively low concentrations of BDE-209 (median: 3500 ng/g, range: 550-15000 ng/g; median: 8100 ng/g, range: 200-71000 ng/g respectively), unlike homes and cars (median: 13000 ng/g, range: 140-650000 ng/g; median: 26000 ng/g, range: 14-680000 ng/g respectively). Highest concentrations of DBDPE were observed in schools (median: 10000 ng/g, range: 620-540000 ng/g respectively), followed by cars, offices and homes (median: 7700 ng/g, range: <LOQ-190000 ng/g; median: 6100 ng/g, range: <LOQ-130000 ng/g; median: 4200 ng/g, range: 410-460000 ng/g respectively) (Figure 6-1).

Concentrations of BFRs in air samples were as expected lower than recorded in dust. The highest concentration was recorded for BDE-209 in schools (median: 410 pg/m³, range: 3.8-21000 pg/m³), followed by homes (median: 410 pg/m³, range: 3.8-5500 pg/m³), offices (median: 240 pg/m³, range: 1.6-1600 pg/m³), and cars (median: 200 pg/m³, range: 3.8-7100 pg/m³). The highest concentration of DBDPE at 7000 pg/m³ has been observed in homes.
Concentrations of PBDEs found in this study are comparable with concentrations detected in other European countries, however concentrations of DBDPE are higher, suggesting that DBDPE is commonly used in Ireland.

Analysis for HBCDDs in air and dust samples is currently ongoing. Air, dust and water samples will be analysed for PFOS in February 2018. Breastmilk samples of Irish primiparous will be analysed for BFRs and PFOS in July 2018 and results from the full study will be available at the end of 2018.

7 Conclusion
The connection between aerosolized particles and long-range transport of POPs is not well studied, and further research of aerosolised POP-exposure to the Irish population is desperately needed. This research will be completed in Irish homes, cars, offices and schools, and will evaluate the human exposure through its different pathways. Aerosol particles are not only found in the atmosphere, they can also bind to deposited dust and by linking those different pathways, new data will be developed to further aid research in this field. Preliminary results of dust and air indicate the presence of POPs in occupational as well as private environments. With this new data it will be possible to incite reductions in human body burdens in Irelands in keeping with the tenets of the Stockholm Convention and, furthermore, fulfil Ireland’s obligation as a signatory to the Treaty. The gathered information will be fundamental to developing policies that will reduce the exposure of the Irish population.

8 Acknowledgements
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9 References


