Occurrence and fate of emerging and legacy flame retardants: from indoor environments to remote areas
Seth Newton
Occurrence and fate of emerging and legacy flame retardants: from indoor environments to remote areas

Seth Newton
This thesis is dedicated to my parents. Without your love and encouragement, I would be nowhere.
List of Papers

I. Atmospheric deposition of persistent organic pollutants and chemicals of emerging concern at two sites in northern Sweden


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II. Emerging Flame Retardants, PBDEs, and HBCDDs in Indoor and Outdoor Media in Stockholm, Sweden


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III. Concentrations of legacy and emerging flame retardants in air and soil on a rural-urban transect in the UK West Midlands

Drage, D.; Newton, S.; de Wit, C.A.; Harrad, S. *Manuscript to be submitted*.

IV. Comparisons of indoor active and passive air sampling methods for emerging and legacy halogenated flame retardants in Beijing, China offices

Newton, S.; Sellström, U.; Harrad, S.; Yu G.; de Wit, C.A. *Manuscript*
Contribution to Papers

I. I was responsible for development of analytical methodology, analytical work, data analysis, and took the lead writing the paper.

II. I was responsible for sampling, analytical work, data analysis, and took the lead writing the paper.

III. I was involved in a small part of the sampling, but performed all analytical work for HBCDDs and EFRS, data analysis for these compounds and some PBDE data, and wrote the parts of the paper concerning HBCDDs and EFRs.

IV. I took part in sampling and did all analytical work, data analysis, and took the lead writing the paper.
Abstract

Persistent organic pollutants (POPs) are toxic chemicals that can be found in various matrices in all corners of the planet, including remote areas such as the Arctic. Several POPs are known and monitored but given the abundance of new chemicals in commerce about which little is known, chemicals that may be new POPs are constantly being screened for. The use of flame retardants, particularly brominated flame retardants (BFRs), has been increasing for decades. PBDEs and HBCDDs are two types of BFRs that have historically been used in large volumes but recently faced legislative restrictions. However, in order to meet fire safety standards, these BFRs have been replaced by a variety of emerging flame retardants (EFRs) about which little is known especially concerning their toxicity, production volumes, and environmental behavior. The main purpose of this thesis was to investigate the occurrence and fate in indoor and outdoor environments of several EFRs and compare them with PBDEs, HBCDDs, and legacy POPs.

Several indoor environments in the city of Stockholm, Sweden were sampled for dust, indoor air, and ventilation system air (Paper II). Results from these samples revealed a number of EFRs that humans are exposed to and that are emitted from buildings through ventilation systems. These included DDC-CO, DBE-DBCH, PBT, HBB, EHTBB, and BEH-TEBP. PBDE levels seem to be declining compared to previous studies in Stockholm. Outdoor air and soil were sampled across transects of Stockholm (Paper II) and Birmingham, United Kingdom (Paper III). Results from these samples showed the presence of many of the same EFRs in the outdoor environment that were found in indoor environments. Urban pulses in air were discovered for PBDEs in both cities and for some EFRs in Stockholm, indicating that the cities are sources of EFRs to the outdoor environment. Atmospheric deposition samples were taken at two sites in northern Sweden (Paper I). Three EFRs (DDC-CO, DBE-DBCH, and BTBPE) and two current-use pesticides (trifluralin and chlorothalonil) were identified, indicating these compounds’ potential for long range transport and global contamination. Other legacy POPs such as HCH, PCBs, and PBDEs were measured in the deposition samples as well. The bulk of deposition was comprised of HCH and PCBs with only minor contributions from PBDEs, chlordanes, and emerging compounds. Finally, passive and active air sampling methods were compared for BFRs in offices in Beijing, China. Some EFRs were identified in indoor air from China; however, BDE-209 was the most predominant compound found (Paper IV). Air samples collected with passive samplers generally had measured FR concentrations within a factor of 2-3 of those collected with active samplers.
The use of a GFF in the passive samplers resulted in concentrations of particle-bound contaminants such as BDE-209 that were more comparable to those in active samples. The positioning of the PUF in the passive samplers affected the sampling rates for gaseous compounds and particle retention on PUFs was shown to be a large source of uncertainty in passive sampling.
Persistenta organiska miljöföroreningar (POPs) är giftiga kemikalier som återfinns i många typer av matriser från jordens alla hörn. Många POPs är kända och följs upp med miljöövervakning, men givet den mängd av nya kemikalier som florerar om vilka väldigt lite är känt, behövs det ständigt screenas för att upptäcka andra, hittills okända POPs. Användningen av flamskyddsmedel (FR) och särskilt då bromerade FR (BFR) har ökat under årtionden. Två BFR, PBDE och HBCDD, som historiskt sett har använts i stora volymer, har nu belagts med restriktioner och ersatts av nya FR (EFR) för att kunna uppfylla gällande brandsäkerhetsnormer. Väldigt lite är känt om dessa EFR, speciellt vad gäller giftighet, produktionsvolymer och miljöbeteende. Det främsta syftet med den här avhandlingen har varit att undersöka förekomst och öde för ett antal EFR i inom- och utomhusmiljöer och att jämföra dem med PBDE, HBCDD och äldre POPs.

Abbreviations

AAS  Active air sampler
ATE  allyl 2,4,6-tribromophenyl ether
BATE 2-bromoallyl 2,4,6-tribromophenyl ether
BDE-47 2,2′,4,4′-tetrabromodiphenyl ether
BDE-99 2,2′,4,4,5-pentabromodiphenyl ether
BDE-100 2,2′,4,4′,6-pentabromodiphenyl ether
BDE-153 2,2′,4,4,5,5′-hexabromodiphenyl ether
BDE-154 2,2′,4,4,5,6′-hexabromodiphenyl ether
BDE-183 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether
BDE-197 2,2′,3,3′,4,4′,6,6′-octabromodiphenyl ether
BDE-209 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether
BEH-TEBP bis(2-ethyl-1-hexyl)tetrabromophthalate
BFR  Brominated flame retardant
BTBPE 1,2-bis(2,4,6-tribromophenoxy)ethane
CUP  Current-use pesticide
DBDPE  Decabromodiphenylethane
DBE-DBCH 1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane
DDC-CO 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro-1,4:7,10-dimethanodibenzo[a,e]cyclooctene, or Dechlorane Plus
DecaBDE  Technical DecaBDE mixture
ECNI  Electron capture negative ionization
EFR  Emerging flame retardant
EH-TBB 2-ethylhexyl-2,3,4,5-tetrabromobenzoate
EI  Electron impact ionization
FR  Flame retardant
GC  Gas chromatography
GFF  Glass fiber filter
HBB  Hexabromobenzene
HBCDD  Hexabromocyclododecane
HCH  Hexachlorocyclohexane
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPV</td>
<td>High production volume</td>
</tr>
<tr>
<td>HRMS</td>
<td>High resolution mass spectrometry</td>
</tr>
<tr>
<td>$K_{OA}$</td>
<td>Octanol-air partitioning coefficient</td>
</tr>
<tr>
<td>$K_{OW}$</td>
<td>Octanol-water partitioning coefficient</td>
</tr>
<tr>
<td>mLOD</td>
<td>Method limit of detection</td>
</tr>
<tr>
<td>mLOQ</td>
<td>Method limit of quantification</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>PAS</td>
<td>Passive air sampler</td>
</tr>
<tr>
<td>PBDE</td>
<td>Polybrominated diphenyl ether</td>
</tr>
<tr>
<td>PBT</td>
<td>Pentabromotoluene</td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated biphenyl</td>
</tr>
<tr>
<td>PentaBDE</td>
<td>Technical PentaBDE mixture</td>
</tr>
<tr>
<td>PLE</td>
<td>Pressurized liquid extraction</td>
</tr>
<tr>
<td>POP</td>
<td>Persistent Organic Pollutant</td>
</tr>
<tr>
<td>PUF</td>
<td>Polyurethane foam</td>
</tr>
<tr>
<td>OctaBDE</td>
<td>Technical OctaBDE mixture</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi-volatile organic compound</td>
</tr>
<tr>
<td>UPLC</td>
<td>Ultra-performance liquid chromatography</td>
</tr>
</tbody>
</table>
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1. Introduction

1.1 Why should we care about halogenated flame retardants?

In the US, it is estimated that there are more than 85,000 chemicals in commerce, of which 2,500 are high production volume chemicals (HPV, more than 1 million pounds or about 450,000 kg produced annually). Of the HPV chemicals, it is estimated that nearly 45% are lacking adequate toxicity data. Some chemicals meet the persistence criteria to be defined as a Persistent Organic Pollutant (POP) under the Stockholm Convention. To be a POP, a chemical must be persistent in the environment, exhibit toxicity, be bioaccumulative, and be capable of long range transport. Only 23 substances have been listed as POPs under the Stockholm Convention, all of which are halogenated. However, it is suggested that because of the lack of data on the great number of chemicals in commerce, other POPs may exist. Of the overwhelming number of potential POPs, those with similar structures to chemicals already known to be POPs are the most suspect. Several flame retardants (FRs) fit into this category, especially those containing halogens such as chlorine or bromine.

Among the first FRs to be recognized as potential POPs were polybrominated diphenyl ethers (PBDEs). PBDEs have a very similar structure to the well-known and well-studied legacy POPs polychlorinated biphenyls (PCBs) which have been the subject of much research because of their POP properties. PBDEs have been used as flame retardants since the 1970s. As the demand for the use of bromine as an antiknock gasoline additive declined due to phase-outs of leaded gasoline, the use of bromine for producing FRs increased. However, PBDEs did not become a concern to human health until the late 1990s when their concentrations were observed to be increasing at alarming rates in archived Swedish breast milk samples from 1972-1997. PBDEs have also been linked to negative effects in humans including on neurobehavioral development, thyroid hormones and reproduction.

Thus, PBDEs have been subjected to regulation in several countries and two of the three technical products, PentaBDE (contains BDE-47, -99, -100, -153, -154) and OctaBDE (BDE-153, -154, -183) are now included in the Stockholm Convention. The DecaBDE technical product, containing primarily BDE-209, was phased out in North America and Europe at the end of 2013, but may still be produced in China. Hexabromocyclododecane (HBCDD) is another flame retardant still in use but has recently been added to the Stockholm Convention on POPs and the European Commission recently announced a ban set for mid-2015. The
HBCDD technical product contains primarily three stereoisomers, α-, β- and γ-HBCDD.\textsuperscript{17}

1.2 Emerging Flame Retardants

Legislative regulation of PBDEs and HBCDDs does not translate into a cessation in the use of FRs, only to a shift in product. For example, as a replacement for PentaBDE, Chemtura Corporation introduced Firemaster 550, which contains BEH-TEBP and EHTBB\textsuperscript{18} shown in Table 1. Other known PBDE replacements include BTBPE, which is a replacement for OctaBDE, and DBDPE which is a replacement for DecaBDE. PBDE replacements are not limited to these compounds though. It is suspected that some FRs, which have been used for many years in low volumes, are now seeing increased usage as PBDE replacements. An example of this is Dechlorane Plus (DDC-CO), which has been a known FR since the 1970s but not found in the environment until 2006.\textsuperscript{19} Recently, Firemaster 550 was shown to have endocrine disrupting effects in rats indicating that some EFRs may be problematic chemicals.\textsuperscript{20}

Only limited information is released about FR products and typically only about those products that are in high production. This leaves scientists with a bit of detective work as to which chemicals should be sought after. The use of production volumes and quantitative structure-activity models based on physical-chemical properties has helped some scientists prioritize which chemicals should be sought after as potential POPs.\textsuperscript{3, 4} Some of these compounds are EFRs and were included in this thesis such as DBE-DBCH, BEH-TEBP, DDC-CO, HBB, and BTBPE. A summary of the FRs included in this thesis and their physical-chemical properties is given in Table 1.
Table 1 - Abbreviations, full names, CAS numbers, log $K_{OA}$, and log $K_{OW}$ of FRs included in this thesis. a) Calculated using Spark on-line calculator b) Calculated using EPI Suite 4.1

<table>
<thead>
<tr>
<th>Common name</th>
<th>Full Name</th>
<th>CAS number</th>
<th>Structure</th>
<th>log $K_{OA}$</th>
<th>log $K_{OW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-47</td>
<td>2,2',4,4'-tetabromodiphenyl ether</td>
<td>5436-43-1</td>
<td><img src="image" alt="Structure" /></td>
<td>10.53$^{21}$</td>
<td>7.16$^a$</td>
</tr>
<tr>
<td>BDE-99</td>
<td>2,2',4,4',5-pentabromodiphenyl ether</td>
<td>60348-60-9</td>
<td><img src="image" alt="Structure" /></td>
<td>11.31$^{21}$</td>
<td>7.94$^a$</td>
</tr>
<tr>
<td>BDE-153</td>
<td>2,2',4,4',5,5'-hexabromodiphenyl ether</td>
<td>68631-49-2</td>
<td><img src="image" alt="Structure" /></td>
<td>12.1$^{21}$</td>
<td>8.73$^a$</td>
</tr>
<tr>
<td>BDE-209</td>
<td>2,2',3,3',4,4',5,5',6,6'-decabromodiphenyl ether</td>
<td>1163-19-5</td>
<td><img src="image" alt="Structure" /></td>
<td>16.77$^{22}$</td>
<td>12.04$^a$</td>
</tr>
<tr>
<td>DBE-DBCH</td>
<td>1,2-dibromo-4-(1,2-dibromoethyl) cyclohexane</td>
<td>3322-93-8</td>
<td><img src="image" alt="Structure" /></td>
<td>8.01$^d$</td>
<td>4.82$^{23}$</td>
</tr>
<tr>
<td>DDC-CO</td>
<td>Dechlorane Plus</td>
<td>135821-74-8</td>
<td><img src="image" alt="Structure" /></td>
<td>13.10$^b$</td>
<td>10.12$^{23}$</td>
</tr>
<tr>
<td>PBT</td>
<td>pentabromotoluene</td>
<td>87-83-2</td>
<td><img src="image" alt="Structure" /></td>
<td>9.66$^{24}$</td>
<td>5.87$^{25}$ 5.43$^{25}$ 6.25$^{23}$</td>
</tr>
<tr>
<td>HBB</td>
<td>hexabromobenzene</td>
<td>87-82-1</td>
<td><img src="image" alt="Structure" /></td>
<td>10.26$^{24}$</td>
<td>5.85$^{25}$ 6.07$^{25}$ 6.11$^{23}$</td>
</tr>
<tr>
<td>ATE</td>
<td>1,3,5-tribromo-2-(2-propen-1-yloxy)-benzene</td>
<td>3278-89-5</td>
<td><img src="image" alt="Structure" /></td>
<td>5.59$^b$</td>
<td>4.97$^{25}$ 5.04$^{23}$</td>
</tr>
<tr>
<td>BATE</td>
<td>2-bromoallyl 2,4,6-tribromophenyl ether</td>
<td>-</td>
<td><img src="image" alt="Structure" /></td>
<td>9.65$^b$</td>
<td>5.98$^b$</td>
</tr>
<tr>
<td>DBDPE</td>
<td>decabromodiphenyl-ethane</td>
<td>84852-53-9</td>
<td><img src="image" alt="Structure" /></td>
<td>19.22$^b$</td>
<td>11.1$^{25}$</td>
</tr>
<tr>
<td>BTBPE</td>
<td>1,2-bis(2,4,6-tribromophenoxy) ethane</td>
<td>37853-59-1</td>
<td><img src="image" alt="Structure" /></td>
<td>15.67$^b$</td>
<td>7.88$^{25}$ 8.31$^{23}$</td>
</tr>
<tr>
<td>EHTBB</td>
<td>2-ethylhexyl-2,3,4,5-tetabromobenzoate</td>
<td>183658-27-7</td>
<td><img src="image" alt="Structure" /></td>
<td>12.34$^b$</td>
<td>7.73$^{23}$</td>
</tr>
<tr>
<td>BEH-TEBP</td>
<td>bis(2-ethyl-1-hexyl) tetabromophthalate</td>
<td>26040-51-7</td>
<td><img src="image" alt="Structure" /></td>
<td>16.86$^b$</td>
<td>9.34$^{23}$</td>
</tr>
<tr>
<td>HBCDD</td>
<td>1,2,5,6,9,10-hexabromocyclododecane</td>
<td>134237-50-6</td>
<td><img src="image" alt="Structure" /></td>
<td>9.62-10.79$^{26}$</td>
<td>7.92$^{23}$</td>
</tr>
</tbody>
</table>
1.3 Indoor exposure and outdoor contamination

FRs are almost exclusively used in consumer products intended for indoor use such as furniture foams, textiles, building insulation and electrical and electronic equipment. As a result, indoor environments have been found to be contaminated with much higher concentrations of PBDEs than outdoor environments\(^\text{12, 27}\) and PBDEs have been labeled “indoor POPs”\(^\text{28}\) as a distinction from many of the original 12 legacy POPs put on the Stockholm Convention, which largely had outdoor applications. Given the amount of time humans spend indoors, direct exposure to indoor POPs (e.g. via dust ingestion and air inhalation) may be a significant exposure pathway.\(^\text{29-31}\)

Via air exchange of buildings (i.e. ventilation), PBDEs originating from indoors have been found to contaminate outdoor environments.\(^\text{12, 32}\) Once the contaminants have reached the outdoors via ventilation, they may be transported long distances depending on their persistence in the environment. The ubiquity of PBDEs in the outdoor environment is well established\(^\text{33, 34}\) and several EFRs have been reported in outdoor studies as well, indicating that they may undergo long range atmospheric transport (LRT).\(^\text{25, 35-37}\) It is thus important to understand the transfer of these EFRs from indoors to the outdoor environment. It is also important to understand which of these EFRs are persistent enough to undergo LRT once they reach the outdoor environment. Indirectly, this also has consequences for human exposure as persistent FRs that become global pollutants can end up in the food web making diet another significant exposure pathway to many POPs.\(^\text{38}\)

1.4 Urban pulses

If air exchange with indoor environments is a major source of FRs to the outdoor environment, then concentrations of FRs in outdoor media can be expected to increase with population density, due to the concentration of buildings containing FR-treated products. This has in fact been observed for both PCBs and PBDEs along rural-urban transects of Birmingham, UK\(^\text{39}\) and for PBDEs in Toronto, Canada.\(^\text{40, 41}\) Elevated concentrations were observed in air at sites closest to the city centers (highest population densities) compared to those sites upwind and downwind from the cities, creating an “urban pulse” of FRs in the outdoor environment. HBCDDs and EFRs were not included in these studies.
1.5 Long Range Transport (LRT)

Once indoor contaminants reach the outdoor environment, the next important question to assess is if they are capable of being transported long distances. In order to be transported long distances, a chemical must be resistant to degradation (persistent) by sunlight, microbial degradation, hydrolysis, and other environmental degradation processes. It must also be transported through the environment in some way. Physical-chemical properties are important for understanding how chemicals move through the environment. Of particular importance are octanol-air and octanol-water partitioning coefficients (\(K_{OA}\) and \(K_{OW}\), respectively). Octanol can be thought of as surrogate for carbon-based molecules such as organic carbon in soils or lipids. Therefore, the way a chemical behaves in a biological system or in an aquatic system with suspended organic carbon can be understood by understanding its \(K_{OW}\). The way a chemical behaves in the atmosphere and how it interacts with aerosol particles and soil can be understood by understanding its \(K_{OA}\). Wania\(^42\) classified global pollutants as swimmers, single hoppers, and multihoppers based on physical-chemical properties. Swimmers are polar contaminants that can be transported via the oceans. The FRs included in this thesis are very hydrophobic (\(\log K_{OW} \approx 5-12\), Table 1) so none of them are expected to be swimmers. Multihoppers are semi-volatile and can undergo several cycles of deposition and revolatilization. Many of the EFRs and some of the lower brominated PBDEs (e.g. DBE-DBCH, BATE, BDE-47) likely fall into this category based on their \(K_{OA}\) values (Table 1). Single hoppers are less volatile than the multihoppers, have higher \(K_{OA}\) values, and are transported bound to aerosol particles (e.g. BDE-209 and DDC-CO). Once a single hopper has deposited from the atmosphere to the earth’s surface, it is less likely to be revolatilized, thus to undergo LRT it must be carried from its source in a single “hop”.

1.6 Comparing air sampling methodology

Both active air sampling (AAS) and passive air sampling (PAS) methods are common to measure FRs and other POPs in indoor and outdoor air.\(^43\) Each has advantages and disadvantages, however, there are some knowledge gaps about how comparable the data are that the two methodologies produce.\(^44\), \(^45\) AAS requires a pump to pull air through an adsorbent. Large air volumes can be sampled over a rather short time period allowing for samples with rather high time resolution. With AAS, a flow meter is often attached to the pump to measure the air volume sampled and the calculated concentrations are considered more accurate than PAS.
The samplers used in PAS are much simpler, do not require a pump and therefore electric power is not needed. PAS require longer sampling times so with this technique integrated concentrations of compounds over a longer time period are measured. Because influences on uptake rates are less well understood, PAS is considered only semi-quantitative. Air particles are to some extent also collected by the PUFs in the PAS but the mechanism for this is currently not understood and the uptake rates for particle-bound contaminants (e.g. BDE-209) are largely uncertain. Only recently have filters been used in PAS to sample particle-bound contaminants. More direct comparisons between AAS and PAS are needed as well as comparisons between PAS with and without a filter.

1.7 Questions addressed in this thesis

1. Are EFRs present in air and dust from indoor environments and if so, how do their concentrations compare to those of legacy FRs?
2. Are FRs from indoor environments emitted to the outdoor environment via ventilation systems?
3. Do EFRs and HBCDDs show similar environmental behavior as PBDEs, e.g. urban pulses and long range transport?
4. How comparable, both qualitatively and quantitatively, are data from different active and passive indoor air sampling methods for FRs?
2. Methods

2.1 Sampling

In order to address these questions, a number of different samples (air, dust, soil, atmospheric deposition) were collected. The locations, matrices and sampling methods used in the different papers are given in Table 2. The different techniques used are summarized below.

Table 2 - Location, matrices, and sampling methods used in each paper included in this thesis.

<table>
<thead>
<tr>
<th>Matrices sampled</th>
<th>Sampling methods</th>
<th>Sampling location</th>
<th>Paper number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric deposition</td>
<td>Passive deposition sampler</td>
<td>Northern Sweden</td>
<td>Paper I</td>
</tr>
<tr>
<td>Dust</td>
<td>Cellulose filter on vacuum cleaner</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indoor and ventilation system air</td>
<td>Low-volume active samplers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outdoor air</td>
<td>High-volume active samplers</td>
<td>Stockholm, Sweden</td>
<td>Paper II</td>
</tr>
<tr>
<td>Soil</td>
<td>Top-soil grab samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outdoor air</td>
<td>Passive samplers</td>
<td>Birmingham, United Kingdom</td>
<td>Paper III</td>
</tr>
<tr>
<td>Soil</td>
<td>Top-soil grab samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indoor air</td>
<td>Passive samplers (two types) and low-volume active samplers</td>
<td>Beijing, China</td>
<td>Paper IV</td>
</tr>
</tbody>
</table>

2.1.1 Air sampling

AAS for semi-volatile organic compounds (SVOCs) typically consists of a filter to trap particles followed by a gas-phase adsorbent connected to a pump that pulls air through the sampler. Common filter types include quartz fiber and glass fiber (GFFs). Two commonly used adsorbents to collect SVOCs present in the gas-phase are XAD and polyurethane foam.
(PUF). Air samplers using a low volume pump (< 3 m$^3$ h$^{-1}$) typically sample acceptable volumes for indoor use over a period of 24-48 hours. Outdoor air sampling often requires a large amount of air to be sampled to accumulate detectable levels of SVOCs because the compounds are more diluted. Therefore, high volume pumps are often employed for outdoor air sampling, typically sampling at rates of 15-80 m$^3$ h$^{-1}$ and common total volumes are between 500-1500 m$^3$.

In this thesis, similar filter/adsorbent systems were used (GFFs and PUFs) for both indoor and outdoor air (Papers II and IV). GFF diameters (low-volume, 2.5 cm; high-volume 29.3 cm) and typical flow rates (low-volume, 0.18 m$^3$ h$^{-1}$; high-volume, 25 m$^3$ h$^{-1}$), resulted in similar linear velocities (0.037 m$^3$ h$^{-1}$ cm$^{-2}$) for both systems. Low-volume AAS (Figure 1) were used in Paper II to sample indoor and ventilation system air from different microenvironments (offices, apartments, stores and schools) in order to test questions 1 and 2. The sampling campaign was conducted during the heating season in Stockholm (February – May, 2012) so that indoor air was leaving the buildings through ventilation systems rather than open windows. High-volume AAS (Figure 1) were used in Paper II to sample outdoor air at 7 sites along a west to east transect over Stockholm to address question 3 regarding urban pulses. This sampling campaign was conducted during two periods: April 30$^{th}$ – May 2$^{nd}$, 2012 and May 29$^{th}$ – June 4$^{th}$, 2012.

Passive air samplers (PAS) typically consist of an adsorbent positioned inside a protective housing to control air exchange rates with the sampled environment. Similar absorbents are used for gaseous compounds that are used in AAS (PUFs and XAD are common). The uptake rates for gaseous compounds are both compound- and sampler-specific and are heavily correlated with log $K_{OA}$ (Figure 2 in Paper IV).

In Paper III, PAS fitted with PUFs and GFFs (Figure 1) were used for outdoor sampling at eight locations along a transect of Birmingham, UK in the direction of the prevailing wind. This study was setup to explore question 3 and samples were collected over 28 day periods from June 2012 until January 2013.

Parallel sampling with active and passive air samplers was conducted in Paper IV to test how well they agree, and to answer question 4. This was done in indoor microenvironments (3 offices) in Beijing, China. Two PAS configurations were tested, one using only a PUF and the other with both a PUF and a GFF in combination (Figure 1). In order to try and mimic the PAS, an AAS with a low volume pump was run for 2.5 hours per day for the 28-day sampling period alongside the PAS. A more traditional AAS was done at the end of each 28-day period with the pump running continuously (about 2.5 days, referred to as “snapshot” AAS) until it had sampled the same amount of air as the 28-day sample.
2.1.2 Atmospheric deposition, soil, and dust sampling

Atmospheric deposition is the process of air-borne contaminants (particle-bound or gaseous) transferring to a surface. Deposition can be “wet”, meaning compounds (or the particles they are adsorbed to) are scavenged from the atmosphere by precipitation, or “dry”, meaning compounds either condense to the surface or the particles to which they are bound settle from the air. Surface soils contain the remnants of previously deposited compounds and in the absence of other contamination sources, such as in remote areas like the Arctic, soil concentrations can be indicative of previous deposition. In a similar manner, dust could be considered as a type of indoor atmospheric deposition. Strictly speaking however, measuring deposition is the measurement of a process, not a medium. Therefore, a flux is calculated rather than a concentration.
In Paper I, atmospheric deposition was sampled at two locations in northern Sweden (Figure 2) to test for long range atmospheric transport (question 3). A funnel-shaped bulk deposition sampler (Figure 3), collecting both wet and dry deposition was used. The precipitation was passed through an adsorbent to collect hydrophobic organic contaminants, and settled particles were wiped from the funnel surface at the end of the sampling period and combined with the adsorbent. This sampler had previously been validated for PAHs and PBDEs. The sampling time was two months for each sample, and the sampling campaign took place between October 2009 and November 2010.

Figure 2 - Location of atmospheric deposition sampling sites (Paper I).
Surface soil was used in this thesis in addition to air samples to calculate air-soil equilibrium and provide environmental levels. For this purpose, surface soil (top ~5 cm) must be used as deeper soil is hindered from exchange with ambient air. Samples must be taken from open areas, since vegetation can influence the amount of atmospheric deposition, known as the forest filter effect. In Paper II, soil was collected from an open, undisturbed area (about 1 m²) close to the AAS after sampling had finished. In Paper III, soil was collected from the same sites as the PAS after the sampling campaign had finished (January 2013).

The precise location in an indoor environment of where to sample dust has been the subject of discussion, as concentration of FRs in dust can be very heterogeneous. Some researchers have simply taken dust from vacuum cleaner bags of homes. This has the advantage of giving an integrated sample of dust from the entire indoor environment as well as being simple and quick. The disadvantage is possible contamination from the vacuum cleaner itself as each participant uses their own vacuum cleaner. To solve this, some researchers use their own vacuum to collect dust samples, collecting the dust in a filter before it enters the vacuum cleaner (e.g. nylon sock or cellulose filter). Some researchers sample floor dust while others sample undisturbed areas above the floor. The selection of where to sample dust should be determined by the research questions. If investigation of human exposure is the purpose of the study, perhaps floor dust is more relevant than above-ground settled dust, especially if the
exposure involves toddlers. If the study involves fate and behavior of FRs, then undisturbed settled dust may be more relevant.

To address question 1 and explore the indoor fate of FRs, indoor dust was sampled on a cellulose filter attached to the vacuum cleaner inlet. Surfaces at least 1 m above the floor in the same rooms as the AAS mentioned above were sampled after the air sampling was completed (Paper II). In stores, surfaces of products suspected to be flame retarded were sampled directly and a separate sample was taken from areas around those products.

2.2 Extraction

The compounds studied in this thesis are traditionally extracted from complex matrices with organic solvents in different combinations. The choice of extraction method depends on type of matrix and also on sample size. It is desirable to keep the solvent consumption low both for environmental reasons and also to minimize possible contamination of analytes from the solvents.

Dust samples are often extracted with repeated volumes of solvents in test tubes in an ultra-sonic bath.\textsuperscript{13} Since these samples are generally small, the solvent consumption can still be kept low, and many samples can be extracted simultaneously. In Papers II and IV, dust and low-volume AAS were extracted ultrasonically using dichloromethane (DCM) as solvent, as it contained only low concentrations of BDE-209. The sampling media used for high-volume AAS and PAS were larger in size, and for these Soxhlet extraction with DCM (AAS, Paper II) or pressurized liquid extraction (PLE) with a mixture of n-hexane and DCM (PAS, Paper III) was applied to keep the solvent consumption down. Soxhlet extraction uses hot solvent that is distilled after each extraction and reused several times. In PLE, both elevated temperature and pressure are applied to increase extraction efficiency.\textsuperscript{55} PLE with n-hexane and acetone was used for the atmospheric deposition samples in Paper I.

The soil samples (Papers II and III) were extracted with combinations of acetone and n-hexane in a mechanical rotator according to Nylund et al.\textsuperscript{56} With this method, many samples can be extracted simultaneously and it has been shown to efficiently extract these types of compounds from soil.\textsuperscript{56}

2.3 Sample Clean-up

The extraction step is followed by one or several clean-up steps in order to reduce the amount of co-extracted interferences from the sample.
extract before the instrumental analysis. Treatment with concentrated sulfuric acid is an effective method to remove less persistent interferences from the extract that can be used when the analytes of interest do not degrade from such a treatment (e.g. PBDEs, PCBs, and many other POPs). Non-destructive, pre-separation of sample extracts on chromatographic columns, i.e. fractionation of classes of compounds due to different physical-chemical properties, are often used to reduce interferences from co-eluting compounds before the final analysis.\(^{57}\)

Some EFRs included in this thesis (EHTBB and BEH-TEBP) degrade in sulfuric acid and were separated from other analytes on a silica gel column in a fractionation step. Three fractions were collected; fraction 1 contained most of the analytes included (i.e. PBDEs, DBDPE, DBE-DBCH, PBT, HBB, DDC-CO, hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO) and octabromo-1,3,3-trimethyl-1-phenylindane (OBTMPI)). This fraction was subsequent treated with concentrated sulfuric acid. Fraction 2 contained BTBPE and the acid-sensitive analytes (EHTBB, and BEH-TEBP) and was further cleaned-up on an aminopropyl column. Fraction 3 contained the HBCDDs and was also treated with concentrated sulfuric acid. This clean-up method was used for all samples in Papers II-IV and is described briefly in Paper II (details can be found in Sahlström et al.\(^{58}\)).

For the atmospheric deposition samples in Paper I a non-destructive, chromatographic clean-up method on a Florisil column was used.

2.4 Instrumental analysis

The final separation of most of the analytes covered in this thesis is commonly done using gas chromatography (GC). Much consideration must be taken for the GC analysis of especially BDE-209 as it can be degraded both in the injector and in the column. To minimize degradation in both of these areas, the use of a programmable temperature vaporizing PTV injector is recommended over a split/splitless and a 15 m column with a thin stationary phase (0.1 µm) is recommended for BDE-209 analysis.\(^{59, 60}\) Although a 30 m column is most common for the analysis of lower brominated PBDEs, a 15 m column was used in this thesis (Papers II-IV), as all analytes in fractions 1 and 2 from the silica gel were found to resolve sufficiently on this column.

The GC is most frequently connected to a mass spectrometer (MS) for the detection of the analytes. The MS can be operated in either the electron capture negative ionization (ECNI) or electron impact (EI) mode. ECNI offers higher sensitivity over EI for many halogenated compounds, such as PBDEs and EFRs. However, fragmentation is reduced compared to EI and for many brominated compounds (e.g. lower brominated PBDEs),
Bromide ions are the predominant (only) ions produced. Higher brominated PBDEs (hepta-deca), however, also form higher mass fragments (phenoxide ions) under ECNI conditions, allowing for the use of isotopically labeled surrogate standards for these. For most of the analyses in Papers II-IV, GC-MS/ECNI was used.

HBCDD isomers cannot be separated on a GC column, so for the isomer specific analysis of HBCDD in dust, air, and soil (Papers II-IV), liquid chromatography (LC), coupled to an MS was used. LC techniques have sometimes, albeit infrequently, been used for the analysis of PBDEs to overcome many of the degradation problems for higher brominated PBDEs as discussed above, resulting in increased sensitivity. For the analysis of BDE-209 in Paper III, an LC-MS/MS method was used. Tri-heptaBDEs in Paper III were analyzed using GC-MS operated in the EI mode.

For increased sensitivity and selectivity, high resolution MS (HRMS) can be used. HRMS has the ability to resolve ions that have the same nominal mass (sum of all the protons and neutrons) but differ in exact mass. This difference is known as a mass defect and is caused by some of the mass of an atom being converted to energy, known as the nuclear strong force, required to overcome the repulsion of protons to each other in the nucleus. There is a significant mass defect for chlorine and bromine atoms, causing their nominal mass to differ from the exact mass and making them ideal candidates for analysis by HRMS. This increased selectivity is especially useful when identifying emerging contaminants at low levels. For these reasons, atmospheric deposition samples (Paper I) were analyzed using GC-HRMS.

2.5 Quality control

To test the ability of PUFs to trap analytes in the AAS, an experiment was performed in which the filters were spiked with standard and run for 24 and 48 hours. Another sampler was run in parallel to correct for target compounds that might be present in the air. Filters, the front PUF, and the back PUF were analyzed separately. Results showed that the target analyte with the lowest $K_{OA}$, DBE-DBCH ($\log K_{OA} = 8.01$), was not fully captured by the PUFs (~50%), while compounds with $\log K_{OA} > ~12$ were not fully volatilized from the filter and BDE-209 was not volatilized at all (Figure S1 in Paper II). The total recovery (filter + PUFs) for most compounds (except DBE-DBCH) was >80%, implying that the air sampling method is acceptable for compounds in this $K_{OA}$ range, however, DBE-DBCH concentrations may be underestimated in this thesis.

The use of isotopically labeled standards as surrogates allows for correction of any losses during the analytical procedure. Low recoveries may result in inaccurate quantification and in some cases, compounds may
not be quantified if the recoveries are not sufficient (e.g. DBDPE in air and HBCDDs in soil in Paper III). A number of different labeled surrogate standards were used in this thesis (see individual papers for more details).

Field blanks as well as laboratory blanks were analyzed in parallel to the samples to check for and, if necessary, correct for background contamination of the analytes. If present in the blanks, the level there determined the method’s limit of detection (mLOD) for that compound. If not present in the blanks, the size of the chromatographic peak determined the mLOD. In Papers II and IV, a method limit of quantification (mLOQ) was also established. This allowed for some compounds to be detected but not quantified and in these cases, the compound’s level is reported as a range from the mLOD to the mLOQ. Further details can be found in the respective papers (Papers I-IV).

Degradation of BDE-209 into nona-BDEs is unavoidable during the analytical procedure but can be corrected for by measuring the degree to which $^{13}$C-BDE-209 degrades in $^{13}$C-nonaBDEs and assuming the same degree of degradation for the native compound.
3. Results

Table 3 summarizes the results for FRs in all matrices included in this thesis.

3.1 PBDEs and HBCDDs

PBDEs in the Penta- and OctaBDE technical products were found in almost all samples, including PentabDE congeners in deposition samples in the Arctic (Table 3). BDE-209 was also often found and was the predominant BDE in most samples. Levels of PBDEs in air and dust from indoor environments in Stockholm (Paper II) were lower than those found in a 2006 study of similar microenvironments in Stockholm. The most predominant compounds in indoor and outdoor air in Stockholm were BDE-47 and -209 which originate from the Penta- and DecaBDE technical mixtures, respectively. In indoor air, the levels of BDE-47 were slightly higher in Stockholm (Paper II) than in Beijing offices (Paper IV), however, levels in both studies were close to detection limits. BDE-209 concentrations, however, were 1-2 orders of magnitude lower in Stockholm than in Beijing. In outdoor air and soil, Stockholm had far lower PBDE concentrations than Birmingham (Figure 4).

HBCDD was seldom detected in indoor or outdoor air in Stockholm but was detected in all dust and soil samples. It was detected much more frequently in indoor air in Beijing (mean = 300 pg m\(^{-3}\)) and in outdoor air in Birmingham (mean = 99 pg m\(^{-3}\) when a generic sampling rate of 4 m\(^3\) day\(^{-1}\) was used). Isomer patterns of HBCDD differed in dust in Stockholm depending on the specific location sampled (Paper II). Dust taken from areas surrounding products had a higher relative abundance of the α-HBCDD isomer than dust taken directly from the product. It has been shown by Harrad and Abdallah\(^{52}\) that photolytic isomerization of HBCDD isomers can occur and formation of the α-HBCDD isomer is favored.

Outdoor concentrations of PBDEs and EFRs were much lower than indoor concentrations for the same compounds in Stockholm (Paper II). However, there were no significant differences in concentrations of any compounds in indoor and ventilation system air (p < 0.05, Paper II). This indicates that indoor air containing FRs may be an important source to the outdoor environment via emissions of ventilation air, as has been seen previously for PBDEs.\(^{12}\)
3.2 Emerging Flame Retardants

Several EFRs, including DBE-DBCH, PBT, HBB, and DDC-CO, were commonly found in many of the samples presented in this thesis (Table 3). However, the predominant EFRs found were DBE-DBCH and DDC-CO. Both of these FRs were reported in samples from studies presented in all four papers, including in deposition samples (Paper I) showing that they are capable of LRT to the Arctic. EFR concentrations were often in the same range as for single BDE congeners, depending on the matrix and sampling site (see Table 1 in Paper I; Figure 2 in Paper II; Tables 2 and 3 in Paper III; Figure 3 in Paper IV). Their presence in indoor air and dust indicate that human exposure is probably occurring. In support of this, there have been some reports of the presence of DDC-CO and DBE-DBCH in human serum.62,63

DDC-CO has previously been reported in outdoor environments19,36,64 including remote areas of the Arctic and Antarctic.36 However, the only report of DBE-DBCH in the environment is one study which found this compound in beluga whales from the Canadian Arctic.65 Recently, it has been reported as a common pollutant in indoor air and dust in Norway62. In this thesis, it was found in indoor air and dust, and outdoor air in Sweden (Paper II), outdoor air in the UK (Paper III), and in indoor air in China (Paper IV) (Table 3). Thus, these two compounds show POP-like behavior and potential for human exposure and should be the subject of further study in the future.

BATE was prevalent in air samples in Birmingham (Paper III), whereas ATE was prevalent in soil samples in Birmingham (Paper III) (Table 3). These are related compounds, that are synthesized from 2,4,6-tribromophenol (TBP).66 It is unclear whether or not these compounds have a common source. Other EFRs found in some sample types were BTBPE, EH-TBB, BEH-TEBP and DBDPE (Table 3). These results indicate that EFRs are now in widespread use as replacements for PBDEs and HBCDDs. BTBPE was detected in deposition samples but could not be quantified (Paper I).
Table 3 - Median concentrations (range) of selected FRs from various matrices included in this thesis. \( \Sigma \text{DBE-DBCH} = \sum \alpha \cdot \text{DBE} + \beta \cdot \text{DBE-DBCH}, \) \( \Sigma \text{DDC-CO} = \sum \text{syn DDC-CO} + \text{anti DDC-CO}, \) \( \Sigma \text{HBCDD} = \sum \alpha \cdot \text{HBCDD} + \beta \cdot \text{HBCDD} + \gamma \cdot \text{HBCDD}. \) ND = not detected. NA = not analyzed. a) represents sum of BDE-99+BDE-100.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Units</th>
<th>Location</th>
<th>Paper</th>
<th>Dust</th>
<th>Indoor Air</th>
<th>Outdoor Air</th>
<th>Soil</th>
<th>Outdoor Air</th>
<th>Soil</th>
<th>Indoor Air</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ng m(^{-2}) month(^{-1})</td>
<td>Atmospheric Deposition</td>
<td>Stockholm</td>
<td>55 (7.0-130)</td>
<td>0.46 (0.18-2.4)</td>
<td>ND</td>
<td>2.0 (&lt;0.14-41)</td>
<td>ND</td>
<td>9.5 (&lt;0.15-80)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ng g(^{-1})</td>
<td>Stockholm</td>
<td>1.2 (&lt;0.073-3.8)</td>
<td>1 (&lt;0.019-4800)</td>
<td>&lt;36 (&lt;36-48)</td>
<td>ND</td>
<td>1.0 (&lt;0.40-14)</td>
<td>&lt;0.64 (&lt;0.64-71)</td>
<td>2.0 (&lt;0.016-4.5)</td>
<td>110 (11-810)</td>
</tr>
<tr>
<td>( \Sigma \text{DBE-DBCH} )</td>
<td>(4.5 (&lt;0.45-59))</td>
<td>Stockholm</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>II</td>
<td>III</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>( \Sigma \text{DDC-CO} )</td>
<td>(1.9 (&lt;0.56-11))</td>
<td>Northern Sweden</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>PBT</td>
<td>NA</td>
<td>Stockholm</td>
<td>1.1 (&lt;0.066-5.5)</td>
<td>11 (2.6-29)</td>
<td>0.17 (0.066-0.50)</td>
<td>0.013 (&lt;0.00085-0.018)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>8.8 (&lt;1.1-24)</td>
</tr>
<tr>
<td>HBB</td>
<td>NA</td>
<td>Stockholm</td>
<td>3.1 (&lt;0.26-69)</td>
<td>3.6 (&lt;5.1-64)</td>
<td>&lt;0.053 (&lt;0.053-0.26)</td>
<td>&lt;0.0028 (&lt;0.00079-0.61)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>6.4 (&lt;4.9-210)</td>
</tr>
<tr>
<td>EHTBB</td>
<td>ND</td>
<td>Stockholm</td>
<td>9.1 (&lt;2.5-65)</td>
<td>ND</td>
<td>0.13 (&lt;0.029-0.47)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.9 (&lt;1.4-26)</td>
</tr>
<tr>
<td>BEH-TEBP</td>
<td>NA</td>
<td>Stockholm</td>
<td>140 (&lt;33-1500)</td>
<td>&lt;35 (&lt;35-150)</td>
<td>ND</td>
<td>ND</td>
<td>Detected, not quantified</td>
<td>Detected, not quantified</td>
<td>Detected, not quantified</td>
<td></td>
</tr>
<tr>
<td>DBDPE</td>
<td>NA</td>
<td>Stockholm</td>
<td>12 (&lt;0.41-2200)</td>
<td>&lt;90 (&lt;90-250)</td>
<td>0.15 (&lt;0.12-0.33)</td>
<td>0.91 (0.20-160)</td>
<td>Detected, not quantified</td>
<td>0.35 (&lt;0.022-0.99)</td>
<td>16 (&lt;15-62)</td>
<td></td>
</tr>
</tbody>
</table>

Note: \( \Sigma \text{DBE-DBCH} = \sum \alpha \cdot \text{DBE} + \beta \cdot \text{DBE-DBCH}, \) \( \Sigma \text{DDC-CO} = \sum \text{syn DDC-CO} + \text{anti DDC-CO}, \) \( \Sigma \text{HBCDD} = \sum \alpha \cdot \text{HBCDD} + \beta \cdot \text{HBCDD} + \gamma \cdot \text{HBCDD}. \) ND = not detected. NA = not analyzed. a) represents sum of BDE-99+BDE-100.
<table>
<thead>
<tr>
<th>Location</th>
<th>Paper</th>
<th>Units</th>
<th>BTBPE</th>
<th>ATE</th>
<th>BATE</th>
<th>ΣHBCDD</th>
<th>BDE-47</th>
<th>BDE-99</th>
<th>BDE-153</th>
<th>BDE-209</th>
</tr>
</thead>
<tbody>
<tr>
<td>Northern Sweden</td>
<td>I</td>
<td>ng m(^2) month(^{-1})</td>
<td>17 (&lt;0.76-150)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>ng g(^{-1})</td>
<td>&lt;0.077 (&lt;0.077-0.26)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Stockholm</td>
<td>II</td>
<td>pg m(^{-3})</td>
<td>&lt;0.077 (&lt;0.077-0.26)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Stockholm</td>
<td>II</td>
<td>pg m(^{-3})</td>
<td>&lt;0.077 (&lt;0.077-0.26)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Stockholm</td>
<td>II</td>
<td>ng g(^{-1}) OM</td>
<td>17 (&lt;0.76-150)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
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<tr>
<td>Stockholm</td>
<td>III</td>
<td>pg m(^{-3})</td>
<td>ND</td>
<td>0.14 (0.010-0.69)</td>
<td>ND</td>
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<tr>
<td>Beijing</td>
<td>IV</td>
<td>pg m(^{-3})</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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</tr>
<tr>
<td>Birmingham</td>
<td>III</td>
<td>pg m(^{-3})</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
<td>Birmingham</td>
<td>III</td>
<td>ng g(^{-1}) OM</td>
<td>ND</td>
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<tr>
<td>Beijing</td>
<td>IV</td>
<td>pg m(^{-3})</td>
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<td>Beijing</td>
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</tr>
</tbody>
</table>

\(^a\) Detected, not quantified
3.3 Usage patterns in various countries

Usage patterns in various countries are often reflected in environmental levels. A good example of this is the stark contrast of levels of HBCDD in air between Sweden and the UK (Figure 4). HBCDD was virtually non-detectable in indoor and outdoor air in Stockholm. However, HBCDD levels rivalled those of PBDEs in outdoor air from Birmingham (Papers II and III). HBCDD levels were higher indoors in Beijing than in Stockholm. Levels of BDE-209 showed a similar pattern, with higher outdoor concentrations in Birmingham than Stockholm, and higher indoor concentrations in Beijing than Stockholm (Figure 4). The higher concentrations in Birmingham reflect the more stringent fire regulations in the UK than in Sweden. For Beijing, this is a reflection of China being the only country that still produces BDE-209 and of having historically consumed large volumes of the DecaBDE technical product.\textsuperscript{15, 67}

Levels of DBE-DBCH were similar in indoor air in Beijing and Stockholm but levels in outdoor air in Birmingham were 1-2 orders of magnitude higher than in Stockholm. Again, this may be reflective of the more stringent fire regulations in the UK. Little is known about the usage of this compound so speculation is difficult as to what the sources may be. DDC-CO was higher in Beijing indoor air than in Stockholm, possible as a result of the compound being manufactured in China.\textsuperscript{64} DDC-CO was not detected in outdoor air in Stockholm but it was found in most outdoor air samples in Birmingham. Levels in soil were 2-3 orders of magnitude lower in Stockholm than Birmingham. Möller et al.\textsuperscript{36} found elevated concentrations of DDC-CO in the English Channel, suggesting Western Europe as a source for this compound.
Figure 4 - Mean concentrations of selected compounds in A) indoor air, B) outdoor air, and C) soil in different countries.
3.3 Urban Pulses

Urban pulses were observed for PBDEs in both Stockholm (Paper II) and Birmingham (III) and for several EFRs that were found in at least 50% of samples in Stockholm (DBE-DBCH, PBT, EHTBB, and DBDPE). These results indicate that cities are sources of FRs to the outdoors, probably due to emissions from indoor environments in buildings via ventilation systems as discussed above. The fact that an urban pulse exists for EFRs in Stockholm indicates that our understanding of PBDE environmental behavior can be extended somewhat to some EFRs.

One measure for an urban pulse is the ratio of the concentration in the most urban area to the average concentration of all other sites. The pulse for PBDEs was more pronounced in Stockholm than it was for Birmingham. For ΣPBDEs, BDE-209, and tri-hexaBDEs the strength of the urban pulse in Stockholm was 2.3, 1.9, and 2.2, respectively (Paper II), while in Birmingham it was 1.1, 0.87, and 2.2, respectively (Paper III). The strength of the urban pulse is influenced by the gradient of population density (or degree of urbanization) from the urban to rural sites, as well as the background concentrations in air entering the city. Both of these factors explain the high urban pulse strength for Stockholm as the most rural sites were scarcely populated (especially, the two rural east sites found on the Stockholm archipelago) compared to some of the rural sites in Birmingham which were semi-populated. Also, the background air entering Birmingham had higher concentrations of PBDEs, diluting the urban pulse.

3.4 Long Range Transport

Air and soil samples from rural sites (Paper II) and deposition samples from remote sites (Paper I) can indicate which compounds are capable of undergoing LRT. DDC-CO was found in all rural soil sites from Paper II as well as deposition from both sites in Paper I. It was not detected in air. DBE-DBCH was found in all air samples and in atmospheric deposition at both sites in Paper I. It was not found in soil, however, perhaps because of its relatively low $K_{OA}$ ($\log K_{OA}$ \~8). BTBPE was found in air at two rural sites in Paper II and in atmospheric deposition at both sites in Paper I, although was not quantified. Some current use pesticides (CUPs) were included in Papers I and II, trifluralin and chlorothalonil, were discovered in the deposition samples. Given that there are no agricultural
activities in the vicinity of either sampling site, these likely underwent atmospheric LRT.

BDEs -47, -99, -100, and -209 were found in air at rural sites (Paper II) and BDEs -47, -99, and -100 were found in atmospheric deposition (Paper I). BDE-209, which is more particle-bound, was not analyzed for in Paper I but it has been previously found in both biotic and abiotic samples in the Arctic. Thus, both gaseous (multi-hoppers) and particle-bound (single hoppers) SVOCs have the potential for LRT and this was confirmed for several of the EFRs studied. DBE-DBCH is more volatile than the lower brominated BDEs, whereas DDC-CO is expected to be more particle-bound, behaving similarly to BDE-209.

For some compounds, isomers have different physical-chemical properties and degradation rates in the environment. For these, the relative abundance of isomers can change with distance from sources. For example, Möller et al. showed that there was an increase in the fraction of the anti-DDC-CO isomer relative to the syn isomer (expressed as F_{anti}) with distance from mainland Europe. This was also observed in Paper I. Samples from the Krycklan sampling site showed an F_{anti} of 0.62, which was closer to that of the technical mixture (0.65-0.75) than was found at the Abisko (Arctic) site (0.25).

In Paper I, air mass back trajectories were used to explore possible source regions for target compounds. While air sources varied greatly over the two month sampling periods, a general trend was observed regarding the two most abundant compound classes, HCHs and PCBs. The ratio of ΣHCHs to ΣPCBs was higher during periods when a greater part of the air masses had travelled over the oceans and lower when the air had travelled over land. This supported models of POP transport which suggest that PCBs enter the atmosphere mainly by primary and secondary emissions from continental sources while HCHs are volatilized more from oceans.

3.5 Deposition and fugacity fractions

Fugacity fractions can be calculated using measured air and soil concentrations, K_{OA}, and measured organic matter content. The resulting number represents a measure of the compound’s need to deposit vs. its need to volatilize in order to reach equilibrium. At equilibrium, the fugacity ratio is 0.50. In Paper II, fugacity ratios were extremely low for most compounds, meaning they were not in equilibrium and net deposition was strongly favored. This can be attributed to the compounds having high K_{OA} values and ongoing emissions to air, promoting disequilibrium.

Atmospheric deposition was measured in Paper I. This is a measure of the transfer of chemicals from the atmosphere to the surface but does not give information about equilibrium. It is useful, though to compare relative
deposition fluxes of chemicals, e.g. emerging chemicals vs. legacy chemicals. Paper I revealed that legacy chemicals are still more predominant than emerging chemicals in remote areas and that even among legacy POPs, HCHs and PCBs made up the bulk of the deposition. This is consistent with findings from air samples taken from Bjørnøya (Bear island), Norway in which HCHs, PCBs, and hexachlorobenzene made up 70-90% of the POPs measured. While other compounds were present in deposition (e.g. PBDEs, CUPs, EFRs), these only made up a minor portion of the total deposition of the compounds measured (Figure 1 in Paper I).

3.6 Comparability of air sampling methods

As discussed previously, active and passive air sampling each have strengths and weaknesses but the comparability of the data they each produce remains to be fully explored. Paper IV revealed that the concentrations measured by each is typically within a factor of 2-3 as previously observed. Concentrations of particle-bound contaminants, such as BDE-209, were less comparable, sometimes differing by as much as two orders of magnitude. Furthermore, more BDE-209 by mass was accumulated by the PUF disk placed in the center of the sampler (PUF-only PAS) than the GFF placed in the same place (Combo PAS). Differences between passive sampling configurations for more volatile compounds (DBE-DBCH, PBT, HBB, and BDE-47) were observed as well. Placement of the PUF disk in the center of the sampler, as opposed to against the top, resulted in greater uptake of these compounds. The retention capacity of PUFs for particles is thought to be the largest source of uncertainty in passive sampling for SVOCs.
4. Conclusions and recommendations for future work

Beyond contributing to the understanding of the behavior of POPs and emerging POP-like chemicals, perhaps the most important finding from this thesis is simply reporting the occurrence of several EFRs and two current-use pesticides about which little was previously known. Two EFRs stand out in their widespread occurrence in indoor and outdoor media and their potential for long range transport – DDC-CO and DBE-DBCH. DDC-CO was a predominant compound found at the remote Arctic sampling site (Abisko) in Paper I, indicating that it is persistent in the environment and can be transported long distances. Coupled with several other reports of its occurrence in the environment, its recent detection in human serum, and its similarity in structure to several banned pesticides such as dieldrin, aldrin, endosulfan, etc., this compound should be studied further for its toxicity and monitored for its environmental occurrence. DBE-DBCH was ubiquitous in indoor air in Stockholm and Norway. It was also found in Birmingham outdoor air, indoor air from Beijing offices, and atmospheric deposition from northern Sweden. People are clearly exposed to this compound, as seen in its presence in some serum samples, as well as in food items and it can be transported long distances. Further study of its toxicity and environmental monitoring is also warranted. These two FRs may thus be potential POPs.

Other EFRs that may be of concern are EHTBB, BEH-TEBP, BTBPE, DBDPE, PBT, and HBB and further studies are also needed. These EFRs were found in air and dust in several indoor environments, indicating humans are exposed to them, but also found in ventilation system air indicating they reach the outdoors. The urban pulses observed in Birmingham and Stockholm for PBDEs further indicate that indoor air is a source of these compounds to the outdoor environment. An urban pulse was also observed for some EFRs in Stockholm and DBE-DBCH in Birmingham indicating that they seem to behave environmentally in a similar manner as PBDEs.

The need for more comparison between active and passive air sampling methods was highlighted in Paper IV. The understanding of the processes that govern the uptake of particles in PUFs is perhaps the largest source of uncertainty in passive sampling. The use of a GFF has improved the sampling of particle-bound contaminants in PAS. However, the PUF placed against the top of the sampler was found to contain particle-bound
contaminants such as BDE-209, showing that there is still some adsorption of particles to the PUF. Particle-bound contaminants are also found on PUFs in active samples (Papers II and IV) indicating that BDE-209 may sorb to particles which may be too small to be trapped by the filter. Study of the retention capacity of PUFs for different sized particles would be most beneficial for PAS.

In a broader context, the ultimate goal is to contribute to the understanding of which chemicals have POP-like properties so we can avoid compounds like this in the future. The first step in achieving this is identifying which chemicals being used right now have POP-like properties. There has been a cycle in which chemicals are introduced to the marketplace, they are found to be more POP-like than previously thought, and then regulated several years later, leaving a legacy of environmental contamination and human exposure. This has been described as a game of “whack-a-mole”.73 Approximately one new chemical comes to market every 2.6 seconds and global chemical production is projected to double every 25 years.74 We need to better evaluate chemicals before they are used and have better methods to monitor those that are in use.
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