Comparison of sampling methods for measurements of atmospheric deposition of POPs

Atlasi Daneshvar, Karin Wiberg
Department of Aquatic Sciences and Assessment
Swedish University of Agricultural Sciences (SLU)

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Abbreviations

ABD: Atmospheric bulk deposition
ACE: Acetone
DCM: Dichloromethane
DD: Dry deposition
GFF: Glass fiber filter
GW: Glass wool
MIC: Meteorological Instruments of Canada
PAHs: Polycyclic aromatic hydrocarbons
PBDEs: Polybrominated diphenyl ethers
PCBs: Polychlorinated biphenyls
PCDDs: Polychlorinated dibenzo-\(p\)-dioxins
PCDD/Fs: Polychlorinated dibenzo-\(p\)-dioxins and polychlorinated dibenzofurans
PCDFs: Polychlorinated dibenzofurans
PUF: Polyurethane foam
QW: Quartz wool
RDS: Resin deposition sampler
SPE: Solid phase extraction
SS: Stainless steel
WD: Wet deposition
WIS: Wet integrating sampler
1. Introduction

A standard sampling method to monitor atmospheric deposition of Persistent Organic Pollutants (POPs) in Sweden was first developed within the framework of the national environmental monitoring in the 1990s (Brorström-Lundén 1995). In this method, atmospheric deposition (rain, snow and particles) is collected in a Teflon-coated funnel (1 m²), which is equipped with polyurethane foam (PUF) plugs as adsorbents (IVL 2006). The sampler was validated for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), but has been used within the Swedish monitoring for other POPs as well (e.g. polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (IVL 2006, IVL 2011). Many other sampling methods for POPs in atmospheric deposition have been developed. The purpose of the current study was to compile and compare recently used methods. A review of available sampling methods was conducted by searching the scientific literature and by questioning key persons in the area of environmental monitoring of POPs in Europe.

We focused on legacy (Stockholm Convention) POPs and other organic pollutants that are frequently monitored in air and atmospheric deposition, such as PCBs, PAHs, PCDDs, PCDFs and polybrominated diphenyl ethers (PBDEs). These compound groups are all highly hydrophobic, but span differently over the hydrophobicity range (Table 1). We aimed for recently conducted studies and limited the time frame of the studies to 2001-2013.

Table 1: Octanol-water partition coefficients (log \( K_{ow} \)) of the studied compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>( \log K_{ow} )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBs</td>
<td>5.3-7.2</td>
<td>Beyer et al. 2002</td>
</tr>
<tr>
<td>PAHs</td>
<td>3.4-6.8</td>
<td>Bergknut 2006</td>
</tr>
<tr>
<td>PBDEs</td>
<td>4.9-8.4</td>
<td>Sheryl et al. 2009</td>
</tr>
<tr>
<td>PCDDs</td>
<td>4.8-8.3</td>
<td>Aberg et al. 2008</td>
</tr>
<tr>
<td>PCDFs</td>
<td>3.9-8.0</td>
<td>Aberg et al. 2008</td>
</tr>
</tbody>
</table>
2. Overview of atmospheric deposition sampling methods

We identified approximately 20 recent (2001-2013) studies that included measurements of atmospheric deposition of the target POPs. Many different sampling methods were identified including various collection principles (on/off-site adsorption/extraction, filter/no-filter, etc.), sampler designs and sampler surface materials. Four different adsorbents were used: XAD-2, Amberlite IRA-743, PUFs and SPE disk (ENVI-18). We divided the studies into five categories according to the collection principle:

1. Filter (on-site) + adsorbent (on or off-site)
2. Glass or quarts wool (GW or QW) + adsorbent (on-site)
3. Glass microfiber extraction thimble (on-site)
4. PUF (on-site)
5. Bulk sampling (on-site) + extraction (liquid-liquid) (off-site)

A complete list of the identified studies is presented in Table 2. In more than 70% of the studies, the deposition (snow, rain and particles) either passed through a filter followed by an adsorbent (Category 1) or through glass or quartz wool (GW or QW) followed by Amberlite IRA-743 or XAD-2 (Category 2). The filters and the GW/QW are meant to collect the particulate phase, while the adsorbents (Amberlite, XAD-2, SPE disks and PUFs) are believed to collect both the dissolved and particulate phase by adsorption and filtration, respectively (Gocht et al., 2007a). The Category 2 sampler described under 2a-2c (see also Gocht et al., 2007a) is validated as a national standard for PAHs in Germany (VDI, 2003). The German standard for sampling of PCDD/Fs (VDI, 2002b) goes even further and uses a combination of Category 2 and 3 (glass microfiber thimble + GW + XAD-2).

Samplers belonging to Categories 3-5 appear to be less commonly applied. Category 5 includes bulk sampling of the wet and dry deposition in the field, followed by liquid-liquid extraction off-site. This sampling method is efficient (Gómez-Belinchón et al., 1988), but has a limited sampling volume capacity and is mostly appropriate for short-term sampling (typically 1-2 weeks); otherwise they require high maintenance to avoid overflows. Category 3 and 4 can be considered as the two extremes. An extraction thimble (Category 3) will only efficiently collect the particulate fraction and is thus only appropriate for highly hydrophobic
POPs. This type of sampler has previously been shown to effectively collect >90% of the PCDD/Fs in precipitation (McLachlan et al., 1998). On the other hand, PUF is a very porous material, and a PUF-only sampler (Category 4) will discriminate the particulate fraction to some extent. This discrimination is partly overcome by cleaning the surface after the sampling period using filter and solvent and by combining these with the PUF-plugs in the analysis (Brorström-Lundén 1995). It has been shown that a significant portion of PAHs and PCBs are attached to the sampler surface (approx. 20-60%, Figure 4.4 and 4.5 in Brorström-Lundén 1995), and that the proportion varies largely between sampling occasions depending on weather conditions (rain, temperature, etc.). The cleaning procedure is therefore part of the normal sampling routine. However, even if this procedure is used, there is a breakthrough of pollutants. It has been assessed that the lost fractions for PAHs and PCBs are 5-15% and 5-10% respectively (Brorström-Lundén 1995). The fraction for even more hydrophobic pollutants is likely higher.

The sampling efficiency of an adsorbent varies depending on the characteristics of the adsorbent (e.g. sorption coefficient ($K$) and wettability) and characteristics of the chemicals (e.g. hydrophobicity). Some guidance on this topic can be found in the literature. For example, PUF was shown to be superior to XAD-2 in adsorbing hydrophobic organic chemicals (hydrocarbons, PCBs and fatty acids) from sea water (Gómez-Belinchón et al., 1988). It has also been argued that XAD-2 is a more efficient adsorbent for PCDD/Fs than PUF (Hovmand et al. 2007). In a study by Grathwohl and Schiedek (1997), it was found that in addition to the sorption coefficients of the adsorbents also the wettability is important for the collection efficiency. Moderately hydrophobic solid phases such as C18-coated solid phases and Amberlite IRA-743 were recommended as the most suitable adsorbents for hydrophobic organic contaminants, while activated carbon, XAD and PUF adsorbents were considered as less good options. Although there is some knowledge in this research area, there are no recent comprehensive studies including the compounds of interest in the current study.

3. Comparison of samplers

The research group of Karin Wiberg carried out a limited screening study in which the two extremes Category 3 (glass microfiber filter thimble) and Category 4 (PUF-plugs) were
compared in a field study at the Svartberget field station (Vindeln, Västerbotten, unpublished). In the figures below, the amounts of PCDD/Fs (Figure 1) and PCBs and hexachlorobenzene (HCBz) (Figure 2) collected in a sampler equipped with a glass fiber thimble (Category 3) and a sampler equipped with PUF plugs (Category 4) are shown. The sampling took place at Svartberget field station (Vindeln) with a 1-month sampling time (February 2008). The PUF sampler (Category 4) is identical with those used in the Swedish national monitoring (Sampler 4-a in Table 2), while the sampler equipped with the glass microfiber thimble was identical with Sampler 3-a in Table 2.

**Figure 1: Amounts (pg) of homologue groups of PCDD/Fs (sum of all congeners) per sample in Sampler types 4-a (PUFs) and 3-a (glass fiber thimble) used in a field study in Svartberget (Vindeln), sampling duration 1 month (Febr. 2008).**
Figure 2: Amounts (pg) of PCB congeners and hexachlorobenzene per sample in Sampler type 4-a (PUFs) and 3-a (glass fiber thimble) used in a field study in Svartberget (Vindeln). The sampling duration was 1 month (Febr. 2008).

The results show that for very hydrophobic pollutants, such as highly chlorinated DD/Fs, the thimble (Sampler 3-a) is more efficient than the PUF (Sampler 4-a). The thimble collected 2.1-2.9 times higher amounts of HpCDD and OCDD and 1.3-1.5 times higher amounts of HpCDFs and OCDF. For the less chlorinated congeners, the PUF was more efficient and collected 1.2-1.6 times higher amounts of tetra- and penta-CDFs (TCDFs and PCDFs) and TCDDs. As atmospheric deposition is dominated by hepta- and octa-substituted CDD/Fs, the thimble (Sampler 3-a) appears to be the better choice among the two, while the PUF sampler (Sampler 4-a) will significantly underestimate deposition fluxes of PCDD/Fs.

The results for the PCBs are consistent with those for the PCDD/Fs in that sense that the more polar (less hydrophobic, lightly chlorinated) the compound is, the PUF is a better collector than the thimble. Consequently, the PUF sampler appears to be the better choice for PCBs and HCBz (Figure 2) as they generally are less hydrophobic (Table 1) and do not partition to particles to the same extent as PCDD/Fs. Looking at Table 2, it can be concluded that the thimble sampler (3-a) has exclusively been used for PCDD/Fs, and not for any other compound groups. However, Sampler 4-a has been used more broadly, and deposition fluxes
(ng m$^-2$ day$^-$1) for PCBs, PAHs as well as PCDD/Fs and PBDEs have been reported (IVL 2006, IVL 2011).

It should also be noted that other sampler types (including those in Category 1, 2 and 5) may be even more efficient than the two tested in this screening study. Very few attempts have been made to compare sampling efficiencies, especially in the field. It is possible, or even likely, that different sampling methods lead to significant differences in deposition fluxes, even if the same chemical is measured at the same site and the same time. It was shown by Bergknut et al. (2011), that annual deposition of PCDD/Fs were approximately 4 times higher using a Category 2 sampler (GW+Amberlite IRA-743) than using a Category 3 sampler (glass microfiber thimble) (Bergknut et al. 2011). This could be due to differences in collection materials (filters, adsorbents, etc.), but also to differences in sampler surface material (e.g., revolatilization from hot metal surfaces during summer season), sampler design (e.g., sampling area in relation to volume) and permeability of the adsorbent (over-flows) (Bergknut et al. 2011; Gocht et al 2007a). A glass microfiber thimble is inert and primarily promoting retention of the particle associated fraction (highly chlorinated compounds), while a combination of GW and Amberlite will have the potential to collect both the particulate and the dissolved phase. In the Bergknut study, differences in collection efficiency were supported by a shift in the congener pattern of the PCDD/Fs with better sampling efficiency for less hydrophobic congeners in the Amberlite sampler (Category 2) as compared to the thimble sampler (Category 3).

On the other hand, there are also other aspects than collection efficiencies that have to be considered in environmental monitoring of pollutants, e.g., the possibility to be able to sample in the field with low maintenance efforts and sometimes without access to electricity. The final choice of sampler may have to be a compromise between many aspects including both collection efficiency and practical issues.
Table 2: Summary of identified sampling methods for atmospheric deposition of POPs

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Sampler type</th>
<th>Description</th>
<th>Method</th>
<th>Time or volume</th>
<th>Location</th>
<th>Validation of method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>Mirror-polished SS cylindrical vessel (D: 500 mm, H: 600 mm)</td>
<td>Deposition filtered through GFF followed by PUF on-site (portable system) Deionized water added to the bottom of sampler to prevent re-suspension of dry deposition.</td>
<td>1 month</td>
<td>Taiwan</td>
<td>Chi et al. 2009</td>
<td>Chi et al. 2013</td>
</tr>
<tr>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>Automated sampler: 2 deposition vessels, for dry/wet dep.</td>
<td>Deposition filtered through GFFs (5 μm and 0.3 μm) followed by PUF on-site.</td>
<td>1 month</td>
<td>Taiwan</td>
<td></td>
<td>Chi et al. 2009</td>
</tr>
<tr>
<td>PBDE/PCB</td>
<td>ABD</td>
<td></td>
<td>Deposition filtered through GFF (47 mm) to collect particles followed by two PUF plugs connected in series (27 x 40 mm) on-site. Funnel washed and rinsed with distilled water, which is passed through the filter setup</td>
<td>4 days</td>
<td>Central basin of Baltic Sea</td>
<td>ter Schure et al. 2002</td>
<td>ter Schure et al. 2004</td>
</tr>
<tr>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>SS pots with inner diameter of 30 cm and a height of 30 cm</td>
<td>Deposition filtered through GFF (47 mm, 0.45 μm) followed by SPE disk (ENVI-18 DISK, 47 mm) off-site. Purified water added to the bottom of sampler to prevent re-suspension of dry deposition.</td>
<td>3-4 months</td>
<td>South Korea</td>
<td>Horstmann &amp; McLachlan 1997</td>
<td>Fang et al. 2011</td>
</tr>
<tr>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>Glass pot (50x50x40 cm)</td>
<td>Deposition filtered through GFF (1.0 μm) followed by SPE disk (ENVI-18 DISK, 47 mm) off-site. Water added to bottom of sampler to prevent re-suspension of dry deposition.</td>
<td>1 month</td>
<td>Japan</td>
<td>Ogura et al. 2001</td>
<td></td>
</tr>
</tbody>
</table>

Filter (on-site) + adsorbent (on or off-site)
<table>
<thead>
<tr>
<th>1-g</th>
<th>PCDD/PCDF</th>
<th>ABD</th>
<th>SS pots with inner diameter of 50 cm and a height of 50 cm</th>
<th>Deposition filtered through GFF (47mm, 0.7 μm) followed by SPE disk (ENVI-18 DISK, 47 mm) off-site. Purified water added to the bottom of sampler to prevent re-suspension of dry deposition.</th>
<th>1 month</th>
<th>South Korea</th>
<th>Ogura et al. 2001</th>
<th>Moon et al. 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-h</td>
<td>PCDD/PCDF/PCB/PAH/PBDE</td>
<td>ABD</td>
<td>Glass funnel</td>
<td>Deposition passed through a filter followed by XAD-2 resin.</td>
<td>4 months</td>
<td>Germany, Switzerland, Austria</td>
<td>VDI, 2002a</td>
<td>Offenthaler et al. 2009</td>
</tr>
<tr>
<td>1-i</td>
<td>PCB/PAH</td>
<td>WIS</td>
<td>MIC rain sampler</td>
<td>Deposition passed through GFF followed by XAD-2 resin on-site</td>
<td>USA</td>
<td>Baker et al. 1992</td>
<td>Park et al. 2002</td>
<td></td>
</tr>
<tr>
<td>1-j</td>
<td>PCB</td>
<td>“Baker” wet only sampler</td>
<td>Deposition passed through GFF (and GW) followed by XAD-2 resin on-site</td>
<td>USA</td>
<td>Baker et al. 1992</td>
<td>Park et al. 2001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**GW or QW + adsorbent (on-site)**

<table>
<thead>
<tr>
<th>2-a</th>
<th>PCB/PBDE</th>
<th>ABD</th>
<th>Deposition passed through GW and Amberlite IRA-743 on-site</th>
<th>3-4 months</th>
<th>South Korea</th>
<th>Gocht et al. 2007a, Gocht et al. 2007b, Fang et al. 2011</th>
<th>Fang et al. 2012</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PCDD/PCDF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-b</td>
<td>PCDD/PCDF/PCB</td>
<td>ABD</td>
<td>0.25 m diameter borosilicate glass funnel (area : 0.05 m²), sample collector volume 0.020 m³</td>
<td>Deposition passed through GW and Amberlite IRA-743 on-site</td>
<td>2 months</td>
<td>Sweden</td>
<td>Gocht et al. 2007a, Gocht et al. 2007b</td>
</tr>
<tr>
<td>2-c</td>
<td>PAH</td>
<td>ABD</td>
<td>Borosilicate glass funnel</td>
<td>Deposition passed through GW and Amberlite IRA-743 on-site.</td>
<td>6-8 weeks</td>
<td>Germany</td>
<td>Martin &amp; Grathwohl 2002</td>
</tr>
<tr>
<td>2-d</td>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>Borosilicate glass funnel (sampling area:0.06 m²)</td>
<td>Deposition filtered through QW followed by XAD-2 on-site. Quarts-wool and XAD-2 removed, funnel washed with ACE &amp; toluene which were collected separately</td>
<td>1-2 months</td>
<td>Denmark</td>
<td>Horstmann &amp; McLachlan 1997, Knoth et al. 2000</td>
</tr>
<tr>
<td></td>
<td>ABD</td>
<td>Collection Method</td>
<td>Description</td>
<td>Collection Period</td>
<td>Country</td>
<td>Reference 1</td>
<td>Reference 2</td>
</tr>
<tr>
<td>----</td>
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<tr>
<td>2-a</td>
<td>PCBs</td>
<td>WIS</td>
<td>0.212 m² SS funnel</td>
<td>Deposition passed through GW(?) and XAD-2 resin on-site</td>
<td>12-24 day</td>
<td>USA</td>
<td>Totten et al. 2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Glass microfiber thimble (on-site)</td>
<td>WIS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-a</td>
<td>PCDD/PCDF</td>
<td>ABD</td>
<td>1 m² rectangular SS funnel, sample collector volume of 0.16 m³</td>
<td>Deposition passed through glass microfiber Soxhlet extraction thimble (22 x 80 mm) on-site. Between samples, funnel surface wiped with GFF moistened with ethanol (included in the sample)</td>
<td>1 month</td>
<td>Sweden</td>
<td>McLachlan &amp; Sellström 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PUF (on-site)</td>
<td>PUF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-a</td>
<td>PCDD/F, PAH, PCB, PBDE</td>
<td>ABD</td>
<td>1 m² Teflon-coated rectangular funnel with a height of 10 cm</td>
<td>Deposition passed through PUF on-site Between samples, funnel wiped with GFF and ethanol (included in the sample)</td>
<td>1 week – 1 month</td>
<td>Sweden/Finland</td>
<td>IVL 2006</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bulk (WD + DD) on-site, extraction (liquid-liquid) off-site</td>
<td>Bulk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-a</td>
<td>PCB</td>
<td>ABD</td>
<td>SS funnel connected (0.36 m² surface) connected to 25 L aluminum bottle</td>
<td>Liquid-liquid extraction off-site using DCM and mechanical shaking</td>
<td>1 week</td>
<td>France</td>
<td>Teil et al. 2004</td>
</tr>
<tr>
<td>5-b</td>
<td>PAH</td>
<td>ABD</td>
<td>A 28 cm-diameter SS funnel. Fallout collected using 5.6 L aluminum bottle</td>
<td>Liquid-liquid extraction off-site using hexane/methylene and mechanical shaking</td>
<td>2 weeks</td>
<td>France</td>
<td>Ollivon et al. 1999</td>
</tr>
<tr>
<td>5-c</td>
<td>PCB/PAH</td>
<td>ABD</td>
<td>Glass funnel (60 mm high, 285 mm diameter) mounted onto a 1L Pyrex glass bottle</td>
<td>Liquid-liquid extraction off-site using DCM pentane or cyclohexane</td>
<td>1 week</td>
<td>Norway</td>
<td>Wania &amp; Haugen 1999</td>
</tr>
</tbody>
</table>
4. Conclusions

- On the basis of the literature study, we conclude that existing methods for sampling of atmospheric deposition of legacy POPs can be divided into 5 categories depending on the collection principle: 1) Filter (on-site) + adsorbent (on or off-site), 2) Glass or quarts wool (GW or QW) + adsorbent (on-site), 3) Glass microfiber extraction thimble (on-site), 4) PUF (on-site), 5) Bulk sampling (on-site) + extraction (liquid-liquid) (off-site).

- The most commonly applied methods, Category 1 and 2, include a combined particulate and dissolved phase retention, where filters and/or GW/QW are used to retain particles and an adsorbent (XAD, Amberlite, PUF and SPE-disk) primarily collects the dissolved phase.

- Two of these categories can be considered as extremes, as they (partly) discriminate the dissolved phase (Category 3, glass microfiber thimble) or the particulate phase (Category 4, PUF-only, and this discrimination occurs even if pollutant residues attached to the sampler surface are included in the analysis).

- A screening study of the sampling efficiency of glass-microfiber-thimble-only (Category 3) and PUF-only (Category 4) samplers indicates that they cannot be considered as good collectors for chemicals including a broad hydrophobicity range. For example, sampling of PCDD/Fs in atmospheric deposition using PUF-only samplers (Category 4) cannot be recommended.

- A field study suggests that a GW+Amberlite IRA-743 sampler (Category 2) has significantly higher collection efficiency for PCDD/Fs than glass-microfiber-thimble-only (Category 3) samplers.

5. Suggestions for future work

Considering the results and conclusions presented here, we suggest that an extended screening study of different samplers for bulk atmospheric deposition of POPs should be conducted. This screening should not only include the two extreme samplers (Category 3 and 4), but also samplers with combined collection principle (Category 1 and 2). Overall, the outcome of this
report highlights the need to validate sampling methods for monitoring of atmospheric deposition of POPs in the Swedish environment.

6. References

Bergknut et al. 2011. Environmental Pollution 159:1592–1598
Bergknut 2006. Ph.D thesis, Department of Chemistry, Umeå University
Chi et al. 2013. Chemosphere 91:150–156
Gocht et al. 2007a. Atmospheric Environment 41:1315–1327
Hovmand et al. 2007. Atmospheric Environment 41:2400–2411
McLachlan et al. 1998. Untersuchung der atmosphärischen belastung, des weiträumigen transports und des verbleibs von polychlorierten dibenzodioxinen, dibenzofuranen und coplanaren biphenylen in ausgewählten gebieten Deutschlands. Report in German. Department of Environmental Chemistry and Geochemistry, Bayreuth University, Germany
Ren et al. 2007. Atmospheric Environment 41:592–605
Totten et al. 2004. Environmental Science and Technology 38:2568–2573
Totten et al. 2001. Environmental Science and Technology 35:3834–3840
deposition of organic trace substances; Funnel adsorber method – Part 2: Determination of polynuclear aromatic hydrocarbons.

**Wania and Haugen 1999.** *Environmental Pollution* 105:381–386

**Yu et al. 2006.** *Atmospheric Environment* 40:96–108