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SAMPLING ARTIFACTS AND UNCERTAINTIES IN ACTIVE AND PASSIVE AIR SAMPLING, AND THE IMPLICATIONS FOR COMPARISON OF MEASUREMENTS OF SVOCs IN AIR

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Introduction

Recent scientific and policy discussion has addressed air sampling of semivolatile organic compounds (SVOCs)/ persistent organic pollutants (POPs), particularly regarding long-term monitoring networks and the data needs of the SVOC community. However, while efforts have been made to synthesize data across monitoring networks, and better integrate active and passive sampling, uncertainties remain in comparability of data due to a lack of systematic efforts to determine sampler comparability and address sampling artifacts that may influence this comparability.[1] A wide range of air sampling configurations are in use (i.e. low/high/very high volume active samplers, and various passive samplers) and data from different sampling configurations are often compared.

In this study, sampling artifacts in active and passive air sampling were addressed in a set of case studies. The particular focus was on gas-phase breakthrough in active samplers, within-sampler degradation in both passive and active samplers, and sources of uncertainty in passive sampler calibration.

Gas-phase breakthrough has previously been identified as a concern in a number of different sampler configurations, particularly for more volatile SVOCs in high-volume active air samplers (AAS) using polyurethane foam (PUF) as gas-phase adsorbent,[2,3] and depends on the properties of the sampling medium and target compound, competition for the sampling medium (i.e. from other gas phase compounds), the sample volume, sample flow rate, temperature, humidity and pressure.

Degradation of SVOCs is a well-identified process in outdoor ambient air. However, the possibility exists for the naturally-occurring degradative processes to continue within active sampling media. This may lead to systematic negative bias of reported concentrations, particularly at longer sampling times and at sites with high levels of reactive trace gases (O₃, OH, NO_x).

Materials and methods

Breakthrough was addressed using specially adapted filter-sorbent sampling trains in three types of AAS. A low-volume AAS, a high volume AAS, and a high volume cascade impactor were run simultaneously at an outdoor suburban site in Brno, Czech Republic in autumn 2012. The samplers were run for sampling periods of 24 hours to 7 days, to collect different sample volumes. A high volume AAS was also run as a reference sampler for 24 hours for each day of the study (28 repeated samples). The sampling trains consisted of quartz fibre filters (QFF) appropriate to the sampler, and PUF sorbent that was subdivided into 5 slices to allow monitoring of the movement of SVOCs through the sorbent.

Degradation was addressed through a case study conducted in Kosetice, Czech Republic, a rural/background air quality monitoring site of the European Monitoring and Evaluation Programme (EMEP). Parallel low volume AAS were deployed containing QFF and PUF. One sampler was deployed in a conventional way, and the second sampler was equipped with a manganese oxide-based denuder to reduce the levels of reactive trace gases (especially O₃) entering the sampler. A series of air samples of different durations (24 hour to 7 days) was collected over a 1-month period in spring 2015. In addition, the possibility for degradation in passive air sampling (PAS) was also explored. Triplicate double-bowl PUF-PAS were deployed for 1 month, and at the same time, a series of triplicate PUF-PAS were deployed for 1-week periods. Thus, comparison of these samplers should provide insight into the temporal influence of within sampler degradation, and whether greater degradative losses occurred with longer sampling periods.

All samples were processed and analyzed in the Trace Analytical Laboratories of the Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University, Czech Republic, according to validated methods.[4] The target compounds in the study were polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and flame retardants (polybrominated diphenyl ethers – PBDEs, and novel flame retardants – NFRs).

Results and Discussion

In the breakthrough case study, separate quantification of QFFs and PUF slices indicated differing potential for breakthrough according to compound volatility. The distributions of compounds with vapour pressures >0.5 Pa suggested breakthrough losses in active air samples of 700 m^3 (e.g., as seen for acenaphthylene, Figure 1a), while for compounds with lower vapour pressures showed no evidence of breakthrough at these sampling temperatures (e.g., PCB 28 Figure 1b).

Comparison of large volume samples (up to 11000 m^3 in 7 day samples) indicated a further relationship with sample volume. Sample volumes $700\text{--}10000\text{ m}^3$ led to breakthrough for compounds with vapour pressures between $0.005\text{--}0.5$ Pa. For example, fluorene, which did not exhibit breakthrough in 700 m^3 samples, had $>20\%$ breakthrough at sample volumes $>1000\text{ m}^3$ (Figure 2).

The degradation case study did not find consistent evidence of within-sampler degradation for halogenated compounds in AAS. However, there was evidence for degradative losses of particle-phase PAHs. The concentrations measured by the AAS equipped with the denuder were consistently higher than those measured by conventional AAS for 1 to 7 day sampling periods (Figure 3a). This loss pathway was confirmed by losses of ^{13}C -labelled PAHs that were spiked onto the air samplers at the time of deployment (Figure 3b).

In the PAS, there were consistently lower concentrations in the longer deployment PAS than in the shorter deployment PAS for all PCBs, all flame retardants, and the majority of PAHs and OCPs. The degradation case study suggests that degradation can lead to underestimates of particle-bound PAHs in AAS and all compounds in PAS, particularly at high ozone conditions.

These case studies suggest that breakthrough and degradation may both contribute to uncertainties in air monitoring, and particularly when comparing between sites with different sampling configurations (e.g., different sample volumes or sorbent types), or sites with very different levels of reactive trace gases. Moreover, the differences in 1-week to 1-month PAS suggest a temporal aspect to degradative losses that may be particularly relevant for passive sampling.

Acknowledgements

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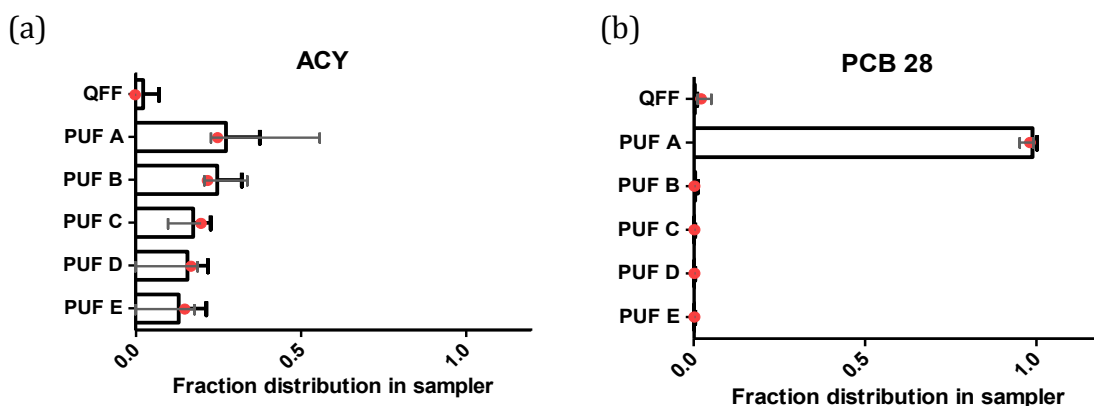


Figure 1: Distribution of volatile SVOCs within high volume AAS collecting 700 m³ of air for (a) acenaphthylene and (b) PCB 28. Black bars indicate measured distributions and red points indicate estimates.

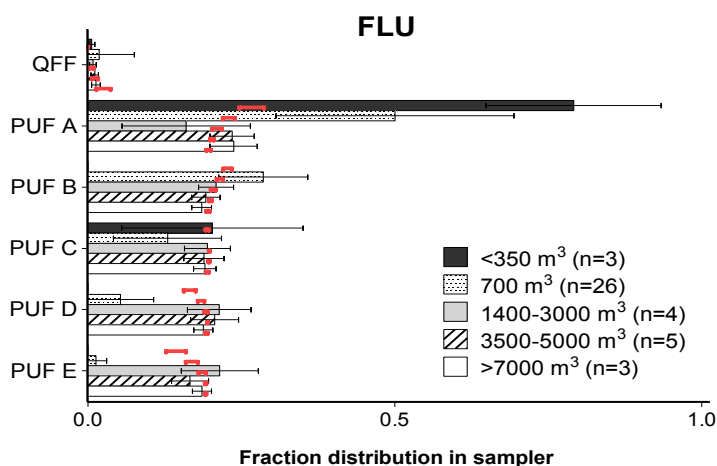


Figure 2: Distribution of fluorene in AAS at sample volumes from ~350 to >7000 m³. Black bars indicate measured distributions and red lines indicate estimates.

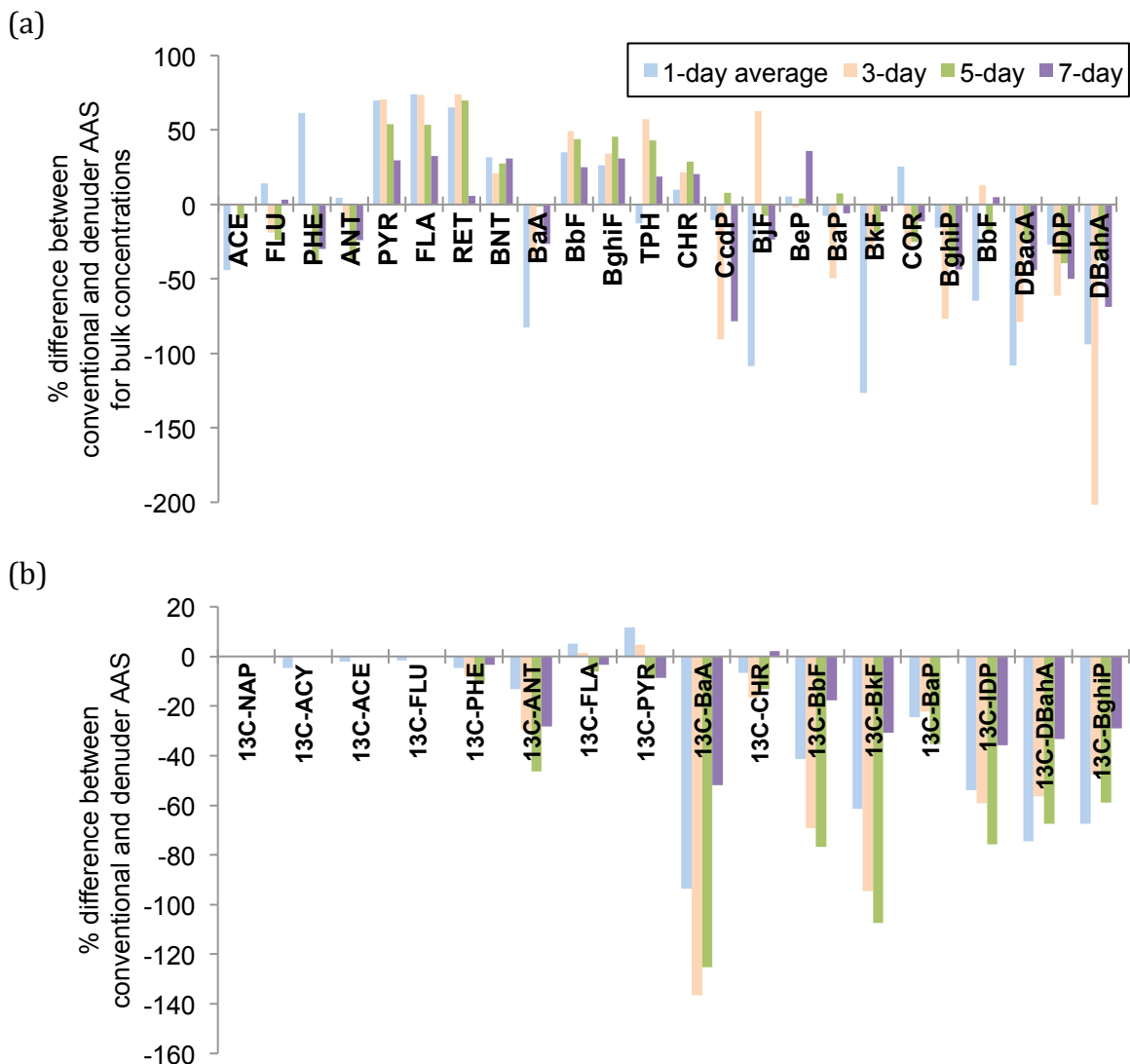


Figure 3: Percent difference between bulk (gas+particle phase) air concentrations of PAHs from AAS with and without denuder. Negative values indicate that the denuder AAS recorded higher concentrations than the conventional AAS (without denuder).