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APPLICATION OF THE PAS-DD PASSIVE SAMPLER FOR ASSESSING ATMOSPHERIC DEPOSITION AND PARTICLE CHARACTERIZATION OF ORGANOPHOSPHORUS FLAME RETARDANTS (OP FRs) AND POLYCYCLIC AROMATIC COMPOUNDS (PACS)

T. Harner¹, N. Jariyasopit¹, A. Eng¹, L. Jantunen¹, J. Martin², Y. Zhang²

¹*Air Quality Processes Research Section, Environment and Climate Change Canada, Toronto, ON Canada, M3H 5T4*

²*Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3*

Introduction. Atmospheric deposition is a key pathway for the delivery of airborne chemicals from the air to terrestrial surfaces (e.g. vegetation, soil, water). Once deposited, these chemicals can be accumulated and may pose a threat to the environment and food-chain. Therefore, it would be advantageous to have a simple method for measuring atmospheric deposition directly for priority air chemicals, particularly for chemicals that are associated with particles in air. The passive dry deposition sampler (PAS-DD) (Tisch Environmental, Cleaves, OH) is a new sampling device that was designed to address challenges with estimating the deposition of priority chemicals in air (i.e. particle deposition and dry gaseous deposition) (Eng et al., 2014; Sajjadi et al., 2016) and for resolving errors associated with model-derived deposition estimates, which can be uncertain if key input parameters are not available – e.g. wind speed, particle size distribution, surface properties. The PAS-DD sampler operates without the need for electricity and is therefore well-suited for deployment in remote and undeveloped environments and/or for concurrent deployment across many sites, over extended time periods. Because it has a uniform deposition surface and geometry, gas-phase and particle deposition to the PAS-DD sampler is easily characterized and therefore provides comparable data. This is advantageous in spatial studies designed to investigate differences in deposition loadings among several sites. The use of a polyurethane foam (PUF) disk as the collection substrate in the PAS-DD sampler also has the benefit that the analysis methods are harmonized with the conventional PUF disk air sampler that is widely used for measuring concentrations of target compounds in air (e.g. Pozo et al., 2009) (Figure 1). This contributes to the comparability of the complementary data generated by the two devices. The use of a common substrate also resolves challenges experienced using bio-monitoring approaches such as lichen sampling, where lichen properties can vary across sampling stations. Furthermore, because PUF is a porous substrate, deposited particles become well entrained in the PUF, thereby eliminating artefacts associated with particle blow-off. The porous structure of the PUF provides a 3-dimensional surface for deposition and also allows for individual particles to be observed and analyzed through microscopic methods which can yield insights for source attribution. In this study we present results on the characterization of the PAS-DD through field trials against the conventional PUF disk sampler targeting organophosphorus flame retardants (OP FRs) and polycyclic aromatic compounds (PACs). We also present novel microscopic techniques applied to PUF disk samples to yield information on the sources of collected particles.

Material and Methods. Field deployment and sample analysis: The PAS-DD sampler was deployed alongside the PUF disk sampler in two campaigns.

i.) Comparison of OP FRs in Toronto (summer vs winter) – during this campaign, two PAS-DD samplers were deployed in parallel with two PUF disk samplers for 2 months in both summer and winter of 2012. The samplers were mounted approximately 2 m above ground at the Environment Canada (Downsview) field station (background urban site). Samples (n = 8) and field blanks (n = 3) were analyzed gas chromatography-mass spectrometry (GC-MS).

ii.) Comparison of polycyclic aromatic compounds in the oil sands region (spatial study) – during this campaign, the samplers were co-deployed at 5 sites for a 2-month period during October-November, 2015. Samples were analyzed for PAHs, alkylated PAHs and PAH transformation products – nitro- and oxy-PAHs, according to methods described in Jariyasopit et al. (2015).

Microscopic analysis: Individual particles that were entrained on the PUFs of the PAS-DD and PUF disk sampler were inspected and analyzed using optical microscopy and scanning electron microscopy (SEM). The SEM analysis was coupled with energy dispersive x-ray spectroscopy (EDS) to provide information on the elemental composition of the particles. For instance, this technique has been used to identify petroleum coke particles by their high sulfur content; such particles are believed to be a major

source of PAC deposition in the oil sands region (Zhang et al., 2016). Particles originating from other sources may be distinguished by enrichment in other elements e.g. silicone, for particles of crustal origin.

Results and discussion: The PAS-DD sampler was applied for the first time to measure deposition of OP FRs. The results were consistent with results for particle-phase PACs reported by Eng et al. (2014) and show enhancement of OP FRs in the PAS-DD compared to the conventional PUF disk sampler (Figure 2). This is consistent with the particle-bound nature of OP FRs (due to their low volatility, Brommer et al., 2014). Thus, PUF disk and PAS-DD are shown to be complementary tools for investigating the occurrence, transport and deposition of OP FRs which are known to be abundant in air (e.g. Salamova et al., 2014).

The comparison of PACs in PAS-DD and PUF disk samplers also demonstrated enhancement in PAS-DD for the less volatile and particle-bound PACs, consistent with other results as already discussed. Interestingly, the PAS-DD is able to capture site-to-site variability that was not observed in model estimates of deposition (Zhang et al., 2015). Ongoing comparison of PAS-DD and POUF disk samplers will provide further insight to their performance and resolution against predicted values. Lastly, figure 4 shows how microscopic and analytical techniques such as SEM and EDS can be used qualitatively and quantitatively to characterize the deposited particles and to support source attribution.

Acknowledgements

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Figure 1. Illustration of the PAS-DD sampler (bottom) and the PUF disk sampler for assessing priority chemicals in air (from Eng et al., 2014).

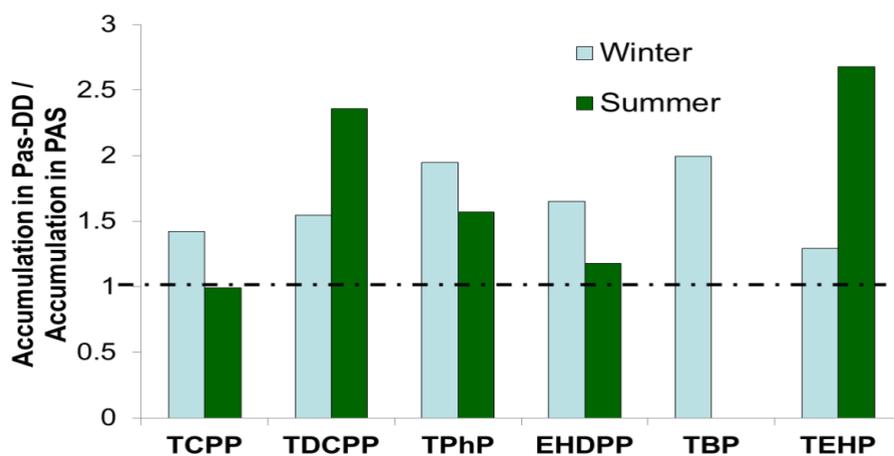


Figure 2. Enhancement ratios (ERs) greater than 1 for OP FRs during summer and winter periods due to greater collection of depositing particles by the PAS-DD sampler compared to the conventional PUF disk samplers. TCPP=Tris(2-chloroisopropyl)phosphate; TDCPP=Tris(1,3-dichloro-2-propyl)phosphate; TPhP=Triphenylphosphate; EHDPP=Ethylhexyl diphenyl; TBP=Tributyl phosphate; TEHP= Tris(2-ethylhexyl).

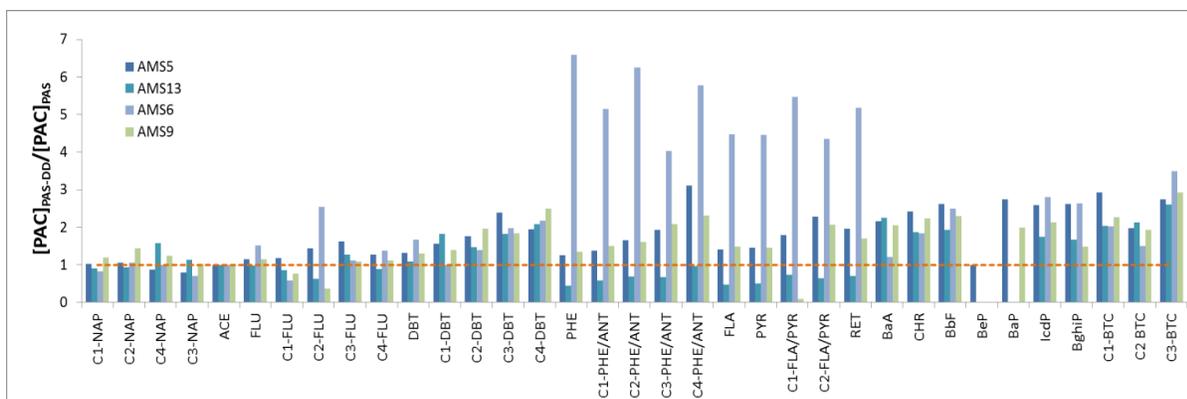


Figure 3. Enhancement ratios (accumulation in PAS-DD relative to PUF disk sampler) of selected PACs across 4 sites in the oil sands region during Oct-Nov 2015. Note: PACs are arranged according to volatility with mainly gas-phase compounds on the left and mainly particle-phase compounds on the right.

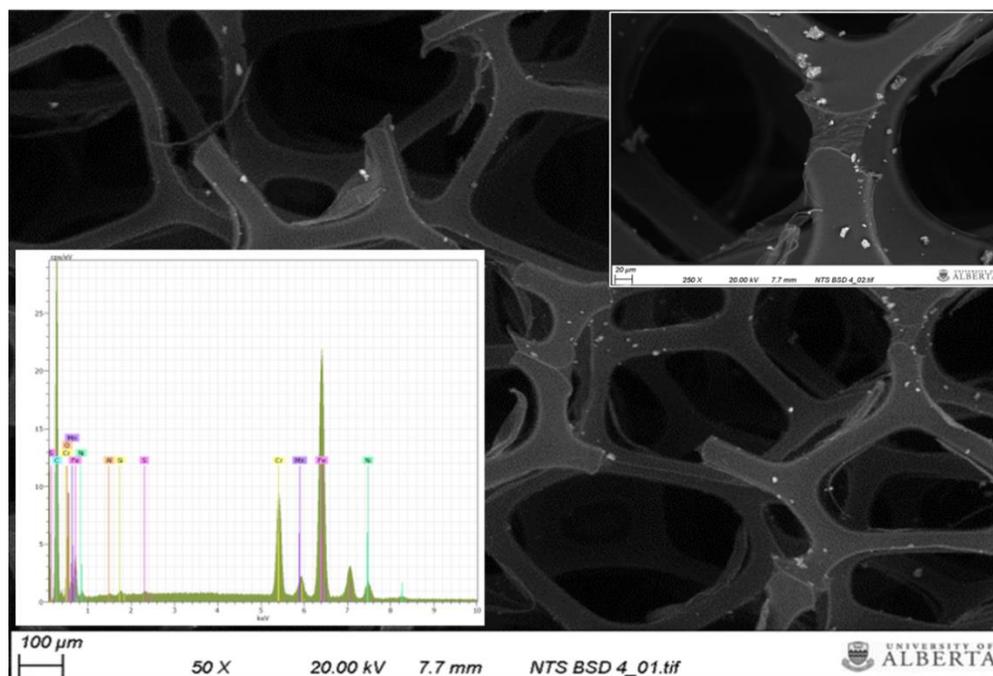


Figure 4. Scanning electron microscopy (SEM) images (50X and 200X (top inset)) of particles deposited onto PUF and elemental analysis (bottom inset) of a single particle using Dispersive X-Ray Spectroscopy (EDS).