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Analysis of polycyclic aromatic hydrocarbons (PAHs) in air using passive sampling calibrated with active measurements[☆]

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ABSTRACT

There are limited ambient air measurements of extended (beyond EPA Priority 16) lists of polycyclic aromatic hydrocarbons (PAHs). We measured air concentrations of 45 PAHs using passive and active air sampling at 15 sites in a central urban community and one rural site for two years. Passive sampling was conducted with cylindrical XAD-based samplers deployed to capture spatial variability. High volume active samplers with quartz fiber filters for particles and XAD-4 absorbent for gases were deployed at two urban sites and the rural site to calibrate the passive measurements directly. Estimated passive sampling rates (PSRs) were evaluated as functions of meteorological data, seasons, locations, study year, and compared with other studies. Possible particle collection by the passive samplers was evaluated using a variety of particle measurements (TSP, PM_{10}, $PM_{2.5}$ and ultrafines <100 nm). Total PAHs were statistically associated with ultrafine particle concentrations and to a lesser extent $PM_{2.5}$ and PM_{10}, but not TSP. PSRs were more variable when PAH mass loadings were lower and near method detection limits; this occurred more often at the rural site. The PSRs were not statistically associated with meteorological conditions in this study, but wind speed had the highest potential to impact PSR results. The resulting passive PAH measurements are reported with respect to proximity to major roadways and other known air emissions types. PSRs were quantifiable for some PAHs that were found predominantly in the particulate phase in active sampling. This information, together with particle fraction calculations from active sampling, were used to estimate the particulate PAH capture of the passive sampler. Summed PAH (∑PAH) passive concentrations were measured within the range of 10–265 ng/m3, with the highest concentrations from naphthalene and the lowest detected concentrations from anthracene. These results indicated a stronger seasonal signal within 200 m of a major roadway.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a category of substances that are emitted to the air mainly from anthropogenic combustion sources (Ravindra et al., 2008). PAH sources do not typically emit a single PAH, but emit complex and somewhat reactive parent PAH and substituted PAH mixtures into the air. PAHs are semi-volatile substances that can be present in the atmosphere in the gas phase, the particle phase, or both, depending on the environmental conditions and individual PAH vapor pressure. Toxicity and potency varies among individual PAHs, and many of them are known carcinogens, respiratory irritants, and/or are classified as persistent, bioaccumulative toxicants (PBTs).

Ambient air is measured using active or passive sampling techniques, where active samplers pull ambient air through a filter and sorbent material using an air pump. Passive air sampling is the collection of air pollutants by the diffusion of gases, and to a lesser extent particle entrainment, onto and into a sampling medium

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(Górecki and Namieśnik, 2002). Passive sampling compliments active air sampling by providing methods that are lower cost, require less security, are noiseless, and do not require power (Gouin et al., 2005). This allows the deployment of more samplers giving higher spatial resolution that is otherwise cost prohibitive. Higher density air sampling in a defined location such as a neighborhood is especially important to public health agencies who aim to answer questions from concerned citizens about potential health effects. However, if passive sampling methods are used either in isolation or in complement to active measurement methods, it is inherent that individual PAH concentrations are determined using PAH specific passive sampling rate (PSR) values in order to evaluate the toxicity or the cancer potency of these complex mixtures in ambient air (MDH, 2016; USEPA, 2010).

Passive air sampling was first used in the late 1920s, but did not become a quantitative methodology until the 1970s (Palmes et al., 1976). Since then, it has grown in use and by the variety of analytes and types of samplers to the present. There are passive air sampling devices for many air toxics and criteria pollutants (Nash and Leith, 2010) including semi-volatiles (Chaemfa et al., 2008; Jaward et al., 2004). Since the effective volume (V_{eff}) of air to the passive sampling media is unknown, the estimation of a PSR is required for the estimation of air concentrations. PSRs may be calculated by a theoretical model (Armitage et al., 2013; Herkert et al., 2016; May et al., 2011), utilized from past studies (Barthel et al., 2012), calculated based on activity of depuration or performance reference compounds (Moeckel et al., 2009), or PSRs may be estimated based on direct calibration from collocated active air measurements (Klanova et al., 2006; Liu et al., 2016; Wania et al., 2003). The use of direct calibration is considered the gold standard for PSR estimation (Herkert et al., 2016), in part because a PSR is estimated for each individual pollutant and site specific characteristics such as ambient temperature and wind speed are reflected in the measurements. The direct calibration of passive samplers to active sampler measurements is well established in the literature (Saini et al., 2015; Armstrong et al., 2014), however, less is known about the particle collection of passive samplers (Markovic et al., 2015).

This manuscript builds upon past investigations of gas and particle sampling rates (Holt et al., 2017), and incorporates the estimation of particulate phase PAH sampling by the passive sampler inferred from associations between ultrafine counts, total PAHs concentrations, particle fraction estimates, and sampling rates for the cylindrical XAD passive sampler. We present active and passive air monitoring results, and the corresponding PSRs for an extended list of PAHs (Table S1) measured over a two-year time period using measurements from co-located passive and active samplers. The study was a collaborative multi-agency effort between the Minnesota Pollution Control Agency (MPCA), the Minnesota Department of Health, and the Mille Lacs Band of Ojibwe Department of Natural Resources and Environment. In this manuscript, (1) we estimate sampling rates from direct calibration of passive samplers, (2) we investigate the potential for uptake of particulate phase PAHs by the XAD passive sampler from in situ particulate measurements (collocated TSP, PM_{10}, $PM_{2.5}$ and ultrafine measurements), (3) we investigate the seasonal and pollutant variability of sampling rates, and (4) we compare the estimated PSRs from this manuscript to PSRs from the existing literature.

2. Materials and methods

Site Selection: Air sampling took place in South Minneapolis and on Mille Lacs Band of Ojibwe land in Minnesota USA (Fig. 1, Table S2). The Minneapolis study location is an urban community of high-density residential areas near major highways, whereas the Mille Lacs study location is a forested area on the banks of one of the largest lakes in Minnesota (Lake Mille Lacs). Active samplers were placed at three existing fixed platform ambient air network sites (MPCA, 2016) with collocated active samplers at the Minnesota network ambient monitoring site Near Roadway (Site ID 962). Passive samplers were co-located with each active sampler, and duplicate passive samplers were sited at Mille Lacs, and Near Roadway. Fourteen passive-only monitors were also sited in South Minneapolis based on modeled results (Pratt et al., 2012), known PAH air emissions sources, demographics, and community member input. The sampling network was dense enough to compare locations for intra-urban variability.

Air Sampling: Active air samples were collected from June 2013 to June 2015 at a frequency of 1 in 12 days for 72 h at stationary fixed platform sites using Tisch Environmental PUF110V high volume samplers set at a flow rate of $120 m^3$/day. The sampling train included a quartz fiber filter (QFF) (particle), a stainless steel screen, and sieved XAD-4 (gas). Passive sampling was conducted seasonally over the same time period with an XAD-4 resin tube inside a cylindrical passive sampler housing (Schrlau et al., 2011; Zhang et al., 2011). XAD-4 was used instead of the more commonly used XAD-2 due to its higher sorptive capacity from increased pore volume and at least twice the surface area (Lee et al., 2004). Samplers were sited on trees and non-wood utility poles to avoid potential contamination from wood treatment (Kohler et al., 2000).

The MPCA runs an extensive ambient air monitoring network, following USEPA quality assurance plans and standard operating procedures. The fine particle data ($PM_{2.5}$) were collected using a Met One Instrument BAM-1020 (BAM) continuous mass monitor that collects and report hourly concentrations. The coarse particles (PM_{10}) were collected hourly using a Federal Equivalent Method (FEM), similar to $PM_{2.5}$. PM_{10} was collected using a monitor Met One Instrument BAM-1020 (BAM), but set up with a PM_{10} cut-off. The hourly concentrations were averaged to the 72 h sample deployment time of the PAH ambient air monitoring. Total suspended particulate is still measured in Minnesota because of an existing state ambient air quality standard for that pollutant. These mass based measurements are 24 h integrated collections using a Tisch Environmental high volume air sampler. The ultrafine particles were collected for the years 2014 and 2015 using a TSI™ Model 3031 ultrafine particle monitor. These 15 min data were reported in 5 channels (20–30 nm, 30–50 nm, 50–70 nm, 70–100 nm, and 100–200 nm), they were summed to <100 nm, and 72 h means were calculated for comparison with the active PAH monitoring data.

Sample Media Preparation and Chemical Analysis: Extraction and chemical analysis of PAHs followed, EPA Method 8270D, Revision 4 (USEPA, 1998a), EPA Method 3545A, Revision 1, Modified (USEPA, 1998b), and a modified EPA Compendium Method Toxics Organics-13A (USEPA, January 1999). Sampler housing and media were cleaned, set up, bagged, and refrigerated at the MDH-PHL (Public Health Laboratory) prior to field deployment. After each use the sampler housings were washed with soap and water and rinsed with deionized water. Before initial use, the raw XAD-4 was washed with deionized water to remove the brine solution and sieved to remove fines (No.30 sieve). After each use, the XAD-4 was cleaned with multiple dichloromethane (DCM) extractions using an Accelerated Solvent Extraction (ASE) apparatus. The cleaned XAD-4 was extracted a final time with acetone to remove DCM for safety reasons and stored in air tight jars in a freezer. The QFF were baked in a muffle furnace at 450 °C for 4 h to remove any organic compounds.

Air samples were held at ≤ 4 °C until the PAH fractions were extracted from QFF or XAD-4 by an ASE method using dichloromethane. The extract was concentrated to 1.0 mL and analyzed by injection of 2.0 μL of the extract into a multimode inlet with a