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Atmospheric polycyclic aromatic hydrocarbon profiles and sources in pine needles and particulate matter in Dayton, Ohio, USA

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) were measured in pine needles (passive sampling) and on high-volume particulate matter (PM) filters (active sampling) over a period of eight to ten months at two separate sites in the Dayton, Ohio, USA metropolitan area: Moraine and Yellow Springs. Total PAH concentrations for PM ranged from 77.4 $\mu g\ g^{-1}$ to 837 $\mu g\ g^{-1}$ (dry wt.) at both sites with high molecular weight PAHs being the predominant form that tended to be higher in concentration during the colder months. Total PAH concentrations for pine needles varied by tree species and location. With an average concentration of 4187 $ng\ g^{-1}$, Austrian pine (*Pinus nigra*) needles in Moraine ranged from 2543 $ng\ g^{-1}$to 6111 $ng\ g^{-1}$ (dry wt.) with the lowest and highest concentrations occurring in October and August, respectively. The amount of phenanthrene was extremely high for August, 4200 ± 112, which could have resulted from the close proximity of the tree to the parking lot at a firehouse. White pine (*Pinus strobus*) needles in Yellow Springs had an average concentration of 384 $ng\ g^{-1}$and ranged from 127 $ng\ g^{-1}$ to 589 $ng\ g^{-1}$ (dry wt.) with September and November, respectively, having the lowest and highest PAH concentrations. The 2- and 3-ring PAHs were the predominant form in *P. nigra*, while the 4-ring PAHs predominated in *P. strobus*. Total PAH concentrations in *P. nigra* were an order of magnitude greater than for *P. strobus*. A bivariate plot of BaA/(BaA + Chry) versus Flt(Flt + Pyr) allowed the PM and pine needle data to be included in the same source analysis and indicated sources of PM at both sites were biomass and/or coal combustion. This plot also suggested PAHs in Yellow Springs *P. strobus* originated from petroleum combustion sources, whereas PAHs in Moraine *P. nigra* originated from petroleum combustion with some sources more aged or remote.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a set of ubiquitous pollutants formed naturally (e.g., forest fires) or released through anthropogenic activities involving combustion processes (McGowin, 2006). Due to significant variations in molecular weight and physical properties of PAHs, atmospheric monitoring requires a combination of sampling techniques, each with its own unique bias. Although the United States Environmental Protection Agency (USEPA) has identified sixteen PAHs of serious concern due to their potential carcinogenic and mutagenic properties, there are no standards for ambient air quality in the United States other than the Occupational Safety and Health Administration (OSHA, 29 CFR part 1910 subpart Z) 8-h limit of 0.2 $mg\ m^{-3}$ total atmospheric PAH in the workplace.

Atmospheric PAHs are transported from the source to the surrounding area either in the gaseous phase or bound to particles and then deposited in the environment via direct impact onto a surface or by sorption/partitioning into lipophilic substances (Motelay-Massei et al., 2006). PAHs with two or three rings are more volatile and remain in the vapor phase to a greater degree, which allows them to travel much farther and even accumulate in polar regions (Masclet et al., 1995). Lighter PAHs can re-enter the atmosphere from the Earth's surface after initial deposition and travel by atmospheric winds. Heavier PAHs (five or more rings) will primarily adsorb to particulate matter (PM) and have lower mobility thereby precipitating closer to the source (McGowin, 2006). As a result of their intermediate vapor pressures, PAHs with only four rings are partitioned between the vapor phase and the particle phase, which makes their mobility more dependent upon temperature (Maliszewska-Kordybach, 1999). They are found in greater concentrations sorbed to particulate matter in winter and early spring months (Li et al., 2010) and at night compared to during the day (Wu et al., 2010).

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Sampling PAHs from the atmosphere falls under two categories: active and passive. In active sampling methods, sequential sampling trains are constructed to collect PAHs with a wide range of physical properties. US EPA Method TO-13A (US EPA, 1999) employs a high-volume air vacuum system, filters, and other chemical/physical sorbents. Active samplers have drawbacks, such as expensive equipment, maintenance, and operation, and require a power supply that limits deployment (Esteve-Turrillas et al., 2008). Two common types of passive samplers used for atmospheric PAHs are semi-permeable membrane devices (SPMDs) (Huckins et al., 1990) and vegetation (Simonich and Hites, 1994; Srogi, 2007). Long deployment times to collect long-term data, ease of use, and low cost are advantages of SPMDs (Söderström and Bergqvist, 2003). The main disadvantage is that analytes are recovered through dialysis requiring copious amounts of solvent and long extraction times.

Vegetative sampling for PAHs is a more economical alternative because special sampling equipment is not needed. Various plants have been used to assess atmospheric PAHs (Simonich and Hites, 1995; Ratola et al., 2006; Srogi, 2007) and can be collected from the field or deployed for specified time periods. Pine needles have an advantage over other plants because they are available for sampling year round and can be differentiated into yearly growths. PAH accumulation into pine needles has been shown to be inversely temperature dependent (Piccardo et al., 2005) and strongly dependent on tree species (Ratola et al., 2011a).

Ratios of less stable to more stable PAH isomer concentrations in various matrices have been used to estimate the distance of the receptor from the source (Yunker et al., 2002; Ravindra et al., 2008) as the concentration of the less stable isomer declines over time and distance. Yunker et al. (2002) also evaluated ratios of more stable PAH isomers to determine their origins and developed a classification system for source determination. Although Yunker's classifications were initially applied to sediments, these classifications have also been applied to PM (Sofowote et al., 2010; Yang et al., 2010) and pine needles (Lehndorff and Schwark, 2004; Hwang and Wade, 2008; Ratola et al., 2011b).

Few studies have examined the results obtained from active and passive sampling methods applied simultaneously at the same site (Nakajima et al., 1995; Chun, 2011). This study measured the concentrations of PAHs in pine needles (passive sampling) and on PM filters (active sampling) with overlapping sampling times over a period of eight to ten months at two separate sites in the Dayton, Ohio, USA metropolitan area. Potential PAH sources and the relative distances from these sources at the two locations were evaluated using bivariate plots of isomer ratios. Since two identical pine species could not be located at each site, two different pine tree species were analyzed; a *Pinus nigra* at one site and a *Pinus strobus* at the other.

2. Experimental

2.1. Materials

Calibration standards composed of the EPA 16 PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene) were prepared from a 4000-μg mL^{-1} or a 200-μg mL^{-1} mixed standard (Accustandard, New Haven, CT). The 4000 μg mL^{-1} solution was diluted first to 100 μg mL^{-1} for calibration standards in (1:1) GC grade hexane:dichloromethane (Fisher Scientific, Fairlawn, NJ or Sigma–Aldrich, St. Louis, MO). The internal standard used was p-terphenyl (Chem Service, West Chester, PA). A 100-μg mL^{-1} mixed stock solution of five perdeuterated standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) was used to assess recoveries (Accustandard, New Haven, CT). All other solvents were GC grade.

2.2. Sampling

Sampling for PAHs on particulate matter was done at Moraine, Ohio and at Yellow Springs, Ohio. These two sites are about 30 km apart with one located south and the other northeast of the City of Dayton. An Anderson Instruments Model 1200 high-volume sampler (Anderson Instrument Company, Fultonville, NY) was previously installed atop the Moraine firehouse [39°42′52.23″N, 84°13′04.93″W], which was located about 500 m from an interstate highway on one side and about 100 m from a large train junction on the other side. In Yellow Springs, a Wedding and Associates Model 600 high-volume sampler (Wedding and Associates, Fort Collins, CO) was previously installed atop the Yellow Springs Government offices [39°48′30.07″N, 83°53′15.45″W]. It was situated about 200 m from a road with light vehicle traffic and to its east, State Highway 68. Both active samplers were equipped with EPM 2000 grade high purity quartz microfiber filters (Whatman Inc., Piscataway, NJ) and employed a gravimetric filter-based technique to measure PM_{10}. A 24-hour PM_{10} average was generated once every six days. The six-day filter samples were provided by the Regional Air Pollution Control Agency (RAPCA) in Dayton, OH. New filters were equilibrated in desiccators for at least 24 h and weighed on a Mettler type H balance (Mettler Instrument Corp, Highstown, NJ). The tare weight was recorded and the filter placed in an envelope prior to deployment. Used filters were removed from the samplers and folded in half with the particle-containing sides together. They were placed in a desiccator for 24 h and re-weighed to obtain the PM_{10} weight. A knife was used to cut a 3.2 cm by 20.4 cm strip out of the filter while the filter was folded with the dirty sides together. This strip was then placed in a labeled, pre-cleaned 120-mL amber jar and stored in a refrigerator prior to extraction. Since only a subsample of the larger filter was analyzed, a correction factor was applied to account for the edges of the filter covered by the filter frame. Moraine PM_{10} samples were analyzed in August, October, and December of 2009 and in February and April of 2010. Yellow Springs PM_{10} samples were analyzed in September and November of 2009 and in January, March, and May of 2010.

In Moraine, Ohio, an Austrian pine (*P. nigra*) was sampled near the firehouse [39° 42′ 49.57″ N. 84° 13′ 01.82″W]. In Yellow Springs a *P. nigra* could not be located near the PM_{10} sampler so a white pine (*P. strobus*) was selected 135 m from the active sampler [39° 48′ 34.28″N, 83° 53′ 15.25″W]. Clean surgical scissors were used to cut 100-g samples of whole needles taken from randomly selected branches around the breathing zone, about 1.5 m high. Needles were placed upright in a clean amber jar and stored in a refrigerator prior to extraction. Third-year needles were identified and selected by gaps between growing segments on *P. nigra*. Third-year needles were not identifiable on the *P. strobus* in Yellow Springs so second-year needles were sampled. The *P. nigra* was sampled in August, October, and December of 2009 and February of 2010. The *P. strobus* was sampled in September and November of 2009 and in January and March of 2010.

2.3. Filter extraction

Filters were removed from the refrigerator and allowed to come to room temperature. They were weighed using a Mettler AE240S (Mettler Instrument Corp, Highstown, NJ) balance and then unfolded with the sample side facing up on a clean watch glass. Each filter was spiked with 80 μL of 100-μg mL^{-1} deuterated mixed