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A Comparison of Atmospheric PAHs in Pine Needles and High-Volume Sampler Filters in the Dayton Metro Area

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A COMPARISON OF ATMOSPHERIC PAHS IN PINE NEEDLES
AND HIGH-VOLUME SAMPLER FILTERS
IN THE DAYTON METRO AREA

A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science

By

TIMOTHY ALEXANDER TOMASHUK
B.S., Wright State University, 2008

2010
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY
Timothy Alexander Tomashuk ENTITLED A Comparison of Atmospheric PAHs in Pine
Needles and High-volume Sampler Filters in the Dayton Metro Area BE ACCEPTED IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT


Samples of filters from High-volume (HiVol) samplers of particulate matter (PM) with a size of 10 micrometers or less were deployed in Moraine and Yellow Springs, OH, by the Regional Air Protection Control Agency and analyzed for five months for the Environmental Pollution Agency (EPA) 16 polycyclic aromatic hydrocarbons (PAHs). Pine needles on trees near the HiVol samplers were also collected and analyzed for a comparison with the active samplers to estimate atmospheric PAH concentrations. Pine needles were found to collect lower molecular weight (LMW) compounds far more than HiVol sampler and thus their profiles shown to compliment the HiVol sampler profile which collect higher molecular weight (HMW) compounds. Concentrations for filters and Yellow Springs pine needles, except for Moraine pine needles, increased as the average temperature decreased. The atmospheric concentrations ($\sum_{PAH_{atm}}$) were calculated for the last ten PAHs that overlapped in the pine needle and filter profiles (Fluoranthene-Benzo(ghi)perylene). The $\sum_{PAH_{atm}}$ calculated for Moraine ranged from 0.32 ng/m$^3$ to 1.69 ng/m$^3$ while Yellow Springs ranged from 0.32 ng/m$^3$ to 4.16 ng/m$^3$. These values are lower than expected especially for Moraine since there is industry nearby. PAH compounds from the pine needles were mostly associated with the vapor phase while the filters collected PAHs in the PM10 phase. Pine needles have been shown to be useful
in showing the additional LMW PAHs present in the atmosphere which HiVol samplers fails to collect.
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INTRODUCTION

Many types of samplers have been used to trap polycyclic aromatic hydrocarbons (PAHs) from the air. These compounds vary significantly in physical properties and thus require a combination of sampling techniques. Each sampling technique has its own unique bias. Often, they are combined in “sampling trains” in order to collect as wide a range of PAHs as possible (McGowin, 2006). An alternative to traditional sampling trains is to use passive samplers like plants or lichens (Piccardo et al., 2005). A comparison between PAH profiles of the most commonly used sampler (high-volume sampler) and plants can indicate the degree of bias associated with each method.

PAHs are a set of ubiquitous pollutants that are formed by natural (forest fires) or anthropogenic sources, such as incomplete fossil fuel combustion (vehicular traffic) or incinerators (Piccardo et al., 2005). Composed of fused aromatic rings, PAHs can be divided into three groups, one with ring counts of two or three, a 4-ring group and the other with ring counts of five to six. Physical properties vary considerably with the molecular weight. The higher the molecular weight the lower the rate of evaporation and water solubility will be and the lipophilicity increases as well (Maliszewska-Kordybach, 1999). PAHs and their derivatives are well known for their carcinogenic, mutagenic and toxic properties. The carcinogenicity of PAHs is attributed to bay-regions which form vicinal epoxides and phenols within the body that bind to DNA bases and lead to mutations (Goldman et al., 2001, Samanta et al., 2002). The United States Environmental Protection Agency (USEPA) has identified 16 PAHs of serious concern due to their potential carcinogenic and mutagenic properties but there are still no standards for ambient air quality (US EPA, 1999). The Occupational Safety and Health
Administration (OSHA) set an air quality limit of 0.2 mg/m$^3$. Benz(a)pyrene B(a)P is considered an air quality indicator since it is a probable human carcinogen. Many countries have adopted B(a)P atmospheric limit values and annual average guide value (Ravindra et al., 2008).

A portion of atmospheric PAHs are transported from the source to the surrounding area either in the gaseous phase or bound to particles. The compounds are then deposited either by direct impact onto a surface or by sorption (partitioning) (Motelay-Massei et al., 2005). The typical distance traveled from the source is dependent upon the number of rings the PAH has. PAHs with 2-3 rings are more volatile and stay in the vapor phase to a greater degree than larger PAHs allowing them to travel much farther and even accumulate in polar-regions (Masclet et al., 1994). The phenomenon associated with accumulation in polar-regions is known as a multi-hop process or grasshopper effect. Lighter PAHs can re-enter the atmosphere from the Earth’s surface after initial deposition and travel by atmospheric winds. Heavier compounds perform a one hop process by depositing to the Earth’s surface and never returning to the atmosphere (Macdonald et al., 2000). The heavier PAHs (five or greater rings) will primarily adsorb to particulate matter and have lower mobility and remain much closer to the source. PAHs with only four rings are partitioned between the vapor and particle phase. Their phase is dependent upon temperature which results in accumulation in mid-latitudes (Maliszewska-Kordybach, 1999, De Nicola et al., 2005).

Due to their harmful nature and potential for atmospheric transport, sampling methods for PAHs have been developed to estimate their concentrations in the atmosphere. Sampling PAHs from the atmosphere falls under two categories: active and passive sampling. In active
sampling methods, sequential sampling trains are often constructed in order to collect PAHs with a wide range of physical properties. The smaller particulate matter (PM) fraction is then adsorbed to a quartz or glass fiber filter. US EPA Method TO-13A is currently the most commonly used method for sampling atmospheric PAHs (USEPA, 1999). This method requires the use of a high-volume air sampler and a quartz fiber filter to collect particulate bound PAHs and polyurethane foam to collect the more volatile PAHs. Some problems with this type of setup include adsorption artifacts and sorbed PAHs reacting with atmospheric ozone (McGowin, 2006). A variation of the high-volume sampler is the addition of a denuder which prevents adsorption of gases onto particulate phase by diffusing the volatile PAHs onto a coating while the PM passes through and is trapped onto a filter (Gundel et al., 1995). Another attempt to prevent adsorption artifacts is the addition of an electrostatic precipitator to trap the negatively charged PM. This aggregation reduces the surface area of the exposed particles thus reducing the evaporation of PAHs. A disadvantage of this technique is the creation of artifacts from the reaction of PM with ozone and the corona-generated free radicals (Ning et al., 2008). Active samplers have drawbacks that include expensive preparation, maintenance and operation. A high-volume sampler also requires a power supply which limits the number of places they can be stationed (Esteve-Turrillas et al., 2008).

Passive samplers collect PAHs by allowing them to diffuse onto or into the needle. Two samplers that are most commonly used for atmospheric PAHs are semi-permeable membrane devices (SPMD) and vegetation. SPMDs were first introduced by Huckins et al. (1990) in 1990. A SPMD is a layflat polyethylene membrane tube filled with a nonpolar high molecular weight lipid (>600 dalton) such as triolein. Advantages that SPMDs have over other samplers include
long deployment times to collect long-term data, ease of use, and low cost. SPMDs are used to mimic the transfer of compounds through cell membranes and partitioning into simulated adipose tissue such as triolein. SPMDs were first introduced in aqueous environments to measure bioconcentration in aquatic animals. However, SPMDs have also been employed to sample the air (Söderström et al., 2003). Sorbed PAHs are recovered through dialysis of the tube and its contents. The dialysis extraction is a disadvantage for SPMDs because it requires copious amounts of solvent (usually hexane) and large amounts of time (24 to 72 h). SPMDs are subject to the biofouling effect where bacteria and other flora and fauna may create a biofilm on the membrane surface. This creates an additional barrier causing a decrease in sampling rates by slowing the transfer rate across the membrane (Esteve-Turrillas et al., 2008).

Vegetative sampling for PAHs is a newer alternative that is more economical as no equipment is needed so deployment and maintenance is avoided. Many types of plants have been used to assess atmospheric PAHs such as lichens, mosses, kale, leaves of evergreen trees, pine needles and pine bark. Previously studied analytes include polychlorinated biphenyls, organochlorine pollutants, PAHs, polychlorinated dibenzodioxins and furans (Ratola et al., 2006); all nonpolar to slightly polar persistent organic contaminants (PACs).

PACs enter the plant through three different pathways; through the roots from the soil, by deposition from contaminated atmospheric particles, and as vapors (Bacci et al., 1990). The amount of pollutants that enter plants via the root system has been demonstrated to be dependent upon the compound's water solubility which for PAHs is generally low due to their low polarity/high lipophilicity. It has been shown that atmospheric PAH uptake through the
root system is negligible (Simonich and Hites, 1995). Controlled studies of different lipophilic compounds (polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans) has shown that uptake of these compounds through the roots is not a significant pathway of accumulation due to their strong sorption to soil (Wang et al., 1994, Welsch-Pausch et al., 1995). For the most part, lipophilic compounds are not translocated within the plant and therefore metabolism does not play a significant role (Trapp et al, 1990). Since PAHs are highly lipophilic, the primary way into the plant is from the air onto the leaf surface.

The main pathway for PAHs to enter the plant is through the leaf’s waxy cuticle (particle-phase deposition) or through the stomata (gas phase). Leaves have many different features (surface area, cuticular waxes, hairs, and number of stomata) that affect PAH accumulation (Srogi, 2007). Generally a large $K_{oa}$ value indicates that the pollutant is more likely to partition into the leaf surface (Simonich and Hites, 1995). $K_{oa}$ is the partition coefficient for a compound between octanol and air. The leaf or needle has two main compartments; the outer compartment where the waxy cuticle is and the inner compartment of the leaf. The outer compartment can reach equilibrium quickly in a matter of minutes while the inner compartment can take up to several weeks to reach equilibrium (Wang, 2008).

Pine trees have a few advantages over other plants that make them stand out as excellent passive samplers. Unlike deciduous plants, pine needles are available for sampling all year round. Another useful feature of pine needles is that they can be differentiated into yearly growths. On any given branch one to four year growths can be seen. Knowing a needle’s age allows for the evaluation of temporal trends of PAH pollution. PAH accumulation into pine
needles has also been shown to be inversely temperature dependent. As the temperature increases, the evaporation rate goes up decreasing the PAH concentration within the needle (Piccardo et al., 2005).

Analysis of PAH profiles have been done in pine needles and PM10 (particulate matter 10 micrometers or less) samplers to determine source apportionment. Source apportionment is often determined through ratios of isomeric compounds by an increase or decrease in the less stable kinetic isomer relative to the more stable thermodynamic isomer. Increases in the less stable isomer are a sign of anthropogenic input. Ratio data cannot be used to determine a specific point source since the PAHs within samples originate from a variety of sources (Yunker et al., 2002) but can give clues as what the source may be (anthropogenic or natural). PAHs are categorized by their source as pyrogenic and petrogenic. Pyrogenic PAHs are produced from incomplete, high temperature combustion processes and are associated with the soot carbon produced in the process. The PAHs and soot carbon remain together until deposition. Petrogenic PAHs formed at low temperatures and over geologic time scales escape into the atmosphere from petroleum use (Burgess, 2003). PAHs with 4-6 rings are more often produced by pyrogenic (crude oil, organic materials and wood) sources. Pyrogenic sources are often characterized by an abundance of high molecular weight (HMW) compounds. Petrogenic PAHs are low molecular weight (LMW) compounds are often from refined petroleum products such as gasoline and diesel used by vehicular traffic (Doong, 2003). A ratio of the sum of combustion specific PAHs (ΣCOMB) to total PAHs (ΣPAHs) alongside PAH profiles has been shown to be useful in comparison of different sites. Nine of the EPA 16 PAHs that are combustion specific are fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene,
benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene (Hwang et al, 2003).

Four major extraction techniques are commonly used to extract PAHs from plants including Soxhlet, pressurized liquid extraction (PLE), ultrasonic extraction (USE), and supercritical fluid extraction (SFE). These techniques have been reviewed extensively along with other less used techniques (Dean, 2000, Lau, 2010, McGowin, 2006). USE has become increasingly popular in the extraction of PAHs in solid environmental samples (Sun et al., 1998, Rey-Salgueiro et al., 2009). USE has been shown to have extraction efficiencies as good as or better than Soxhlet extraction while requiring significantly less solvent and time for the extraction. Equipment is much less expensive than PLE and SFE since only a sonication bath and solvent are required.

Sample cleanup is commonly performed with three adsorbents which are Florisil, silica and alumina. According to Ratola (2006), Florisil and silica produce biased results because of the high recoveries (> 140%) for fluoranthene and benzo[a]pyrene. However, Florisil was shown to have the best recoveries for the less volatile PAHs. Florisil was also shown to have comparable or better recoveries for many of the PAHs.

This study attempts to understand the bias between plant (passive) and high-volume samplers (active) by comparing the PAH profiles of each over a period of ten months at two sites in the Dayton, Ohio, USA area. One site, Yellow Springs, Ohio, is a small town with limited industrial activity near a state highway. The other site is near a fire station in Moraine, Ohio with considerable traffic and more industrial activity. PM 10 filters obtained from the local air
quality agency were compared to pine trees within 140 meters of the high-volume samplers.

Samples were analyzed at these same sites over the course of 10 months.
EXPERIMENTAL

Materials

A set of calibration standards composed of five deuterated standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{10} and perylene-d_{12}) and the EPA 16 PAHs (naphthalene, acenaphthene, acenaphthylene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylenne, indeno[1,2,3-cd]pyrene were prepared from a 4000-ppm (µg/L) (Accustandard, New Haven, CT) mixed solution and a 200-ppm (µg/L) (Accustandard, New Haven, CT) standard. The 4000 ppm solution was diluted to 100-ppm for making the calibration standards in (1:1) hexane:dichloromethane mix (GC grade, Fisher, Fair Lawn, NJ). The internal standard used was p-terphenyl (Chem Service, West Chester, PA). All solvents were GC-grade from Sigma-Aldrich or Fisher.

Sampling

Sampling for PAHs was done at Moraine, Ohio, and at Yellow Springs, Ohio. An Anderson Instruments model 1200 high-volume sampler (Anderson Instrument Company, Fultonville, NY) on top of the Moraine firehouse in Moraine, OH [39°42′52.23″N, 84°13′04.93″W] was used to sample the air. The Moraine filter is located near the interstate and a large train junction lies directly behind a tree line. In Yellow Springs, a Wedding & Associates model 600 high-volume sampler (Wedding & Associates, Fort Collins, CO) that was installed on top of the Yellow Springs Government offices in Yellow Springs, Ohio [39°48′30.07″N, 83°53′15.45″W] was utilized. The filter is about 200 m from a light-traffic road
and to its east is State Highway 68. These two active samplers were both equipped with EPM 2000 grade high purity quartz microfiber filters (Whatman Inc., Piscataway, NJ). Both samplers use a gravimetric filter-based technique to measure PM10. A 24-hour PM10 average is generated once every six days. The filter samples were provided by the Regional Air Pollution Control Agency (RAPCA), Dayton, OH. Before placing the filters in the samplers, clean filters were equilibrated in desiccators for at least 24 h. The filters were then weighed on a Mettler type H balance. The tare weight was recorded and the filter placed into an envelope. When the dirty filters were removed from the samplers, the filters were folded in half long ways with the particle-containing sides together. They were placed in a desiccator again for 24 h and then re-weighed to record the PM10 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 placed in the refrigerator.

Near each of these locations, a pine tree was chosen. In Moraine, Ohio an Austrian pine was sampled behind a nearby building [39°48'34.28''N, 83°53'15.25''W]. The Austrian pine (pinus nigrus) was identified by its clusters of needles that grow in bundles of two that are about 8-cm long or longer. In Yellow Springs a white pine (pinus strobes) was selected 135 m from the active sampler [39°42'49.57''N 84°13'01.82''W] and is 86.62 m from the parking lot. Yellow Springs did not have an Austrian pine and Moraine did not have a white pine. It was identified by its needles that grow in bundles of five and are usually 5-13 cm long. Clean surgical scissors were used to cut needles off the branch and are then placed into a clean 1-L amber jar. Third year needles were identified by gaps between growing segments of the Austrian pine branch. Third year needles were not identifiable on the white pine in Yellow
Springs, Ohio, and so second year needles were sampled. They were placed in the jar so that they were standing straight up and not bent or broken in the jar. These needles were then placed in the refrigerator.

Filter Extraction

Filters were taken out of the refrigerator and allowed to come to room temperature. They were then weighed on a Mettler AE240S (Mettler Instrument Corp, Highstown, NJ) balance. The filters were placed on a clean watchglass and unfolded with the dirty side facing up. They were spiked with 8000 ng of each surrogate standard using a 100-µL syringe (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₀, and perylene-d₁₂).

The filters are then allowed to air dry for 20 min inside the amber jars with the lid ajar. Extraction procedure by ultrasonication was taken from Ratola (2006). To samples, 60 mL of 1:1 hexane/dichloromethane were added to amber jars with filters inside. Ratola (2006) used 30 mL but a larger volume was required due to the volume of sample. The lids were tightened and the jars placed in a 150 W FS14H ultrasonicator from Fisher Scientific (Fair Lawn, NJ) for 10 min. The supernatant in the amber jar was then pipetted into a 300-mL round bottom flask covered with aluminum foil and the extraction was repeated two more times using a fresh aliquot of solvent. The combined 180-mL extracts were rotory evaporated down to 2-3 mL.

A cleanup column was prepared with 5.0 g of Florisil (Supelco, Bellefonte, PA) and 1.0 g of Na₂SO₄ (Fisher, Fair Lawn, NJ) with glass wool (Supelco, Bellefonte, PA) on the top and bottom. It was then conditioned with 50 mL of GC-grade hexane/dichloromethane (1:1). The extracts were added to the column and eluted with 30 mL of hexane/dichloromethane (1:1) into an
aluminum foil covered 250-mL round bottom flask. The extract was rotary evaporated down to 2 mL and transferred to a graduated centrifuge tube and diluted to 4.00 mL. 2.00 mL of extract were placed into a GC vial with 40 µL of 25 ppm p-terphenyl as internal standard while the other 2 mL was reserved. P-terphenyl was used because it is composed of aromatic rings and falls in the middle of the chromatogram between ions 228 and 202.

Pine Needle Preparation

Pine needles were allowed to air dry overnight in the dark to remove external moisture. They were cut with clean scissors into 2-cm lengths and placed into a coffee grinder with a blade (Hamilton Beach, Washington, NC). The grinder was then run at the highest setting twice. The chopped needles were sieved to a No. 10 mesh or Tyler equivalent 9 mesh. An amber 120-mL jar was filled with 10 g of ground pine needles. Four replicates were prepared alongside a blank of clean sand (Fisher Scientific, Fair Lawn NJ). Each jar was then spiked with 8000 ng of each surrogate standard. The rest of the pine needle extraction was then followed the same way as the filter extraction. Moraine extracts were a clear dark green and Yellow Spring extracts were clear light green in color.

Instrumental Analysis

Samples were analyzed on one of the following two GC/MS systems. August 2009 to December 2009 samples were analyzed using a HP 5890 GC oven coupled with a HP5972 mass spectrometer. Enhanced Chemstation G1701BA V B.01.00 was used to interface with the GC/MS. Separation of the compounds was done on a 30 m x 0.250 mm HP-5MS (J&W Scientific, Santa Clara, CA) column coated with (5%-Phenyl)-methylpolysiloxane with a film
thicknes of 0.25 µm. Temperature program started at 80 °C and was then raised to 190 °C at
10 °C/min. The temperature was then raised to 250 °C at a rate of 8 °C/min. The temperature
was then raised to 320 °C at a rate of 4 °C/min and then held at that temperature for 5 minutes.
Injection was in splitless mode and the purge was turned on after 0.50 min. The carrier gas was
helium. The injector, transfer line, and MS were set at 320 °C, 300 °C and 175 °C, respectively.

Samples from January 2010 to May 2010 were run on a HP 6890 GC and analyzed with a
5973 MSD. The program used was ChemStation D.01.02.16 by Agilent Technologies (Santa
Clara, CA). The initial temperature of 40 °C was held for 2 min. The temperature was raised to
190 °C at a rate of 10 °C/min and then to 250 °C at a rate of 8 °C/min. The temperature was
then raised again to 300 °C at a rate of 4 °C/min and then held for 43 min to remove higher
molecular weight compounds. All other parameters were the same as parameters on the HP
5890 GC. Samples on both GC/MS were run in selected ion monitoring (SIM) mode. The ions
monitored can be seen in Table 1. Duplicate injections of each sample were run.

Calibration curves were generated for each of the EPA 16 and deuterated compounds
with R² values ranging from 0.9764 to 0.9977. Deuterated standards were not used to correct
PAH concentrations but to check the validity of the results. Acenaphthene-d10 coeluted with
matrix components so it was not evaluated in the August through December samples.

Needle moisture and lipid concentration

Moisture content was determined by measuring 5 g sample and drying them at 120 °C for
24 hrs and reweighed. Analyses were done in triplicate. Lipid content of the needles were
measured to normalize the PAH concentrations of Moraine and Yellow Springs. Dry needles
were sonicated for one hour twice in 30 mL of fresh hexane:acetone (50:50). The lipid extract
was then placed in a pre-weighed beaker and the solvent was allowed to evaporate overnight. The difference in mass was the lipid weight for that particular tree.
RESULTS AND DISCUSSION

Moraine filter concentrations are shown in Table 1 of the sixteen PAHs (µg/g) analyzed. \( \Sigma \text{PAH} \) concentrations ranged from 171 µg/g to 641 µg/g dry wt. (PAH mass/PM10 mass). Over a ten month period, Moraine filters averaged 420 µg/g dry wt. Only 4- to 6-ring compounds were detectable with filters collecting mostly 5- to 6-ring compounds composing 58.8% to 75.4% of the total PAH mass except for August where no HMW compounds were measured. The calculated \( \Sigma \text{EPA}_{16} \) atmospheric concentrations ranged from 0.343 ng/m\(^3\) to 2.58 ng/m\(^3\) based upon the volume of air passing through the filter. The \( \Sigma \text{EPA}_{16} \) ten month average was 1.46 ng/m\(^3\). These measurements were not similar to those taken elsewhere in urbanized and industrialized areas, for example, an atmospheric concentration of 3.2 ng/m\(^3\) was measured at the north side of the Birmingham University campus which is about 300 m from one of the busiest roads in England (Smith and Harrison, 1995) and an industrial site in France reported an average atmospheric PAH concentration of 22 ng/m\(^3\) (Dejean et al., 2008).

The Yellow Springs (YS) filter concentrations are shown in Table 2. Filter concentrations ranged from 77.4 µg/g to 838 µg/g dry wt. (PAH mass/PM10 mass). YS had an average filter concentration, over 10 months, of 452 µg/g. The filter collected only 4- to 6-ring compounds with 5- to 6-rings as the majority of the compounds collected comprising 40.8% to 60.5% of the total PAH concentration. The volume of air sampled by the YS sampler ranged from 1572 m\(^3\) to 1642 m\(^3\). The calculated \( \Sigma \text{EPA}_{16} \) atmospheric concentrations ranged from 0.319 ng/m\(^3\) to 2.44 ng/m\(^3\) over the test period. Yellow Springs’ average PAH atmospheric concentration was 1.41 ng/m\(^3\) which is surprising because it is not that much different than Moraine’s 1.46 ng/m\(^3\)
which was expected to be much higher than a rural site. The Moraine site may have become more like YS since the closing of the General Motors plant 2.07 km away. A large amount of traffic passed through this area every day while the plant was still open. Since the closing, it is likely that the train junction that brought materials sees little use. Smith and Harrison (1995) reports an atmospheric PAH concentration of 1.13 ng/m$^3$ for a rural area surrounded by farmland 2 km outside Birmingham, England.

Moraine pine needle ΣPAH concentrations ranged from 706 ng/g to 6290 ng/g dry wt. with April having the lowest concentration with August having the highest concentration. An interstate highway is nearby and a large train junction behind the tree line. Semi-urban areas like Moscow, Idaho had pine needle (white pine) concentrations of 498 ng/g to 859 ng/g dry wt. (Lang et al., 2000) and Bloomington, Indiana had white pine needles concentrations of 600 ng/g to 1600 ng/g dry wt. (Simonich and Hites, 1994). Phenanthrene was the predominant compound detected composing 30.9% to 66.9% of the total mass which is in agreement with Hwang and Wade (2008) who found that phenanthrene accounted for approximately 30% of the total PAHs in Pinus Taeda pine needles in Houston, TX. The PAHs collected by the pine needles ranged from 3- to 4-rings except for benz[a]anthracene since the main pathway is through gaseous absorption and the 3- to 4-ring compounds exist mainly in vapor phase (Park et al., 2000). The needles collected also some 5-ring but not the 6-ring compounds with concentrations ranging 21.5 ng/g (August) to 325 ng/g (December) dry wt. Acenaphthene and acenaphthylene may have been there but were not measured due to coelution of the plant matrix.
The Yellow Springs white pine is located in a forested area near a bike path (Table 2). The ΣPAH for YS ranged from 127 ng/g to 2030 ng/g (dry wt.) with September having the lowest PAH concentration and May having the highest concentration. The average concentration in Yellow Springs was 1460 ng/g and exceeded concentration ranges reported by others. Other examples of rural sites include a rural mountain site at Spring Valley which is 20 miles away from Moscow, Idaho, had a concentration of 62 ng/g to 141 ng/g dry wt. (Lang et al., 2000) and in Genoa, Italy 134.95 ng/g to 507.30 ng/g dry wt. was measured in Austrian pine (Piccardo et al., 2005). Only the September's concentration of 343 ng/g falls within any reported ranges. PAHs with 5- to 6-rings were not detected except for in November and composed 35.8% of the total PAH mass. Compared to Moraine where HMW PAHs were detected in pine needles, the absence of 5- to 6-ring compounds may be due to the relative lack of industry in the vicinity. Phenanthrene ranges from 3.02% to 47.3% of the total mass. In general, ΣPAH levels in Moraine Austrian pine were higher than in Yellow Springs white pine. May was the only month where it collected 3.50 times more PAHs than Moraine.

Source Apportionment

To interpret the filter data, atmospheric concentrations needed to be calculated because PAH concentrations vs. PM 10 was misleading and there was very little relationship found between atmospheric PAHs and the mass of PM 10. The amount of PM10 measured did not hold much bearing on the PAH concentration sampled.

Prajapati (2008) divided PAHs into three groups: 2-3 rings, 4-rings and 5-6 rings. This was done to see how ΣPAH concentrations for each ring group changed over time in Ficus
benghalensis. Pine needle concentrations (dry wt.) were graphed against \( \sum \text{PAH} \) concentrations for each ring group. Prajapati showed leaves sampled from five locations throughout an urban area had only concentrations for 4-ring compounds ranging \(~500 \text{ ng/g to ~3000 ng/g (dry wt.)}\).

The author’s low detection of LMW compounds was probably a result of using Soxhlet extraction for sample preparation extraction and thus losing the more volatile compounds through evaporation.

Figures 1a and 1b give a general idea the source of PAHs detected on both Moraine and Yellow Springs filters. Both samplers are on top of buildings surrounded by parking lots. The filters collected 4- to 6-ring compounds which are often pyrogenic in origin and often associated with particulate matter (Burgess, 2003). These compounds, which are in the PM phase, lack the mobility which LMW compounds have due to their low volatility (Maliszewska-Kordybach, 1999). Moraine’s concentrations may be slightly higher due to the additional train junction nearby. The 5- to 6- ring concentrations are generally higher than the 4-ring concentrations.

LMW and medium weight compounds which are found in the pine needles in both sites are mainly from a petrogenic source as can be seen in Figures 3a and 3b due to the high LMW PAH concentrations found over 10 months. The parking lots that are near both trees probably contribute the majority of the PAHs found in the samples. The white pine is 86.62 m whereas the Austrian pine is only 2.76 m from the parking lot making it more susceptible to petrogenic PAHs.
Seasonal trends

Figures 2a and 2b show that filters generally collected higher PAH concentrations of high molecular weight (HMW) and medium molecular weight compounds as the temperature decreases. Moraine and Yellow Springs had the highest PAH filter concentration during December (641 ug/g) and March (838 ug/g), respectively. Higher PAH filter concentrations occurred generally during colder months; which is shown in Figure 4. PAH accumulation on filters is by direct impact and very little by partitioning of PAHs from the atmosphere as is evident by no measurements of LMW PAHs. Yellow Springs has a similar type of filter profile as Moraine. According to Maliszewska-Kordybach (1999), the concentrations of gas-phase compounds increase as temperatures increase whereas particulate-bound PAHs will decrease. During colder months, PAHs will partition to PM causing an increase in PAH filter concentration. The PAH atmospheric concentrations do not seem to be related with the amount of PM 10 in the atmosphere collected but when PM 10 and PAH atmospheric concentrations are graphed against temperature PM 10 and PAH atmospheric concentrations follow each other closely except for in April and May.

Figure 3a and 3b show that pine needles collect LMW and medium weight PAHs higher in colder months. Moraine had an unusually high PAH concentration during August of 6290 ng/g ± 122 ng/g dry wt. during a warm month. Yellow Springs also had a high PAH concentration of 2030 ng/g ± 62.8 ng/g dry wt. during May. The unusually high concentrations in August and May could be a result of a release of PAHs from soil that had partitioned into the soil over the winter months and then were released back into the atmosphere from the soil and partitioned into the pine needles as suggested by Simonich and Hites (1994). After August, PAH
concentrations in Moraine increased with decreasing temperature. Yellow Springs PAH concentrations fluctuate over the sampling period with a large concentration in May. In a study done by Hwang and Wade (2008) in Houston, TX, PAH concentrations were lowest (275 ng/g dry wt.) in months with a high ambient temperature and concentrations highest (361 ng/g dry wt.) in colder months. Hwang also found the highest PAH concentration in April which was concluded to be an outlier. It is possible that this point was caused by PAHs partitioning into the needles from the soil.

PAH air concentrations from pine needles

Comparing plant concentrations and filter concentrations is not possible due to the differences in matrix and sampling rates. Calculating atmospheric concentrations from filters is simple needing only the volume of air sampled and the filter’s PAH concentrations. Calculating atmospheric concentrations from needles proves much more difficult since there are many more variables affecting sampling rate such as time and the volume of air to which the pine needles are exposed. One method has been to give each PAH an air-vegetation partitioning coefficient ($k_v$) (Simonich and Hites, 1994). $k_v$ is an approximation of the equilibrium between air and plant and does not truly exist since the environment is always in flux. This coefficient is also strongly dependent on temperature.

$$\ln k_v = \frac{1000}{T} \times \text{slope} - 35.95$$

Eq. 1
T is the temperature in Kelvin. The slopes for each compound are given by Simonich and Hites (1994). The Weather Underground provided average monthly temperatures that ranged from 270-295K (www.wunderground.com) for the Dayton area over the ten month period. From $k_v$, the atmosphere concentration could be calculated in units of ng/m$^3$.

$$k_v = \frac{[veg]}{[lipid] \times [gas]}$$

Eq. 2

The atmospheric concentration was calculated for the PAHs that overlapped (fluoranthene, pyrene, benz(a)anthracene, and chrysene) in the pine needle and filter profiles. The vegetation concentration was the concentration (ng/g, dry weight) calculated for each PAH. The lipid concentration for Austrian pine and white pine was 5.06% of needle dry weight and 4.98% of needle dry weight, respectively. Comparing atmospheric PAH concentrations calculated from plants to filters shows a large discrepancy. August atmospheric concentrations derived from needles gave the closest results with PM filter data. Fluoranthene, pyrene, benz(a)anthracene and chrysene gave concentrations 0.0880 ng/m$^3$, 0.0323 ng/m$^3$, $1.65 \times 10^{-4}$ ng/m$^3$ and $6.53 \times 10^{-4}$ ng/m$^3$ respectively at an ambient temperature of 295 K. The calculated PAH atmospheric concentrations from filters for the same PAHs were 0.0932 ng/m$^3$, 0.0852 ng/m$^3$, 0.0720 ng/m$^3$, 0.0737 ng/m$^3$ respectively. The predicted PAH atmospheric concentrations for fluoranthene and pyrene came relatively close to the filter predicted atmospheric concentrations. The predicted PAH atmospheric concentrations for benz(a)anthracene and chrysene differed by about two orders of magnitude from the filter predicted atmospheric concentrations. As monthly average temperatures decreased, the predicted atmospheric concentrations
decreased while concentrations calculated from filters increased. The equations given by Simonich and Hites were used for only a small range of temperatures (273-309 K) with the mean temperature being 291 K. It’s possible that when temperatures are closer to the mean temperature atmospheric concentrations are better predicted. The PAH atmospheric concentrations for fluoranthene, pyrene, benz(a)anthracene and chrysene continue to decrease while calculated PAH atmospheric concentrations increase causing an even larger disparity in PAH concentrations from each type of sampler. These equations come with serious limitations allowing for reasonable predictions only for LMW compounds during warmer months.
CONCLUSION

Two different methods, high-volume filters and pine trees, collect two different fractions of PAHs. Filters collect HMW compounds while pine trees sample LMW compounds primarily. By comparing Moraine samplers to the same samplers in Yellow Springs, each type of sampler was able to give a better understanding of PAHs in the atmosphere between a two different sites. Filters sample PAHs that are produced from a pyrogenic source while pine needles sample PAHs mainly from a petrogenic source. Seasonal trends from filters and pine needles were shown to be similar except for a spike in PAH concentration for pine needles that occurs in April and May when PAHs are released from the soil. Filters allow for direct calculation of PAH atmospheric concentrations while pine needles do not. Trying to compare concentrations of filters and pine needles can only be done by calculating air concentrations from each sampler. Using equations provided by Simonich and Hites, it was found that the equations only worked for lighter compounds during warmer months. However for fluoranthene and anthracene, it gave concentrations that came close to the filter predicted concentrations. Using a high-volume sampler and pine needles to sample the atmosphere for PAHs gives a complete picture of PAHs in the atmosphere.
REFERENCES


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Table 2 Yellow Springs white pine
**Figure 1a** Moraine Filter atmospheric concentration vs. ring group concentration

**Figure 1b** Yellow Springs Filter atmospheric concentration vs. ring group concentration
Figure 2a Moraine Filter concentration vs. ring group concentration

Figure 2b Yellow Spring Filter concentration vs. ring group concentration
Figure 3a Moraine Ohio Austrian pine vs. ring group concentration

Figure 3b Yellow Springs Ohio white pine vs. ring group concentration
Figure 4 Filter concentrations vs. average temperature

\[ y = -15.322x + 4664.7 \]

\[ R^2 = 0.2854 \]
Standard Operating Procedures
Preparation of pine needles and filters for PAH analysis by GC/MS

#1

April 22, 2009

By

Timothy Tomashuk
A. SCOPE AND APPLICABILITY

This method is applicable to pine needles and boxwood contaminated with the EPA 16 PAHS. The analysis is to be done by GC/MS.

B. SUMMARY OF METHOD

This method uses an ultrasonic bath to extract the PAHs from pine needles or boxwood with 20 mL hexane/dichloromethane (1:1) for ten minutes followed by a repeat extraction. Combined extracts were cleaned up with SPE cartridges containing Florisil, silica or alumina. The extract is then concentrated in a Rotovap and injected in duplicate into the GC/MS.

C. INTERFERENCES

No interferences from the plant matrix have yet been identified.

D. SAFETY

1. Proper lab technique should be observed. Extraction and sample prep should be done while wearing a lab coat and goggles.

E. APPARATUS AND MATERIALS

1. Sample collection

   GPS
   500-mL amber bottle with lid
   Aluminum Foil

2. Extraction

   50-mL amber bottle with lid
   Hamilton Beach Coffee Grinder Model 80365
   Fisher Scientific FS14H ultrasonic water bath
   Clean scissors

3. Cleanup

   5-g SPE cartridges of Florisil, silica or alumina
   Buchi Rotovapor
   Nitrogen

F. Reagents and Chemicals

1. Organic Solvents
a. Hexane: GC-grade n-Hexane for GC/MS analysis or equivalent.

b. Dichloromethane: GC- or LC-grade dichloromethane for HPLC analysis or equivalent.

2. Spiking Solutions
a. A spiking solution is prepared by SOP#3

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3. Internal Standard
a. A solution of p-terphenyl is made in hexane from a solid provided by Chem Service. A 1000 ppm solution is prepared by weighing 10 mg of p-terphenyl into a 10-mL flask and diluted to the mark with hexane.

4. Calibration Standards
a. A total of five standards ranging from 0.1 ppm to 2.0 ppm of the EPA 16 are made in hexane:methylene chloride
b. The EPA 16

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Compound Name</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Naphthalene</td>
<td>91-20-3</td>
</tr>
<tr>
<td>2</td>
<td>Acenaphthalene</td>
<td>83-32-9</td>
</tr>
<tr>
<td>3</td>
<td>Acenaphthalene</td>
<td>208-96-8</td>
</tr>
<tr>
<td>4</td>
<td>Fluorene</td>
<td>86-73-7</td>
</tr>
<tr>
<td>5</td>
<td>Phenanthrene</td>
<td>85-01-8</td>
</tr>
<tr>
<td>6</td>
<td>Anthracene</td>
<td>120-12-7</td>
</tr>
<tr>
<td>7</td>
<td>Fluoranthene</td>
<td>206-44-0</td>
</tr>
<tr>
<td>8</td>
<td>Pyrene</td>
<td>129-00-0</td>
</tr>
<tr>
<td>9</td>
<td>Benz[a]anthracene</td>
<td>56-55-3</td>
</tr>
<tr>
<td>10</td>
<td>Chrysene</td>
<td>218-01-9</td>
</tr>
<tr>
<td>11</td>
<td>Benzo[b]Fluoranthene</td>
<td>205-99-2</td>
</tr>
<tr>
<td>12</td>
<td>Benzo[k]Fluoranthene</td>
<td>207-08-9</td>
</tr>
<tr>
<td>13</td>
<td>Benzo[a]Pyrene</td>
<td>50-32-8</td>
</tr>
<tr>
<td>14</td>
<td>Dibenzo[a,h]anthracene</td>
<td>53-70-1</td>
</tr>
<tr>
<td>15</td>
<td>Benzo[ghi]pyrene</td>
<td>191-24-2</td>
</tr>
<tr>
<td>16</td>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>193-39-5</td>
</tr>
</tbody>
</table>
G. Sample Collection, Preservation, and Handling

Pine needles of the third generation are cut from the branch and placed in a pre-cleaned 500-mL amber jar with lid. The amber jars are quickly wrapped in aluminum foil to prevent sun exposure. The amber jars are then placed in freezer to prevent the PAHs from volatilizing. GPS coordinates are recorded.

H. Quality Control
Standard reference materials of pine needles are not available.

I. Sample Preparation Procedure

1. Sample Preparation
   a. A blank is to be prepared along with this method.
   b. Clean scissors are used to chop pine needles to fit within the coffee grinder.
      i. Allow the pine needles to air dry for one day.
      ii. The pine needles are then cut with scissors and placed in a clean coffee grinder
      iii. Each setting is labeled from 1 to 5. The fifth setting is used and is run twice.
      iv. Use a spatula to remove the pine needles from the cup into Sieve #10.
      v. Repeat steps ii-iv until there is enough for four 10 g samples.
      vi. From Sieve #10 weigh 10 g of chopped needles into each bottle
   c. Tare a clean 120-mL amber bottle with teflon lid and weigh ~10.00 g of pine needles from the sieve into bottle and secure with lid.
   d. Spike each sample with 80 ul from a 100 ppm solution of surrogate standard.
      i. Leave the top slightly open in the hood to allow the solvent to evaporate for 20 minutes.
   e. Extraction
      i. Add 60.0 mL of hexane/dichloromethane (1:1) using a graduated cylinder and replace cap tightly.
      ii. Make sure water bath is at room temperature.
      iii. Place bottled sample in Fisher Scientific ultrasonic water bath for 10 min.
      iv. Transferred with Pasteur pipette the supernatant into a 250 mL foil wrapped round bottom flask.
      v. Repeat steps i-iv with fresh solvent twice
      vi. Combined extracts are evaporated to about 2-3 mL in a rotary evaporator.
   f. Sample Cleanup
      i. Cartridges (5 g of Florisil and 1.0 g NaSO4) are conditioned with 50 mL of hexane/dichloromethane (1:1).
ii. Extract (2-3 mL) is added to the cartridge and eluted with 30 mL hexane/dichloromethane (1:1).

iii. Extracts are evaporated in the rotary evaporator to 2 mL and transferred to graduated centrifuge tube and then diluted to 4 mL.

iv. Quantitatively transfer to amber storage vial and refrigerate.
Preparation of calibration standards for GC/MS analysis of pine needles

#2

April 27, 2009

By

Timothy Tomashuk
A. SCOPE AND APPLICABILITY

This method is applicable to calibrated standards prepared for PAH analysis using the GC/MS.

B. SUMMARY OF METHOD

This method uses a mixture of the EPA 16 at 4000 ppm to prepare five calibrated standards at concentrations 2.0 ppm, 1.0 ppm, 0.75 ppm, 0.50 ppm, and 0.25 ppm and 0.10 ppm. These standards are analysed with the GC/MS to generate calibration curves.

C. Safety

1. Proper lab technique should be observed. Extraction and sample prep should be done while wearing a lab coat and goggles.

E. APPARATUS AND MATERIALS

1. Solution Prep
   One 4-mL and five 10-mL volumetric flasks with caps
   A 500 µL, 100 µL, and a 25 µL syringes

2. Weighing equipment
   Weigh boats
   Spatula
   AE 240 Mettler Balance

3. Solution storage
   Five clean 20 mL amber vials
   Two clean 5 mL amber vials

F. Reagents and Chemicals

1. Organic Solvents
   a. Hexane: GC-grade n-Hexane for GC/MS analysis or equivalent
   b. Dichloromethane: GC-grade dichloromethane for GC/MS analysis or equivalent

2. Calibration Standards
   a. A total of five standards ranging from 0.1 ppm to 2.0 ppm of the EPA 16 are made in a hexane:dichloromethane (50:50).
   b. The EPA 16
### Peak No. | Compound Name          | CAS No.  
--- | --- | ---  
1   | Naphthalene           | 91-20-3  
2   | Acenaphthalene        | 83-32-9  
3   | Acenaphthalene        | 208-96-8  
4   | Fluorene              | 86-73-7  
5   | Phenanthrene          | 85-01-8  
6   | Anthracene            | 120-12-7  
7   | Fluoranethene         | 206-44-0  
8   | Pyrene                | 129-00-0  
9   | Benz[a]anthracene     | 56-55-3  
10  | Chrysene              | 218-01-9  
11  | Benzo[b]Fluoranethene | 205-99-2  
12  | Benzo[k]Fluoranethene | 207-08-9  
13  | Benzo[a]Pyrene        | 50-32-8  
14  | Dibenz[a,h]anthracene | 53-70-1  
15  | Benzo[ghi]perylene    | 191-24-2  
16  | Indeno[1,2,3-cd]pyrene | 193-39-5  

#### 3. Internal Standard

a. A solution of p-terphenyl [92-94-4] is made in hexane from a solid provided by Chem Service. A 1000 ppm solution is prepared by weighing 10 mg of p-terphenyl into a 10-mL flask and diluted to the mark with hexane.

#### G. Calibration Standards

1. **Cleaning**
   a. All glassware should be cleaned first.
   b. Syringes should be cleaned by drawing up hexane 20 times and dispensing into a waste beaker before and after use. Hexane:dichloromethane should also be allowed to soak after post cleaning.

2. **Internal Standard Prep**
   a. Weigh out 0.01g of p-terphenyl into a 10 mL volumetric flask.
   b. Dilute to the mark with hexane:dichloromethane.

3. **Calibration Standards Prep**
   a. Solutions are prepared from a 200 ppm solution in MeOH:CH₂Cl₂ (1:1) provided by AccuStandard
<table>
<thead>
<tr>
<th>Deuterated Standards from a 100 ppm solution</th>
<th>Native PAHs from a 200 ppm solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Concentration</strong></td>
<td><strong>µL of solution</strong></td>
</tr>
<tr>
<td>2.0 ppm</td>
<td>200</td>
</tr>
<tr>
<td>1.0 ppm</td>
<td>100</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>75</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>50</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>25</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>10</td>
</tr>
</tbody>
</table>

4. **Mixture Storage**
   a. Pour the contents of each flask into a 20-mL amber vial and the 4-mL volumetric’s into the 5-mL vial.
   b. Pour the remaining PAH mixture into a 4-mL amber vial and peel off the label from the original vial and put it on the new vial.
   c. Label each vial, date and initial them.
   d. Place vials in the freezer.
Appendix A: Table of PAHs and Structure
<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Compound Name</th>
<th>CAS No.</th>
<th>Mol. Wt.</th>
<th>Structure</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Naphthalene</td>
<td>[91-20-3]</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Acenaphthalene</td>
<td>[83-32-9]</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Acenaphthalene</td>
<td>[208-96-8]</td>
<td>152</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Fluorene</td>
<td>[86-73-7]</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Phenanthrene</td>
<td>[85-01-8]</td>
<td>178</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Anthracene</td>
<td>[120-12-7]</td>
<td>178</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Fluoranthene</td>
<td>[206-44-0]</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Pyrene</td>
<td>[129-00-0]</td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Benz[a]anthracene</td>
<td>[56-55-3]</td>
<td>228</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Chrysene</td>
<td>[218-01-9]</td>
<td>228</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Benzo[b]fluoranthene</td>
<td>[205-99-2]</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Benzo[k]fluoranthene</td>
<td>[207-08-9]</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Benzo[a]pyrene</td>
<td>[50-32-8]</td>
<td>252</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Dibenz[a,h]anthracene</td>
<td>[53-70-1]</td>
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<td></td>
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<tr>
<td>16</td>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>[193-39-5]</td>
<td>276</td>
<td></td>
</tr>
</tbody>
</table>

*Table 3 List of PAHs and structures*
Appendix B: Filter and pine needle PAH concentrations over time
Figure 5 Moraine plant PAH concentrations

Figure 6 Moraine filter PAH concentrations
Figure 7 Yellow Springs plant PAH concentrations

Figure 8 Yellow Springs filter PAH concentrations
Appendix C: Temperature Graphs
Figure 9 Temperature vs. month

$$y = 1.0189x^2 - 12.057x + 309.08$$

$$R^2 = 0.8883$$

Figure 10 Normalized concentration vs. time (pine needles)

$$y = 0.013x^2 - 0.1862x + 0.9418$$

$$R^2 = 0.1544$$
Appendix D: Vegetation-air partition coefficients
<table>
<thead>
<tr>
<th>Flt</th>
<th>Pyr</th>
<th>BaA</th>
<th>Chry</th>
<th>BbF</th>
<th>BaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>August</td>
<td>0.269409</td>
<td>0.289263</td>
<td>2.158781</td>
<td>1.963025</td>
<td>3.792768</td>
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<tr>
<td>September</td>
<td>0.398021</td>
<td>0.427649</td>
<td>3.264983</td>
<td>2.965742</td>
<td>5.772775</td>
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<tr>
<td>October</td>
<td>0.977441</td>
<td>1.051864</td>
<td>8.462408</td>
<td>7.667896</td>
<td>15.18246</td>
</tr>
<tr>
<td>November</td>
<td>1.403536</td>
<td>1.511364</td>
<td>12.41829</td>
<td>11.24121</td>
<td>22.41119</td>
</tr>
<tr>
<td>December</td>
<td>3.917407</td>
<td>4.226009</td>
<td>36.8641</td>
<td>33.27609</td>
<td>67.64804</td>
</tr>
<tr>
<td>January</td>
<td>6.401433</td>
<td>6.911701</td>
<td>62.04238</td>
<td>55.92836</td>
<td>114.7646</td>
</tr>
<tr>
<td>February</td>
<td>5.788531</td>
<td>6.248834</td>
<td>55.76415</td>
<td>50.28271</td>
<td>102.9826</td>
</tr>
<tr>
<td>March</td>
<td>1.799178</td>
<td>1.938251</td>
<td>16.15803</td>
<td>14.61652</td>
<td>29.27826</td>
</tr>
<tr>
<td>April</td>
<td>0.671278</td>
<td>0.721911</td>
<td>5.682078</td>
<td>5.153912</td>
<td>10.13216</td>
</tr>
<tr>
<td>May</td>
<td>0.524799</td>
<td>0.564138</td>
<td>4.377014</td>
<td>3.972839</td>
<td>7.773817</td>
</tr>
</tbody>
</table>

Table 4 Vegetation-air coefficients
Appendix E: GC 5890/MS 5972 Method
TOLEVEL PARAMETERS
----------------------

Method Information For: C:\HPCHEM\1\METHODS\RAMP2.M

Method Sections To Run:

(X) Save Copy of Method With Data
( ) Pre-Run Cmd/Macro =
(X) Data Acquisition
(X) Data Analysis
( ) Post-Run Cmd/Macro =

Method Comments:

END OF TOLEVEL PARAMETERS
----------------------

INSTRUMENT CONTROL PARAMETERS
----------------------

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

7673 Injector

Front Injector:
Sample Washes
Sample Pumps
Injection Volume
Syringe Size
On Column
Nanoliter Adapter
PostInj Solvent A Washes
PostInj Solvent B Washes
Viscosity Delay
Plunger Speed

Back Injector:
No parameters specified

HP5890 Temperature Parameters

Zone Temperatures: State Setpoint
Inlet A: On 320 C
Inlet B: Off 250 C
Detector A: Off 300 C
Detector B: On 300 C
Auxiliary: Off 50 C

Oven Parameters:
Oven Equib Time: 0.50 minutes
Oven Max: 325 C
Oven State: On
Cryo State: Off
Cryo Blast: Off
Ambient: 25 C

Oven Program:
Initial Temperature: 80 C
Initial Time: 1.00 minutes

<table>
<thead>
<tr>
<th>Rate Level</th>
<th>(C/minute)</th>
<th>Final Temperature (C)</th>
<th>Final Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.0</td>
<td>190</td>
<td>0.00</td>
</tr>
<tr>
<td>2(A)</td>
<td>8.0</td>
<td>250</td>
<td>0.00</td>
</tr>
<tr>
<td>3(B)</td>
<td>4.0</td>
<td>320</td>
<td>5.00</td>
</tr>
</tbody>
</table>
Next Run Time: 42.00 minutes

HP5890 Inlet Pressure Programs

GC Pressure Units: psi

Inlet A:
Constant Flow: On
Constant Flow Pressure: 9.2 psi
Constant Flow Temperature: 300 C
Initial Pressure: 10.4 psi
Initial Time: 0.00 minutes

<table>
<thead>
<tr>
<th>Rate Level</th>
<th>(psi/minute)</th>
<th>Final Pressure (psi)</th>
<th>Final Time (minutes)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2(A)</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>3(B)</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Total Program Time: 0.00 minutes

Column Length: 30.00 m
Column Diameter: 0.320 mm
Gas: He
Vacuum Compensation: On

Inlet B:
Constant Flow: Off
Constant Flow Pressure: 3.2 psi
Constant Flow Temperature: 100 C
Initial Pressure: 0.0 psi
Initial Time: 480.00 minutes

<table>
<thead>
<tr>
<th>Rate Level</th>
<th>(psi/minute)</th>
<th>Final Pressure (psi)</th>
<th>Final Time (minutes)</th>
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<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>2(A)</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td>3(B)</td>
<td>0.00</td>
<td>0.0</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Total Program Time: 480.00 minutes

Column Length: 30.00 m

Column Diameter: 0.250 mm
Gas: He
Vacuum Compensation: On

HP5890 Packed Column Flow Control

Inlet A not used to control packed column flow.
Inlet B not used to control packed column flow.

HP5890 Purge Valve Settings

<table>
<thead>
<tr>
<th>Inlet Purge</th>
<th>Init Value</th>
<th>On Time</th>
<th>Off Time</th>
<th>Splitless Injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Off</td>
<td>0.50</td>
<td>5.00</td>
<td>Yes</td>
</tr>
<tr>
<td>B</td>
<td>Off</td>
<td>0.50</td>
<td>0.00</td>
<td>No</td>
</tr>
</tbody>
</table>

HP5890 Valve and Relay Information

Initial Setpoints:
5890 Valves:
Valve 1: Off
Valve 2: Off
Valve 3: Off
Valve 4: Off
19405 Valves:
Valve 5: Off
Valve 6: Off
Valve 7: Off
Valve 8: Off
19405 Relays:
Relay 1: Off
Relay 2: Off
Relay 3: Off
Relay 4: Off

HP5890 Detector Information

<table>
<thead>
<tr>
<th>Detector</th>
<th>Type</th>
<th>State</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>PID</td>
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</tr>
<tr>
<td>B</td>
<td>---</td>
<td>Off</td>
</tr>
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</table>

HP5890 Signal Information

Save data for signal 1 only.

<table>
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<tr>
<th>Signal</th>
<th>Source</th>
<th>Peak Width</th>
<th>Data Rate</th>
<th>Start Data</th>
<th>Stop Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Compl</td>
<td>0.053</td>
<td>5.000</td>
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<td>25.00</td>
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<td>Testplot</td>
<td>0.053</td>
<td>5.000</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

MS ACQUISITION PARAMETERS

General Information

Tune File: ATUNE.U
Acquisition Mode: SIM
Method: RAMP2.M
MS Information
-- -------

Solvent Delay : 2.50 min
EM Absolute : False
EM Offset : 0
Resulting EM Voltage : 2941.2

[Sim Parameters]

GROUP 1
Group ID : ion
Resolution : Low
Group Start Time : 0.00
Plot 1 Ion : 10.0
Ions/Dwell In Group
( Mass, Dwell)
( 10.0, 10)

GROUP 2
Group ID : Naphthalene
Resolution : Low
Group Start Time : 6.00
Plot 1 Ion : 128.0
Ions/Dwell In Group
( Mass, Dwell) ( Mass, Dwell)
( 128.0, 100) ( 136.0, 100)

GROUP 3
Group ID : Acenaphthalene
Resolution : Low
Group Start Time : 10.00
Plot 1 Ion : 152.0
Ions/Dwell In Group
( Mass, Dwell) ( Mass, Dwell) ( Mass, Dwell)
( 152.0, 100) ( 164.0, 100) ( 154.0, 100)

GROUP 4
Group ID : Fluorene
Resolution : Low
Group Start Time : 11.90
Plot 1 Ion : 166.0
Ions/Dwell In Group
( Mass, Dwell)
( 166.0, 100)

GROUP 5
Group ID : Phenanthrene
Resolution : Low
Group Start Time : 14.00
Plot 1 Ion : 188.0
Ions/Dwell In Group
( Mass, Dwell) ( Mass, Dwell)
( 188.0, 100) ( 178.0, 100)

GROUP 6
Group ID : Fluoranthenes
Resolution : Low
Group Start Time : 17.00
Plot 1 Ion : 202.0
Ions/Dwell In Group
( Mass, Dwell) ( Mass, Dwell)
( 202.0, 100) ( 230.0, 100)

Method: RAMP2.M
Wed Jun 23 15:43:20 2010
Page: 4
GROUP 7
Group ID : Benza(a)/chrys
Resolution : Low
Group Start Time : 21.50
Plot 1 Ion : 228.0
Ions/Dwell In Group ( Mass, Dwell) ( Mass, Dwell)
( 228.0,   100) ( 240.0,   100)

GROUP 8
Group ID : Benzo(b)fluoran
Resolution : Low
Group Start Time : 25.00
Plot 1 Ion : 252.0
Ions/Dwell In Group ( Mass, Dwell) ( Mass, Dwell)
( 252.0,   100) ( 264.0,   100)

GROUP 9
Group ID : indeno/dibenzo
Resolution : Low
Group Start Time : 31.00
Plot 1 Ion : 276.0
Ions/Dwell In Group ( Mass, Dwell) ( Mass, Dwell)
( 276.0,   100) ( 278.0,   100)

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\HPCHEM\1\METHODS\RAMP2.M

Percent Report Settings
Sort By: Retention Time
Output Destination
    Screen: Yes
    Printer: No
    File: No

Integration Events: AutoIntegrate
Generate Report During Run Method: Yes
Signal Correlation Window: 0.020
Qualitative Report Settings
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Peak Location of Unknown: Apex

Library to Search  Minimum Quality
C:\DATABASE\NIST98.L  25
C:\DATABASE\NBS75K.L  0

Integration Events: AutoIntegrate

Report Type: Summary

Output Destination
Screen: Yes
Printer: Yes
File: No

Generate Report During Run Method: Yes

Quantitative Report Settings
-----------------------------

Report Type: Summary

Output Destination
Screen: No
Printer: Yes
File: No

Generate Report During Run Method: Yes

Calibration Last Updated: Wed Jan 06 07:51:58 1999

Reference Window: 5.00 Percent
Non-Reference Window: 5.00 Percent
Correlation Window: 0.10 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information
-----------------------

*** Empty Quantitation Database ***

END OF DATA ANALYSIS PARAMETERS
-----------------------------

TOLEVEL PARAMETERS
---------------------

Method Information For: C:\MSDCHEM\METHODS\PAHMethod2.M
Method Sections To Run:
  ( ) Save Copy of Method With Data
  ( ) MSTOP Pre-Run Cmd/Macro =
  ( ) Instrument Control Pre-Run Cmd/Macro =
  ( ) Data Analysis Pre-Run Cmd/Macro =
  (X) Data Acquisition
  (X) Data Analysis
  ( ) MSTOP Post-Run Cmd/Macro =
  ( ) Instrument Control Post-Run Cmd/Macro =
  ( ) Data Analysis Post-Run Cmd/Macro =
Method Comments:
  This places the instrument in a stand-by mode.

END OF TOLEVEL PARAMETERS
---------------------

INSTRUMENT CONTROL PARAMETERS
---------------------

6890 GC METHOD
--------------------

OVEN
Initial temp: 40 'C (On)
Initial time: 2.00 min
Maximum temp: 325 'C
Equilibration time: 0.50 min

Ramps:
# Rate Final temp Final time
 1 10.00 190 0.00
 2 8.00 250 0.00
 3 4.00 300 43.00
 4 0.0(Off)

Post temp: 0 'C
Post time: 0.00 min
Run time: 80.00 min

FRONT INLET (SPLIT/SPLITLESS)
Mode: Splitless
Initial temp: 320 'C (On)
Pressure: 47.5 kPa (On)
Purge flow: 9.9 mL/min
Purge time: 2.00 min
Total flow: 13.3 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 0.00 min
Gas type: Helium

BACK INLET (UNKNOWN)

COLUMN 1
Capillary Column
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 30.0 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 47.5 kPa
Average velocity: 36 cm/sec

COLUMN 2
(not installed)

Inlet: Front Inlet  
Outlet: MSD  
Outlet pressure: vacuum

FRONT DETECTOR ()  
BACK DETECTOR ()

SIGNAL 1  
Data rate: 20 Hz  
Type: test plot  
Save Data: Off  
Zero: 0.0 (Off)  
Range: 0  
Fast Peaks: Off  
Attenuation: 0

SIGNAL 2  
Data rate: 20 Hz  
Type: test plot  
Save Data: Off  
Zero: 0.0 (Off)  
Range: 0  
Fast Peaks: Off  
Attenuation: 0

COLUMN COMP 1  
(No Detectors Installed)

COLUMN COMP 2  
(No Detectors Installed)

THERMAL AUX 2  
Use: MSD Transfer Line Heater  
Description: Initial temp: 300 °C (On)  
Initial time: 0.00 min  
# Rate Final temp Final time  
1  0.0(Off)

POST RUN  
Post Time: 0.00 min

TIME TABLE  
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:  
Sample Washes 2  
Sample Pumps 2  
Injection Volume 1.0 microliters  
Syringe Size 10.0 microliters  
Nanoliter Adapter Off  
PostInj Solvent A Washes 2  
PostInj Solvent B Washes 2  
Viscosity Delay 1 seconds  
Plunger Speed Fast  
PreInjection Dwell 0.00 minutes  
PostInjection Dwell 0.00 minutes

Back Injector:  
No parameters specified

Column 1 Inventory Number:  
Column 2 Inventory Number:  

MS ACQUISITION PARAMETERS

General Information  
--- ---

Tune File: stune.u  
Acquisition Mode: SIM

MS Information  
--- ---

Solvent Delay: 4.00 min  
EM Absolute: False  
EM Offset: 0

Method: PARMETHOD2.M  
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**[MS Zones]**

- MS Quad: 150 C maximum 200 C
- MS Source: 230 C maximum 250 C

Method: PARMETHOD2.M

Wed Jun 23 15:13:52 2010
DATA ANALYSIS PARAMETERS

Method Name: C:\MSDCHEM1\METHODS\PAHMETHOD2.M

Percent Report Settings
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Sort By: Signal
Output Destination
  Screen: No
  Printer: Yes
  File: No
Integration Events: Meth Default
Generate Report During Run Method: No
Signal Correlation Window: 0.020

Qualitative Report Settings
---------------------------
Peak Location of Unknown: Apex
Library to Search Minimum Quality
  C:\DATABASE\NBS75K.L  0
Integration Events: Meth Default
Report Type: Summary
Output Destination
  Screen: No
  Printer: Yes
  File: No
Generate Report During Run Method: No

Quantitative Report Settings
----------------------------
Report Type: Summary
Output Destination
  Screen: Yes
  Printer: No
  File: No
Generate Report During Run Method: No

### Calibration Last Updated: Fri May 04 12:37:22 2001

Reference Window: 2.00 Minutes  
Non-Reference Window: 1.00 Minutes  
Correlation Window: 0.10 minutes  
Default Multiplier: 1.00  
Default Sample Concentration: 0.00

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Curve Fit: Linear

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Method: PAHMETHOD2.M  
Wed Jun 23 15:13:52 2010  
Page: 5
Appendix G: Calculations
1. Calculating PAH pine needle dry weight concentrations (Yellow Springs, May, Phenanthrene)
   a. Calibration curves
      i. Area count correction-PAH/p-terphenyl=corrected
         1.  $\frac{379828}{130174}=2.92$
      ii. Average corrected area count vs. concentration
      iii. Linear regression equation made
   b. Samples
      i. PAH area counts corrected with p-terphenyl
         1. $\frac{6071}{172364}=0.0352$
      ii. Rearranged regression equations used to calculate PAH concentrations with average corrected PAH areas
         1. $(0.0351+0.1303)/1.5391=0.107 \, \mu g/mL$
        a. Concentrations were left uncorrected due to low recoveries
         2. $0.107 \, \mu g/mL \div 0.543 = 0.200$ (corrected value not used in study)
      iii. Mass of PAH calculated in a 4 mL volume
         1. $0.107 \, \mu g/mL \times 4 \, mL=0.430 \, \mu g$
   iv. Regression equation rearranged to solve for concentration
   v. Samples
      a. PAH area counts corrected with p-terphenyl
         1. $\frac{6071}{172364}=0.0352$
   b. Samples
      i. PAH area counts corrected with p-terphenyl
         1. $\frac{6071}{172364}=0.0352$
      ii. Rearranged regression equations used to calculate PAH concentrations with average corrected PAH areas
         1. $(0.0351+0.1303)/1.5391=0.107 \, \mu g/mL$
        a. Concentrations were left uncorrected due to low recoveries
         2. $0.107 \, \mu g/mL \div 0.543 = 0.200$ (corrected value not used in study)
      iii. Mass of PAH calculated in a 4 mL volume
         1. $0.107 \, \mu g/mL \times 4 \, mL=0.430 \, \mu g$
   iv. PAH concentration in needle calculated on a dry weight basis
1. \( 0.430 \mu g / 1.539 \ g = 0.279 \mu g/ g \)

2. Calculating water content
   a. Initial weight – final weight
      i. \( 4.9432 - 0.7253 = 4.2179 \ g \)
   b. Water ratio
      i. \( 4.2179 \ g / 4.9432 \ g = 0.8581 \)
   c. Average water content for 3 samples calculated
   d. Pine needle replicate water content calculated
      i. \( 10.8458 \ g \times 0.8581 = 9.306 \ g \)
   e. Pine needle dry weight
      i. \( 10.8458 \ g - 9.306 \ g = 1.539 \ g \)

3. Filter PAH concentrations (Yellow Springs, May, fluoranthene)
   a. Calculations same as steps 1) a)-1) b) iv)
   b. Final filter concentrations calculated based on amount of PM10 mass on filter strip
   c. Mass of filter and PM without border
      i. \( 4.4922 - 0.955 \)
         1. \( 0.955 \ g \) was an average of trimmings (or filter border untouched by PM)
            from 6 different filters
   d. (Filter PM 10 mass * filter strip mass)/trimmless filter strip
      i. \( (0.409 \ g \times 0.57711 \ g) / 3.5372 \ g = 0.00667 \ g \)
   e. \( 0.396 \mu g / 0.00667 \ g = 59.4 \mu g/ g \)

4. PAH atmospheric concentrations from filters (fluoranthene)
   a. (Mass *1000)/Volume of air
      i. \( (0.396 \mu g \times 1000) / 1632 \ m^3 = 0.242 \ ng/ m^3 \)

5. PAH atmospheric concentrations from pine needles (fluoranthene)
   a. \( \ln k_v = \frac{1000}{T} \times slope - 35.95 \)
      i. \( e^{(1000/294.56*10.209-35.95)} = 0.269 \)
   b. \( k_v = \frac{[veg]}{[lipid]+[gas]} \)
      i. \( [gas] = (1.20 \ ng/g) /((.269 \ m^3/mg)\times(50.591 \ mg/g)) = .0880 \ ng/m^3 \)
Appendix H: Raw Data sample (February 2010)
| Ion 128.00 (127.70 to 128.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 38 | 9.833 | rBV | 0.101 | 12200 | 9.779 | 9.88 |

| Ion 136.00 (135.70 to 136.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 19 | 9.79 | rBV | 0.16 | 798936 | 9.755 | 9.915 |

| Ion 164.00 (163.70 to 164.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 10 | 13.877 | rBV | 0.18 | 444744 | 13.807 | 13.987 |

| Ion 166.00 (165.70 to 166.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 2 | 15.124 | rVV | 0.174 | 50127 | 15.031 | 15.206 |

| Ion 188.00 (187.70 to 188.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 10 | 17.266 | rBV | 0.116 | 824582 | 17.225 | 17.341 |

| Ion 178.00 (177.70 to 178.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|
| 6 | 17.318 | rBV | 0.157 | 1380685 | 17.249 | 17.405 |
| 7 | 17.44 | rVB | 0.139 | 38148 | 17.405 | 17.545 |

<p>| Ion 202.00 (201.70 to 202.70): 4-30-10v.D | FebPlaMor2-1 | |
|---|---|---|---|---|---|---|---|</p>
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Table 5 February Moraine Austrian pine
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Table 6 February Moraine filter data
Appendix I: Discussion on issues with experiment
There are a few things concerning the experimental that need to be addressed because of the limited amount of time available for method optimization, different passive samplers from each site used and two different GC/MS used during sample analysis.

Using Austrian pine and white pine to collect atmospheric PAHs doesn’t provide a level field for comparison of the two sites. Differences in the needle structure, lipid content and other unknown variables affect the uptake of atmospheric PAHs. Using different trees to compare two different sites could give misleading results. This may not affect qualitative results but quantitative results would be affected due to the differences in PAH uptake.

Recoveries throughout the experiment were low especially for naphthalene-d8 and perlyene-d12. Low recoveries for naphthalene-d8 and perlyene-d12 are likely due to loss in rotary evaporation or from sticking to the column. Acenaphthene-d10 was not detectable throughout the analysis on the GC 5890 due to co-elution. This was a result of a clean-up stage requiring optimization. Ratola (2006) optimized a glass column of Florisil by activating it for 12 h at 400 °C followed with a deactivation with 1.2% of ultrapure water. This would have given a starting point for optimization to increase recoveries.

A complication in the analysis arose from GC 5890/MS 5972 constantly breaking down due to events beyond control (i.e. building power shutdowns). Eventually due to software issues in restarting the instrument, the instrument gave inconsistent area counts for the internal standards showing a decrease in sensitivity. The method also used for this GC/MS was not optimized either due to too high of an initial temperature of 80 °C which should have been 40 °C. Another reason why sensitivity decreased between sample replicates was due to the
column becoming dirty from sample matrix. A much longer baking of the column than 5 min was required to ensure a clean column at the start of another run. Due to the breakdown of the GC 5890/ MS 5972 resulted in using the GC 6890 / MS 5973. The method for this instrument was changed to fix the initial temperature and cleaning the column. The MS 5973 is more sensitive than the MS 5972.
Appendix J: Sample Chromatograms
Figure 11 Moraine Filter Sample
Figure 12 Moraine Plant Sample
Figure 13 Yellow Springs Filter Sample
Figure 14 Yellow Springs Plant Sample
Figure 15 2.0 ppm standard