AN ABSTRACT OF THE DISSERTATION OF

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Title: Local Scale Spatial and Temporal Variation in Wet Deposition of Persistent Organic Pollutants by Snow.

Abstract approved: _____

Staci L. Simonich

The objective of this research was to assess the variability of POP deposition by snow on a 10 km spatial scale by measuring the POP concentrations in fresh-fallen snow from remote alpine sites. Samples of pre-metamorphic snow were concurrently collected from three remote alpine sites, of matched altitude and exposure, along a 10 km transect of the HJ Andrews Research Forest in the Cascade Mountains of Oregon. During ten snow events, eighty-seven samples of pre-metamorphic snow were collected between January 2013 and February 2014. Samples were collected within 12 hours of a snow deposition event, with air temperatures below 0˚C and low solar irradiance for the period between deposition and collection. Samples were extracted using solid phase extraction (SPE) and analyzed by gas chromatography-mass spectroscopy (GC-MS) for 57 persistent organic pollutants, including PAHs and a variety of current and historic-use pesticides and pesticide degradation products. Sixteen of the seventeen PAHs analyzed for were detected in over 35% of the samples collected. Total PAH concentrations in individual samples ranged from

below quantifiable limits to 53.5 ng per liter of snow water equivalents (SWE). The most frequently detected PAH was fluoranthene, which was detected in 69% of all samples, with a maximum measured concentration of 22.2 ng/L_{SWE}. The pesticide degradation products, endosulfan sulfate and heptachlor epoxide, were detected at quantifiable concentrations in all samples, and were the most frequent chlorinated compound detected, with concentration ranges of 0.070 – 1.430 ng/L_{SWE} and 0.983 – 5.83 ng/$L_{SWE,}$ respectively. Dieldrin and chlorpyrifos were detected with maximum measured concentrations of 3.14 ng/L_{SWE} and 3.11 ng/$L_{SWE,}$ respectively. However, detection of each was limited to a single snow event. Of the hexachlorocyclohexanes, α-HCH was detected in 7 of 87 samples, but β-HCH and ϒ-HCH (Lindane) were not detected at quantifiable concentrations in any sample. Detections of chlorodiphenylmethane pesticides and degradation products (isomers of DDT, DDD and DDE) were largely limited to two individual snow events. No statistically significant evidence of between-site differences in POP concentration in fresh-fallen, pre-metamorphic snow was found at the 95% confidence level. Analysis of between-event variance found significant between-event differences in total PAH, total gas-phase PAH, total particulate-phase PAH and total pesticide concentration for all events. Source region impact factors (SRIFs) were used to assess regional contributions to POP deposition at HJ Andrews Experimental Forest. No SRIF positive correlations of total gas-phase PAH or total particulate-phase PAH concentration with any source region were found to be statistically significant at the 95% level. Retene and pyrene concentrations were positively correlated with air mass time in Oregon. A similar analysis showed a statistically significant correlation

at the 95% level between pesticide concentrations and air mass time in Washington and Oregon. No statistically significant correlation was found between total pesticide concentration and the Willamette Valley or Eastern Washington/Oregon source regions. Statistically significant correlations ($p<0.05$) were found between solar irradiance and total gas-phase PAH, total particulate-phase PAH, fluorene, pyrene and endosulfan sulfate concentrations, and between reciprocal snow temperature and phenanthrene concentration.

Local Scale Spatial and Temporal Variation in Wet Deposition of Persistent Organic Pollutants by Snow

by
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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Christopher D. Walsh, Author

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CONTRIBUTION OF AUTHORS

Dr. Staci Simonich assisted with experimental design and manuscript preparation for all chapters.

Chapter 3: Jill Schrlau assisted with method development and manuscript preparation.

Chapter 4: Dan Wang assisted with sample preparation. Chris Heist assisted with optical microscopy.

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Introduction: Persistent Organic Pollutants in Snow

Persistent organic pollutants (POPs) are compounds of concern for environmental or toxicological reasons that, due to their physical-chemical properties, are resistant to both biotic and abiotic degradation.[1-2] Volatilization, atmospheric transport in the gaseous or particulate phase, and subsequent wet deposition by snow provides a pathway for transport of POPs to remote and/or high-elevation ecosystems, including sites which might otherwise be expected to be pristine. [3-13]

In Arctic or high-altitude regions, these pollutants are incorporated into glacial ice and are subject to long-term storage. In warmer regions, the accumulated pollutants are released to the local ecosystem as the snow cover melts. Due to the rapid onset of snowpack metamorphosis and the variety of possible post-depositional fates, published information on the spatial variability of POP deposition by snow and the concentrations of POPs in fresh-fallen snow is scarce. This study was undertaken with the goal of measuring the concentrations of POPs in fresh-fallen snow from alpine sites and comparing the variability of POP deposition by snow in non-urban areas on the 10 km spatial scale.

Atmospheric Transport, Distribution and Deposition

The POPs of interest for this study include 18 polycyclic aromatic hydrocarbons (PAHs) and 57 current or historic use pesticides and pesticide derivatives. A full list of analytes, with chemical structures and physical-chemical properties is provided in Appendix A.

PAHs are released to the atmosphere through a variety of natural and anthropogenic combustion processes, including volcanic eruptions, fossil fuel and biomass burning and

agriculture. Current-use pesticides are released to the atmosphere both through agricultural application and through revolitalization from previously treated soil. Due to their persistence, historic-use pesticides can revolatilize from soil long after their original application and will therefore remain compounds of concern for many years after usage is restricted. Once volatilized, these compounds can undergo atmospheric transport of tens to thousands of kilometers before removal by dry or wet deposition. The distance traveled in the atmosphere is dependent on prevailing meteorological conditions, the compound's physical-chemical properties and gaseous/particulate-phase partitioning behavior. [14-18]

Impact

Atmospheric transport, combined with the temperature dependence of volatilization, drives a net transport of semi-volatile POPs from warm regions to colder, high-altitude or high-latitude regions.[19] After deposition in these remote regions, these compounds may be released to different environmental compartments in the local ecosystem by partitioning to soil, movement with bulk snowmelt runoff or re-volatilization to the atmosphere.[20] POPs released from snowpack are subject to bioaccumulation and subsequent amplification of their toxic and carcinogenic effects. Improved understanding of the spatial and temporal variability of deposition of POPs to remote snowpack could lead to improved assessment of the impact of POP deposition on remote ecosystems and aid in management and mitigation efforts.

Precipitation Scavenging

Precipitation scavenging is an important mechanism for the removal of both gaseous and particulate-phase pollutants from the atmosphere. The formation of cloud droplets around pre-

existing cloud condensation nuclei incorporates particulate-bound pollutants into cloud droplets and ice crystal. As raindrops or snowflakes grow and fall, the concentration of pollutants can increase through in-cloud and below-cloud scavenging of gaseous and particulate pollutants. Due to the increased surface area of snowflakes compared to rain droplets for a given liquid water content, snowfall is a particularly effective mechanism for below-cloud washout of atmospheric pollutants, including sub-micron particulate material.[3, 21] In regions with significant amounts of seasonal snowfall, wet deposition by snow is believed to be the predominant deposition mechanism for semi-volatile organic compounds, including the POPs studied here. [21-23]

Prior Studies of POP concentrations in Snowpack

Samples of snowpack and glacial ice provide a time-integrated record of contaminants deposited by both wet and dry deposition over the entire snow accumulation period. A number of prior studies have examined concentrations of POPs and other semi-volatile organic compounds in seasonal snowpack, multi-season snowpack and glacial ice. [3-4, 7, 9, 13, 24-30] The results of these studies for the compounds of interest in this research are summarized in Table 1.1.

Gregor and Gummer (1989) examined snow from 12 sites distributed across the Northwest Territories, Canada for organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), using liquid-liquid extraction of 40 L samples. They reported the frequent detection of the OCPs endosulfan, dieldrin and α- and γ-hexachlorocyclohexane (HCH), at concentrations ranging from 0.5 to 1.0 ng/L. Heptachlor, *o,p'*-DDT and *p,p'*-DDT were detected in a limited number of samples. The spatial analysis presented was limited, however intersite differences in mean concentration of total HCH were noted, with samples from coastal sites having generally lower concentrations than those from inland sites. [31]

PAH concentrations in superficial snow collected on the Greenland ice sheet were reported by Masclet et al. (2000). Twelve liter snow samples were collected in 10 cm thick layers representing seasonal deposition strata from a 3.5 m snow pit at a site described as being representative of long-range transport effects for the region. Samples were analyzed using high-performance liquid chromatography / UV fluorescence. Fluoranthene and pyrene were the most abundant PAHs measured in snow, with concentrations ranging from 100 – 4700 pg g^{-1}. All PAHs measured, except retene, showed significant interannual variation, with total PAH concentration ranging from 100 to 10000 pg g^{-1}. [30]

Persistent organic pollutants, including PAHs, OCPs and PCBs, were detected in total snowpack cores from European alpine sites by Carrera et al. (2001). Nine total two liter samples were taken at five sites. PAHs were detected in all samples, with phenanthrene, fluoranthere and pyrene detected at the highest concentrations. Total PAH concentration was measured at 16 – 81 ng/l. PAH profiles varied from site to site. The samples with the highest particulate mass load generally had the highest proportion of high molecular weight PAHs. However, this relationship did not hold for all sites, as the site with the highest particle concentration was not enriched in high molecular weight PAHs. Interannual variation in total PAH at the same site was low, with a coefficient of variation (CV) of 18%. Similar PAH species concentration profiles were observed from year to year at each site. Of the OCPs studied, only lindane (γ-hexachlorocyclohexane) was detected at measureable concentrations in a significant number of samples and was reported at concentrations of 0.022 – 1.1 ng/l.[5]

PAHs and OCPs were detected in snow and ice samples from the Baltic Sea region by Melnikov et al. (2003). One liter snow samples were extracted by liquid-liquid extraction and analyzed by gas chromatography / mass spectrometry (GC/MS). PAHs were detected in all

samples, with total PAH concentrations of 25 – 33 μg/L. The most abundant PAHs detected in snow were naphthalene, phenanthrene, flouranthene, pyrene, chrysene, benzo(b)flouranthene and benzo(k)flouranthene. The sampling region was broken into 100 km x 100 km grid boxes for spatial analysis. In contrast to other published studies of POPs in snow, no statistically significant differences in total PAH concentrations were found when comparing all regions and all years together. Total HCH concentrations reported range from 1.7 to 1.4 ng/L, with a CV of 26% for the four regions sampled. Total DDT is reported at 0.6 – 0.9 ng/L with no statistically significant regional or interannual differences. [26]

OCP and PCB concentrations in snow and snowmelt runoff across a single lake catchment in Alberta, Canada were reported by Lafreniere et al. (2006). Nineteen samples were collected over two years. Hexachlorocyclobenzene (HCB), α- and γ-HCH, dieldrin, and DDT were detected in most samples. Significant intersite variations in concentration were noted, with the coefficient of variation (CV) for all samples ranging from 25% to 94%. Open, non-forested sites had 23– 86% higher OCP and PCB concentrations than forested sites. Concentrations of HCH and HCB were strongly correlated to snow water equivalents (SWE).

Finizio et al. (2006) sampled fresh fallen snow at a single site on an Alpine glacier in Italy. Snow samples were collected every 12 hours for 3 days beginning 12 hours after a fresh snow event. Melted snow samples, including their particulate component, were extracted by liquid-liquid extraction using dichloromethane (DCM). Samples were analyzed for DDT, the α- and γ-isomers of hexachlorocyclohexane (HCH) and PCB concentration. Total HCH was measured at concentrations of 10.7 – 234 pg/L. Total DDT concentrations ranged from no detection to 96.2 pg/L. A correlation of log γ-HCH concentration to time since deposition showed an R^2 of 0.81 and was used to calculate a first-order half life for γ-HCH of 18 hours.[8]

POP concentrations in a variety of environmental media were the focus of the Western Airborne Contaminants Assessment Program (WACAP).[32] Samples of annual snowpack, lichen, conifer needles, fish and lake sediment from eight national parks in the western United States were analyzed for a wide range of POPs. Large volume annual accumulation snow samples were collected in open areas on north facing slopes.[28] Fifty liter snow samples were extracted using solid phase extraction, with analysis by GC/MS. The pesticides dacthal, chrolpyrifos, endosulfan, HCH, trifluralin and triallate, as well as the pesticide degradation products endosulfan sulfate and chlorpyrifos oxon were detected. Significant differences in pesticide concentrations between parks were noted.[28] A high degree of spatial variability in POP concentrations was also noted, even for samples collected at closely-spaced sites of similar altitude and aspect. Site replicates showed a mean coefficient of variation of 15%. However, intra-park replicates (concurrently collected samples from sites within the same national park) had a CV of 41%, which was almost as high as the 59% CV seen for interannual replicates from the same sites.[29]

Source of Variability in Snowpack POP Concentrations

While permanent snow and glacial ice may represent a long-term sink for organic pollutants, regions of seasonal snowpack present a more dynamic situation. The changing physical characteristics of aging snowpack drive changes in environmental partitioning and snowpack pollutant content. Figure 1.1 summarizes the sources and sinks of POPs in seasonal snowpack.

Table 1.1 –Concentration of POPs measured in previous studies.

(ng/L, except ** which is µg/L)

	chlorpyrifos	Endosulfan (I & II)	Chlordane (I & II)	HCB	dieldrin	Total HCH	Total PAH	
Gregor and Gummer [1989]		0.10 - 1.34			0.11 - 1.61	0.2 - 8.7		Northwest Territories, Canada
Masclet [2004]							3000 - 5000	Greenland Ice Sheet
Carerra [2000]						0.49 - 1.1	16 - 81	Italian Alps
Melnikov [2003]						1.2 - 2.4	25 -33 **	Baltic Sea Ports (urban)
Lafreniere [2006]		0.035 - 0.30		.028 - .045	0.12 - 0.72	0.05 - 0.43		Banff NP, Canada
Finizio [2006]				.0093 - .095		.349 - .610		Italian Alps
WACAP / Hageman [2010]	2.8	1.5	0.05	0.007	4.8	1.0 - 4.2		US National Parks

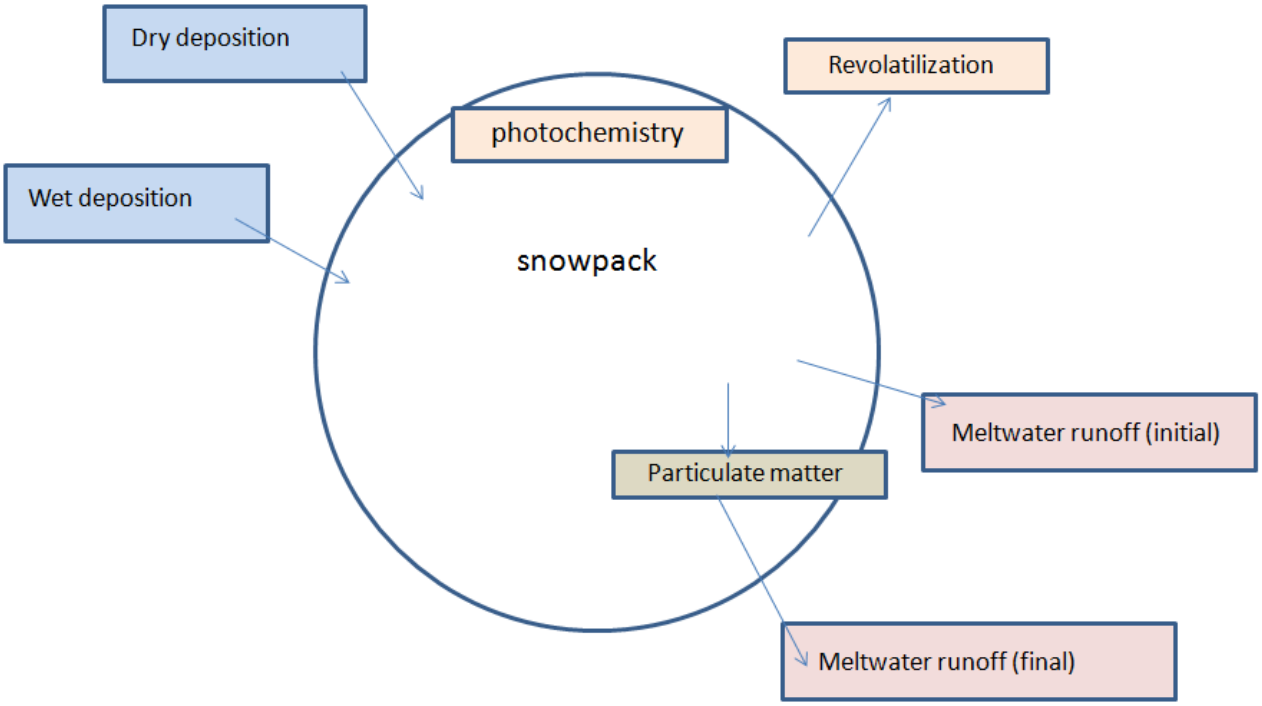

Figure 1.1 – Sources and sinks of persistent organic pollutants in seasonal snowpack.

Freshly deposited snow is subject to rapid and dramatic physical changes as it ages from snow to firn and on to glacial ice.[33] Increases in density as snowpack ages are associated with an increase in the average ice crystal size and changes in the amount and distribution of interstitial airspace. Organic material incorporated into snowpack is subject to physical dislocation in the horizontal or vertical.[33] Revolitalization and atmospheric exchange are ongoing at the snowpack surface.[34] If present, meltwater channels can alter pollutant distribution in an extremely localized manner.[35] The high degree of variation seen in POP concentrations measured by prior studies of snowpack could be the result of localized differences in depositional flux, or could result from the many metamorphic processes that occur as snowpack ages.[22, 36] Modeling predicts that within hours to days of deposition, these snowpack metamorphic processes, including settling and diffusional crystal growth, may cause compounds to undergo highly localized repartitioning, including revolitalization, repartitioning or spatial redistribution.[37] As a result of these metamorphic processes, a study of the variability of POP deposition by snow requires rapid sample collection. Low air temperatures and low solar irradiance for the period from deposition to collection are also required in order to avoid relocation of deposited pollutants prior to sampling.

Research Question and Hypothesis

Studies of snowpack or snow cores give a measure of the POP deposition over the entire period of accumulation. The deposition of POPs resulting from a single snow event can be directly measured using samples of fresh-fallen snow, but due to the logistical difficulties involved in the rapid collection of samples from remote sites, few published studies exist for

POP concentrations in pre-metamorphic or fresh-fallen snow,[8, 23, 38] and none focus on the spatial variability of POP concentration in fresh-fallen snow.

This study was undertaken in order to address the following research question:

- Is the local-scale (10 km) variation in POP concentration typically observed in snow samples due to differences in deposition?

The hypotheses were:

- Between-site variation of POP concentration in fresh-fallen snow for single snow events is statistically indistinguishable from within-site variation for sites of similar elevation and exposure with <10 km separation.
- Significant correlation will be found between deposition profiles and air-parcel source regions, as determined by analysis of model-derived air parcel back-trajectories generated for each snow event.

Experimental Plan

The remainder of this dissertation describes the experimental plan used to test these hypotheses. Chapter Two of the dissertation describes the development of a method for the measurement of POPs in fresh fallen snow using solid-phase microextraction (SPME). This resulted in insufficient sensitivity for the desired application, and so this method was not used. Chapter Three of the dissertation describes the development and validation of an analytical method for the measurement of POPs in five liter samples of fresh-fallen snow using solid phase extraction, and a preliminary field study, including a description of the sampling plan and sampling site parameters. Chapter Four of the dissertation presents the interpretation of POP

concentrations in fresh-fallen snow samples collected for ten snow events over the winters of 2013-2013 and 2013-2014 in the Cascade Range in Oregon, USA. Spatial variability was assessed by comparison the coefficient of variation for within-site and between-site mean concentrations. One-way analysis of variance (ANOVA) was used to test for independence of site means for individual compounds and for inter-event differences in gas-phase PAH, particulate-phase PAH, total PAH, total DDT and total pesticide concentrations. Overall variations in analyte concentrations were examined for correlation with snow density, particulate mass load, snowpack and site temperature and solar irradiance profiles over the accumulation period. The influence of air-parcel source-region was determined by air-parcel back-trajectory modeling and the correlation of POP concentrations to air-parcel source region. Chapter Five summarizes the conclusions of this study and outlines future areas of research on POP deposition by snow and snow scavenging efficiency.

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Development of an Analytical Method Using Solid-Phase Microextraction for the Measurement of Persistent Organic Pollutants in Fresh-Fallen Snow

Introduction

Most published studies of persistent organic pollutant (POP) concentrations in snow present the analysis of seasonal snowpack[1-6] or glacial ice[7-8] and generally find a high degree of within-site, between-site and inter-annual variability. Similar to an intentionally placed passive sampling device, seasonal snowpack and glacial ice samples contain the total deposition over the accumulation period,[9] minus any losses due to revolitalization, loss with meltwater or spatial relocation with snow grains or intrinsic particulate matter.[10] The observed variability in POP concentration could result from variability in the initial deposition by snow, or from differences in post-depositional fate. As of this writing, no published information exists on the spatial variability of POP concentration in pre-metamorphic snow. As significant snowpack metamorphosis and potential analyte repartitioning can occur in hours to days following deposition, the study of variability in POP deposition requires rapid sample collection from sites that are sufficiently remote to avoid impact from local point sources. Published methods for the analysis of POPs in seasonal snowpack samples used sample sizes ranging from 1 L for samples of highly contaminated snow in the Baltic Sea Region[4] to 50 L for samples of snow in remote mountain regions of North America[6]. Due to the logistical difficulties associated with the collection of pre-metamorphic snow samples from multiple remote sites, a sample size of less than 5 liters was desired. For this study, an analytical method was developed using solid-phase

microextraction (SPME) and gas chromatography/mass spectrometry (GC-MS) for the measurement of 18 polycyclic aromatic hydrocarbons and 57 pesticides and pesticide degradation products in small-volume (<1 kg) samples of fresh-fallen snow. Analyte information, including CAS number, structure, quantification and qualifier ion numbers and NIST and experimental reference spectra, is provided in Appendix A of the thesis.

Prior SPME Methods for Determination of POP Concentration in Aqueous Samples

Several prior studies have reported methods for the measurement of polycyclic aromatic hydrocarbons (PAHs) and/or organochlorine pesticides (OCPs) in aqueous samples using SPME.[11-15] The reported method Limits of Detection (mLOD) are summarized in Table 2.1. It was expected that the use of Selected Ion Monitoring (SIM) Mode for mass spectroscopy would allow for improvement over these published mLODs.

Potter and Pawliszyn (1994)[11] were the first to report a method for measurement of PAHs and polychlorinated biphenyls (PCBs) in water, using lab-built SPME fibers and aqueous standards as samples. They report method detection limits for PAHs of 1.25 to 20 ng/L.

The reproducibility of SPME analysis of a variety of pesticides using a commercially available fiber was reported by Magdic and Pawliszyn (1996)[12] for a multi-lab round-robin experiment analyzing aqueous standards. Relative standard deviations of less than 20% are reported for all analytes.

Boyd-Boland et al. (1996)[13] report 1 ng/L mLODs and relative standard deviations of 3-20% for PAHs in contaminated groundwater samples using 100μm PDMS fibers and ion-trap mass spectroscopy. Stiles et. al. (2008)[15] reports a SPME method for the measurement of PAHs, OCPs and other organic contaminants in drinking water using a dual coating PDMS/DVB fiber.

Reported mLOD (ng/L)	Potter (1994)	Magdic (1996)	Magdic (1996)	Boyd-Boland (1996)	Stiles (2008)
	MS	MS	ECD	MS	GC-MS
naphthalene	20				500
anthracene	3				500
phenanthene					500
Benz(a)anthracene	1.25				
Benzo(a)pyrene	1.25				500
fluoranthene					500
"other PAHs"	~2.5				
lindane		200000	1000	1	100
heptachlor		3800	500	1	
aldrin		4500	900	1	
heptachlor epoxide		200	400	1	
endosulfan I		600	300	1	
dieldrin		60	300	1	100
endosulfan II		300	400	1	
endosulfan sulfate		4500	50	1	
chlorpyrifos				1	1000

Table 2.1 Reported method Limits of Detection (mLOD) for persistent organic pollutants by solid-phase microextraction (SPME).

Experimental Materials

A standard reference solution of 16 PAHs was obtained from ChemService (West Chester, PA). Retene, benzo(e)pyrene and triphenylene were obtained from Sigma Aldrich (St. Louis, MO). Pesticide standards were obtained from ChemService and Restek (Belfonte, PA). Isotopically labeled PAHs and pesticides for use as recovery surrogates or internal standards were obtained from CDN Isotopes (Pointe-Claire, Quebec, Canada).

The SPME fibers used for this study were 24 gauge Sigma Aldrich fused silica fibers with 100μm polydimethylsiloxane (PDMS) coating (Sigma Aldrich 57300-U) in a manual holder. This fiber was selected as the commercially available option providing the best overall sensitivity given the wide range of physical-chemical properties of the POPs of interest based on published recommendations.[16]

Prior to use, fibers were conditioned by exposing them in a 280˚ C GC inlet for 60 minutes. After conditioning, the fibers were inspected using optical microscopy for cracks or other defects in the PDMS stationary phase. Optical inspection at 50x magnification was repeated after every five uses. Any fibers with coating loss visible at 50x magnification were discarded. No fiber was used for more than 35 extractions, which is less than the manufacturer's predicted lifetime of 50 uses.

Following sample extraction, fibers were immediately analyzed by GC-MS using an Agilent 6890 gas chromatograph with a Merlin Microseal septum injector seal. The manual fiber holder was positioned to place the exposed fiber in the center of the inlet liner during desorption. Fibers were desorbed in the GC inlet for 5 minutes at 280˚ C. Fibers blanks were performed after every five samples or standards by desorbing and analyzing the fiber without exposing it to samples or standards.

A 30 m DB5-MS column from Agilent (Santa Clara, CA) was used for chromatography. The oven temperature method started at 60˚C with a 0.1 minute hold, a first ramp of 4.0 ˚C/min to 250 ˚C and a second ramp of 15.0 ˚C/min to a final temperature of 320 ˚C. The detector used was an Agilent 5973N MSD using electron ionization (EI) in Selected Ion Monitoring (SIM) mode.

Development of an Object-Oriented Fiber Partitioning Model: SPMEpy

Prior published methods for solid-phase microextraction of POPs have method detection limits ranging from 1 ng/L to 1μg/L[11, 15]. Although it was expected that the use of SIM mode mass spectrometry would provide lower detection limits, the non-exhaustive nature of SPME sampling requires consideration of the possibility of analyte depletion limiting method sensitivity, especially when dealing with small volume samples with low concentrations of the analytes of interest. Prior to physical experimentation, an assessment and prediction tool, SPMEpy, was developed to predict the maximum possible method sensitivity for a given analyte concentration and sample volume. SPMEpy is a partitioning model developed using the open source Python programming language. Model calculations were based on the SPME theory presented in Pawliszyn (1999)[5] and included analyte concentration, fiber and sample partition volume, instrumental limits of detection, and analyte physical-chemical properties. SPMEpy output files reported equilibrium fiber load, post-extraction sample concentration and method limit of detection. The extraction kinetics of solid-phase microextraction are not modeled. Fiber loading is calculated using equation 2.1:

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s} \qquad (2.1)$$

where n is the number of moles of analyte partitioned onto the fiber, K_{fs} is the analyte-specific fiber-solution partitioning constant, V_f is the volume of the fiber coating, V_s is the volume of the sample and C_0 is the initial concentration of the sample. Octanol-water partitioning coefficients (K_{ow}) calculated using the U.S. Environmental Protection Agency's EPI-Suite program[17] were used as surrogate K_{fs} values. SPMEpy output was validated using manual calculations and by reproducing the experimental results of Potter (1994) under their reported experimental conditions.[11] Appendix B contains the source code of the SPMEpy program and validation data.

Virtual experiments using SPMEpy were used to simultaneously calculate fiber loading for a series of experimental conditions for analytes with a wide range of physical-chemical properties. These results were used for sample vial size selection and as an initial assessment of method sensitivity.

SPMEpy Sample Volume Estimates

SPME has been described as volume independent[16], but this is only true when sample volume and concentration are such that overall depletion of the sample over the course of the extraction is negligible. For small volume samples at trace concentrations, the final fiber loading may be limited by the sample volume, due to depletion of the analyte in the aqueous phase.

In order to aid selection of an appropriate sample volume, the SPMEpy model was run for all analytes over a range of sample volumes, given sample concentrations of 10 ng/L for each analyte. Figure 2.1 shows the equilibrium fiber load in ng as a function of sample volume for naphthalene. Similar curves were generated for all analytes. The results indicated that for samples of 100 mL or less, at concentrations of 10 ng/L and below, SPME results are significantly influenced by sample volume.

Figure 2.1 shows the SPMEpy output for the fiber loading of naphthalene, given full equilibrium and a starting concentration of 10 ng/L. By applying equation (1) over a range of sample volumes for all analytes, it was determined that a the largest commercially available SPME vials, with a volume of 40 mL, could obtain over 90% of the maximum possible fiber loading for any sample volume for all analytes. Forty mL vials were used for all subsequent experiments.

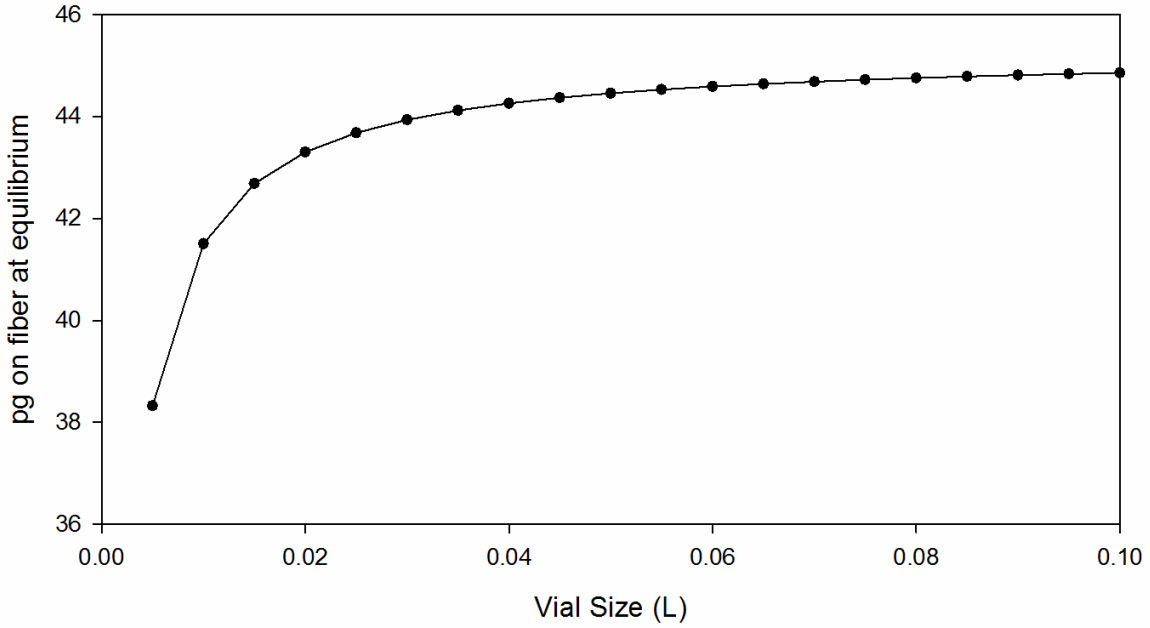

Figure 2.1 – SPMEpy predicted fiber load by vial size for naphthalene, 10 ng/mL starting concentration.

Additionally, it was shown that for 40 mL samples at starting concentrations of 50 ng/L, a single extraction would significantly deplete analyte concentrations. This finding dictated that a single GC/MS analytical method for quantifying all analytes from a single extraction and desorption is required for SPME analysis of low concentration POPs in aqueous samples. SPMEpy derived estimates of equilibrium fiber load and vial depletion are given in Table 2.2.

	equilibrium fiber load (pg)	**% remaining in vial**
naphthalene	42.68	89.3
acenaptheylene	196.64	90.2
acenaphthene	274.21	86.3
fluorene	224.51	88.8
phenanthrene	358.03	82.1
anthracene	358.03	82.1
fluoranthene	582.31	70.9
pyrene	582.31	70.9
retene	741.30	62.9
chrysene	698.31	65.1
triphenylene	698.31	65.1
benzo(b)fluoranthene	736.00	63.2
benzo(k)fluoranthene	736.00	63.2
benzo(e)pyrene	736.00	63.2
benzo(a)pyrene	736.00	63.2
indeno (123-C.D)pyrene	746.35	62.7
1.2:56-dibenzanthracene	746.35	62.7
1,12-benzoperylene	746.35	62.7
benzo(a)anthracene	698.31	65.1
carbofuran	6.06	99.7
trifluralin	669.62	66.5
HCB	725.46	63.7
α-HCH	319.57	84.0
γ-HCH	319.57	84.0
β-HCH	319.57	84.0
δ-HCH	319.57	84.0
heptachlor	725.46	63.7
chlorpyrifos	488.21	75.6
DCPA [Dacthal]	311.15	84.4
chlordane	740.03	63.0
dieldrin	690.00	65.5
Endosulfan I	85.71	95.7
endosulfan sulfate	113.38	94.3

Table 2.2 – SPMEpy derived predictions of equilibrium fiber load and vial depletion. (100μm PDMS fiber, starting concentration of 10 ng/L and vial volume of 40 mL)

SPMEpy method Limit of Detection (mLOD) estimates

SPMEpy fiber loading predictions were also combined with the instrument limits of quantitation for the target analytes in a similar matrix to predict method limits of detection (mLODs). The mLOD is the minimum sample concentration required to give an equilibrium fiber load equal to the instrument limit of quantitation (LOQ) for a given compound. Method LOD was calculated by equation 2.2:

$$mLOD = LOQ \times \frac{K_{fs}\, V_f + V_s}{MW\, K_{fs} V_f V_s} \qquad (2.2)$$

Where K_{fs} is the analyte-specific fiber-solution partitioning constant, V_f is the volume of the fiber coating, V_s is the volume of the sample and MW is the molar mass of the analyte. LOQ was defined as the minimum sample amount introduced to the GC/MS that would give a signal with a sign to noise ratio of 10:1 or better. A conservative instrument LOQ of 50 pg/μL was assumed for all analytes, which is slightly higher than typical lab operational values.

Predicted method limits of detection for pesticides are given in Table 2.3 and for PAHs in Table 2.4. These results suggested that SPME would be an adequate technique for the measurement of PAHs and pesticides in 40 mL snow samples at the concentrations previously observed in prior studies of snow at remote North American sites. Consequently, experiments for the development and optimization of an method using a sample volume of 40 mL were initiated.

	pg on fiber	mLOD [ng/L]
carbofuran	1.22	164
trifluralin	303	0.660
HCB	367	0.545
alpha-HCH	87.1	2.30
gamma-HCH	87.1	2.30
beta-HCH	87.1	2.30
delta-HCH	87.1	2.30
heptachlor	367	0.545
chlorpyrifos	165	1.21
DCPA [Dacthal]	84.0	2.38
chlordane	386	0.518
dieldrin	325	0.616
endosulfan	18.5	10.8
endosulfan sulfate	25.0	7.986
mirex	397	0.503

Table 2.3 – SPMEpy calculated equilibrium fiber load and method limit of detection for selected pesticides and degradation products.

(100μm PDMS fiber, starting concentration of 10 ng/L and vial volume of 40 mL)

	pg on fiber	**mLOD [ng/L]**
naphthalene	8.85	22.6
acenaptheylene	47.0	4.25
acenaphthene	71.1	2.81
fluorene	55.2	3.62
phenanthrene	102	1.96
anthracene	102	1.96
fluoranthene	226	0.884
pyrene	226	0.884
retene	388	0.516
chrysene	334	0.599
triphenylene	334	0.599
benzo(b)fluoranthene	381	0.525
benzo(k)fluoranthene	381	0.525
benzo(e)pyrene	381	0.525
benzo(a)pyrene	381	0.525
indeno (123-C.D)pyrene	395	0.507
1.2:56-dibenzanthracene	395	0.507
1,12-benzoperylene	395	0.507
benzo(a)anthracene	334	0.599

Table 2.4 – SPMEpy calculated equilibrium fiber load and method limit of detection for PAHs.

(assuming 10 ng/Lsample, 40 mL sample, 100 μm PDMS fiber)

SPME Analytical Method Optimization

For reproducible results, SPME must be performed with close control over the conditions that affect partitioning.[16, 18] This is particularly important when full equilibrium partitioning is not achieved for all target compounds. In order to obtain acceptable reproducibility, sampling temperature, sampling time, agitation conditions, desorption temperature and desorption time were all controlled. For maximum sensitivity, agitation method and extraction time were optimized.

Extraction Agitation Experiments

In a perfectly agitated sample, all analyte molecules would have equal access to the SPME fiber throughout the extraction process and the time to equilibrium would be determined by the fiber thickness, F (μm) and the analyte diffusional coefficient in the fiber coating, D_f (μm^2/sec) In this case the time, in seconds, required to reach to 95% of equilibrium during an extraction[18] is given by equation 2.3:

$$t_{95\%} = \frac{2\,F^2}{D_f} \qquad (2.3)$$

Under actual conditions, a layer of fluid directly in contact with the surface of the fiber remains stationary. Fluid movement gradually increases as you move away from the fiber surface until it matches the flow rate of the bulk fluid. Within this static boundary layer, which is known as the Prandtl layer, analyte movement is governed by the diffusional coefficient of the analyte in

the bulk fluid. The thickness of the Prandtl layer is determined by the viscosity of the bulk fluid and the effectiveness of the agitation.[16]

For this study, both mechanical and ultrasonic agitation methods were tested for maximum sorption over a preset sampling time. The agitation methods tested were; no agitation, low shake, high shake and ultrasonic agitation. Standards were prepared by spiking 40 mL of high-purity water in SPME vials to a concentration of 10 ng/L of each of the target analytes via a methanol-based stock solution.

Mechanical agitation was performed using a VWR S-500 platform shaker at settings of 20% (low shake) and 50% (high shake). Ambient air temperature during the mechanically agitated extractions was 28˚ C. Ultrasonic agitation was performed using a Branson 1510 sonicator with the water bath temperature adjusted to 28˚ C, in order to match the room air temperature of the mechanically agitated extractions. All extractions were 45 minutes long, based on the results of Kos et. al (2006),[19] and were performed in triplicate.

The results are shown in Figures 2.2 and 2.3. No agitation and low shake experiments resulted in very low peak areas and seem to represent diffusion-controlled situations. The high shake experiment showed a significant increase in mean peak areas, suggesting that this level of mechanical agitation successfully decreases the thickness of the Prandtl layer. However, for all analytes, ultrasonic agitation was clearly the most effective technique under the conditions tested. Consequently, all following SPME experiments included ultrasonic agitation.

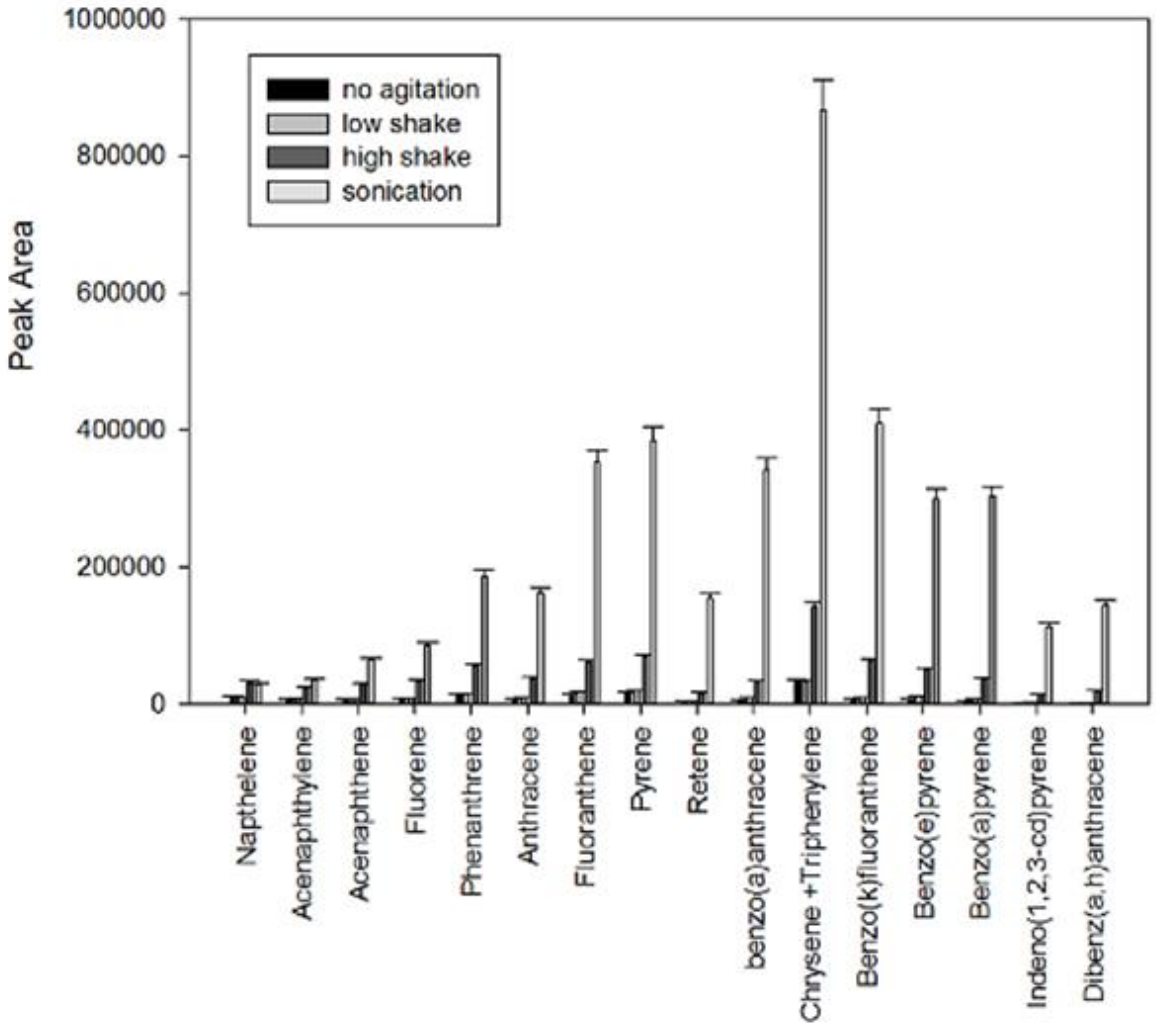

Figure 2.2 –Agitation method comparison for SPME extraction of PAHs.

(40 mL sample, 45 min extraction, 28˚C, n=3, error bars=2 std. dev.)

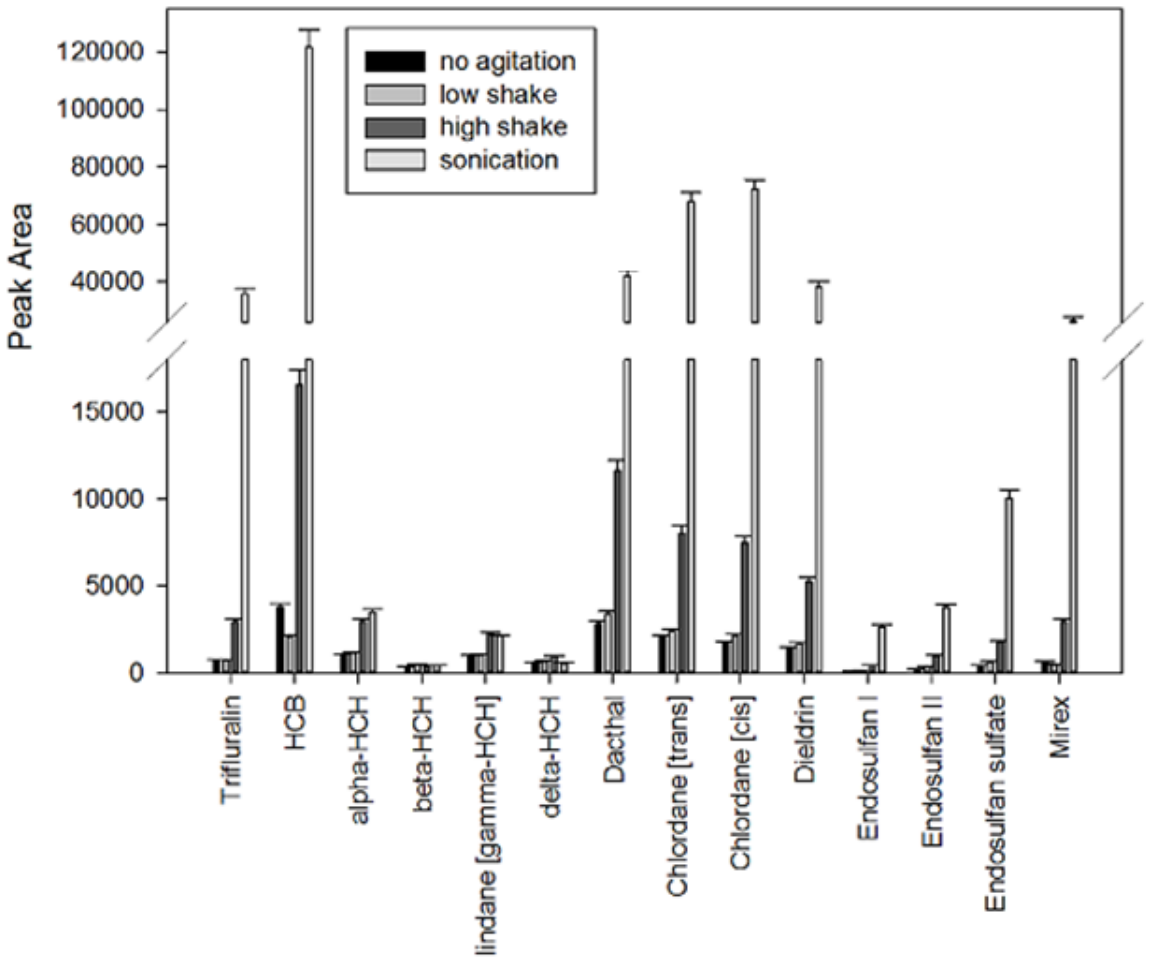

Figure 2.3 – Agitation method comparison for SPME extraction of pesticides

(40 mL sample, 45 min extraction, 28˚C, n=3, error bars=2 std. dev.)

Selection of Extraction Temperature

When using SPME, sample temperature during extraction affects analyte diffusion rates and the time required to reach solution-fiber equilibrium.[18] However, in the absence of thermal degradation, sample temperature does not affect the fiber load at full equilibrium. Maintaining the Branson sonicator's water bath sample at an arbitrary temperature throughout lengthy agitations proved to be problematic. As a result, extraction temperature was optimized for reproducibility. An extraction temperature of 40˚C was selected, as this temperature gave reasonable extraction times and was the most consistently reproducible and maintainable in the water bath of the sonicator.

Extraction Time Experiments

In order to optimize extraction time, a series of extraction time profile experiments were conducted. Forty mL of high-purity water was spiked to a concentration of 10 ng/L of each of the target analytes. Extraction times of 15, 30, 45, 60 and 120 minutes were each tested in triplicate using ultrasonic agitation at a temperature of 40˚C. Extracts were analyzed by GC-MS in SIM mode with Electron Ionization (EI). Figures 2.4, 2.5 and 2.6 show the extraction time profiles for representative low molecular weight PAHs, high molecular weight PAHs and pesticides, respectively.

As expected, the relatively low molecular weight pesticides reached equilibrium in less than 30 minutes. High molecular weight PAHs reached over 80% of maximum response in less than 60 minutes. Low molecular weight PAHs reached equilibrium in approximately 45 minutes, but a decreased response is seen with longer extractions. This decrease in peak area of low molecular weight PAHs seen with longer extraction times may be the result of ultrasonic

degradation of the analyte molecules.[19] Based on these results, an extraction time of 45 minutes was selected as the best compromise for all analytes.

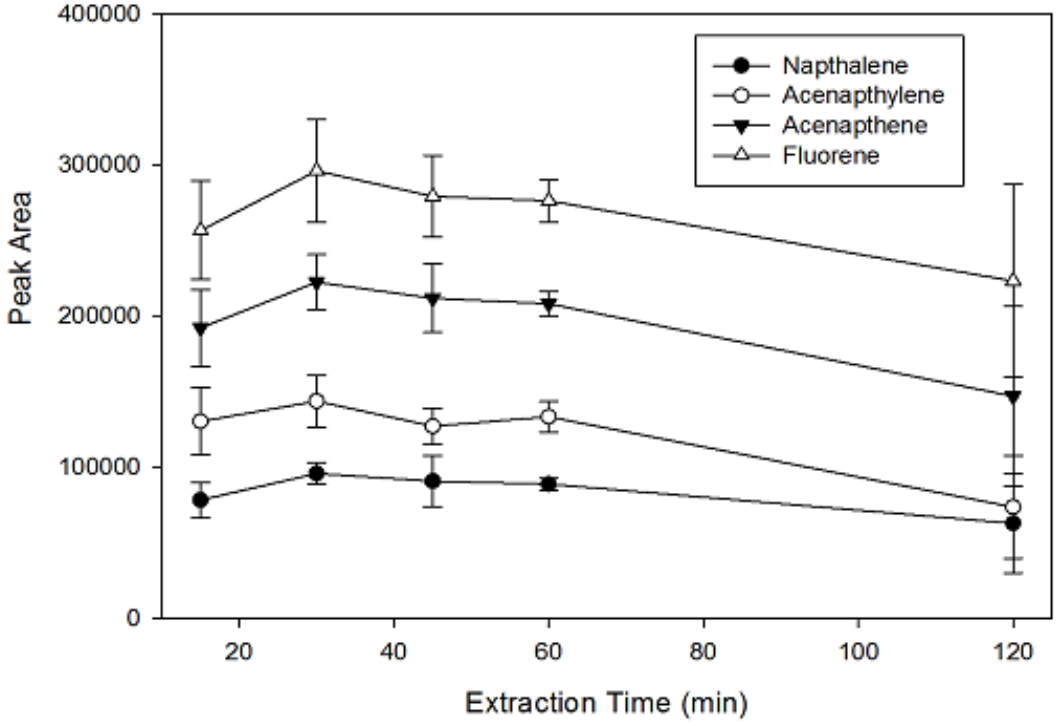

Figure 2.4 – SPME time profile for selected low molecular weight PAHs, ultrasonic agitation, 40 ˚C, 100 µm PDMS fiber, 10 ng/L starting sample concentration.

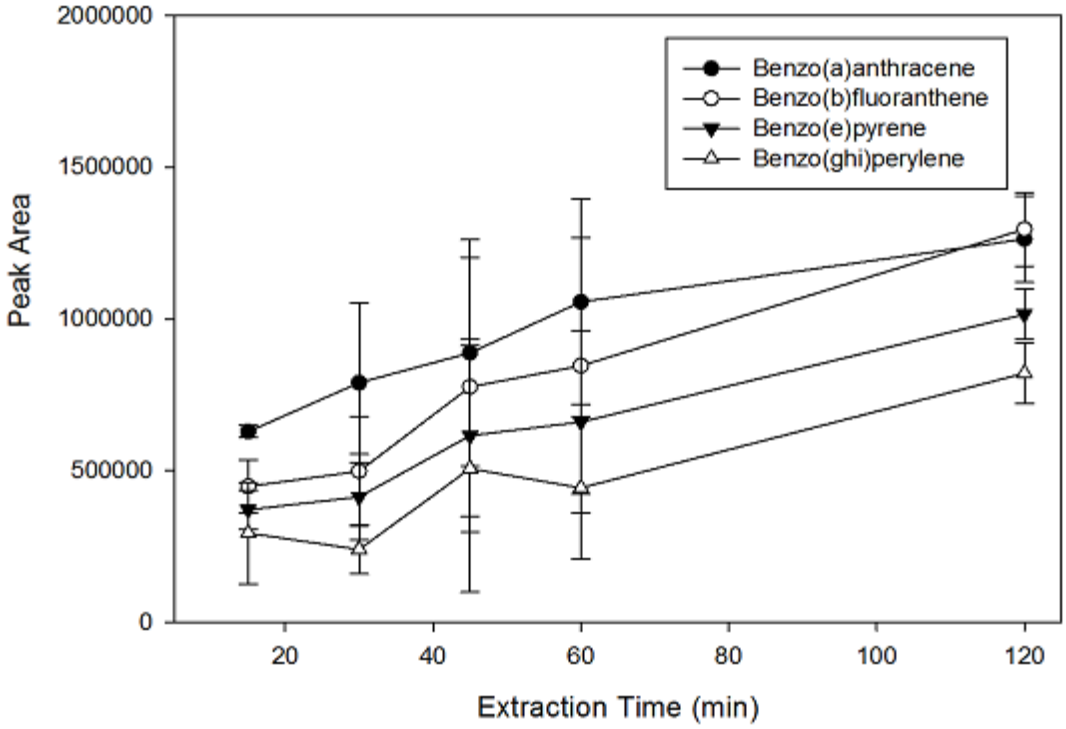

Figure 2.5 – SPME time profile for selected high molecular weight PAHs, ultrasonic agitation, 40 ˚C, 100 μm PDMS fiber, 10 ng/L starting sample concentration.

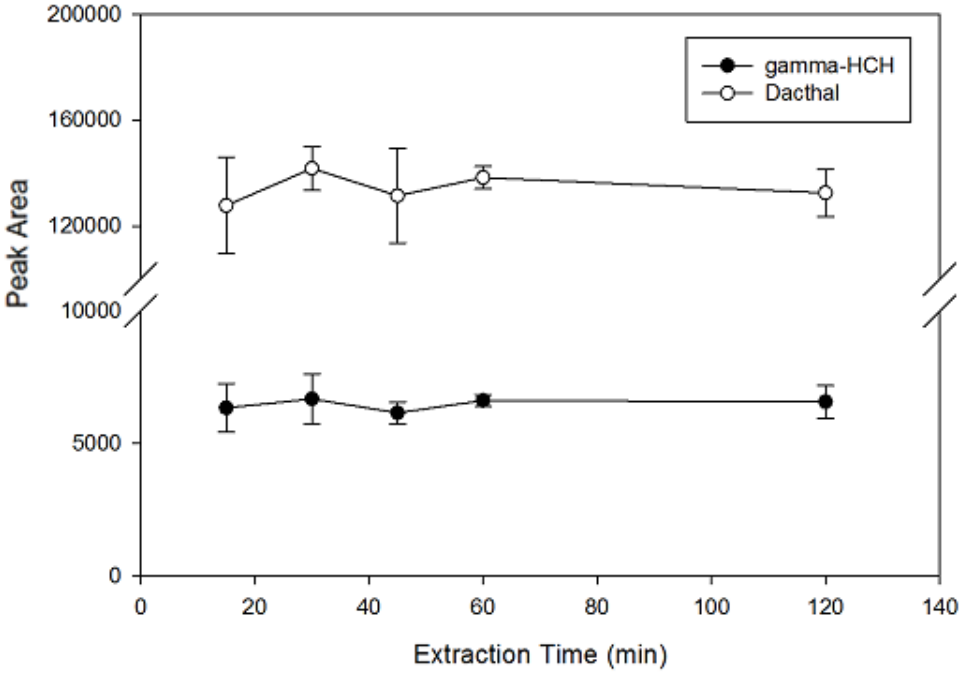

Figure 2.6 –SPME time profile for selected pesticides, ultrasonic agitation, 40 ˚C, 100 μm PDMS fiber, 10 ng/L starting sample concentration.

Reproducibility Experiment

In order to assess method reproducibility, nine 40 mL samples of melted snow collected at HJ Andrews Experimental Forest in the Cascade Range, Oregon, USA, were spiked at 1 ng/mL with target pesticides and PAHs and internal standards. These samples were subsequently extracted by SPME. The extractions conditions were; 40˚C, 45 min extraction time with ultrasonic agitation. Exposed SPME fibers were analyzed by GC-MS in SIM mode with Electron Ionization (EI). Extractions were done three per day over three days with fiber and lab blanks run each day. Peak areas were normalized to internal standards and used to calculate relative standard deviation for individual runs, daily and three day averages. Method three-day percent relative standard deviations (%RSDs) are reported in Tables 2.5 and 2.6.

%RSDs were below 7% for all PAHs except for the high molecular weight PAHs indeno(1,2,3-CD)pyrene, dibenz(a,h)anthracene and benzo(ghi)perylene, which had %RSDs of 12.90%, 11.95% and 9.81% respectively. These three compounds may be particularly sensitive to small variations in sampling time or other sampling conditions, as extraction time experiments indicate that they are being sampled in non-equilibrium mode.

Relative standard deviations were below 10% for all pesticides and pesticide degradation products tested, except for trifluralin, hexachlorcyclobenzene (HCB), beta-hexachlorocyclohexane, heptachlor epoxide and Endosulfan II, which had %RSDs of 33.14%, 17.79%, 13.97% and 14.51% respectively. The high %RSD observed for these five compounds was largely due to their relatively poor ionization in electron ionization mode mass spectroscopy.

	%RSD
naphthalene	3.23
acenaptheylene	2.75
acenaphthene	2.18
fluorene	2.57
phenanthrene	5.61
anthracene	5.72
fluoranthene	3.29
pyrene	2.98
retene	3.76
benzo(a)anthracene	5.39
chrysene +triphenylene	6.56
benzo(b)fluoranthene	2.81
benzo(k)fluoranthene	3.65
benzo(e)pyrene	3.29
benzo(a)pyrene	3.63
indeno(1,2,3-cd)pyrene	12.90
dibenz(a,h)anthracene	11.95
benzo(ghi)perylene	9.81

Table 2.5 Method % Relative Standard Deviations for PAHs

(n=9, 3 per day, 3 days, 45 min, ultrasonic agitation, 40˚C)

	%RSD
trifluralin	33.14
HCB	16.32
alpha-HCH	2.26
beta-HCH	17.79
lindane [gamma-HCH]	9.92
delta-HCH	7.85
dacthal	6.76
heptachlor epoxide	13.97
trans-chlordane	8.77
cis-chlordane	8.83
dieldrin	9.56
endosulfan I	2.66
endosulfan II	14.51
endosulfan sulfate	4.28
mirex	3.90

Table 2.6 Method % Relative Standard Deviations for pesticides.

(n=9, 3 per day, 3 days, 45 min, ultrasonic agitation, 40˚C)

Initial Field Test

Following the optimization of extraction conditions to ultrasonic agitation at 40 ˚C for 45 minutes, the analytical method was given an initial field test using fresh snow and late season snowpack collected at HJ Andrews Experimental Forest in the Cascade Range, Oregon. SPME analysis of these preliminary samples using the conditions described above showed only very small peaks. Figure 2.7 shows the chromatograms generated for a 5 ng/L aqueous sample, as well as samples of fresh-fallen snow collected February 10, 2012 in the HJ Andrews Experimental Forest at the Upper Lookout site and snowpack from the Vanilla site in the HJ Andrews Experimental Forest collected on March 3, 2012. The lack of detection of PAHs called into question the utility of this method for the analysis of POPs at the very low concentrations expected in fresh-fallen snow.

Repeat Extraction Experiment

A repeat extraction experiment was conducted in order to experimentally verify SPMEpy mLOD predictions in the sample matrix. Since SPMEpy gives full equilibrium values with no competing matrix effects, it was expected that experimental LODs would be greater than SPMEpy predictions, which could possibly explain the lack of PAH detection in the initial field trial. The repeat extraction experiment compared SPMEpy predicted extraction efficiencies to values derived from the extraction of spiked natural matrix samples.

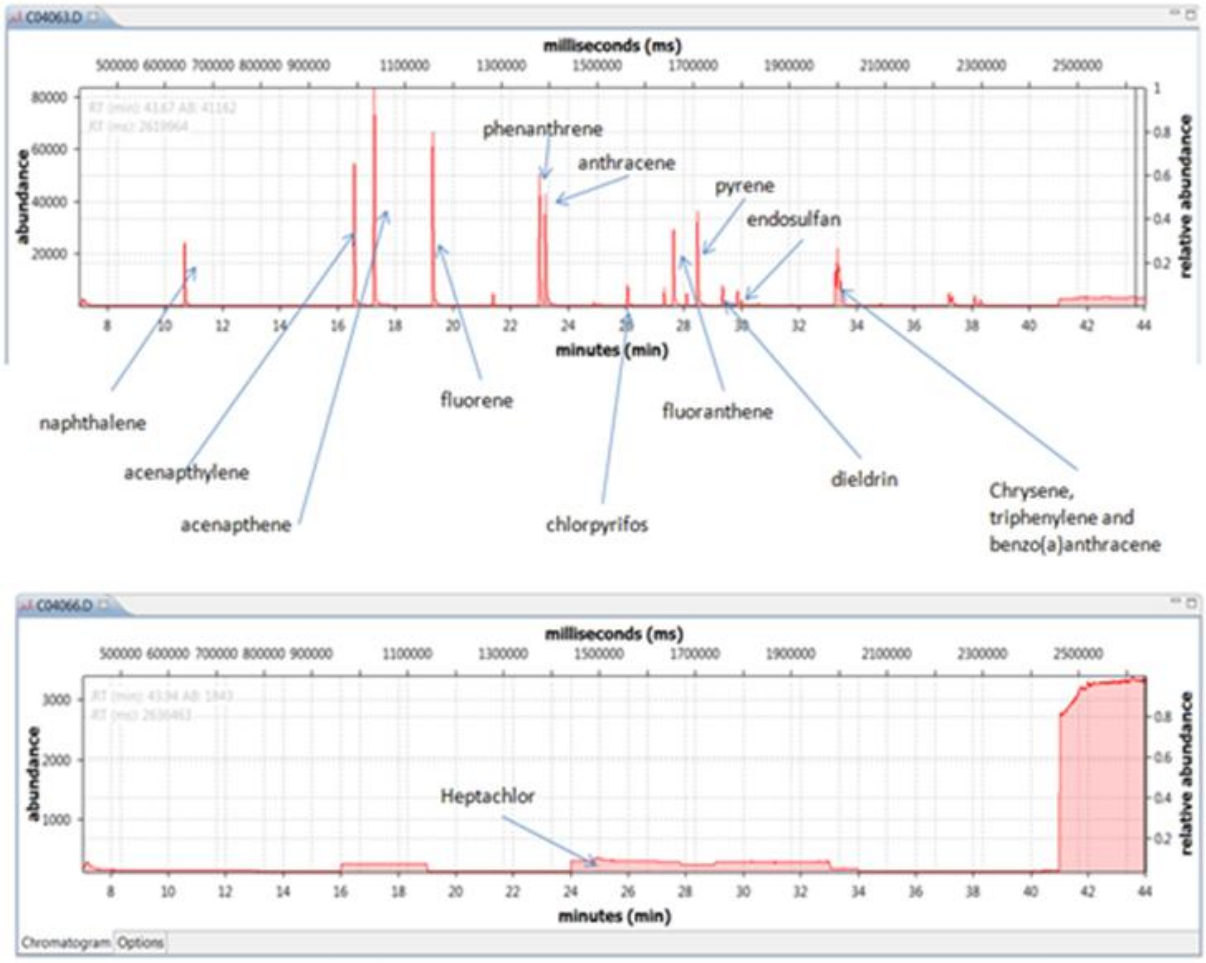

Figure 2.7 – Chromatogram of solid-phase microextraction of a 5 ng/L aqueous standard (top), and of fresh snow from the Upper Lookout Site at HJ Andrews (bottom).

(70eV Electron Ionization, SIM mode, 45 min, ultrasonic agitation, 40˚C)

Three 40 mL freshly melted snow samples were spiked at 10 ng/L with each of the target analytes, as described above. Each sample was extracted five successive times by SPME using the optimized extraction conditions described above. Exponential depletion curves were fitted for each analyte and used to calculate the experimental extraction efficiency for each analyte. Figure 2.8 shows the theoretical and experimental depletion profiles and fitted curve parameters.

Repeat extractions can be modeled using stepwise first-order kinetics. Exponential curve coefficients were fit to the experimental data and used to calculate the fraction remaining in a sample following a single extraction step, as given by equation 2.4, where PA is observed peak area:

$$1 - \frac{PA_1}{PA_2} = e^{-k_{spme}} \qquad (2.4)$$

A comparison of theoretical and experimental depletion values for PAHs and some representative pesticides is shown in Figure 2.9. Most pesticides met model predictions. Lower molecular weight PAHs were slightly more depleted than predicted. However, higher molecular weight PAHs were much less depleted than predicted.

The less than predicted depletion observed for high molecular weight PAHs in the repeat extraction experiment may be caused by the larger molecules not reaching full equilibrium in 45 minutes, even with ultrasonic agitation. Since SPMEpy predictions are based on equilibrium conditions, some overestimation of fiber loading is expected. However, experimental results presented above, and in prior published methods for SPME of PAHs in aqueous samples[19], show a maximum response for high molecular weight PAHs around 45 minutes, with a decreased response for longer sampling times.

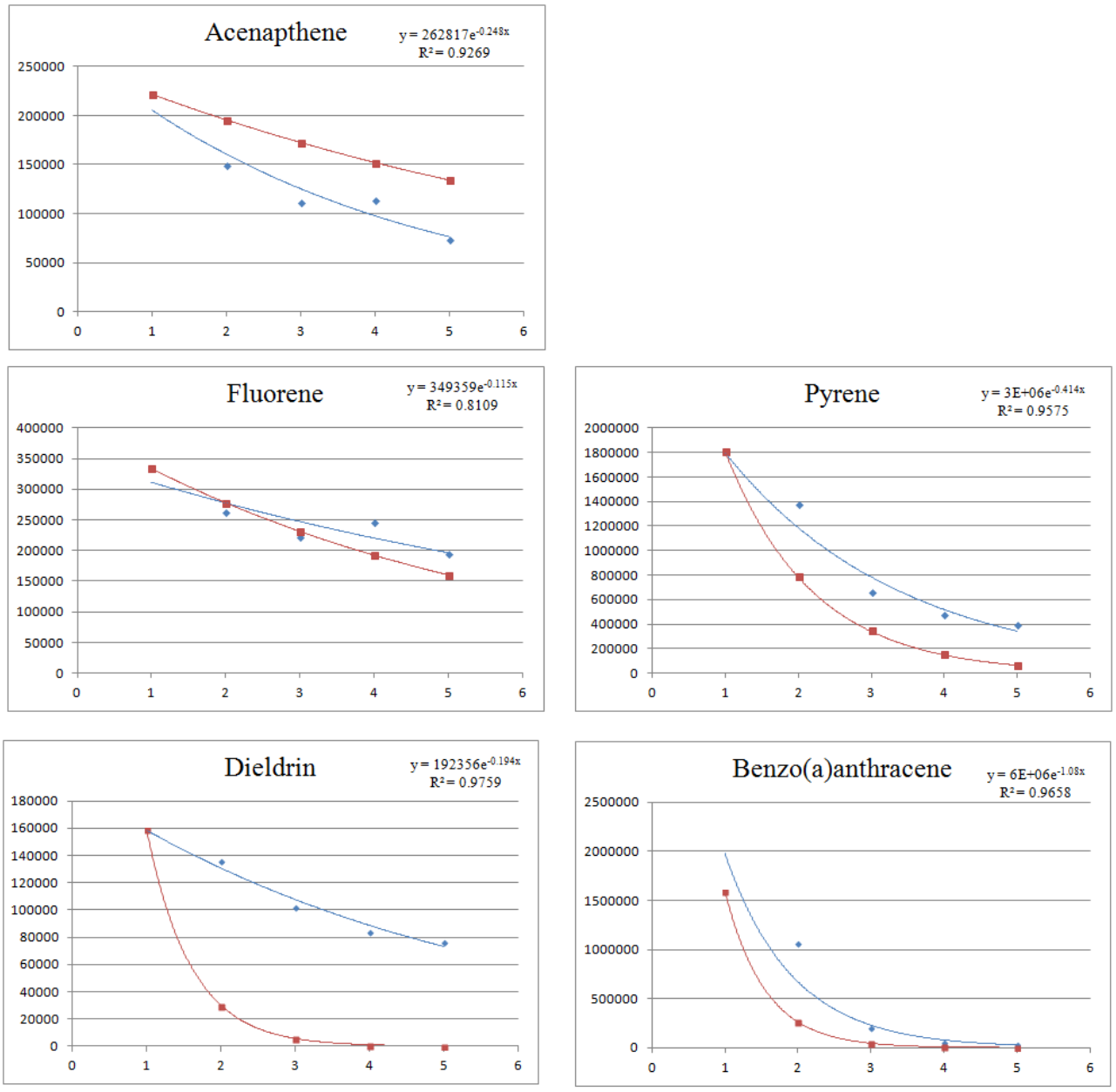

Figure 2.8 – Experimental depletion profile (blue circles, n=3) vs. SPMEpy predicted depletion profile (red squares). The equation shown on each plot is the exponential fit for experimental data used to calculate experimental extraction efficiency.

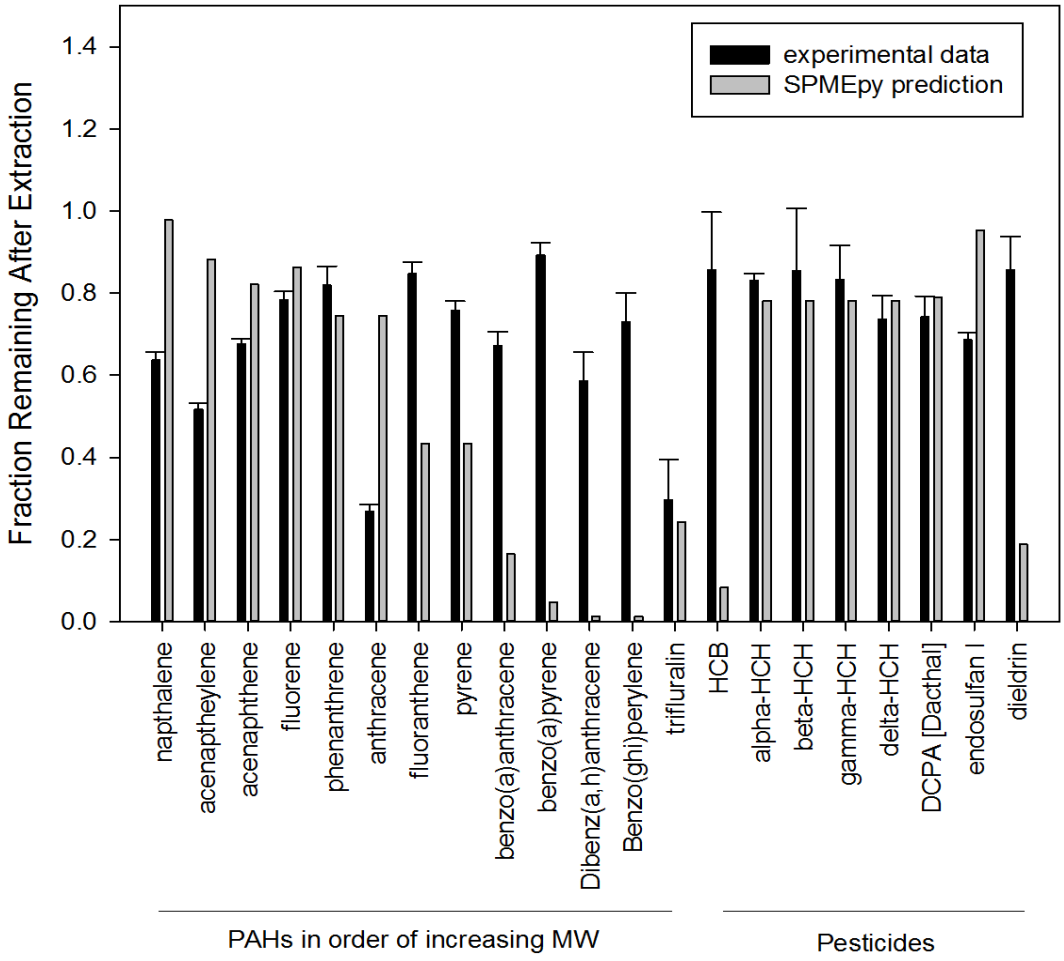

Figure 2.9 – Analyte fraction remaining after a single extraction step. Experimental values are derived from an exponential curve fit to analyte repeat extraction profiles (n=3, error bars = 2 standard deviations).

A second possible explanation for the lower than predicted experimental response is given by modeling results from Meyer and Wania (2011),[20] which show that as ice or snow samples melt, many POPs will repartition from the ice surface to any particulate organic material (POM) present in the sample. When attempting solid-phase microextraction of natural aqueous samples, organic material in the sample may serve as an additional partition in competition with the SPME fiber, leading to decreased fiber loading. Since snow crystals form around pre-existing aerosol particles in the atmosphere, the inclusion of DOC or POM in the SPME sample is likely, and may account for the reduced depletion experimentally seen in spiked snow samples. Additional experiments would be required to test this competitive partitioning hypothesis and allow for the calculation of matrix-specific method limits of detection.

Conclusions

An analytical method was developed and optimized for the analysis of persistent organic pollutants in 40 mL samples of melted snow using a 100 μm PDMS SPME fiber and analysis by GC/MS. A model, SPMEpy, was developed to predict fiber loading at full equilibrium in the absence of matrix effects. Application of the analytical method to samples of fresh fallen snow yielded lower peak areas than the fiber loading model predicted. Subsequent repeat extraction experiments showed that extraction efficiencies in a natural matrix for many desired analytes were lower than SPMEpy predictions for high molecular weight PAHs. Lower than predicted experimental results for analyte concentrations in snow were obtained.

Given the poor effectiveness noted for high molecular weight PAHs in recovery experiments, the results for the preliminary field samples, and the low response and poor % RSDs seen for some pesticides due to the limitations of electron ionization mode mass spectrometry, it was

decided that SPME was not likely to provide the detection limits necessary for the measurement of POPs in fresh-fallen snow. Subsequent method development focused on solid-phase extraction with larger, 5 kg samples, which is described in Chapter Three of the dissertation.

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Development and Use of a Method for the Determination of Polycyclic Aromatic Hydrocarbon and Organochlorine Pesticide Concentrations in Fresh-fallen Snow

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Abstract

An analytical method was developed and validated for the quantitative analysis of 18 polycyclic aromatic hydrocarbons (PAHs) and 57 organochlorine pesticides (OCPs) and degradation products in 5 kg samples of fresh-fallen snow, using Oasis HLB solid phase extraction (SPE) with quantitation by Gas Chromatography/Mass Spectroscopy (GC/MS). The mean method estimated detection limits were 0.658 ng/μL for OCPs and 0.520 ng/μL for PAHs, with most relative standard deviations (RSDs) below 8%. Mean analyte recovery for the entire analytical method was 63% ± 11% for OCPs and 47% ± 11% for PAHs. The method was applied to samples of fresh-fallen, pre-metamorphic snow collected from two remote alpine sites of similar altitude and exposure in the Cascade Mountains of Oregon, USA during the winter of 2012-2013. PAHs were detected in fresh-fallen snow at concentrations of 1.3 – 2.2 ng/L of snow water equivalents (SWE). The pesticides dacthal, α-HCH and chlorpyrifos were detected at concentrations of 45 – 220 pg/L SWE. Spatial analysis showed statistically significant between-site differences in α-HCH, dacthal, fluorene and fluoranthene concentrations, indicating variability in persistent organic pollutant (POP) deposition on the 10 km scale.

Introduction

The atmospheric transport of persistent organic pollutants (POPs), including pesticides, polycyclic aromatic hydrocarbons (PAHs) and their subsequent selective removal via snowfall, provides a mechanism for POP deposition to remote sites, including sites which might otherwise be expected to be pristine.[1-3] POPs deposited by snow are incorporated into seasonal snowpack, thereby providing a time-integrated record of contaminants deposited over the entire snow accumulation period. A number of prior studies have used seasonal snowpack samples to examine seasonal POP deposition rates, typically showing a high degree of spatial variability in POP concentrations, even for samples collected at closely-spaced sites of similar altitude and aspect. [3-16]

The deposition of POPs resulting from a single snow event can be directly measured using samples of fresh-fallen snow. However, modeling predicts that within hours to days of deposition, snowpack metamorphic processes may cause compounds to undergo highly localized repartitioning, revolatilization, sorption to particulate matter and/or spatial redistribution.[17] Rapid changes in distribution have been observed in samples of fresh-fallen snow collected at a single site at twelve hour intervals following deposition.[18] Consequently, information on the spatial variability of POP deposition by snow is quickly obscured. Due to the logistical difficulties involved in the rapid collection of samples from remote sites, few published studies exist for POP concentrations in pre-metamorphic or fresh-fallen snow.[18-19] Here, an analytical method was developed that uses a smaller sample size than is typically required for the quantitative analysis of POPs in snowpack.[9-10, 13, 20] The method involves the use of solid-phase extraction of small-volume (5 kg) fresh-fallen snow samples, with quantitation by gas chromatography-mass spectrometry in selected ion monitoring mode (SIM), using electron ionization (EI) and electron

capture negative ionization (ECNI). This method was used for an initial inter-site comparison of POP deposition for a snow event on April 15, 2013 in the Cascade Range in Oregon, USA. This study is the first publication known to the authors of PAH and pesticide concentrations in fresh-fallen snow from multiple remote sites for the same single snow event.

Materials

The analytes of interest for this study included 18 PAHs and 57 current or historic use pesticides and pesticide derivatives (Tables 1a and 1b), which replicates the POPs selected for analysis in the Western Airborne Contaminant Assessment Program.[10, 20-21] A standard reference solution of 16 PAHs was obtained from ChemService (West Chester, PA). Retene, benzo(e)pyrene and triphenylene were obtained from Sigma Aldrich (St. Louis, MO). Pesticide standards were obtained from ChemService and Restek (Belfonte, PA). Isotopically labeled PAHs and pesticides for use as recovery surrogates or internal standards (Tables 1a and 1b) were obtained from CDN Isotopes (Pointe-Claire, Quebec, Canada). Twenty mL OASIS HLB extraction cartridges with 1 g of sorbent were obtained from Waters, Inc. (Milford, MA, part number 186000117.). Air temperature at the sampling sites was measured using Campbell Scientific (Logan, UT) Model HMP35C probes with Fenwal Electronics (Palatine, IL) UUT51J1 thermistors. Solar radiation was measured using Kipp and Zonnen (Bohemia, NY) model CM-6B pyranometers with thermopile-type sensors.

Experimental Details

Sampling sites were located in the HJ Andrews Experimental Forest (HJA) in the Oregon Cascade Range, adjacent to established back-country meteorological data collection sites operated by HJA personnel. Site access was by snow-cat, with the final 100 m by snowshoe in order to avoid potential contamination from the exhaust of the snow-cat.

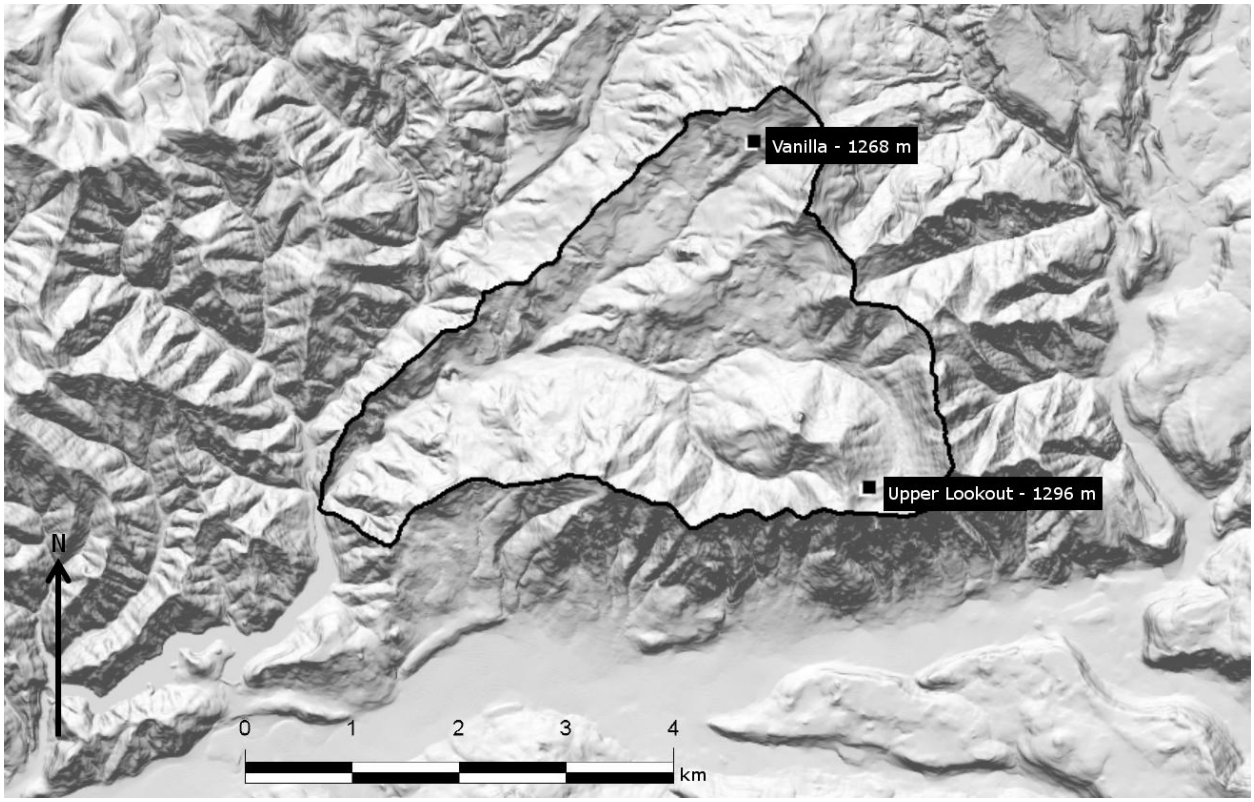

Figure 1 - Map of sampling sites at HJ Andrews Experimental Forest in the Oregon Cascade Range. The basemap is the US Forest Service 30 m digital elevation model.

(HJA data set GI002)

The map in Figure 1 shows the location of the Upper Lookout and Vanilla sites in the experimental forest. The Upper Lookout and Vanilla sites were at an altitude of 1298 m and 1268 m, respectively. Both sampling locations were open clearings, with aspect and exposure similar to the adjacent meteorological site.

All samples were collected within 12 hours of a snow deposition event, with air temperatures below 0˚C and a maximum solar irradiance of les than 150 W/m^2 for the entire period between

deposition and collection. Mixed precipitation events with both snow and rain were excluded. Intrasite replicates were collected within a total of 30 minutes from locations spaced approximately 5 m apart. All samples for a given snow event were retrieved within a 5 hour period. Sample collection was limited to fresh-fallen snow by sampling above the prior snow crust layer, and sampling no deeper than the depth of recent deposition recorded by ultrasonic snow depth gauges at the adjacent meteorological station. Snowpack temperature and density of the fresh-fallen snow were measured at the sampling point using a field sampling kit from Snowmetrics (Boulder, CO). Air-mass back-trajectories for source region analysis were generated using the HYSPLIT model provided by the National Atmospheric and Oceanic Administration.[22] Ten day back trajectories were calculated for the air mass over the HJ Andrews Experimental Forest during the snow event of April 15, 2013, at starting elevations of 1500 m, 2000 m and 2500 m above sea level. The trajectories generated by HYSPLIT were imported into ESRI ArcMap software for GIS analysis.

At each site, replicate 5 kg samples were collected using a stainless steel shovel and stored in Teflon bags (Welch Fluorocarbon, Dover, NH). The stainless-steel shovel was rinsed with reagent-grade methanol and high-purity water between each sample. The collection bags were sealed with zip-ties and stored in opaque 5 gallon food-grade pails with air-tight gasket lids. In order to assess the cleanliness of sampling equipment and potential cross-sample contamination, one field blank was generated per trip by rinsing the shovel with high-purity water between samples and collecting the rinsate in Teflon bags. For each trip, a travel blank of high-purity water, stored in the same Teflon bag and gasketed pail as was used for sample collection, accompanied the sample containers to and from the sampling sites. Three samples were collected at each site on the morning of April 15, 2013, immediately following an overnight snow event.

After collection, samples were directly transported to the campus of Oregon State University in Corvallis, OR and stored at -20˚ C until analysis.

Samples were thawed, still sealed, at room temperature over 24 hours. No heat was applied to accelerate melting. Once melted, isotopically-labeled surrogates were spiked into 2 mL of reagent-grade methanol and added to the sample. A lab blank of high-purity water was extracted with each batch of twelve samples. Sample extraction occurred immediately after melting, with the sample temperature remaining close to 0˚C throughout the extraction. In order to prevent photodegradation, aluminum foil and opaque plastic were used to shield the sample bag, the SPE cartridge and the final extract from light throughout the extraction process.

Pre-weighed solid phase extraction (SPE) cartridges were conditioned with 10 mL each of ethyl acetate (EA), methanol and high-purity water. A Teflon cartridge adapter and sampling tube were used to interface the cartridge to the sample bag. The sample was drawn through the cartridge by vacuum at a rate of 15 mL/min. Teflon valves on the sampling line allowed for the vacuum manifold trap to be periodically emptied without introducing air bubbles into the sampling line or allowing the SPE cartridge to dry out. After extraction of the sample, the sample bag was rinsed with 20 mL of EA and 20 mL of dichloromethane (DCM). The rinse fractions were collected and used as a portion of the elution solvents. The analytes retained on the SPE cartridge were eluted with a total of 40 mL of EA followed by a total of 40 mL of DCM. The EA and DCM elution fractions were recombined before concentration.

After elution, the cartridge was allowed to air-dry to constant mass in order to calculate the mass of particulates retained. It should be noted that this extraction process combines both dissolved-phase and particulate-bound pollutants. However, dissolved and particulate-bound

pollutants are subject to repartitioning as a consequence of melting the snow sample for analysis.[23]

The combined EA and DCM extract was dried with sodium sulfate and filtered with a Whatman 0.45μm PTFE syringe filter. Snowpack samples may include dust from dry deposition, soil, and plant material and so require extensive sample clean-up.[9] However, low particulate mass and lack of extraneous material found in fresh-fallen snow samples allowed for an acceptable chromatographic baseline without any additional sample clean-up. The filtered extract was reduced to a volume of 200 μL and solvent-exchanged to EA under a gentle nitrogen stream in a Turbovap II sample concentrator (Zymark, Hopkinton, MA). Prior to GC/MS analysis, samples were spiked with 500 pg each of isotopically-labeled acenapthene, fluoranthene, benzo(k)fluoranthene and PCB-138 for use as internal standards.

GC/MS analysis was performed on an Agilent 6890 gas chromatograph. Five microliter injections into a cryogenically cooled Programmed Temperature Vaporization (PTV) inlet in solvent vent mode were used to help alleviate the loss in sensitivity expected to result from the reduction of sample size from 50 kg to 5 kg. Large volume injection was particularly effective for analytes detected using electron capture negative ionization mass spectrometry, which provided a very low level of baseline noise. Initial PTV inlet temperature was 30˚C with a pressure of 75 kPA and a 6 second hold. The inlet temperature final temperature was 300˚C with a ramp rate of 600˚C/min. A 30m DB5-MS column from Agilent (Santa Clara, CA) was used. The oven temperature profile for both electron ionization (EI) and electron capture negative ionization (ECNI) modes started at 60˚C with a 0.1 minute hold, a first ramp of 4.0 ˚C/min to 250 ˚C and a second ramp of 15.0 ˚C/min to a final temperature of 320 ˚C. Calibration check standards were run every 10 samples. The detector used was an Agilent 5973N MSD in Selected

Ion Monitoring (SIM) mode. Electronic Ionization (EI) was used for PAHs and some pesticides, and Electron Capture Negative Ionization (ECNI) was used for the remaining pesticides and pesticide degradation products. Full lists of all target analytes, surrogates, and internal standards analyzed and their retention times, ionization mode and quantification and qualification ions using EI and ECNI modes are given in Table 1a and 1b respectively.

Analyte Recoveries

Analyte recovery (%R) across the entire analytical method was determined using a spike and recovery experiment. Three samples of fresh-fallen snow from the Upper Lookout site were melted, spiked with 150 ng of each of the target analytes The spiked samples were run through the full extraction and then spiked with isotopically labeled surrogates prior to quantitation. A fourth snow sample was spiked with surrogates prior to extraction, without being spiked with target analytes, in order to determine background concentrations of analytes in the fresh-fallen snow. A lab blank was also extracted for assessment of possible contamination. The analyte percent recovery was calculated as the percentage of the spiked amount quantified in the sample after extraction, after subtracting the background concentration of analyte in the non-spiked sample. The mean recovery for PAHs over the entire analytical method was 47% ± 7% (Table 2), while the mean recovery for pesticides and degradation products was 63% ± 11% (Table 2).

Table 1a - Quantitation ion (Q1) and qualifier ions (Q2 and Q3) for all analytes, surrogates and internal standards - Electron Ionization.

	m/z				m/z		
target compounds	**Q1**	**Q2**	**Q3**		**Q1**	**Q2**	**Q3**
EPTC	128	132	189	benzo(k)fluoranthene	252	250	253
etridiazole	211	213	183	benzo(e)pyrene	252	250	253
acenapthylene	152	151	76	benzo(a)pyrene	252	250	253
acenaphthene	154	153	152	indeno (123-C.D)pyrene	276	274	277
fluorene	166	165	163	dibenz[a,h]anthracene	278	276	279
propachlor	120	176	93	benzo[ghi]perylene	276	274	277
atrazine desiosopropyl	173	175	158				
atrazine desethyl	172	174	187				
carbofuran	164	149	131				
simazine	201	203	186	**surrogates and**			
atrazine	200	202	215	**internal standards**	**Q1**	**Q2**	**Q3**
phenanthrene	178	176	179	EPTC-d14	142	203	201
diazinon	304	199	137	acenaphthene-d10	164	162	161
anthracene	178	176	179	fluorene-d10	1S76	174	173
triallate	268	270	272	atrazine-d5	205	220	218
acetochlor	146	162	223	phenanthrene - d10	188	189	187
methyl parathion	263	125	109	diazinon-d10	314	138	136
alachlor	188	160	237	acetochlor-d11	173	245	175
malathion	173	158	127	alachlor - d13	200	251	253
metolachlor	162	238	240	methyl parathion-d6	269	115	117
cyanazine	225	240	227	malthion-d6	174	131	133
parathion	291	155	109	parathion - d10	115	117	113
fluoranthene	202	200	203	fluoranthene-d10	212	213	211
opDDE	318	320	316	pyrene-d10	212	213	211
pyrene	202	200	203	ppDDEd8	326	324	322
ppDDE	318	316	320	ppDDT-d8	243	245	241
opDDD	235	237	165	triphenylene-d12	240	241	238
retene	219	234	204	benzo(k)fluoranthene-d12	264	265	263
ppDDD	235	237	165	benzo(a)pyrene-d12	264	265	263
opDDT	235	237	165	benzo(ghi)perylene-d12	288	289	286
ethion	231	153	384				
ppDDT	235	237	165				
benzo(a)anthracene	228	226	229				
methoxychlor	227	228	274				
chrysene and triphenylene	228	226	229				
benzo(b)fluoranthene	252	250	253				

Table 1b -Quantitation ion (Q1) and qualifier ions (Q2 and Q3) for all analytes, surrogates and internal standards - Electron Capture Negative Ionization.

		m/z				m/z	
target compounds	**Q1**	**Q2**	**Q3**	**surrogates and internal standards**	**Q1**	**Q2**	**Q3**
trifluralin	335	336	305	PCB-138-13C	372	374	370
alpha-HCH	71	73	70	trifluralin-d14	349	350	319
HCB	284	286	282	HCB-13C	294	292	290
beta-HCH	71	73	70	Lindane-d6	72	74	263
gamma-HCH	71	73	70	chlorpyrifos-d10	322	324	214
delta-HCH	71	253	255	endosulfan I - d4	376	378	374
triallate	160	161	104	endosulfan II-d4	414	412	410
metribuzin	198	199	184				
heptachlor	268	266	300				
chlorpyrifos oxon	297	298	299				
chlorpyrifos	315	313	214				
DCPA [Dacthal]	332	333	334				
heptachlor epoxide	388	390	392				
trans-chlordane	410	408	412				
endosulfan I	404	372	370				
cis-chlordane	266	264	268				
trans-nonachlor	444	446	442				
dieldrin	346	348	380				
endrin	346	348	380				
endosulfan II	406	408	372				
cis-nonachlor	444	446	442				
endrin aldehyde	380	382	346				
endosulfan sulfate	386	388	422				

Figures 2 and 3 compare this method's extraction efficiency for PAHs and OCPs to the method reported by Usenko et al.[9], which was used for the Western Airborne Contaminants Assessment Program.[10, 13] The WACAP method used 50 kg snow samples with extraction by modified BakerBond Speedisks, and sample cleanup by silica gel chromatography and size exclusion chromatography. No statistically significant differences at the 95% confidence level were found between this method and the WACAP method for OCPs. PAH recovery in this method was decreased by an average of 24% compared to the WACAP method. However, this apparent decrease may be due to the inclusion of the post-extraction concentration step in recovery calculations for this study, while Usenko et al.[9] reported loss from the extraction step only. An additional recovery experiment for the post-extraction sample concentration was conducted for this study. PAH recovery for the sample concentration step was found to be 74% ± 5% to 84% ± 3%, which suggests that loss from just the extraction step in this method is similar to, or less than that reported by Usenko et al.[9]

Figure 4 compares the total recovery efficiency for OCPs from this method to Mast et al.[16] , who used the 1g OASIS HLB SPE cartridge for analysis of organo-chlorine pesticides in 250 ml to 980 ml melted snow samples. DCM and diethyl ether were used by Mast et al. as elution solvents and a post-extraction sample clean-up step with Florisil was also used. Recovery uncertainty for Mast et al.[16] was not available, however comparison suggests somewhat lower recovery of chlordane, nonachlor and endosulfan in our method. This may be due to the difference in elution solvents.

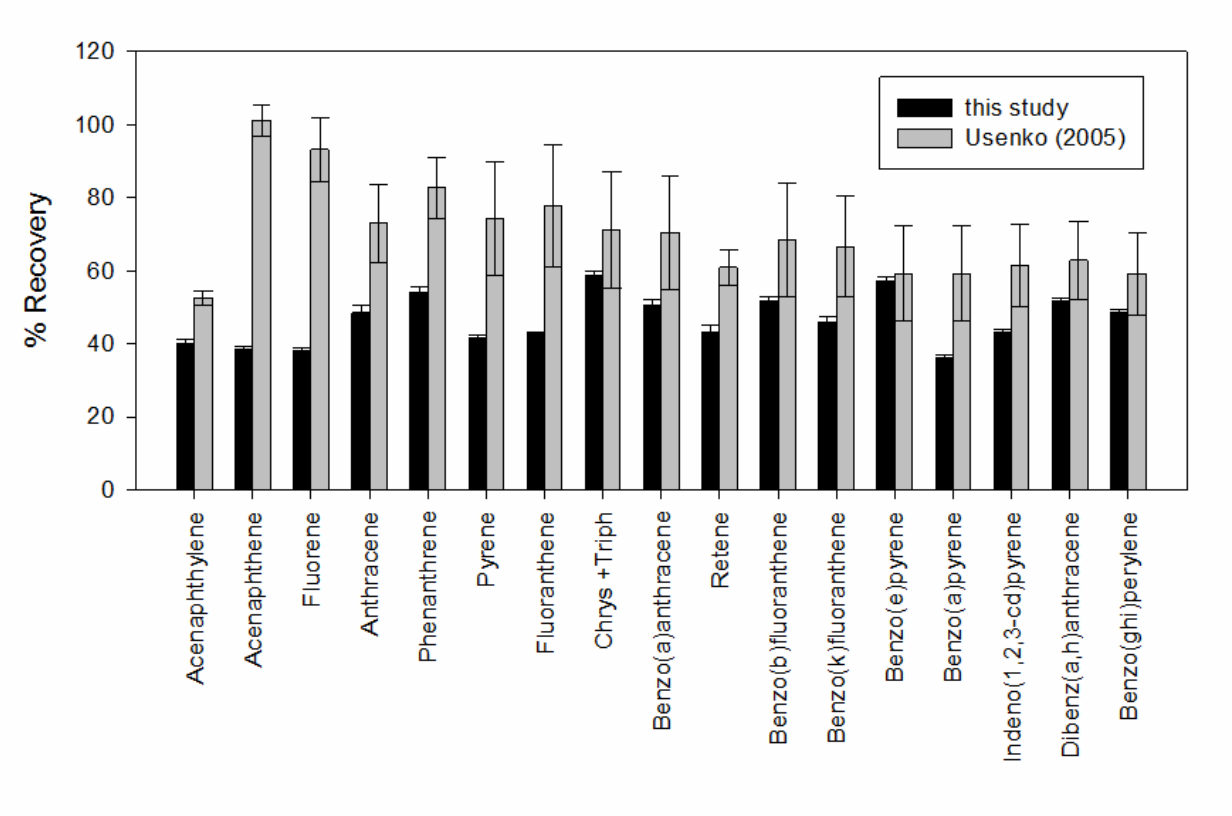

Figure 2 - Mean Extraction Efficiency Comparison for PAHs

(n=3, error bars indicate 2 standard deviations)

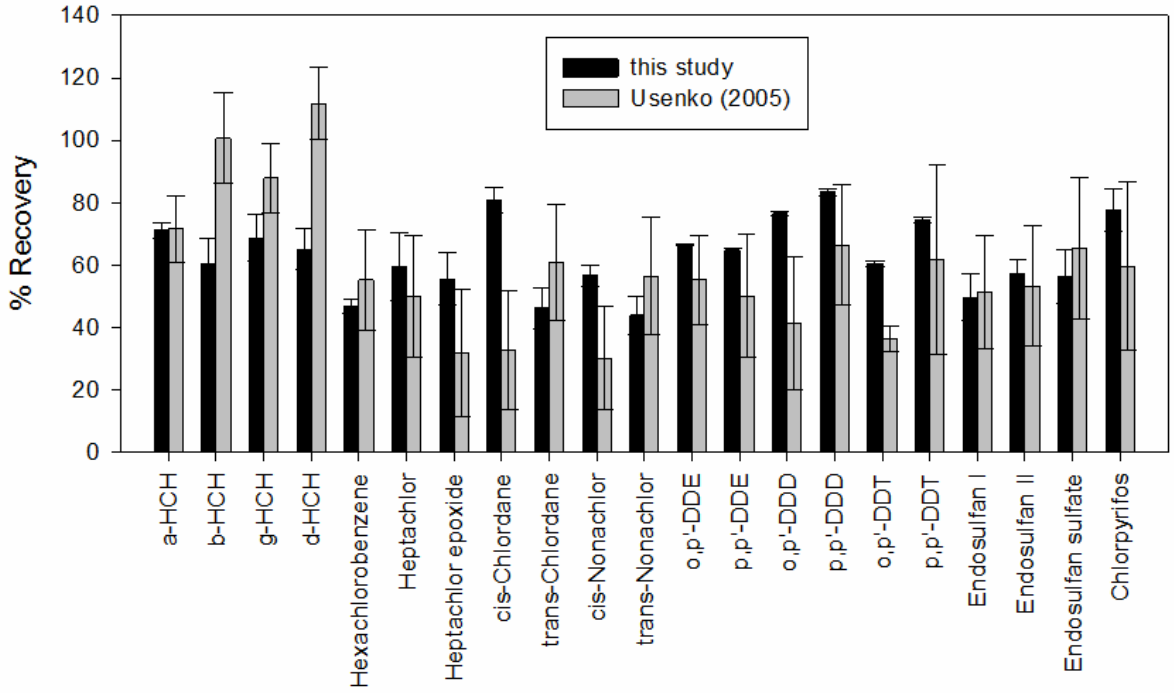

Figure 3 - Mean Extraction Efficiency Comparison for OCPs.

(n=3, error bars indicate 2 standard deviations)

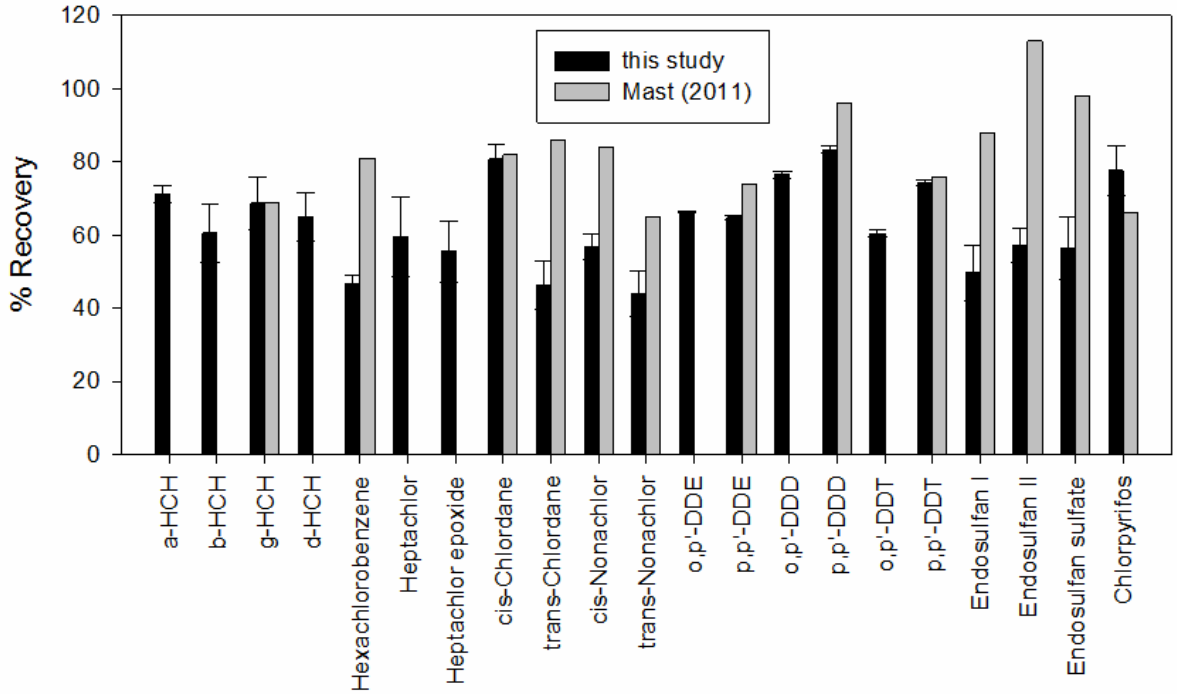

Figure 4 - Mean Extraction Efficiency Comparison for OCPs.

(n=3, error bars indicate 2 standard deviations)

Table 2a - Comparison of Method Percent Recovery (%Recovery), Estimated Detection Limit (EDL) in pg/L and Percent Relative Standard Deviation (%RSD, n=3) for pesticides.

	OASIS HLB			Usenko (2005)		
	%R	**%RSD**	**EDL (pg/L)**	**%R**	**%RSD**	**EDL (pg/L)**
a-HCH	71.2	1.8	27	71.7	7.4	18.8
b-HCH	60.6	6.7	36	100.7	7.2	32.1
g-HCH	68.7	5.4	38	87.9	6.3	12.3
d-HCH	65.0	5.1	49	111.8	5.2	20.7
Hexachlorobenzene	46.8	2.3	5	55.3	14.6	0.2
Heptachlor	59.5	9.1	11	49.9	19.6	121.7
Heptachlor epoxide	55.6	7.5	257	31.8	32.0	14.7
cis-Chlordane	80.7	2.6	51	32.7	29.1	16.3
trans-Chlordane	46.2	7.2	45	60.9	15.3	0.4
cis-Nonachlor	56.7	3.1	11	30.2	27.3	0.6
trans-Nonachlor	44.0	7.0	41	56.4	16.7	0.9
o,p'-DDE	66.5	0.2	63	55.3	12.9	24.7
p,p'-DDE	64.8	0.4	47	50.1	19.6	10.3
o,p'-DDD	76.6	0.6	127	41.5	25.7	24.7
p,p'-DDD	83.4	0.7	589	66.5	14.6	44.0
o,p'-DDT	60.5	0.7	750	36.4	5.6	23.4
p,p'-DDT	74.3	0.6	214	61.9	24.6	26.2
Endosulfan I	49.7	7.6	74	51.3	17.7	4.9
Endosulfan II	57.3	4.1	64	53.3	18.1	2.0
Endosulfan sulfate	56.4	7.7	8	65.4	17.3	1.0
Chlorpyrifos	77.7	4.4	6	59.7	22.5	6.9
mean	**63.0**	**4.0**	**119.7**	**58.6**	**17.1**	**19.4**

Table 2 - Comparison of Method Percent Recovery (%Recovery), Estimated Detection Limit (EDL) in pg/L and Percent Relative Standard Deviation (%RSD, n=3) for PAHs.

	OASIS HLB			Usenko (2005)		
	% Recovery	%RSD	EDL (pg/L)	% Recovery	%RSD	EDL (pg/L)
Acenaphthylene	40.0	1.4	171	52.7	1.8	19.8
Acenaphthene	38.6	1.2	86	101.3	2.1	11.3
Fluorene	38.3	0.9	85	93.2	4.7	8.3
Anthracene	48.6	2.0	82	73.0	7.3	19.9
Phenanthrene	54.2	1.5	53	82.7	5.1	8.8
Pyrene	41.7	0.8	131	74.4	10.5	4.9
Fluoranthene	42.7	0.8	79	77.9	10.7	4.0
Chrys +Triph	58.9	1.0	132	71.2	11.2	13.3
Benzo(a)anthracene	50.8	1.3	70	70.5	11.1	14.6
Retene	43.4	1.9	105	61.0	4.0	33.4
Benzo(b)fluoranthene	51.9	1.1	132	68.4	11.4	6.9
Benzo(k)fluoranthene	46.2	1.3	222	66.7	10.3	5.0
Benzo(e)pyrene	57.3	1.1	112	59.3	10.9	8.9
Benzo(a)pyrene	36.2	1.0	112	59.3	10.9	7.9
Indeno(1,2,3-cd)pyrene	43.4	0.7	112	61.5	9.1	31.5
Dibenz(a,h)anthracene	51.6	0.8	125	62.9	8.5	28.9
Benzo(ghi)perylene	48.8	0.8	92	59.2	9.4	16.5
mean	**46.6**	**1.2**	**111.8**	**70.3**	**8.2**	**14.3**

Analyte Estimated Detection Limits and Reproducibility

Sample specific estimated detection limits (EDLs) were calculated using the method described in EPA Method 8280a [24] and are reported as the amount of target analyte per liter of Snow Water Equivalents (SWE). Tables 2a and 2b show the EDL and %RSD values for all target analytes for the entire method. The EDLs for PAHs were 53 ± 1 pg/L_{SWE} to 222 ± 3 pg/L_{SWE}, while the EDL for pesticides were 5 ± 0.1 pg/L_{SWE} to 750 ± 5 $pg/L_{SWE.}$ EDLs reported for the WACAP method[9] were from 4 ± 0.1 pg/L_{SWE} to 33 ± 1 pg/L_{SWE} for PAHs and from 0.4 ± 0.1 pg/L_{SWE} to 122 ± 24 pg/L_{SWE} for pesticides.

Method reproducibility was assessed by examination of the percent relative standard deviation (%RSD) for each analyte, with %RSD defined as 100 times the standard deviation for three replicates, divided by the mean measured concentration (Tables 2a and 2b). The mean %RSDs for PAHs and pesticides in this study were 1.2% and 4.0% respectively, compared to %RSDs of 17.1% for PAHs and 8.2% for pesticides reported by Usenko et al.[9] This 4% to 16% improvement in reproducibility may result from eliminating the process of manually recombining the sorbent from two SPE cartridges, which our testing suggested was vulnerable to the formation of channels around the edges of the transferred sorbent layer. However, it should noted that the RSDs reported here for this study represent the within-day variability and do not include the between-day variability of the method.

Analysis of Field Samples

This analytical method was used to analyze six fresh-fallen snow samples from a snow event on April 15, 2013. Triplicate samples from the Upper Lookout and Vanilla sites at HJ Andrews Experimental Forest were analyzed. Fluoranthene, pyrene, retene, fluorene, dibenz[a,h]anthracene and benzo(b)anthracene as well as alachlor, propachlor, α-HCH, dacthal,

chlorpyrifos, heptachlor epoxide and endosulfan sulfate were each detected at concentrations greater than their EDL in two or more samples. Low concentrations of fluoranthene, pyrene and retene were measured in lab, field and travel blanks and reported sample concentrations were adjusted by a blank concentration subtraction. Phenanthrene was analyzed for, but not reported here, because significant concentrations of phenanthrene were measured in both lab and field blanks.

The samples from the April 15th snow event were used to perform an initial site-to-site comparison to assess the method's ability to resolve within-site and between-site variation in concentrations. Figure 5 shows the ten day air-mass back-trajectories for April 15, 2013, originating from the HJ Andrews Experimental Forest. Given the largely marine origin of these back-trajectories, it was expected that this sample set would have low overall pollutant concentrations and could serve to assess the impact of local sources on pollutant deposition at the sampling sites.

Figure 6 shows the POP concentrations measured in samples from the Upper Lookout and Vanilla sites for the April 15, 2013 snow event. Four organo-chlorine compounds were detected in all samples at both sites; the pesticides α-hexachlorocyclohexane (α-HCH), dacthal and chlorpyrifos, and the degradation product endosulfan sulfate, which derives from the pesticide endosulfan. Four PAHs; fluorene, fluoranthene, pyrene and retene, were measured at quantifiable concentrations in all samples, at both sites. Table 3 compares the measured concentrations to those reported in prior studies[12-13, 25] of snowpack, at similar sites. Concentrations of all analytes in snow deposited by the April 15th, 2013 snow event were lower than prior studies of accumulated seasonal snowpack. This difference may result from the marine origin of the air mass associated with the April 15th, 2013 snow event.

Figure 5 - Ten day air mass back-trajectories for the snow event on April 15, 2013 generated by the HYSPLIT model provided by the National Oceanic and Atmospheric Administration.

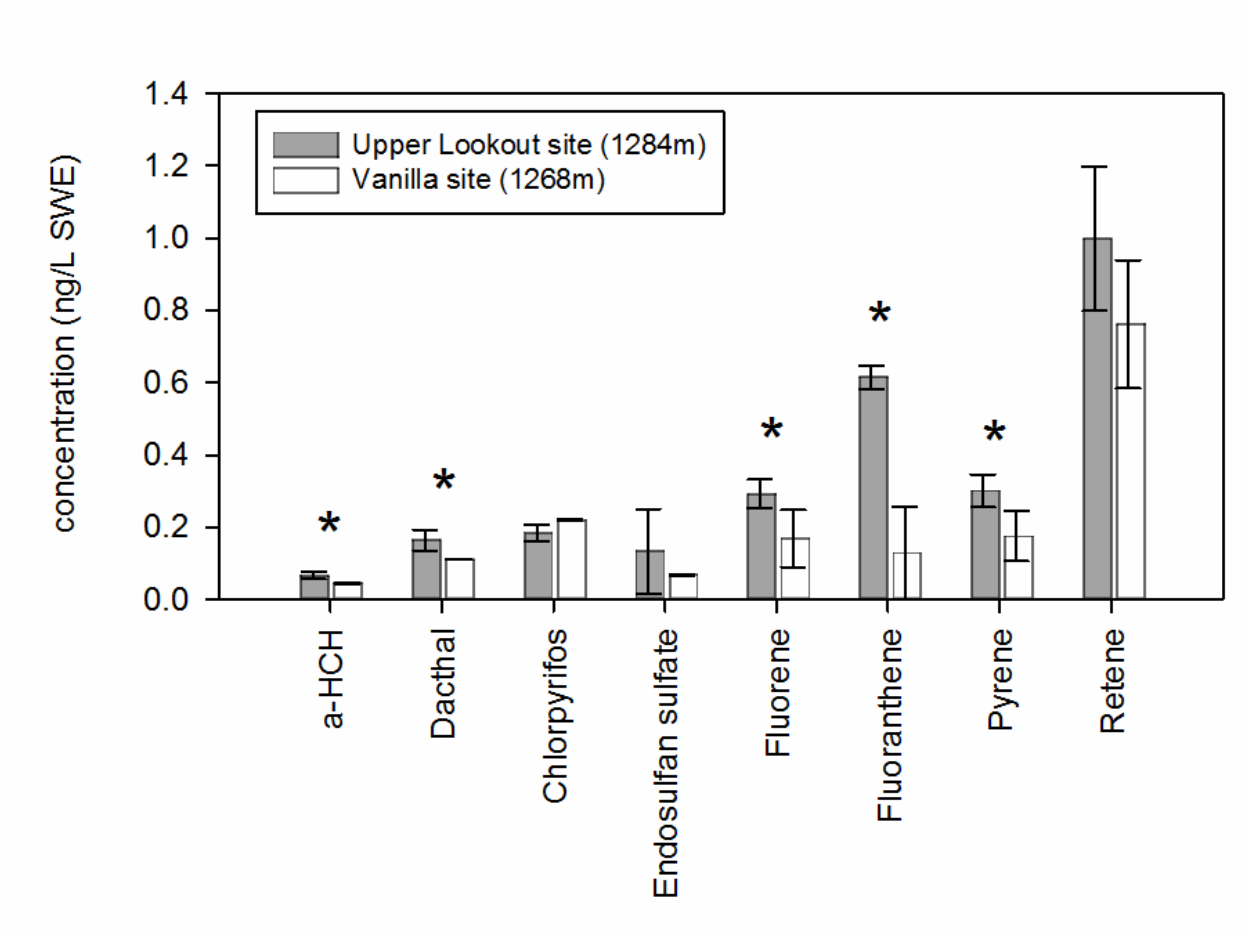

Figure 6 - PAH and OCP concentration in fresh-fallen snow at HJ Andrews Experimental Forest, April 15th, 2013. (n=3, error bars indicate 2 standard deviations; asterisks indicate a statistically significant difference in site means at the 95% confidence level)

Table 3 - Comparison of POP concentrations in fresh snow and snowpack.

(nd = not detected, nr = not reported)

	High-altitude European mtns. Carerra et al [2000]	**Bow Lake Alberta, Canada Lafreniere et al [2006]**	**Snowpack US National Parks Hageman et al [2010]**	**Fresh Snow HJ Andrews E.F. this study**
Σ PAH	16 - 81	nr	nr	1.3 - 2.2
Σ endosulfan	nr	0.035 - 0.30	1.5	nd
Σ chlordane	nr	nr	0.05	nd
HCB	nr	4.6 - 28	0.007	nd
dieldrin	nr	0.12 - 0.72	4.8	nd
Σ HCH	0.49 - 1.1	0.05 - 0.43	1.0 - 4.2	0.045 - 0.066
chlorpyrifos	nr	nr	2.8	0.19 - 0.22

Table 4 - Site and Sample Parameters for April 15th, 2013.

	Upper Lookout		**Vanilla Leaf**	
site altitude	1298	m	1268	m
collection period high air temperature	-1.80	˚C	-1.30	˚C
collection period low air temperature	-3.00	˚C	-2.90	˚C
max collection period solar irradiance	30	W/m^2	28	W/m^2
snow density at time of collection	76	kg/m^3	176	kg/m^3
snow temperature at time of collection	-1.00	˚C	-0.25	˚C
site average particulate mass ratio	7.6	mg / kg	3.9	mg / kg

A two-tailed t-test comparing the Upper Lookout and Vanilla sites showed statistically significant between-site differences in mean concentration at the 95% confidence level for α-HCH, dacthal, fluorene, fluoranthene and pyrene. All compounds detected with statistically significant inter-site differences were present in higher concentration in samples from the Upper Lookout site. Meteorological data collected at the Upper Lookout and Vanilla sites (Table 4) showed similar temperature and solar irradiance profiles at both sites over the accumulation period, with a higher mean particulate mass ratio (Table 4) at the Upper Lookout site. This higher mean particulate mass ratio may account for the higher POP concentrations measured in the Upper Lookout samples. A full interpretation of the influence of meteorological parameters, as well as source-region influences, will require additional samples.

Conclusions

An analytical method was developed which reduces the sample size needed for the analysis of PAH and OCP concentrations in snow samples from 50 kg to 5 kg, with percent recovery and estimated detection limits sufficient for examination of within-site and between-site variation in concentration. This method had a mean EDL of 120 pg/L SWE (±4% RSD) for OCPs and 112 pg/L SWE (±1.2% RSD) for PAHs. Triplicate samples were collected from two remote sites of similar altitude and aspect in the Oregon Cascade Range for a snow event on April 15, 2013, with similar temperature and solar irradiance profiles at both sites over the accumulation period. Analysis of these near-concurrently collected fresh-fallen snow samples showed statistically significant between-site concentration differences in 2 of 4 pesticides and 3 of 4 PAHs detected. Where statistically significant differences were shown, higher analyte concentrations were associated with the site with the higher mean particulate mass ratio. Additional sampling and analysis is ongoing to more fully characterize the influence of meteorological parameters and

source-region influences, and to assess the within-site, between-site, within-event and between-event variability associated with the deposition of PAHs and OCPs by single snow events.

Acknowledgements

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Local Scale Spatial and Temporal Variability in Wet Deposition of Persistent Organic Pollutants by Snow

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Abstract

The objective of this research was to assess the variability of POP deposition by snow on a 10 km spatial scale by measuring the POP concentrations in fresh-fallen snow from remote alpine sites. Samples of pre-metamorphic snow were concurrently collected from three remote alpine sites, of matched altitude and exposure, along a 10 km transect of the HJ Andrews Research Forest in the Cascade Mountains of Oregon. Eighty seven samples of pre-metamorphic snow were collected from three sites, over ten separate storm events, between January 2013 and February 2014. Samples were extracted using solid phase extraction (SPE) and analyzed by gas chromatography-mass spectroscopy (GC-MS) for 57 persistent organic pollutants, including PAHs and a variety of current and historic-use pesticides and pesticide degradation products. Sixteen of the seventeen PAHs analyzed for were detected in over 35% of the samples collected. Total PAH concentrations in individual samples ranged from below quantifiable limits to 53.5 ng per liter of snow water equivalents (SWE). The most frequently detected PAH was fluoranthene, which was detected in 69% of all samples, with a maximum measured concentration of 22.2 ng/L_{SWE}. The pesticide degradation products, endosulfan sulfate and heptachlor epoxide, were detected at quantifiable concentrations in all samples, and were the most frequent chlorinated compounds detected, with concentration ranges of 0.070 – 1.430 ng/L_{SWE} and 0.983 – 5.83 $ng/L_{SWE,}$ respectively. Dieldrin and chlorpyrifos were detected at maximum measured concentrations of 3.14 ng/L_{SWE} and 3.11 $ng/L_{SWE,}$ respectively. However, detection of each was limited to a single snow event. Of the hexachlorocyclohexanes, α-HCH was detected in 7 of 87 samples, but β-HCH and ϒ-HCH (Lindane) were not detected at quantifiable concentrations in any sample. Detections of chlorodiphenylmethane pesticides and degradation products (isomers of DDT, DDD and DDE) were largely limited to two individual snow events. Comparison of

within-site and between-site coefficients of variance and one-way ANOVA for differences in site means revealed no evidence of between-site differences in POP concentration in fresh-fallen, pre-metamorphic snow ($p<0.05$). Analysis of between-event variance found significant between-event differences ($p<0.05$) in total PAH, total gas-phase PAH, total particulate-phase PAH and total pesticide concentration for all events. Source region impact factors (SRIFs) were calculated from HYSPLIT-derived 10-day air parcel back trajectories and correlated to total gas-phase PAH, total particulate-phase PA, phenanthrene, fluoranthene, retene, and pyrene concentrations. No correlations for total gas-phase PAH or total particulate-phase PAH concentration with any SRIFs were found to be statistically significant ($p<0.05$). Retene and pyrene concentrations were positively correlated with air mass time in Oregon. A similar analysis resulted in a statistically significant correlation ($p<0.05$) between pesticide concentrations and air mass time in Washington and Oregon. No statistically significant correlation was found between total pesticide concentration and the Willamette Valley or Eastern Washington/Oregon source regions. Measured POP concentrations were also examined for correlations with sample particulate mass, reciprocal maximum air temperature and maximum solar irradiance over the accumulation period, reciprocal snowpack temperature and snow density. Statistically significant correlations ($p<0.05$) were found between solar irradiance and total gas-phase PAH, total particulate-phase PAH, fluorine, pyrene and endosulfan sulfate concentrations, and between reciprocal snow temperature and phenanthrene concentration. No statistically significant ($p<0.05$) correlations were found with reciprocal maximum air temperature.

1.0 Introduction

Persistent organic pollutants (POPs) are compounds of concern for environmental or toxicological reasons that, due to their physical-chemical properties, are resistant to abiotic and biotic degradation.[1-2] The temperature dependence of volatilization and the effectiveness of precipitation scavenging and washout of gaseous and particulate-bound pollutants by snow create an effective and well documented pathway for the transport of POPs from regions of anthropogenic activity to remote and/or high-elevation ecosystems, including sites which might otherwise be expected to be pristine.[3-17] POPs deposited by snow are incorporated into seasonal snowpack, and seasonal snowpack samples have been used to provide a time-integrated record of POPs deposited over the entire snow accumulation period.[12, 18-22] Such studies typically show a high degree of spatial variability in POP concentrations in seasonal snowpack, even for samples collected at sites of less than 10 km spacing, with similar altitude and aspect.[21-22] The high degree of observed variability in POP concentration could result from variability in the initial deposition by snow, or from differences in post-depositional fate. Within hours to days of deposition, snowpack metamorphic processes may cause highly localized repartitioning, including revolatilization, sorption to particulate matter and/or spatial redistribution.[23-24] Consequently, studies of seasonal snowpack provide little information on the spatial or temporal variability of POPs in snow upon initial deposition. The goal of this research was to measure POP concentrations in fresh-fallen, pre-metamorphic snow, and assess the within-site, between-site, within-event and between-event variability in wet deposition of POPs by snow on the 10 km scale, as well as to identify potential source regions.

2. Materials and Methods

2.1 Site Descriptions

Sampling sites for this study were located in the HJ Andrews Experimental Forest (HJA), a research facility located in Willamette National Forest in the Oregon Cascade Range and jointly operated by the US Forest Service, the National Science Foundation, and Oregon State University. HJA covers the entire drainage basin of Lookout Creek, with an elevation range of 410 m to 1630 m and is one of the major sites for the National Science Foundation's Long-Term Ecological Research Project. [25]

Each of the three sampling sites was adjacent to an established back-country meteorological data collection site which provided supporting meteorological data. All sites are in regions of the forest closed to the public during the snow season. Site access was by snow-cat, with the final 100 m by snowshoe. All three sampling locations were open clearings, with aspect and exposure similar to the adjacent meteorological site. Sampling locations were chosen to minimize site-to-site differences in altitude and exposure as much as possible. A total of ten separate snow events over the snow seasons of 2012-2013 and 2013-2014 were sampled, yielding 87 individual 5 kg samples. Figure 4.1 shows a map of the HJ Andrews Forest, indicating the location of the Upper Lookout (UpLo), Center (Ctr) and Vanilla (Van) sites. Table 5.1 gives site coordinates and altitudes.

2.2 Sampling Procedure

For each snow event analyzed, samples were collected at all three sites within 12 hours of deposition, with air temperatures below 3˚C at all collection sites for the entire period between deposition and collection. Maximum solar irradiance at the collection sites for the entire period between deposition and collection was typically below 150 W/m^2, and was below 200 W/m^2 for all but one snow event collected. Mixed precipitation events with both snow and rain were not

collected. Site meteorological parameters and sample physical parameters for each snow event sampled are given in Table 4.2.

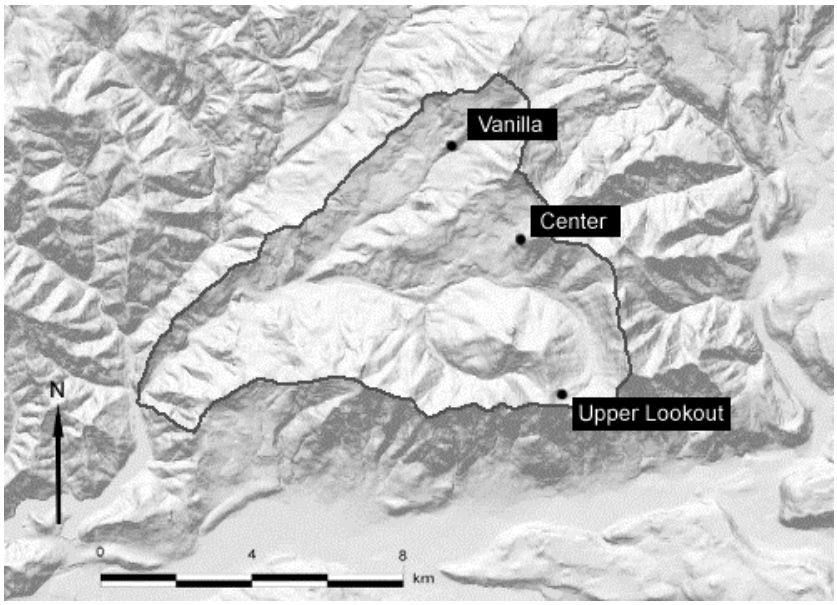


Figure 5.1 – Sampling Site locations within the HJ Andrews Experimental Forest

Table 4.1 –Sampling Site Locations and Altitudes. Max temperature and max solar irradiance are the maximum values measured over the ten-hour period preceding sample collection.

	latitude	longitude	elevation (m)	% slope	aspect (deg)	max temp (˚C)	max solar irradiance (W/m2)
Upper Lookout Meteorological Station (UpLo)	-122.120	44.207	1284	14.1	72	-2.42	103.2
Central Meteorological Station (Ctr)	-122.141	44.243	1028	21.57	224	-0.40	123.3
Vanilla Leaf Meteorological Station (Van)	-122.149	44.272	1268	9.6	183	-0.52	73.7

Intra-site replicates were collected within a total of 30 minutes from locations spaced 5-10 m apart. Samples from all three sites, for a given snow event, were retrieved within a 5 hour period. Sample collection was limited to fresh-fallen snow by sampling above the prior snow crust layer

and sampling no deeper than the depth of recent deposition, as recorded by ultrasonic snow depth gauges at the adjacent meteorological station. Samples were collected using a stainless steel shovel and stored in Teflon bags (Welch Fluorocarbon, Dover, NH). The stainless-steel shovel was rinsed with reagent-grade methanol and high-purity water between each sample. The collection bags were sealed with zip-ties and stored in opaque 5 gallon food-grade pails with air-tight gasket lids. Samples were transported, still frozen, to the laboratory and stored in a -20°C freezer within 5 hours of collection. Air temperature at the sampling sites was measured using Campbell Scientific (Logan, UT) Model HMP35C probes with Fenwal Electronics (Palatine, IL) UUT51J1 thermistors. Solar radiation was measured using Kipp and Zonnen (Bohemia, NY) model CM-6B pyranometers with thermopile-type sensors. Snowpack temperature and density of the fresh-fallen snow were measured at the sampling point using a field sampling kit from Snowmetrics (Boulder, CO).

2.3 Analytical Method

Samples were melted at room temperature over 24 hours while still sealed in buckets. Melted samples were spiked with isotopically labeled recovery surrogates prior to solid phase extraction using Waters Oasis HLB SPE cartridges (Milford, MA, part number 186000117) with elution by dichloromethane and ethyl acetate. No sample clean-up was performed other than filtration of the extract through Whatman 0.45 μm PTFE syringe filters. Extracted samples were concentrated in a Turbovap II sample concentrator (Zymark, Hopkinton, MA) and analyzed for POP concentrations using an Agilent 6890 GC-MS with Programmed Temperature Vaporization and electron impact (EI) or chemical ionization (CI) in selected ion monitoring mode. The analytes of interest for this study included 18 PAHs and 57 current or historic use pesticides and pesticide derivatives. A full list of the analytes, isotopically labeled recovery surrogates and internal

standards is given in table S1 in the supplementary information. Full details of the analytical method used, including percent recovery values, relative standard deviations and method limits of detection are given in Walsh et. al (*in press*).

2.4 Source Region Impact Factor Analysis

Air parcel back trajectories were generated for each storm event using the HYSPLIT model provided by the National Atmospheric and Oceanic Administration.[26] Ten day back trajectories were calculated for the air mass over the HJ Andrews Experimental Forest at starting elevations of 1500 m, 2000 m and 2500 m above sea level. Maps of the trajectory ensembles generated are shown along with concentration profiles, source region impact factors and site data are presented in Figures 4.2 – 4.11.

A custom program, TRAJpy, was written in the open source Python language, to process HYSPLIT model output files and classify each of the generated endpoints in the trajectory ensemble into geographic regions, including Asia, Siberia, Alaska, British Columbia, and the states of Washington and Oregon (Figure S.1). Local region boxes were also designated, including urban Oregon and urban Washington regions and agricultural regions in Western Washington and Oregon, the Willamette Valley in Oregon and the Central Valley of California (Figure S.2). Region boundaries were chose to coincide with regions used for prior published studies of PAHs and pesticides in air samples at high altitude sites, including a site within 50 km of the sites used for this study.[27-28] Boundary coordinates for each source region box (Table S.15) are given in the supplementary information. Source code of the TRAJpy program is provided in Appendix C.

For each snow event, a source region impact factor (SRIF) was generated for each of the local and regional source region boxes. The SRIF for a given region is the percentage of trajectory

endpoints in the generated ensemble located in the designated region. For this study, 10-day back-trajectories with three starting altitudes were used, giving an ensemble, with 720 individual hourly trajectory endpoints. SRIFs are calculated using equation 4.1:

$$SRIF\ (\%) = [[\sum_{n=1}^{240}(n(T_{sr=1}; otherwise = 0))]hours/720\ hours\ ] \times 100 \qquad (4.1)$$

2.5 Data Quality Assurance Procedures

Lab, field and travel blanks were collected in order to assess potential sample contamination. Lab blanks consisted of 5 L of high-purity water which was processed in the same manner as melted snow samples. Travel blanks, consisting of 5 L high-purity water samples, stored in the same containers used for sample collection, travelled to and from the sampling sites once per season and were processed in the same manner as melted snow samples. Field blanks were obtained by rinsing the stainless steel shovel used for sample collection with ethyl acetate following the standard post-collection cleaning procedure. The ethyl acetate rinsate was collected, concentrated, and analyzed using the same GC-MS method as extracted samples. No target compounds were detected at quantifiable concentrations in field blanks. The PAHs acenaphthene, fluorene, phenanthrene and anthracene, and the pesticides alachlor and p-p'-DDT were detected at quantifiable concentrations in both lab and travel blanks. Reported concentrations for these compounds were blank corrected by the mean of the lab blank concentrations for that season (n=3). Any detection with a blank value of more than 33% of the sample value was excluded from the data set.

For multi-site and multi-event analysis of variance (ANOVA), detections below the limit of quantitation were substituted with one half of the sample specific detection limit for that

compound. Only one substituted value per compound per site per event was permitted before rejection of that set from ANOVA. No substituted values are used in the calculation of means or coefficients of variation.

3. Results and Discussion

3.1 POP Concentrations in Fresh-Fallen Snow

Sixteen of the seventeen PAHs analyzed for were detected in over 35% of the samples collected. Total PAH concentrations in individual samples ranged from below quantifiable limits to 53.5 ng per liter of snow water equivalents (SWE). The most frequently detected PAH was fluoranthene, which was detected in 69% of all samples with a maximum measured concentration of 22.2 ng/L_{SWE}. Pyrene and retene were each detected in 57% of all samples, with maximum measured concentrations of 3.80 ng/L_{SWE} and 15.9 ng/L_{SWE} respectively. Phenanthrene was detected in 44% of all samples, with measured concentrations ranging from 2.08 – 25.2 ng/L_{SWE}. Anthracene, a photo-reactive gas-phase PAH with a short atmospheric half life of one day, was not detected at quantifiable concentrations in any samples, indicating no contamination from local sources. The absence of anthracene also indicates that the collected samples are not contaminated by the exhaust of the snow-cat used for site access. Gaseous-phase PAHs, defined as those with two or three fused rings, were more frequently detected than particulate-phase PAHs (four or more rings).

Of the 57 pesticides and pesticide degradation products analyzed for, only 14 were detected at quantifiable concentrations in any samples, including trifluralin, triallate, metribuzin, heptachlor, chlorpyrifos, cis-chlordane, endosulfan sulfate, dieldrin, heptachlor epoxide, α-HCH, op-DDD, pp-DDD, op-DDT and pp-DDT. The pesticide degradation products endosulfan sulfate and heptachlor epoxide, were detected at quantifiable concentrations in all samples, and were the

most abundant chlorinated compounds detected, with concentration ranges of 0.070 – 1.430 ng/L_{SWE} and 0.983 – 5.83 ng/$L_{SWE,}$ respectively. Dieldrin and chlorpyrifos were detected with maximum measured concentrations of 3.14 ng/L_{SWE} and 3.11 ng/$L_{SWE,}$ respectively. However, detection of each was limited to a single snow event. Of the hexachlorocyclohexanes, α-HCH was detected in 7 of 87 samples, but β-HCH and ϒ-HCH (Lindane) were not detected at quantifiable concentrations in any sample. Hexachlorochclobenzene (HCB) was also not detected at concentrations above the limit of quantitation in any samples. Detections of chlorodiphenylmethane pesticides and degradation products (isomers of DDT, DDD and DDE) were largely limited to the snow events on December 7, 2013 and February 7, 2014 and may be related to historic use of DDT within the experimental forest. No detections of op-DDE or pp-DDE were made, but matrix interferants in the relevant region of the chromatogram are likely to have obscured any signal present for these compounds. Figures 4.2-4.11 show concentration profiles, air parcel back-trajectory maps and source region data for each of the snow events sampled. Individual concentrations for all compounds detected, including total gas-phase PAH, total particulate-phase PAH, total DDT and total pesticides are given in tables S2 – S12 in the supplemental information.

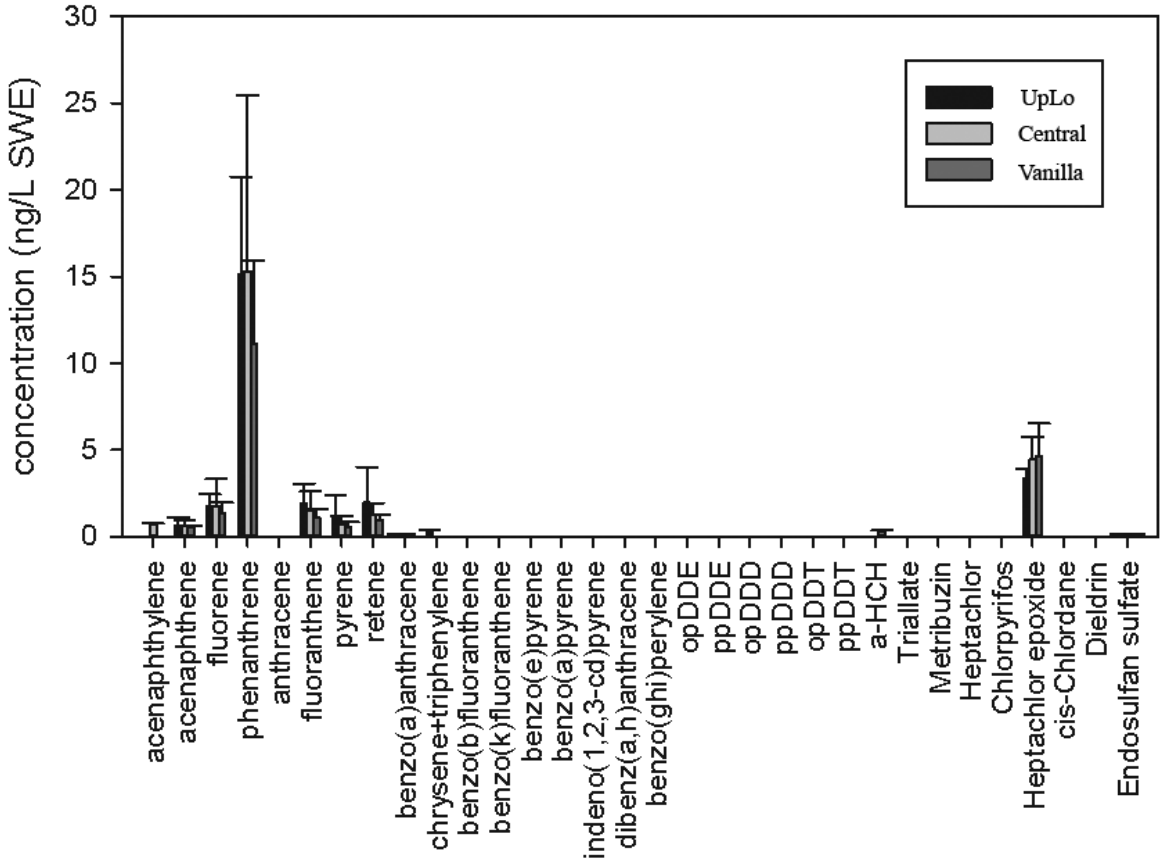
3.2 Local Scale Spatial Variability of Wet Deposition of POPs by snow

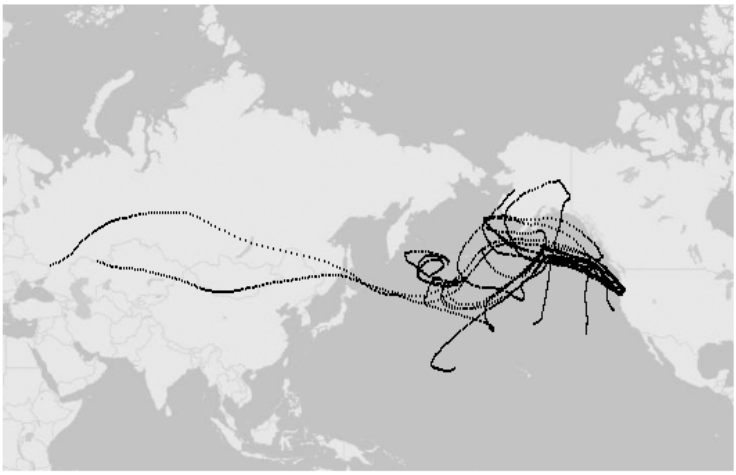
3.2.1 CV comparisons

Several prior studies have established the high degree of spatial variability of POP concentrations in samples of seasonal snowpack. Persistent organic pollutants, including PAHs, OCPs and PCBs, were detected in total snowpack cores from European alpine sites by Carrera et al. (2001). PAH profiles varied from site to site, with the samples with the highest particulate mass load having the highest proportion of high molecular weight PAHs. However, this

relationship did not hold for all sites, as the site with the highest particle concentration was not enriched in high molecular weight PAHs. Inter-annual variation in total PAH concentration at the same site was low, with a coefficient of variation (CV) (standard deviation divided by the mean) of 18%.[5]

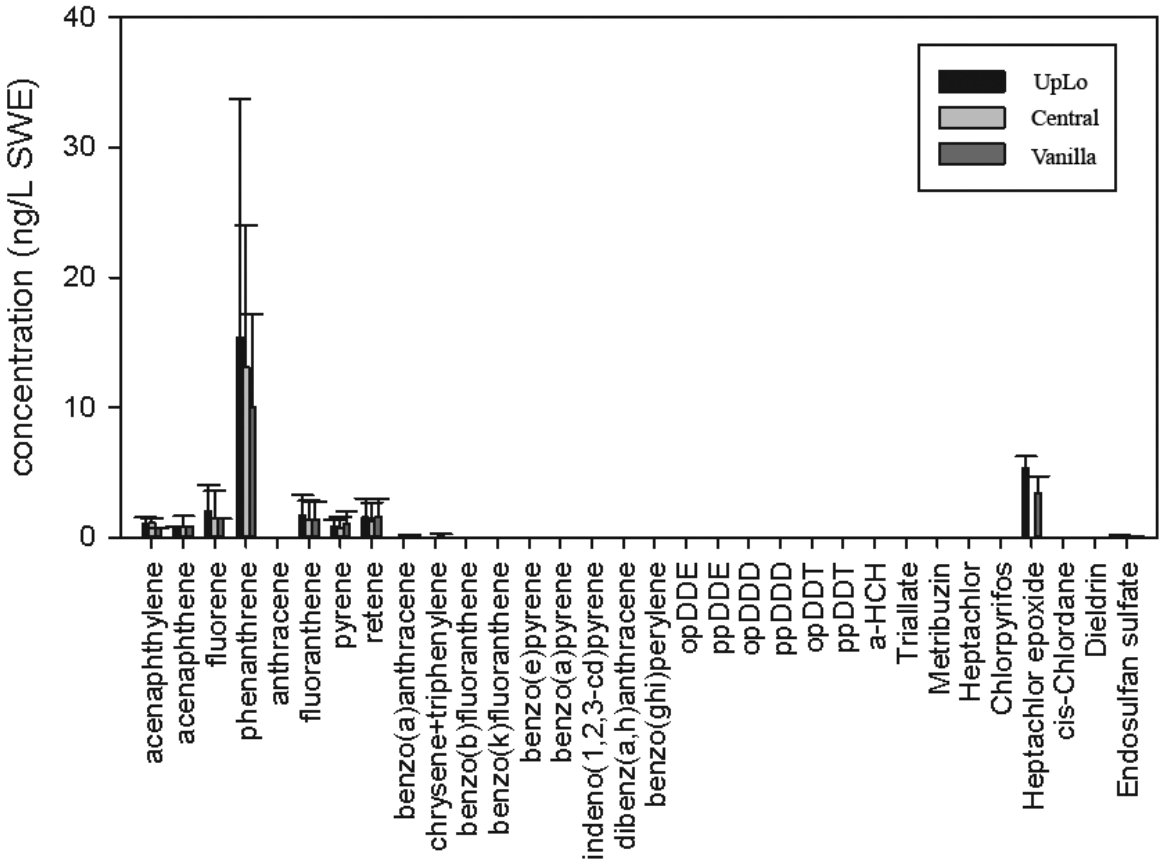
PAHs and OCPs concentrations in aged snow and ice samples from polluted sites in the Baltic Sea region were reported by Melnikov et al. (2003) for sampling regions broken into 100 km x 100 km grid boxes for spatial analysis. In contrast to other published studies of POPs in snow, no statistically significant differences in total PAH concentrations were found when comparing all regions and all years together. Total HCH concentrations ranged from 1.7 to 1.4 ng/L, with a CV of 26% for the four regions sampled. Total DDT is reported at 0.6 – 0.9 ng/L, with no statistically significant regional differences.[19] OCP and PCB concentrations in snow and snowmelt runoff across a single lake catchment in Alberta, Canada were reported by Lafreniere et al. (2006). Nineteen samples were collected over two years. Significant inter-site variations in pesticide concentration were noted, with the coefficient of variation (CV) for all samples ranging from 25% to 94%. POP concentrations in samples of seasonal snowpack were collected as part of the Western Airborne Contaminants Assessment Program (WACAP).[29] Samples from eight national parks in the western United States were analyzed for a wide range of POPs. Large volume annual accumulation snow samples were collected in open areas on north facing slopes.[21] The pesticides, dacthal, chrolpyrifos, endosulfan, HCH, trifluralin and triallate, as well as the pesticide degradation products, endosulfan sulfate and chlorpyrifos oxon were detected. Site replicates showed a mean coefficient of variation (CV) of 15%. However, intra-park replicates (concurrently collected samples from sites within the same national park) had a CV of 41%, which was almost as high as the 59% CV seen for inter-annual replicates from the same sites.[22]

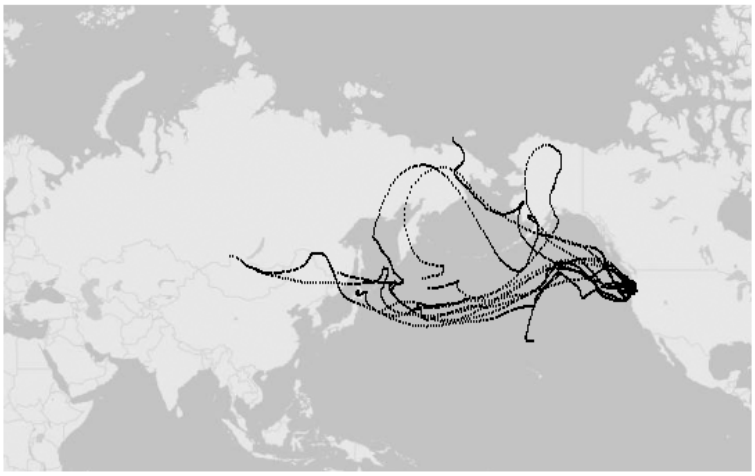




1/28/2013	
Asia	15.45
Siberia	4.44
Alaska	10.59
BC	1.84
WA	0.10
OR	6.67
urban WA	0.00
urban OR	2.53
Eastern WA and OR	0.00
Willamette Valley	2.53
CA Central Valley	0.00

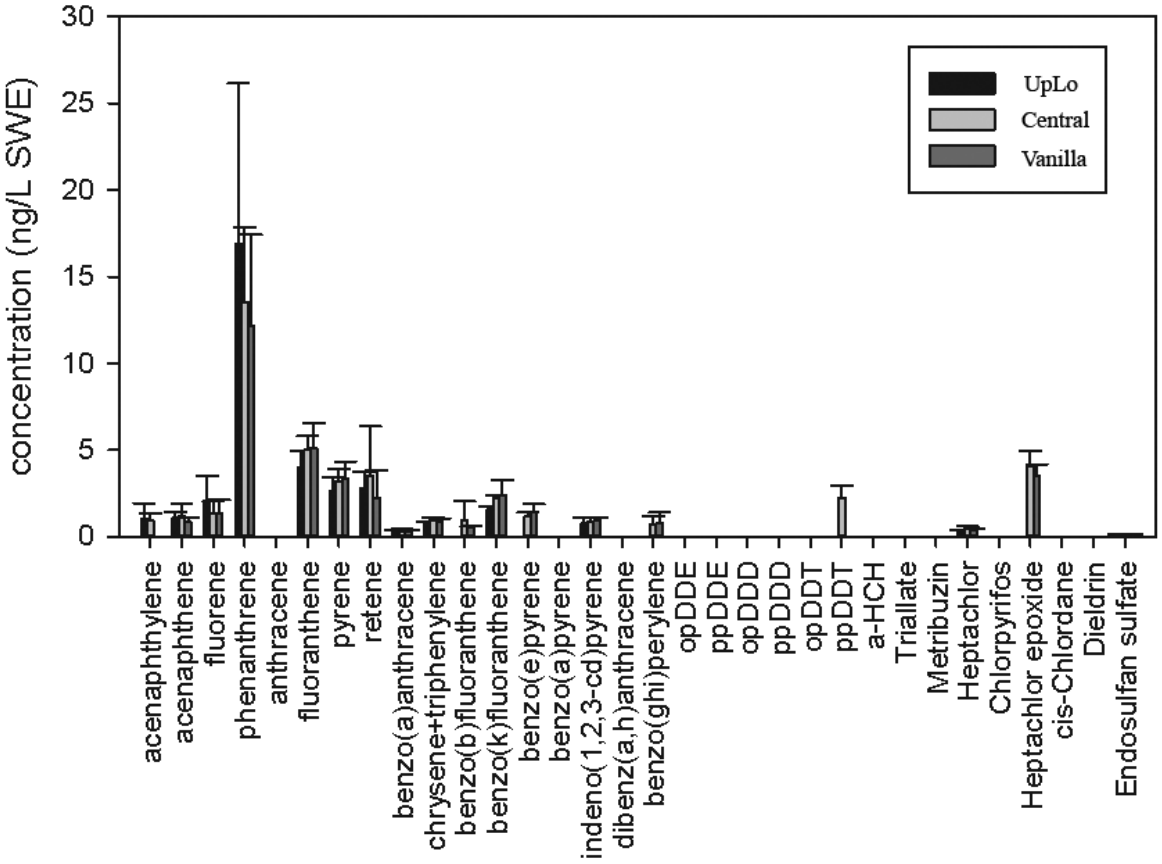
Figure 4.2 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for January 28, 2013.

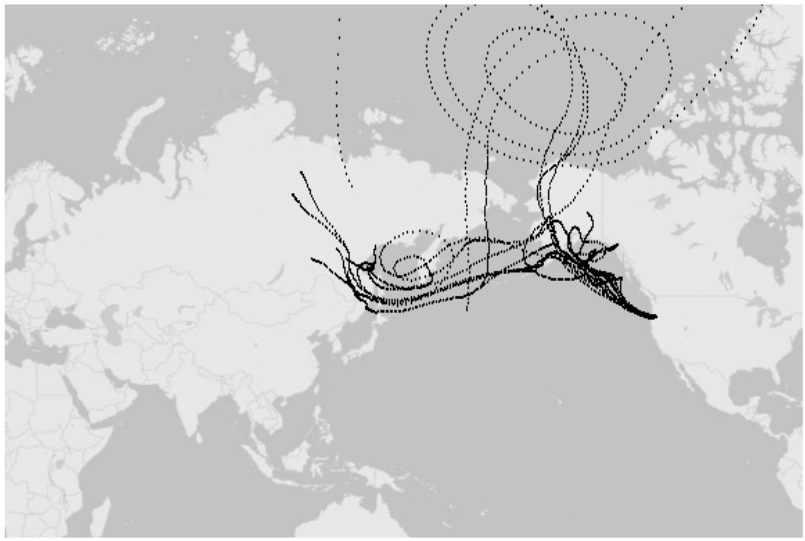




2/21/2013	
Asia	25.94
Siberia	9.27
Alaska	8.40
BC	0.80
WA	0.87
OR	9.51
urban WA	0.00
urban OR	4.13
Eastern WA and OR	0.00
Willamette Valley	4.13
CA Central Valley	0.00

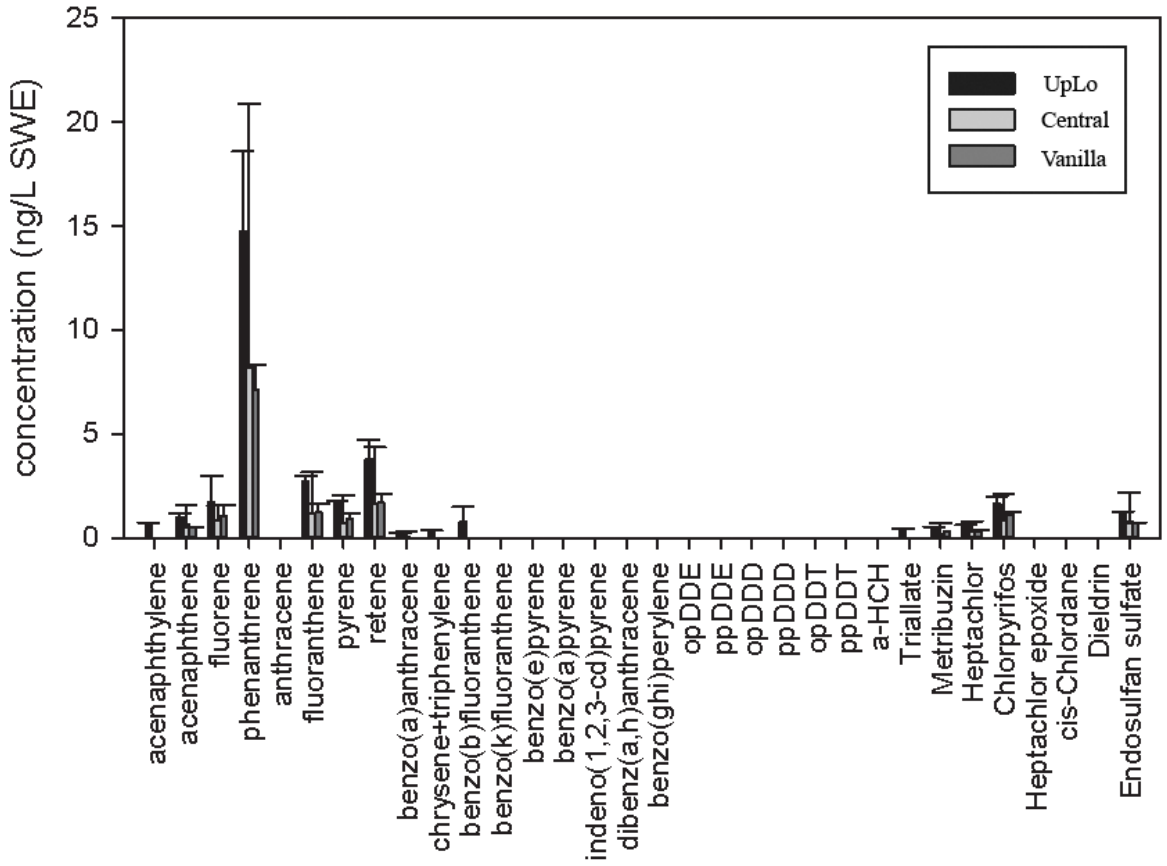
Figure 4.3 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for February 21, 2013.

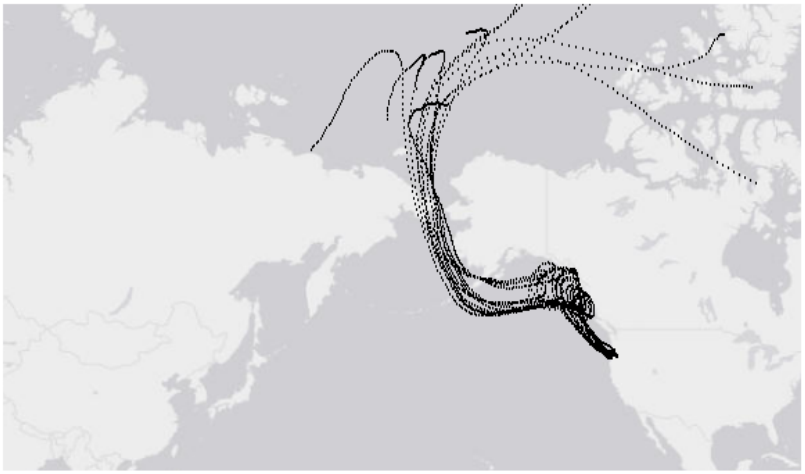




3/21/2013	
Asia	7.64
Siberia	22.92
Alaska	23.47
BC	0.00
WA	0.00
OR	3.23
urban WA	0.00
urban OR	1.56
Eastern WA and OR	0.00
Willamette Valley	1.56
CA Central Valley	0.00

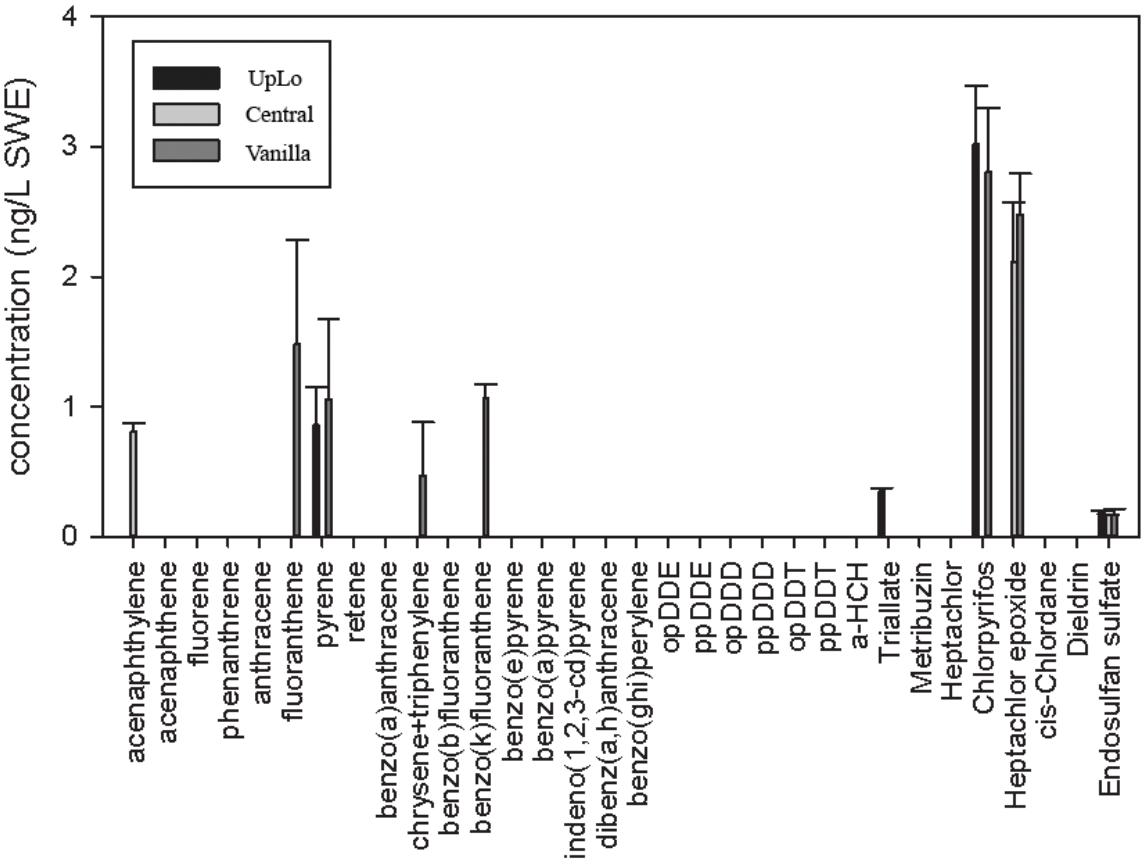
Figure 4.4 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for March 21, 2013.

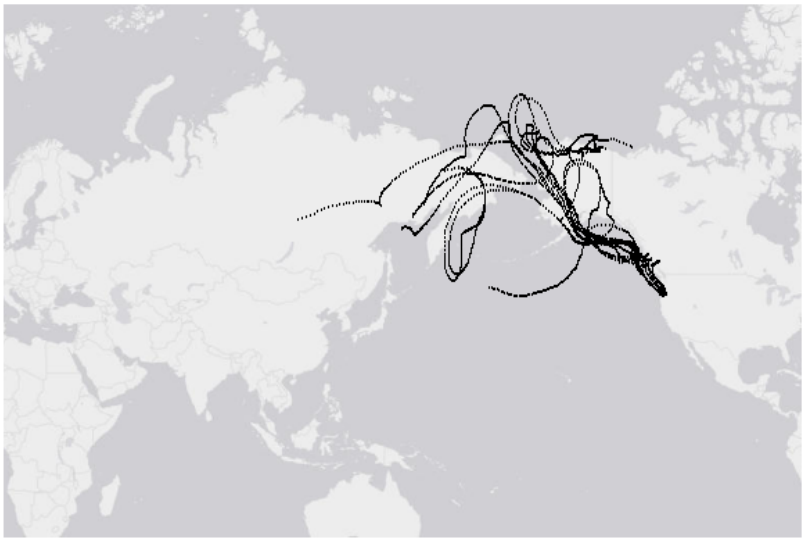




4/15/2013	
Asia	0.00
Siberia	0.00
Alaska	14.86
BC	6.35
WA	0.17
OR	11.22
urban WA	0.00
urban OR	7.08
Eastern WA and OR	0.00
Willamette Valley	7.08
CA Central Valley	0.00

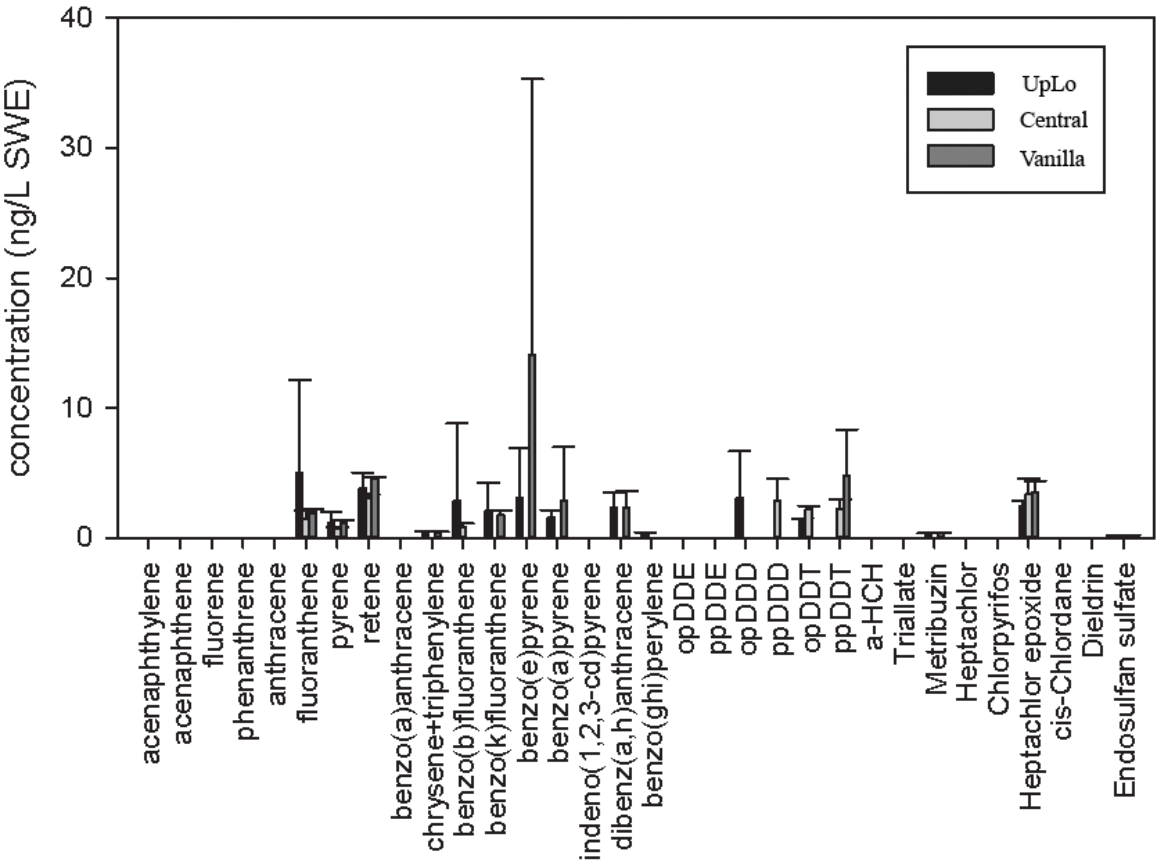
Figure 4.5 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for April 15, 2013.





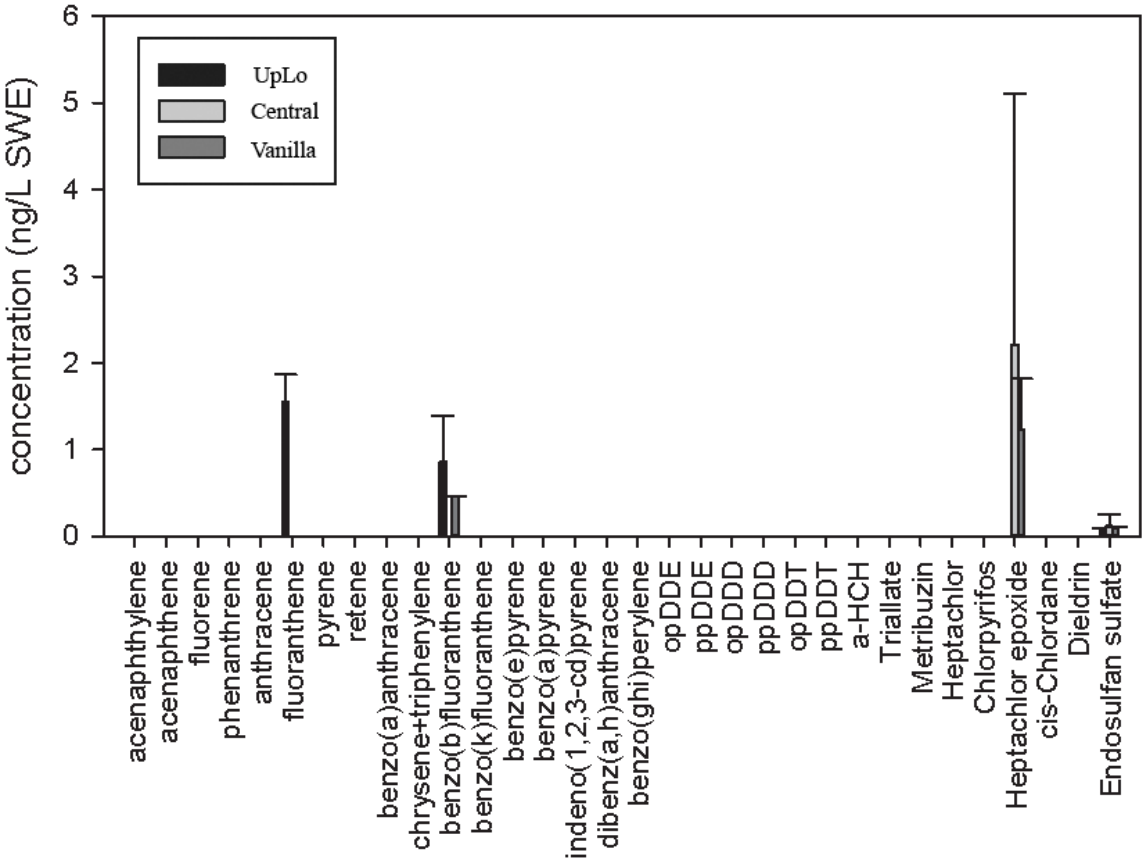
12/3/2013	
Asia	1.28
Siberia	16.74
Alaska	33.02
BC	6.46
WA	0.56
OR	5.07
urban WA	0.14
urban OR	3.47
Eastern WA and OR	0.00
Willamette Valley	3.47
CA Central Valley	0.00

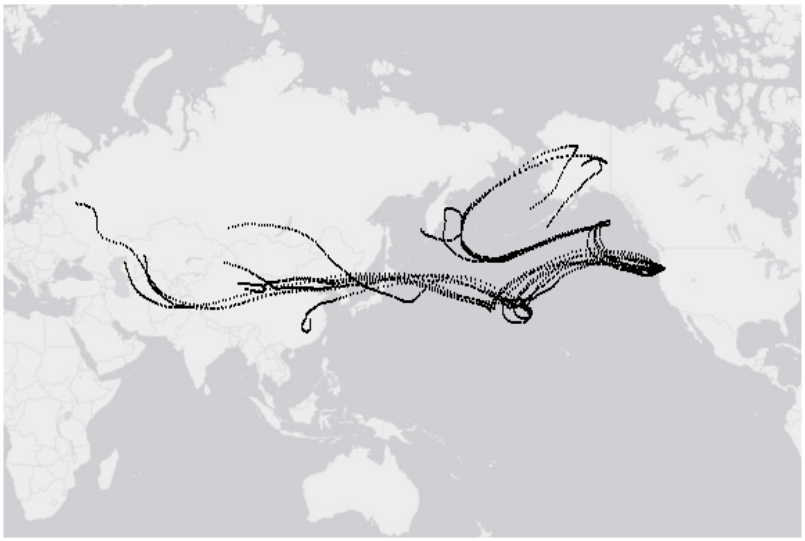
Figure 56 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for December 3, 2013.



12/7/2013	
Asia	3.75
Siberia	4.10
Alaska	10.14
BC	11.08
WA	2.67
OR	18.44
urban WA	0.59
urban OR	3.06
Eastern WA and OR	5.73
Willamette Valley	3.06
CA Central Valley	0.00

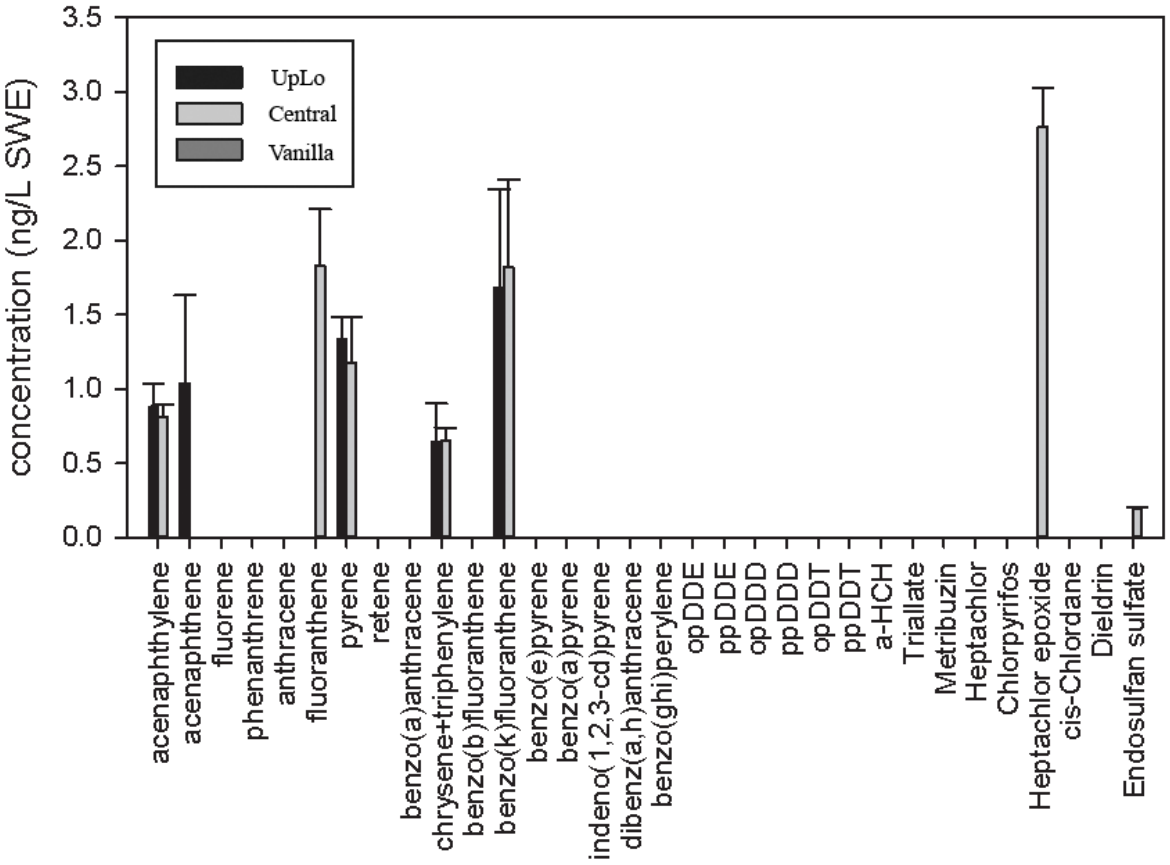
Figure 4.7 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for December 7, 2013.

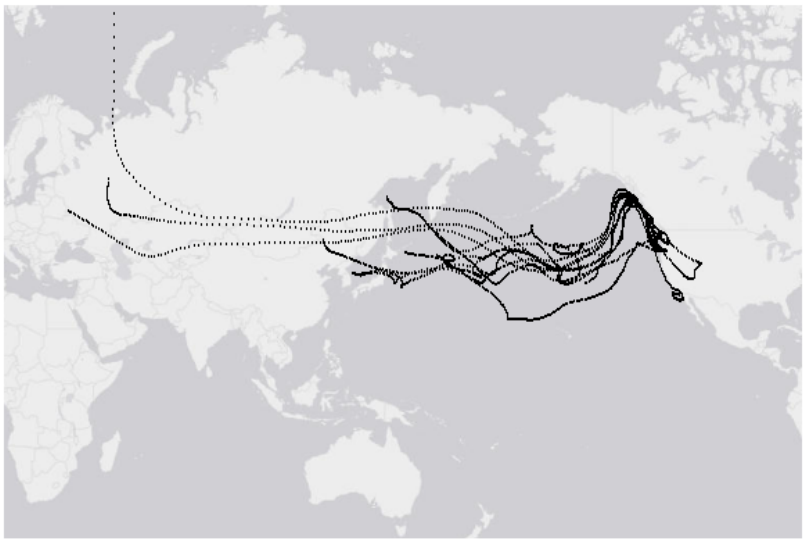




1/13/2014	
Asia	31.98
Siberia	6.28
Alaska	5.52
BC	0.00
WA	0.00
OR	4.10
urban WA	0.00
urban OR	1.60
Eastern WA and OR	0.00
Willamette Valley	1.60
CA Central Valley	0.00

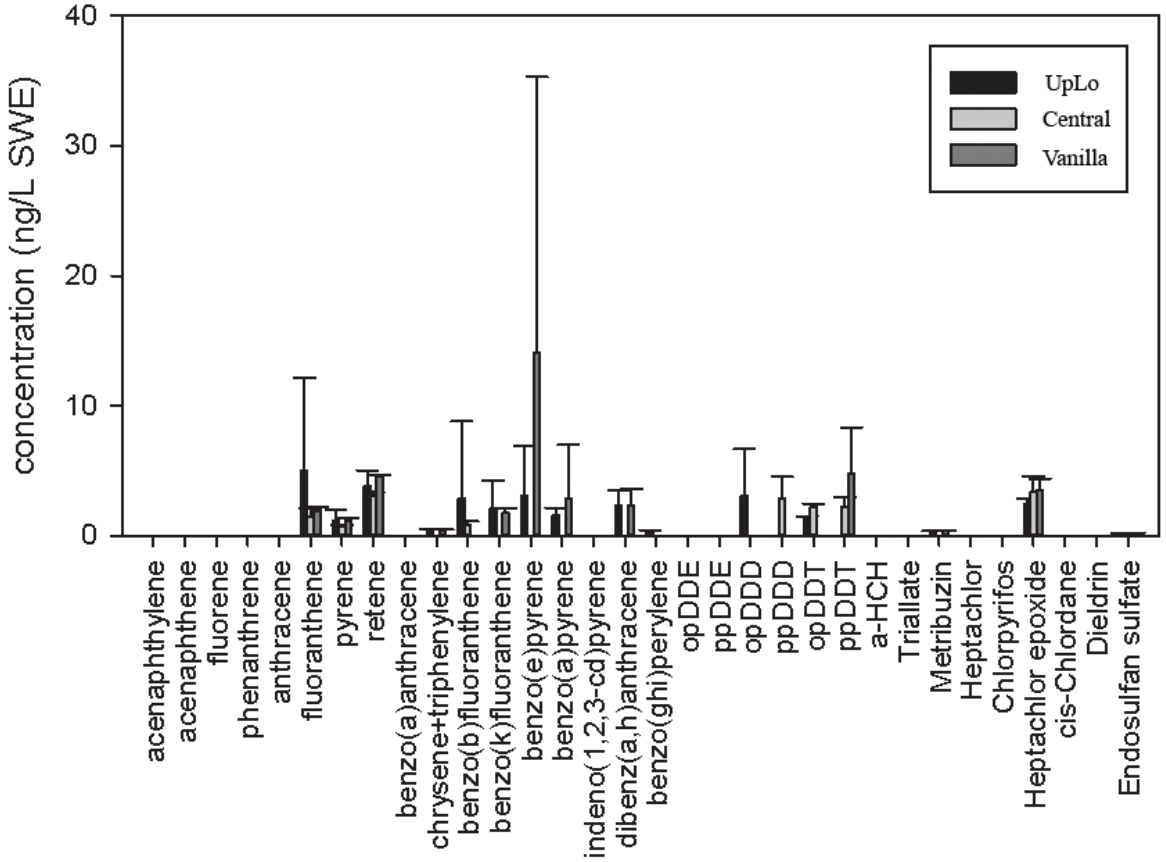
Figure 4.8 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for January 13, 2014.

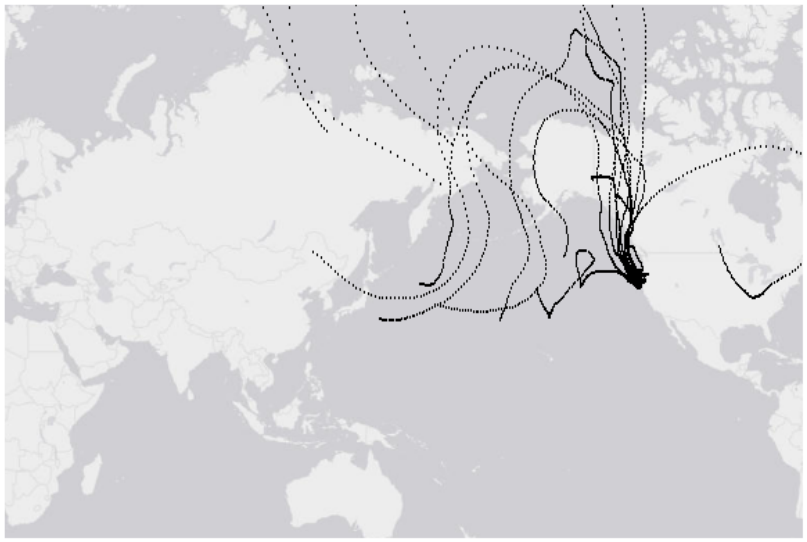




1/30/2014	
Asia	21.49
Siberia	4.86
Alaska	0.21
BC	6.88
WA	3.61
OR	4.06
urban WA	2.64
urban OR	1.91
Eastern WA and OR	0.07
Willamette Valley	1.91
CA Central Valley	0.17

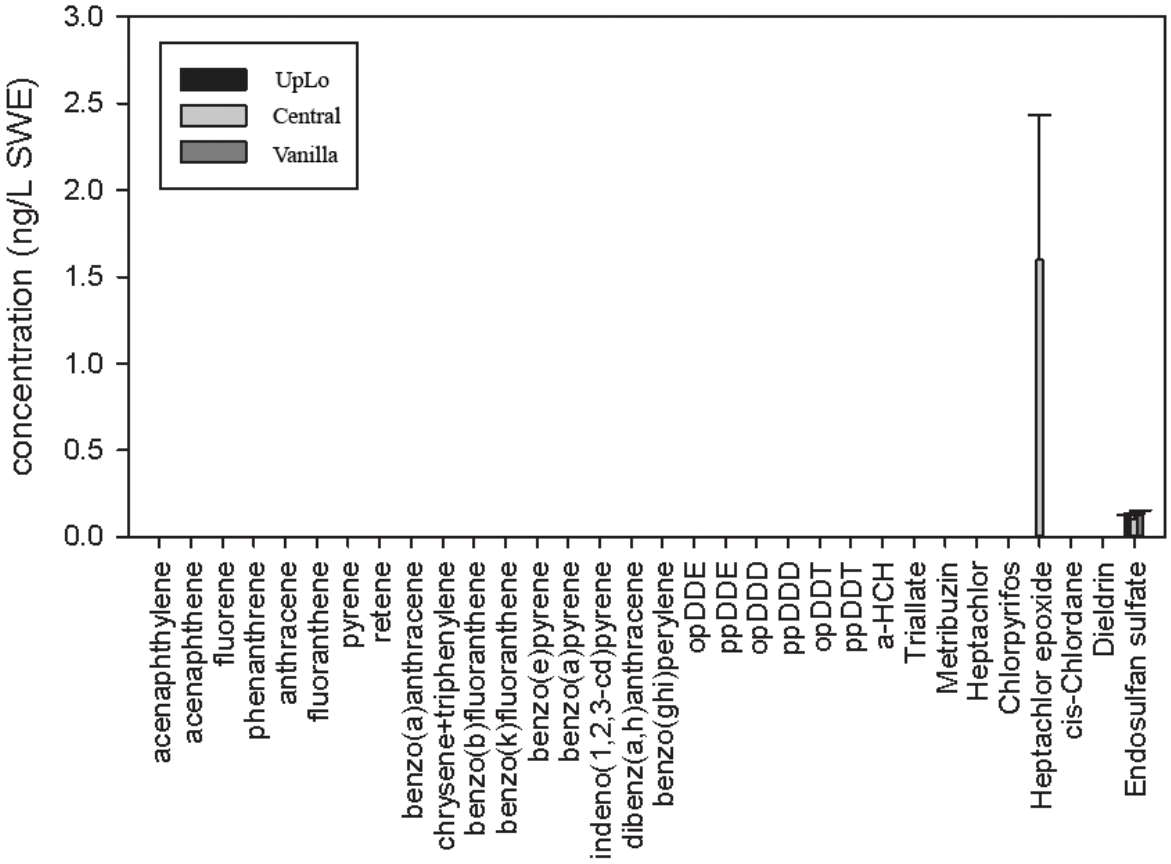
Figure 4.9 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for January 30, 2014.





2/7/2014	
Asia	4.58
Siberia	2.78
Alaska	3.26
BC	9.69
WA	0.14
OR	9.93
urban WA	0.03
urban OR	1.39
Eastern WA and OR	0.00
Willamette Valley	1.39
CA Central Valley	0.00

Figure 4.10 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for February 7, 2014.



2/21/2014	
Asia	12.05
Siberia	12.22
Alaska	4.31
BC	0.03
WA	0.00
OR	5.38
urban WA	0.00
urban OR	2.26
Eastern WA and OR	0.00
Willamette Valley	2.26
CA Central Valley	0.00

Figure 4.11 – Concentration profile, 10 day air-parcel back-trajectory map and Source Region Impact Factors for February 21, 2014.

For this study, individual single-event means and coefficients of variation CV were calculated for each sampling site for all compounds with more than one detection within a single site. Results from all events sampled were used to calculate a mean CV for each detected compound, at each individual site, mean intra-site CVs, mean inter-site CVs and mean event CVs. The results are presented in Table 4.2.

Table 4.2 –Mean single site %CVs (n=3), mean intra-site site %CVs (n=9) and mean inter-site %CVs for all samples for a single event (n=9)

	UpLo	Ctr	Vanilla	Mean intra-site CV	Mean inter-site CV	Event CV
acenaphthylene	25	11	3.0	13	16	13
acenaphthene	15	27	8.0	17	15	18
fluorene	37	43	18	33	34	33
phenanthrene	30	30	22	27	30	27
fluoranthene	27	31	34	31	36	31
pyrene	30	54	46	433	45	44
retene	33	32	36	34	34	34
benzo(a)anthracene	12	7.0	12	10		10
chrysene+triphenylene	14	14	16	15		15
benzo(b)fluoranthene	47	40	6.0	31		31
benzo(k)fluoranthene	29	12	15	19		17
benzo(e)pyrene	62	11	46	39		41
benzo(a)pyrene	16		74	45		45
indeno(1,2,3-cd)pyrene	23	12	10	15		15
dibenz(a,h)anthracene	22		26	24		22
benzo(ghi)perylene	3.0	38	37	26		26
total g-p PAH	**47**	**59**	**64**	**57**	**63**	**57**
total p-p PAH	**77**	**107**	**75**	**86**	**80**	**86**
total PAH	**42**	**60**	**47**	**49**	**52**	**49**
op'-DDT	2.0	33		17		22
pp'-DDT		24	38	31		27
metribuzin	3.0	7.0	3.0	4.0	4.0	4.0
heptachlor	8.0	11	6.0	8.0	7.0	8.0
mean for all compounds	**23**	**25**	**25**	**25**	**26**	**25**

Mean within-site variability for POP concentration in fresh-fallen snow was 25% in this study, compared to 15% previously reported for pesticide concentrations, by the WACAP study, in seasonal snowpack in North American National Parks.[22] However, mean inter-site and mean event variability were both 25% in this study, much lower than the 41% inter-site and 59% inter-annual variability reported by WACAP.[22] The 25% inter-site and event variability measured in this study are similar to the 26% regional variability in PAH concentrations reported by Melnikov et al. (2003) for snow with PAH concentrations several orders of magnitude higher than those measured for this study.

Differences in mean event CV from the corresponding within-site or between-site mean CV range from 0-6%. These results support the hypothesis that there is no greater variability in POP concentrations in fresh-fallen snow for sites of approximately 10 km separation for a single event, than for samples collected with 10 m separation, within a single site, for that same single event.

3.2.2 ANOVA of within-site vs. between-site POP concentrations

A primary objective of this research was a comparison of the variability in POP concentrations in fresh-fallen snow on the 10 m (within-site) and 10 km (between-site) spatial scales. Forty seven instances were located where an individual compound was detected for all nine samples of a given snow event. The twelve compounds meeting these criteria were; acenaphthylene with 1 instance, acenaphthene with 3 instances, fluorene with 5 instances, phenanthrene with 4 instances, fluoranthene with 5 instances, pyrene with 5 instances, retene with 6 instances, chrysene and triphenylene (co-eluting and analyzed together) with 3 instances, heptachlor with 2 instances, chlorpyrifos with 1 instance, heptachlor epoxide with 3 instance sand endosulfan sulfate with 6 instances. One-way lysis of variance was used to test the null hypothesis of no

significant difference in site means for each of the 47 instances. No evidence to reject the null hypothesis was found for 41 of the 47 instances, indicating no statistically significant difference at the 95% confidence level in site mean concentration on the 10 km scale. Test reports, including the dates, F, F_{crit}, and P-values for all comparisons are given in Table S13 in the supplemental information.

All of the six instances with statistically significant evidence of between-site differences in concentration at the 95% confidence level were associated with the snow event on April 15, 2013. The compounds showing evidence of a difference in site means at the 95% confidence level were the PAHs acenaphthene, phenanthrene, fluoranthene, retene, pyrene and the pesticide chlorpyrifos. These PAHs were detected in most snow samples, but no evidence of a difference in site means was found for any other events. April 15, 2013 was the only event sampled where chlorpyrifos was detected at quantifiable concentrations in more than one sample. Figure 4.2 shows the PAH concentrations and PAH profile at each site for the April 15, 2013 snow event. The PAH profile is consistent across all three sites, with reduced concentrations of acenaphthene, phenanthrene, fluoranthene, pyrene and retene at the Vanilla site, which is the most distant from the nearest road of the three sites.

The analysis of variance was used to test a null hypothesis of no difference in group means for all of the groups included. A rejection of the null hypothesis gave no information on which group mean or means differed from the others. To further investigate this episode of between-site variability, episodes with ANOVA results indicating a difference in means were subjected to two-sample, two-tailed t-tests comparing each site's mean concentration to the concentration at the other two sites.

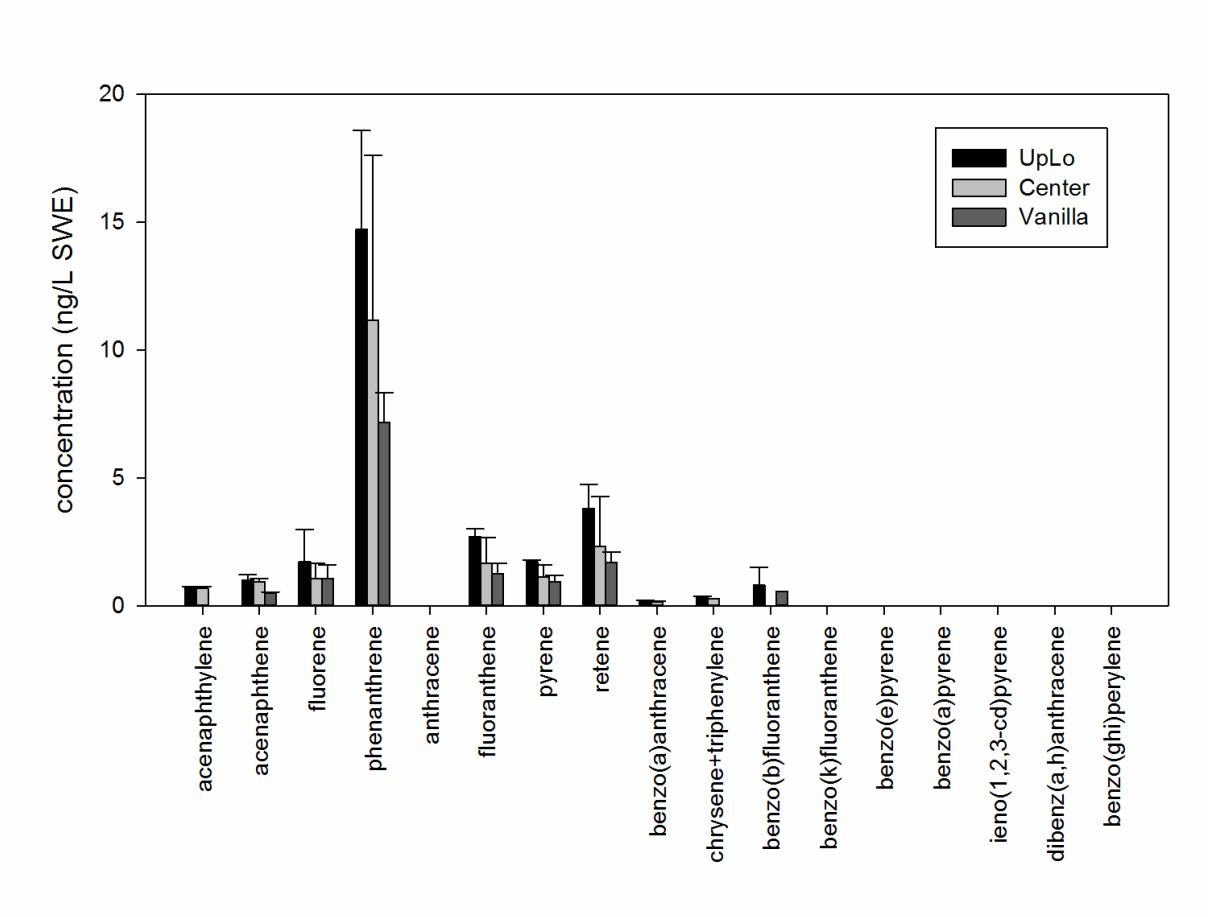


Figure 4.12 - PAH concentrations at HJ Andrews Experimental Forest, April 15, 2013 (n=3, error bars=2 std. dev.)

Concentrations of the individual compounds acenaphthene, phenanthrene, fluoranthene, pyrene, retene and chlorpyrifos, as well total concentrations of gas-phase PAH, total particulate-phase PAH, total PAH and total pesticide were tested. The only evidence of a statistically significant difference in site means at the 95% confidence level was the site-to-site comparisons of acenaphthene concentrations for UpLo vs. Vanilla and for Center vs. Vanilla. Test and critical values for the comparisons conducted are given in table S.14 in the supplemental information. The rest of the t-tests conducted revealed no evidence of a difference in site mean concentrations

within any single snow event. As with the measured CVs, this finding suggests that there is no greater variability in POP deposition by snow on the 10 km scale than on the 10 m scale.

3.3 Local Scale Temporal Variability in Wet deposition of POPs by snow

3.3.1 ANOVA of events

Given the findings from the comparison of within-site to between-site variability in POP deposition by snow, samples from all three sites, for a given snow event, were averaged together for analysis of between-event variability. Mean event total gas-phase PAH, total particulate-phase PAH, total DDT and total pesticide concentrations were tested by one-way analysis of variance against the null hypothesis of no difference in event means. Significant evidence to reject the null hypothesis was found for all comparisons, indicating definite between-event differences in POP deposition for all compounds analyzed ($p<0.05$). Individual mean concentrations of phenanthrene, fluoranthene, pyrene and retene were also tested by one-way ANOVA for events when they were detected at quantifiable concentrations. Evidence was found to reject the null hypothesis of no difference in event means ($p<0.05$) for all individual compounds tested, except phenanthrene. Table S.14 in the supplemental information gives the F, F_{crit}, and P-values for these tests.

3.3.2 SRIF analysis

SRIF analysis revealed five days (January 28, 2013, February 21, 2013, January 13, 2014 and January 30, 2014) with an Asia SRIF greater than 10%. The highest Asia SRIF was on February 21, 2013, with an Asia SRIF of 25.9%. Only four of the ten events sampled (February 21, 2013, April 15, 2013, December 7, 2013, and February 7, 2014) had an Oregon SRIF greater than 6%, with the highest Oregon SRIF of 18.4% on December 7, 2013. That same event on December 7, 2014 was the only event with a non-zero SRIF for the source region defined of agricultural areas

of Eastern Washington and Oregon. No non-zero SRIFs were found for the source regions covering the Northern and Southern California urban areas or the agricultural regions of the California Central Valley. The trajectories generated and the SRIF results show that air masses associated with wintertime precipitation at HJ Andrews Experimental Forest have a large Pacific maritime influence, episodic inputs from Asia and Alaska and relatively little impact from Pacific Northwest urban or agricultural regions.

A prior published study by Primbs et. al (2005) [28] reported PAH concentrations in air samples collected at Mount Bachelor, located approximately 40 km SE and 1500 m higher in altitude from the sampling sites used for this study. Gas phase PAH concentrations were significantly positively correlated ($p<0.05$) with air time in Oregon, as measured by SRIF. Concentrations of retene, a marker for wood combustion, were also correlated with increased air time in Oregon. Concentrations of particulate-phase PAHs were significantly (p-value > 0.5) positively correlated with Asia SRIFs and not correlated at the 95% confidence level with air mass time in North America.

In this study, correlation coefficients were calculated for total gas-phase PAH, total particulate-phase PA, phenanthrene, fluoranthene, retene, and pyrene concentrations with SRIFs for Asia, Siberia, Washington, Oregon, urban Washington and urban Oregon. No statistically significant ($p<0.05$) correlations for total gas-phase PAH or total particulate-phase PAH with any source region were found. Similar to the results of Primbs et. al (2005), retene concentrations were positively correlated with Oregon SRIF values, as were pyrene concentrations.

A similar analysis showed a statistically significant correlation at the 95% level between pesticide concentrations the Washington and Oregon SRIFs. No statistically significant correlation was found between total pesticides and the Willamette Valley or Eastern

Washington/Oregon SRIFs. An insufficient number of quantifiable detections were made for SRIF analysis of individual pesticides. However, it should be noted that all of the quantifiable detects of chlorodiphenylmethane pesticides and degradation products were made on December 7, 2013. This was the only storm event with a SRIF for the agricultural regions of Eastern Washington and Oregon that was greater than 1%, and the highest urban Oregon SRIF, at 18.44%. These samples showed a visible yellow tint after extraction and exhibited mildly degraded peak shapes. Full-scan chromatograms of samples from this date also showed several large non-analyte peaks. The baseline noise level for some analytes in SIM mode mass spectrometry was slightly increased. Chromatography returned to normal peak shapes after the first 10 cm of the chromatographic column was trimmed and the GC inlet liner was changed.

3.4 Correlation of Site Meteorological Parameters

Analysis of variance showed that there was no greater variability in deposition of POPs by snow on the 10 km (inter-site) scale than the 10 m (intra-site) scale. However, this is, in part, due to the relatively high degree of variability observed on the intra-site scale. Maximum air temperature and solar irradiance over the snow accumulation period and snowpack temperature at time of collection were assessed as possible contributors to spatial variation. Pierson's correlations coefficients were calculated for concentrations of gas-phase PAH, particulate-phase PAH, total PAH, total DDT, total pesticides and the individual PAHs phenanthrene, fluoranthene, pyrene and retene and pesticide degradation products endosulfan sulfate and heptachlor epoxide with reciprocal maximum air temperature, reciprocal snow temperature, and maximum solar irradiance for the collection period and compared to the critical value corresponding to a 95% confidence interval for that set. Values for n, r and $r_{critical}$ for all correlations tested are presented in Table S.16 in the supplemental information. Statistically

significant positive correlations ($p<0.05$) were found between solar irradiance and total gas-phase PAH, total particulate-phase PAH, fluorine, pyrene and endosulfan sulfate concentrations, and between reciprocal snow temperature and phenanthrene concentration. No statistically significant ($p>0.05$) positive correlations were found with reciprocal maximum air temperature.

The lack of detection of any target compounds in samples from the February 21, 2014 snow event may be related to sampling conditions. This was a large snow event, with over 400 cm of snow accumulation in the 48 hours prior to sampling. Samples for this event were collected from the upper layers of this accumulation, and did not reach down to the crust from prior accumulation. Precipitation scavenging and below-cloud washout are efficient processes, which typically lead to the highest concentration of pollutants being found in the earliest hours of deposition.[30] It is possible that the snow sampled during this event represents snow that fell after the surrounding atmosphere had been "cleaned" by earlier snowfall.

3.4.2 Particulate-phase PAHs and particle mass load.

The solid-phase extraction method used for this study excluded large (>1 mm) debris, but included small particulate matter such as cloud condensation nuclei and other atmospheric aerosols swept out by the falling snow. Any POPs sorbed onto the surface of small particulate matter in the sample were extracted along with the melted snow. Particulate mass concentration was obtained by weighing dried SPE cartridges post-extraction, using a Mettler high-precision analytical balance, and subtracting their pre-extraction mass. (Figure 4.13)

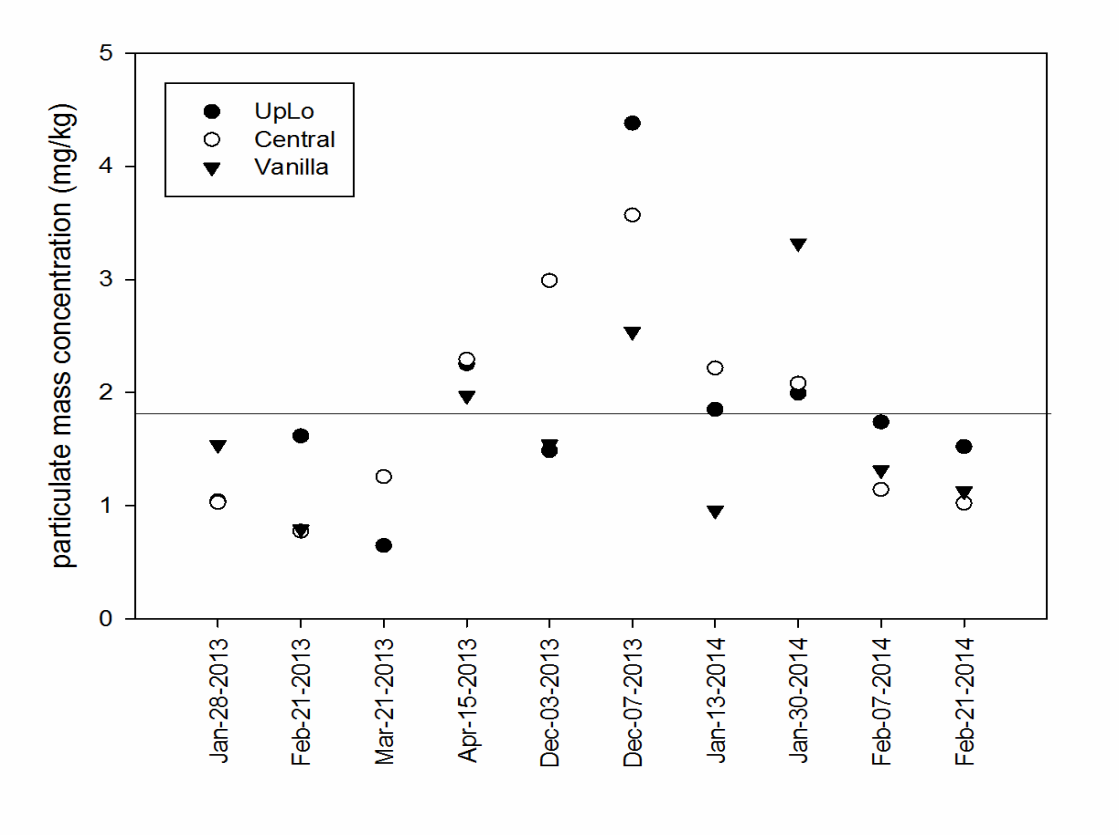


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Figure 4.13 – Particulate Mass concentration in snow samples from HJ Andrews Experimental Forest, January 2013 – February 2014. The line indicates the mean particulate matter concentration for all samples.

We hypothesized that the particulate-phase PAH concentrations would correlate with particulate matter concentrations in the samples. However, a correlation of particulate phase PAH concentration vs. particulate matter concentration was not statistically significant at the 95% confidence level. Several SPE cartridges, including those with the highest particulate matter concentrations, were disassembled and the interior glass frits were imaged using a Zeiss optical microscope. Figure 4.14 shows an image of some of the particulate matter collected during extraction

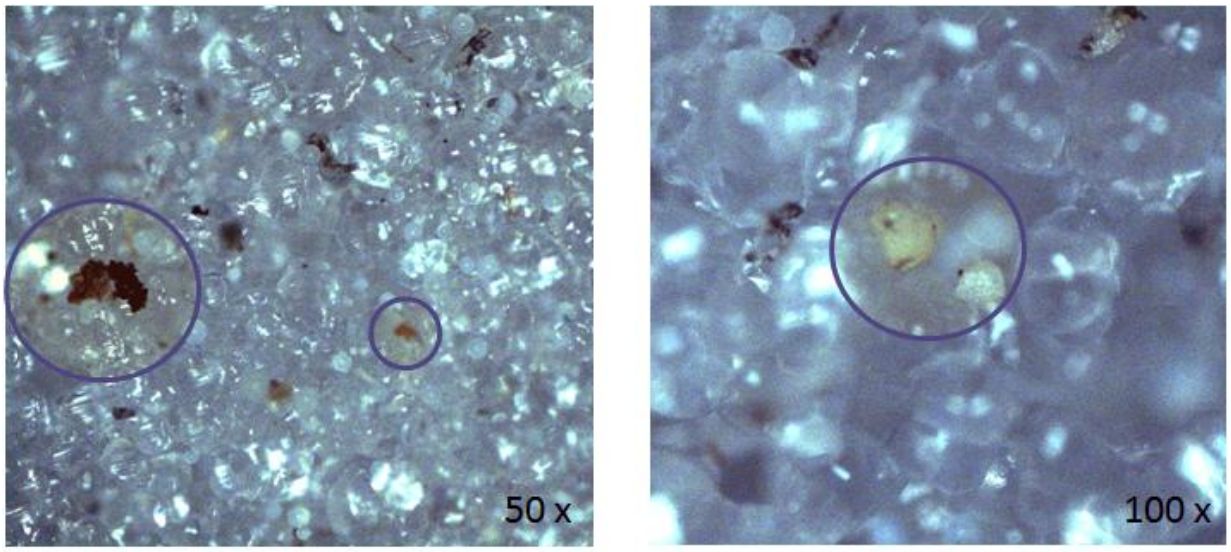

Figure 4.14 - Particulate matter collected in SPE cartridge from December 7, 2014, Upper Lookout site sample.

Grains of the glass frit and the smooth spheres of sorbent particles, as well as single-particle carbon, carbon-aggregate and mineral dust particles are shown in the image. Wind-blown mineral dust washed out by snow may account for variable amounts of the particulate mass measured in the samples. The samples with the highest particulate matter concentration do not correlate with the Asia source region, but occur in samples with elevated SRIFs for the Oregon, Washington and British Columbia regions, which suggests the inclusion of mineral dust from the Pacific Northwest. This finding may explain the unexpected lack of correlation between particulate matter concentration and particulate-phase PAH concentrations.

4. Conclusions and Future Work

During ten snow events between January 2013 and February 2014, 87 samples of fresh-fallen, pre-metamorphic snow were collected at three remote sites of similar altitude and exposure, located along a 10 km transect in the Cascade Mountains in Oregon, USA. Comparison of

between-site and within-site coefficients of variation for site mean concentrations and analysis of variance of between-site differences suggested no difference in spatial variability of POP deposition by snow on the 10 km scale than on the 10 m scale for nine of ten events sampled.

For improved accuracy in future studies assessing the POP concentration in fresh-fallen snow on the 10 km scale, the number of replicate samples collected at a single site that is representative of the altitude and solar exposure of the region to be assessed should be increased, rather than increasing the number of sampling locations throughout the region.

In the future, enlarging the data set through continued sampling of snow events at HJ Andrews would increase understanding of between-event differences in deposition, with the ultimate goal of establishing the temporal frequency of sampling necessary for accurate characterization of POP deposition on the 10 km scale.

In addition to the POPs described in this study, a variety of PAH photo-degradation products, including nitro-, oxy- and hydroxyl- derivatives are emerging contaminants of interest and may have toxic and environmental impacts that exceed those of their parent compounds. Analysis of samples of fresh-fallen snow for these emerging contaminants would provide information on atmospheric formation. Production of these compounds in snowpack should be investigated by repeat sampling of deposited snow from a single site.

This research showed a higher mean within-site CV for POP concentrations (25%) in fresh-fallen snow than was seen in prior studies of North American snowpack (15%). However, between-site variability for fresh-fallen snow was also shown to 25%, while between site CVs for POP concentrations in snowpack have been reported at 41%-94%. These results suggest that post-depositional transport and fate of POPs has a significant component of local variability. A future study with repeat sampling both deposition events and periodic total columns of seasonal

snowpack would greatly increase our understanding of the factors affecting variability of POP concentrations in snowpack and further assist impact assessment and environmental modeling efforts.

5. Acknowledgements

The authors would like to thank the staff and administration of the HJ Andrews Experimental Forest and the National Park Service Willamette National Forest for logistical support, assistance with site access and providing supporting meteorological data. The Andrews forest is jointly administered by the USDA Forest Service Pacific Northwest Research Station and Oregon State University, with additional funding from the National Science Foundation. Additional thanks are given to Chris Heist at Oregon State University for assistance with microscopy and to Dan Wang for assistance with sample preparation.

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Conclusions and Future Work

This research was undertaken for the analysis of the spatial and temporal variability in wet deposition by snow of persistent organic pollutants (POPs), including polycyclic aromatic hydrocarbons (PAHs) and both current-use and historic-use pesticides. The research question was:

- Is the local-scale (10 km) variation in POP concentration typically observed in snow samples due to differences in deposition?

The hypotheses tested were:

- Between-site variation of POP concentration in fresh-fallen snow for single snow events is statistically indistinguishable from within-site variation for sites of similar elevation and exposure with <10 km separation.
- Significant correlation will be found between deposition profiles and air-parcel source regions, as determined by analysis of model-derived air parcel back-trajectories generated for each snow event.

An analytical method using solid-phase microextraction (SPME) was assessed. Method limits of detection were modeled using a custom-developed Python program, SPMEpy, which encouraged method development experiments. The method was optimized for extraction conditions using aqueous standards. However, preliminary application to field samples of melted snow and urban streamwater exhibited low peak areas. A repeat extraction experiment was conducted and experimental depletion coefficients calculated for comparison to model predictions of depletion coefficients. Experimental extractions were show to have less sensitivity

than predicted for high molecular weight PAHs. Due to this lack of sensitivity in the natural sample matrix, this method was not used for the field study.

A second analytic method was developed involving solid phase extraction with Oasis HLB SPE cartridges. Percent recovery values, matrix-specific method limits of detection and percent relative standard deviations were for the method were calculated for each compound of interest. Sensitivity and reproducibility were judged to be suitable for the analysis variability in POP concentrations at the concentrations expected to be present in North American snow.

Eighty seven samples of fresh-fallen, pre-metamorphic snow were collected at three remote sites of similar altitude and exposure, located along a 10 km transect in the Cascade Mountains in Oregon, USA .Ten separate snow events were sampled. All samples and associated blanks were processed by the solid-phase extraction method described in Chapter 3 of the thesis, and analyzed for POP concentration. Sixteen of the seventeen PAHs analyzed for were detected in over 35% of the samples collected. Total PAH concentrations in individual samples ranged from below quantifiable limits to 53.5 ng per liter of snow water equivalents (SWE). The most frequently detected PAH was fluoranthene, which was detected in 69% of all samples with a maximum measured concentration of 22.2 ng/L_{SWE}. Pyrene and retene were each detected in 57% of all samples, with maximum measured concentrations of 3.80 ng/L_{SWE} and 15.9 ng/L_{SWE} respectively. Phenanthrene was detected in 44% of all samples, with measured concentrations ranging from 2.08 – 25.2 ng/L_{SWE}. Anthracene, a photo-reactive PAH with a short atmospheric half life, was not detected at quantifiable concentrations in any samples, indicating no contamination from nearby sources. The absence of anthracene also indicates that the collected samples are not contaminated by the exhaust of the snow-cat used for site access. Gaseous-phase

PAHs, defined as those with two or three fused rings, were more frequently detected than particulate-phase PAHs (four or more rings).

Of the 57 pesticides and pesticide degradation products analyzed for, only 14 were detected at quantifiable concentrations in any samples, including trifluralin, triallate, metribuzin, heptachlor, chlorpyrifos, cis-chlordane, endosulfan sulfate, dieldrin, heptachlor epoxide, α-HCH, op-DDD, pp-DDD, op-DDT and pp-DDT. The pesticide degradation products endosulfan sulfate and heptachlor epoxide, were detected at quantifiable concentrations in all samples, and were the most frequently detected chlorinated compounds, with concentration ranges of 0.070 – 1.430 ng/L_{SWE} and 0.983 – 5.83 ng/$L_{SWE,}$ respectively. Dieldrin and chlorpyrifos were detected with maximum measured concentrations of 3.14 ng/L_{SWE} and 3.11 ng/$L_{SWE,}$ respectively. However, detection of each was limited to a single snow event. Of the hexachlorocyclohexanes, α-HCH was detected in 7 of 87 samples, but β-HCH and ϒ-HCH (Lindane) were not detected at quantifiable concentrations in any sample. Hexachlorochclobenzene (HCB) was also not detected at concentrations above the limit of quantitation in any samples. Detections of chlorodiphenylmethane pesticides and degradation products (isomers of DDT, DDD and DDE) were largely limited to the snow events on December 7, 2013 and February 7, 2014. No detections of op-DDE or pp-DDE were made, but matrix interferants in the relevant region of the chromatogram are likely to have obscured any signal present for these compounds.

Comparison of between-site and within-site coefficients of variation for site mean concentrations and showed a 1% difference in within-site and between-site mean CVs. Analysis of variance of between-site differences showed no evidence of difference in means at the 95% confidence level for nine of ten events sampled. Two-way t-tests of individual compound for the

date indicating a difference in site means revealed statistically significant ($p>0.05$) evidence in site means for just one compound, acenaphthene.

Consequently, for improved accuracy in future studies assessing the POP concentration in fresh-fallen snow on the 10 km scale, the number of replicate samples collected at a single site that is representative of the altitude and solar exposure of the region to be assessed should be increased, rather than increasing the number of sampling locations throughout the region.

Future Work:

In the future, enlarging the data set through continued sampling of snow events at HJ Andrews would increase understanding of between-event differences in deposition, with the ultimate goal of establishing the temporal frequency of sampling necessary for accurate characterization of POP deposition on the 10 km scale. Increasing the number of site replicates collected for future snow events could reduce within-site %CVs.

In addition to the POPs described in this study, a variety of PAH photo-degradation products, including nitro-, oxy- and hydroxyl- derivatives are emerging contaminants of interest and may have toxic and environmental impacts that exceed those of their parent compounds. Analysis of samples of fresh-fallen snow for these emerging contaminants would provide information on atmospheric formation. Production of these compounds in snowpack should be investigated by repeat sampling of deposited snow from a single site.

This research showed a higher mean within-site CV for POP concentrations (25%) in fresh-fallen snow than was seen in prior studies of North American snowpack (15%). However, between-site variability for fresh-fallen snow was also shown to 25%, while between site CVs for POP concentrations in snowpack have been reported at 41%-94%. These results suggest that post-depositional transport and fate of POPs has a significant component of local variability. A

future study with repeat sampling both deposition events and periodic total columns of seasonal snowpack would greatly increase our understanding of the factors affecting variability of POP concentrations in snowpack and further assist impact assessment and environmental modeling efforts.

Acknowledgements

The authors would like to thank the staff and administration of the HJ Andrews Experimental Forest and the National Park Service Willamette National Forest for logistical support, assistance with site access and providing supporting meteorological data. The Andrews forest is jointly administered by the USDA Forest Service Pacific Northwest Research Station and Oregon State University, with additional funding from the National Science Foundation.

Table S.2a – Measured concentrations (ng/L SWE) and CVs for PAHs, January 28, 2013

	0128UpLo1	0128ctr2	0128UpLo3	0128ctr1	0128UpLo2	0128ctr3	0128van1	0128van2	0128van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	<	<	<	0.726	0.703	<	<	<	<	0.715	0.016	0.022		0.022		
acenaphthene	0.463	0.635	0.898	0.492	0.803	0.536	<	0.529	0.575	0.616	0.156	0.252	0.329	0.276	0.059	0.230
fluorene	1.44	2.12	1.68	0.973	2.57	1.66	1.05	1.47	1.61	1.62	0.495	0.305	0.194	0.462	0.213	0.295
phenanthrene	13.3	18.3	13.8	9.41	18.2	18.2	8.48	13.0	11.9	13.8	3.73	0.269	0.184	0.331	0.213	0.246
anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
fluoranthene	1.34	1.98	2.46	0.961	2.05	1.49	0.824	1.23	1.28	1.51	0.543	0.358	0.292	0.363	0.227	0.299
pyrene	0.331	0.509	0.907	0.653	0.525	0.969	0.223	0.422	0.664	0.578	0.248	0.430	0.506	0.320	0.506	0.429
retene	1.07	1.66	3.09	<	1.50	1.04	<	0.865	1.06	1.47	0.770	0.522	0.535	0.255	0.148	0.360
total g-p PAH	**17.9**	**25.2**	**22.8**	**13.2**	**26.4**	**23.9**	**10.5**	**17.5**	**17.1**	**19.4**	**5.50**	**0.283**	**0.169**	**0.330**	**0.260**	**0.251**
benzo(a)anthracene	0.135	<	0.152	<	0.127	0.129	<	<	0.272	0.163	0.062	0.378	0.082	0.010		
chrysene+triphenylene	<	0.234	0.323	<	0.263	<	<	<	<	0.273	0.046	0.167	0.227			
benzo(b)fluoranthene	<	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(k)fluoranthene	<	<	<	<	<	<	<	<	<							
benzo(e)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
indeno(1,2,3-cd)pyrene	nd	<	nd	nd	nd	nd	<	<	<							
dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd	nd	<							
total p-p PAH	**0.135**	**0.234**	**0.475**	**0.000**	**0.390**	**0.129**	**0.000**	**0.000**	**0.272**	**0.182**	**0.175**	**0.962**	**0.621**	**1.15**	**1.73**	**0.973**
total PAH	**18.1**	**25.5**	**23.3**	**13.2**	**26.8**	**24.0**	**10.5**	**17.5**	**17.4**	**19.6**	**5.60**	**0.200**	**0.100**	**0.300**	**0.200**	**0.200**

Table S.2b – Measured concentrations (ng/L SWE) and CVs for pesticides, January 28, 2013

	0128UpLo1	0128ctr2	0128UpLo3	0128ctr1	0128UpLo2	0128ctr3	0128van1	0128van2	0128van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	<	<	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDT	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDT	<	<	nd	<	<	<	<	nd	<							
total DDT	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	<	<	nd	<	nd	<	<	0.318	0.263	0.290	0.039	0.133			0.133	
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	<	<	<	<	<	<	<	nd	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.318**	**0.263**	**0.065**	**0.129**	**1.99**			**0.877**	**0.877**
Trifluralin	<	<	<	<	<	<	<	<	<							
Triallate	nd	nd	<	nd	nd	nd	nd	nd	nd							
Metribuzin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor	nd	nd	0.392	nd	nd	nd	nd	nd	nd							
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Chlordane	<	nd	<	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.158	0.148	0.149	0.148	0.139	0.156	0.133	0.147	0.131	0.146	0.009	0.065	0.035	0.058	0.062	0.051
Dieldrin	nd	nd	nd	nd	nd	<	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	<	3.12	3.53	4.15	4.02	5.20	5.31	3.95	<	4.18	0.810	0.193	0.087	0.145	0.208	0.153
total pesticides	**0.158**	**3.27**	**4.07**	**4.30**	**4.16**	**5.35**	**5.44**	**4.10**	**0.131**	**3.44**	**1.98**	**0.576**	**0.827**	**0.142**	**0.857**	**0.531**

Table S.3a – Measured concentrations (ng/L SWE) and CVs for PAHs, February 21, 2013

	0221UpLo1	0221UpLo2	0221UpLo3	0221Ctr1	0221ctr2	0221ctr3	0221Van1	0221Van2	0221Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	0.864	0.949	1.344	1.249	<	0.961	0.711	0.703	<	0.969	0.248	0.256	0.243	0.184	0.008	0.162
acenaphthene	<	0.877	0.873	1.12	<	0.571	<	<	0.876	0.865	0.197	0.228	0.004	0.462		
fluorene	0.883	2.90	2.19	2.66	0.706	1.12	<	1.42	1.42	1.66	0.825	0.495	0.515	0.689	0.002	0.419
phenanthrene	7.02	25.2	13.7	19.4	9.65	10.2	5.92	11.6	12.4	12.8	6.09	0.476	0.600	0.418	0.356	0.474
anthracene	nd	<	nd	nd	nd	nd	nd	nd	nd							
fluoranthene	0.950	2.49	1.65	2.15	0.665	1.19	0.732	1.45	2.08	1.48	0.658	0.443	0.456	0.563	0.475	0.494
pyrene		0.663	1.14	0.271	1.06	<	0.395	<	0.662	0.699	0.348	0.498	0.377	0.838	0.358	0.518
retene	<	2.07	1.04	1.78	<	0.785	1.21	1.161	2.40	1.49	0.598	0.399	0.466	0.551	0.440	0.481
total g-p PAH	**9.72**	**35.1**	**22.0**	**28.6**	**12.0**	**14.8**	**8.98**	**16.4**	**19.9**	**18.6**	**8.81**	**0.473**	**0.571**	**0.479**	**0.369**	**0.486**
benzo(a)anthracene	<	0.195	<	0.176	nd	nd	<	0.149	0.141	0.165	0.025	0.151			0.037	
chrysene+triphenylene	<	0.356	<	0.261	nd	nd	<	0.240	0.262	0.280	0.052	0.186			0.064	
benzo(b)fluoranthene	nd	<	nd	nd	nd	nd	nd	nd	nd							
benzo(k)fluoranthene	<	<	<	<	<	<	<	<	<							
benzo(e)pyrene	<	nd	<	nd	nd	nd	nd	nd	nd							
benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
indeno(1,2,3-cd)pyrene	<	<	<	nd	nd	nd	nd	nd	nd							
dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(ghi)perylene	<	<	<	nd	nd	nd	nd	nd	nd							
total p-p PAH	**0.000**	**0.551**	**0.000**	**0.437**	**0.000**	**0.000**	**0.000**	**0.388**	**0.403**	**0.198**	**0.239**	**1.20**	**1.73**	**1.73**	**0.866**	**1.34**
total PAH	**9.72**	**35.7**	**21.9**	**29.08**	**12.08**	**14.85**	**8.98**	**16.8**	**20.3**	**18.8**	**9.00**	**0.478**	**0.579**	**0.488**	**0.377**	**0.494**

Table S.3b – Measured concentrations (ng/L SWE) and CVs for pesticides, February 21, 2013

	0221UpLo1	0221UpLo2	0221UpLo3	0221Ctr1	0221ctr2	0221ctr3	0221Van1	0221Van2	0221Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd	nd	nd	<							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	nd	nd	nd	<	nd	nd	nd	nd							
opDDT	nd	nd	nd	nd	2.45	nd	nd	nd	nd							
ppDDT	nd	<	<	<	nd	nd	nd	nd	<							
total DDT	**0.000**	**0.000**	**0.000**	**0.000**	**2.45**	**0.000**	**0.000**	**0.000**	**0.000**	**0.273**	**0.820**	**3.000**		**1.732**		**1.732**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	<	<	nd	nd	nd	nd	nd	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**					
Trifluralin	<	<	<	<	<	<	<	<	<							
Triallate	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Metribuzin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	0.298							
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Chlordane	<	<	<	<	<	0.307	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.146	0.132	nd	0.136	0.132	nd	0.131	0.139	0.132	0.135	0.006	0.041	0.071	0.020	0.033	0.042
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	5.055	4.967	5.829	nd	nd	3.440	3.891	2.973	nd	4.359	1.095	0.251	0.090		0.189	
total pesticides	**5.20**	**5.09**	**5.82**	**0.136**	**0.132**	**3.74**	**4.02**	**3.11**	**0.430**	**3.07**	**2.28**	**0.743**	**0.074**	**1.56**	**0.741**	**0.471**

Table S.4a – Measured concentrations (ng/L SWE) and CVs for PAHs, March 21, 2013

	0321UpLo1	0321UpLo2	0321UpLo3	0321ctr1	0321ctr2	0321ctr3	0321van1	0321van2	0321van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	1.32	<	0.656	1.18	0.907	0.816	<	<	<	0.977	0.272	0.278	0.477	0.196		
acenaphthene	0.924	1.06	1.26	1.48	1.31	0.836	0.980	0.781	0.768	1.04	0.257	0.245	0.158	0.278	0.141	0.200
fluorene	2.83	1.38	1.50	1.23	1.71	1.02	1.79	1.29	1.07	1.54	0.554	0.360	0.421	0.269	0.269	0.332
phenanthrene	21.9	12.7	15.9	13.2	15.8	11.5	14.5	12.6	9.39	14.2	3.54	0.250	0.274	0.158	0.214	0.220
anthracene	<	<	<	nd	nd	nd	nd	nd	nd							
fluoranthene	3.90	3.52	4.50	5.00	5.45	4.70	5.53	5.51	4.22	4.70	0.733	0.156	0.125	0.074	0.147	0.115
pyrene		2.25	2.58	0.391	3.318	3.49	0.358	3.79	3.38	2.44	1.37	0.561	0.096	0.726	0.747	0.526
retene	2.47	2.63	3.34	2.92	5.11	2.37	2.98	2.37	1.38	2.84	1.01	0.355	0.165	0.417	0.358	0.318
total g-p PAH	**33.3**	**23.6**	**29.7**	**25.4**	**33.6**	**24.8**	**26.2**	**26.3**	**20.2**	**27.0**	**4.4**	**0.164**	**0.170**	**0.176**	**0.145**	**0.164**
benzo(a)anthracene	0.342	0.235	0.249	0.313	0.402	0.291	0.362	0.236	0.314	0.305	0.058	0.191	0.210	0.175	0.209	0.197
chrysene+triphenylene	0.816	0.682	0.710	0.883	1.02	0.937	0.899	0.975	0.840	0.864	0.115	0.133	0.095	0.078	0.075	0.082
benzo(b)fluoranthene	<	<	<	0.583	0.648	1.577	0.569	0.542	<	0.784	0.445	0.568		0.594	0.035	
benzo(k)fluoranthene	1.68	1.53	1.49	2.21	2.17	2.32	2.13	2.89	2.11	2.06	0.442	0.214	0.065	0.034	0.187	0.101
benzo(e)pyrene	1.51	<	<	1.06	<	1.23	1.16	1.57	1.54	1.35	0.220	0.163		0.106	0.159	
benzo(a)pyrene	nd	<	<	<	<	<	<	<	<							
indeno(1,2,3-cd)pyrene	0.897	0.644	<	0.884	0.752	0.956	0.839	0.997	1.009	0.872	0.125	0.144	0.232	0.120	0.100	0.146
dibenz(a,h)anthracene	nd	nd	nd	<	<	<	nd	<	nd							
benzo(ghi)perylene	0.624	<	<	0.804	0.391	0.865	0.464	0.952	1.02	0.731	0.243	0.332		0.376	0.374	
total p-p PAH	**5.88**	**3.09**	**2.45**	**6.74**	**5.40**	**8.18**	**6.43**	**8.17**	**6.84**	**5.91**	**2.01**	**0.340**	**0.479**	**0.206**	**0.127**	**0.233**
total PAH	**39.2**	**26.7**	**32.2**	**32.2**	**39.0**	**32.9**	**32.6**	**34.5**	**27.0**	**32.9**	**4.37**	**0.133**	**0.191**	**0.107**	**0.124**	**0.140**

Table S.4b – Measured concentrations (ng/L SWE) and CVs for pesticides, March 21, 2013

	0321UpLo1	0321UpLo2	0321UpLo3	0321ctr1	0321ctr2	0321ctr3	0321van1	0321van2	0321van3		event			Intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	<	<	<	<	<	<	<	<	nd							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDT	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDT	<	<	<	2.50	1.98	nd	<	<	<	2.24	0.369	0.164		0.164		
total DDT	**0.000**	**0.000**	**0.000**	**2.50**	**1.98**	**0.000**	**0.000**	**0.000**	**0.000**	**0.498**	**0.998**	**2.001**		**0.883**		**0.883**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**					
Trifluralin	<	<	<	<	<	<	<	<	<							
Triallate	nd	nd	nd	<	nd	<	nd	nd	nd							
Metribuzin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor	<	0.304	0.342	0.424	0.519	<	0.395	0.417	0.451	0.407	0.070	0.173	0.082	0.143	0.068	0.101
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Chlordane	<	<	<	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.162	0.147	0.158	0.143	0.164	0.148	0.142	0.136	0.140	0.149	0.010	0.068	0.050	0.072	0.020	0.048
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	nd	<	nd	3.73	<	4.34	3.87	3.32	3.21	3.71	0.442	0.119		0.107	0.098	
total pesticides	**0.162**	**0.451**	**0.500**	**4.30**	**0.683**	**4.49**	**4.41**	**3.94**	**3.81**	**2.53**	**1.99**	**0.787**	**0.492**	**0.680**	**0.078**	**0.349**

Table S.5a – Measured concentrations (ng/L SWE) and CVs for PAHs, April 15, 2013

	0415UpLo1	0415UpLo2	0415UpLo3	0415ctr1	0415ctr2	0415ctr3	0415van1	0415van2	0415van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	0.715	0.678	<	0.683	<	<	<	<	<	0.692	0.020	0.029	0.038			
acenaphthene	0.934	0.979	1.127	0.919	0.912	1.023	0.494	0.507	0.530	0.825	0.245	0.297	0.100	0.065	0.036	0.073
fluorene	2.19	1.96	0.997	0.726	1.28	1.19	<	0.883	1.25	1.31	0.513	0.391	0.369	0.281	0.245	0.310
phenanthrene	16.40	12.60	15.12	8.16	14.5	10.7	7.77	7.07	6.61	11.0	3.787	0.344	0.131	0.288	0.082	0.174
anthracene	nd	nd	nd	nd	nd	nd	<	nd	nd							
fluoranthene	2.71	2.53	2.83	1.16	2.17	1.64	1.22	1.03	1.45	1.86	0.710	0.381	0.057	0.306	0.172	0.156
pyrene		1.75	1.68	0.035	0.879	1.34	0.665	1.02	0.815	1.02	0.565	0.552	0.029	0.883	0.216	0.271
retene	4.11	3.25	4.02	1.25	3.15	2.57	1.86	3.47	1.75	2.82	1.02	0.363	0.125	0.420	0.409	0.285
total g-p PAH	**27.0**	**23.7**	**25.7**	**12.9**	**22.9**	**18.5**	**12.0**	**14.0**	**12.4**	**18.8**	**6.16**	**0.327**	**0.066**	**0.277**	**0.082**	**0.137**
benzo(a)anthracene	0.214	0.191	0.200	<	0.161	0.170	<	<	<	0.187	0.022	0.116	0.058	0.039		
chrysene+triphenylene	0.330	0.277	0.317	<	0.273	<	<	<	<	0.299	0.028	0.095	0.089			
benzo(b)fluoranthene	<	0.549	1.048	<	<	<	<	0.567	<	0.722	0.283	0.392	0.442			
benzo(k)fluoranthene	<	<	<	<	<	<	<	<	<							
benzo(e)pyrene	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(a)pyrene	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
indeno(1,2,3-cd)pyrene	Nd	nd	nd	nd	nd	<	nd	nd	nd							
dibenz(a,h)anthracene	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(ghi)perylene	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
total p-p PAH	**0.544**	**1.01**	**1.56**	**0.000**	**0.434**	**0.170**	**0.000**	**0.567**	**0.000**	**0.478**	**0.532**	**1.11**	**0.490**	**1.09**	**1.73**	**0.738**
total PAH	**27.6**	**24.7**	**27.3**	**12.9**	**23.4**	**18.7**	**12.0**	**14.5**	**12.4**	**19.3**	**6.5**	**0.3**	**0.059**	**0.286**	**0.106**	**0.141**

Table S.5b – Measured concentrations (ng/L SWE) and CVs for pesticides, April 15, 2013

	0415UpLo1	0415UpLo2	0415UpLo3	0415ctr1	0415ctr2	0415ctr3	0415van1	0415van2	0415van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	<	nd	<	<	<	<	nd	<	<							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	2.273	nd	nd	nd	nd	nd	nd	nd							
opDDT	nd	2.733	nd	nd	nd	nd	nd	nd	nd							
ppDDT	nd	<	nd	<	<	<	<	<	<							
total DDT	**0.000**	**5.005**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.556**	**1.66**	**3.000**	**1.73**			**1.73**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	0.254	0.234	0.268	<	<	<	<	0.264	0.238							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	<	nd	nd	nd	<	<	<	<	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.254**	**0.234**	**0.268**	**0.000**	**0.000**	**0.000**	**0.000**	**0.264**	**0.238**	**0.140**	**0.133**	**0.952**			**0.869**	
Trifluralin	<	<	<	<	<	<	<	<	<							
Triallate	0.419	0.375	<	nd	<	nd	nd	nd	<	0.397	0.031	0.078	0.078			
Metribuzin	0.510	0.468	<	<	0.383	0.358	nd	0.312	0.312	0.390	0.082	0.211	0.061	0.047	0.000	0.040
Heptachlor	0.560	0.494	0.584	0.477	0.446	0.405	0.350	0.318	0.336	0.441	0.096	0.219	0.085	0.081	0.048	0.074
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	1.58	1.51	1.85	1.23	1.24	1.19	1.20	1.11	1.15	1.34	0.250	0.186	0.109	0.023	0.039	0.063
cis-Chlordane	<	<	<	<	<	<	<	<	<							
trans-Chlordane	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	1.16	1.08	1.20	0.93	1.43	0.813	0.711	0.711	0.726	0.976	0.260	0.266	0.055	0.310	0.012	0.136
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	0.389							
Heptachlor epoxide	2.37	<	<	2.94	<	<	nd	<	nd	2.65	0.408	0.153				
total pesticides	**6.61**	**3.93**	**3.64**	**5.59**	**3.50**	**2.76**	**2.26**	**2.45**	**2.91**	**3.74**	**1.46**	**0.392**	**0.346**	**0.370**	**0.131**	**0.306**

Table S.6a – Measured concentrations (ng/L SWE) and CVs for PAHs, December 3, 2013

	1203UpLo1	1203UpLo2	1203UpLo3	1203ctr1	1203ctr2	1203ctr3	1203van1	1203van2	1203van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	0.951	<	<	0.776	0.833	0.831	<	<	<	0.848	0.074	0.087		0.039		
acenaphthene	<	<	<	<	<	<	nd	nd	nd							
fluorene	<	nd	<	<	<	<	nd	<	<							
phenanthrene	<	nd	<	<	nd	<	<	<	nd							
anthracene	nd	nd	<	nd	nd	nd	<	nd	<							
fluoranthene	<	<	22.2	<	<	<	1.200	1.765	<	8.395	11.975	1.427			0.270	
pyrene	<	0.651	<	0.295	<	<	<	1.335	1.117	0.849	0.467	0.550			0.125	
retene	<	<	15.8	<	<	<	<	11.4	<	13.6	3.11	0.228				
total g-p PAH	**0.951**	**0.651**	**38.0**	**1.07**	**0.833**	**0.831**	**1.20**	**14.5**	**1.11**	**6.58**	**12.6**	**1.91**	**1.62**	**0.152**	**1.37**	**1.48**
benzo(a)anthracene	<	nd	nd	<	<	<	<	<	<							
chrysene+triphenylene	<	<	0.741	<	<	<	0.392	0.704	0.316	0.538	0.216	0.400			0.437	
benzo(b)fluoranthene	<	nd	nd	<	<	<	<	<	<							
benzo(k)fluoranthene	<	nd	2.01	<	<	<	1.10	1.02	<	1.38	0.549	0.397			0.049	
benzo(e)pyrene	<	<	nd	<	<	<	<	nd	<							
benzo(a)pyrene	nd	nd	1.64	<	nd	1.53	<	<	<	1.59	0.074	0.046				
indeno(1,2,3-cd)pyrene	<	nd	2.85	<	<	<	<	nd	nd							
dibenz(a,h)anthracene	<	<	8.21	<	<	<	<	<	<							
benzo(ghi)perylene	<	<	Nd	<	<	<	<	nd	<							
total p-p PAH	**0.000**	**0.000**	**15.4**	**0.000**	**0.000**	**1.53**	**1.49**	**1.73**	**0.316**	**2.28**	**5.00**	**2.19**	**1.73**	**1.73**	**0.642**	**1.54**
total PAH	**0.951**	**0.651**	**53.5**	**1.07**	**0.833**	**2.36**	**2.69**	**16.2**	**1.43**	**8.86**	**17.4**	**1.97**	**1.65**	**0.580**	**1.21**	**1.48**

Table S.6b – Measured concentrations (ng/L SWE) and CVs for pesticides, December 3, 2013

	1203UpLo1	1203UpLo2	1203UpLo3	1203ctr1	1203ctr2	1203ctr3	1203van1	1203van2	1203van3		event			intrasite		intersite
													UlpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	<	nd	nd	nd	nd	nd	nd	nd							
opDDT	nd	<	nd	nd	nd	nd	nd	nd	nd							
ppDDT	nd	nd	nd	nd	nd	nd	<	1.891	nd							
total DDT	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**1.891**	**0.000**	**0.210**	**0.630**	**3.000**			**1.73**	**1.732**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	<	<	<	<	nd	<	nd	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	<	<	<	<	<	nd	<	<							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**					
Trifluralin	nd	<	nd	nd	nd	nd	nd	nd	nd							
Triallate	nd	<	0.328	nd	nd	nd	nd	nd	nd							
Metribuzin	0.369	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor	Nd	nd	nd	nd	nd	nd	nd	nd	nd							
Dacthal	Nd	<	<	nd	nd	nd	nd	nd	nd	0.097						
Chlorpyrifos	0.975	2.69	<	<	<	<	<	<	<							
cis-Chlordane	3.34	<	<	<	<	<	2.63	<	2.98							
trans-Chlordane	<	<	<	<	<	<	<	<	<							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	<							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Dieldrin	0.190	nd	0.198	0.160	0.166	0.166	0.148	0.192	0.170							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	Nd							
Heptachlor epoxide	nd	nd	nd	nd	nd	nd	nd	nd	Nd							
total pesticides	**3.35**	**<**	**nd**	**1.85**	**2.29**	**2.20**	**2.63**	**2.48**	**2.32**	**2.45**	**0.466**	**0.191**		**0.108**	**0.063**	

Table S.7a– Measured concentrations (ng/L SWE) and CVs for PAHs, December 7, 2013

	1207UpLo1	1207UpLo2	1207UpLo3	1207ctr1	1207ctr2	1207ctr3	1207van1	1207van2	1207van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	<	<	<	<	<	<	<	<	<							
acenaphthene	nd	<	<	nd	nd	nd	<	<	<							
fluorene	<	<	<	<	<	<	<	<	<							
phenanthrene	<	<	<	<	<	<	<	<	<							
anthracene	<	nd	<	<	<	nd	nd	nd	<							
fluoranthene	1.76	nd	1.47	nd	nd	nd	1.52	15.2	1.65	4.33	6.11	1.41	0.126		1.28	
pyrene		nd	nd		nd	0.829		0.700	2.202	1.244	0.833	0.669			0.732	
retene	12.6	3.47	10.6	<	7.49	10.0	2.68	15.9	2.84	8.23	4.95	0.602	0.542	0.207	1.06	0.574
total g-p PAH	**14.4**	**3.47**	**12.1**	**0.000**	**7.49**	**10.8**	**4.21**	**31.9**	**6.70**	**10.1**	**9.34**	**0.922**	**0.578**	**0.909**	**1.07**	**0.877**
benzo(a)anthracene	<	nd	nd	nd	nd	nd	nd	nd	nd							
chrysene+triphenylene	0.689	nd	0.544	nd	0.408	nd	0.278	0.409	0.337	0.444	0.149	0.337	0.166		0.193	
benzo(b)fluoranthene	1.14	1.06	nd	nd	nd	nd	0.849	nd	0.708	0.940	0.199	0.211	0.057		0.128	
benzo(k)fluoranthene	1.41	<	<	nd	<	nd	1.03	<	1.50	1.317	0.251	0.190			0.264	
benzo(e)pyrene	<	nd	nd	nd	nd	nd	<	<	<							
benzo(a)pyrene	<	1.10	<	<	<	1.57	<	1.21	<	1.29	0.242	0.187				
indeno(1,2,3-cd)pyrene	0.660	nd	nd	nd	nd	0.672	<	<	<	0.666	0.009	0.013				
dibenz(a,h)anthracene	2.34	1.86	1.65	<	1.30	1.48	<	nd	<	1.72	0.399	0.231	0.181	0.091		
benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	<	nd	<							
total p-p PAH	**6.24**	**4.02**	**2.19**	**0.000**	**1.71**	**3.72**	**2.16**	**1.62**	**2.55**	**2.69**	**1.78**	**0.661**	**0.489**	**1.029**	**0.221**	**0.540**
total PAH	**20.6**	**7.49**	**14.3**	**0.000**	**9.20**	**14.6**	**6.37**	**33.5**	**9.25**	**12.8**	**9.73**	**0.758**	**0.466**	**0.931**	**0.911**	**0.751**

Table S.7b – Measured concentrations (ng/L SWE) and CVs for pesticides, December 7, 2013

	1207UpLo1	1207UpLo2	1207UpLo3	1207ctr1	1207ctr2	1207ctr3	1207van1	1207van2	1207van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	4.157	nd	nd	nd	nd							
ppDDD	nd	nd	2.39	3.40	<	4.37	nd	<	nd	3.39	0.990	0.292		0.178		
opDDT	nd	nd	2.78	3.84	2.29	7.67	nd	4.67	nd	4.25	2.12	0.499		0.601		
ppDDT	nd	nd	6.00	8.02	7.98	14.73	nd	nd	<	9.18	3.81	0.415		0.379		
total DDT	**0.000**	**0.000**	**11.1**	**15.2**	**14.4**	**26.7**	**0.000**	**4.67**	**0.000**	**8.03**	**9.51**	**1.18**	**1.73**	**0.367**	**1.732**	**0.666**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	nd	<	nd	nd	nd	<	<	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**					
Trifluralin	nd	nd	nd	nd	nd	nd	nd	0.097								
Triallate	nd	nd	nd	nd	nd	nd	0.283	nd								
Metribuzin	nd	nd	0.293	0.326	0.287	0.350	nd	nd		0.314	0.030	0.094		0.099		
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd								
Dacthal	<	<	<	<	<	<	<	<								
Chlorpyrifos	nd	nd	<	<	nd	nd	3.115	nd								
cis-Chlordane	<	<	<	<	<	<	<	<								
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd								
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd								
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd								
Endosulfan sulfate	0.188	nd	nd	nd	nd	nd	nd	nd								
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd								
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd								
Heptachlor epoxide	2.568	3.609	2.453	3.344	<	5.690	nd	nd		3.53	1.30	0.369	0.221	0.367		
total pesticides	**2.75**	**3.60**	**2.74**	**3.67**	**0.287**	**6.04**	**3.39**	**0.097**	**0.000**	**2.51**	**2.03**	**0.808**	**0.163**	**0.868**	**1.66**	**0.706**

Table S.8a– Measured concentrations (ng/L SWE) and CVs for PAHs, January 13, 2014

	0113UpLo1	0113UpLo2	0113UpLo3	0113ctr1	0113ctr2	0113ctr3	0113van1	0113van2	0113Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	<	<	<	<	<	<	<	<	<							
acenaphthene	nd	<	<	nd	nd	nd	nd	<	nd							
fluorene	nd	nd	nd	nd	nd	<	nd	<	nd							
phenanthrene	nd	nd	nd	nd	nd	nd	nd	<	<							
anthracene	<	nd	nd	nd	nd	nd	nd	nd	nd							
fluoranthene	1.71	1.53	1.39	0.430	nd	nd	nd	nd	0.480	1.11	0.609	0.549	0.104			
pyrene		<	<		<	<		<	<							
retene	<	<	<	nd	nd	nd	nd	<	1.80							
total g-p PAH	**1.71**	**1.53**	**1.39**	**0.430**	**0.000**	**0.000**	**0.000**	**0.000**	**2.28**	**0.817**	**0.910**	**1.11**	**0.104**	**1.73**	**1.73**	**0.705**
benzo(a)anthracene	nd	nd	nd	nd	nd	nd	nd	<	<							
chrysene+triphenylene	nd	<	<	<	<	<	<	<	<							
benzo(b)fluoranthene	0.964	1.05	0.550	0.415	<	<	<	0.466	0.464	0.652	0.281	0.431	0.314		0.002	
benzo(k)fluoranthene	<	<	<	<	<	<	<	<	<							
benzo(e)pyrene	<	<	<	<	<	<	<	<	nd							
benzo(a)pyrene	nd	Nd	nd	nd	nd	nd	nd	nd	nd							
indeno(1,2,3-cd)pyrene	<	<	<	<	<	<	nd	<	nd							
dibenz(a,h)anthracene	<	<	<	nd	nd	nd	<	<	<							
benzo(ghi)perylene	<	<	<	<	<	<	<	<	nd							
total p-p PAH	**0.964**	**1.05**	**0.550**	**0.415**	**0.000**	**0.000**	**0.000**	**0.466**	**0.464**	**0.435**	**0.395**	**0.908**	**0.314**	**1.73**	**0.866**	**0.595**
total PAH	**2.67**	**2.58**	**1.94**	**0.845**	**0.000**	**0.000**	**0.000**	**0.466**	**2.75**	**1.25**	**1.22**	**0.979**	**0.167**	**1.73**	**1.37**	**0.628**

Table S.8b– Measured concentrations (ng/L SWE) and CVs for pesticides, January 13, 2014

	0113UpLo1	0113UpLo2	0113UpLo3	0113ctr1	0113ctr2	0113ctr3	0113van1	0113van2	0113Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	<	<	nd	nd	nd	nd	nd	<	nd							
opDDT	<	<	nd	nd	nd	nd	nd	<	nd							
ppDDT	<	<	<	nd	nd	nd	nd	<	<							
total DDT	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	nd	<	nd	nd	nd	<	<	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Trifluralin	nd	nd	nd	nd	nd	0.148	nd	nd	nd							
Triallate	nd	nd	nd	nd	nd	0.401	nd	nd	nd							
Metribuzin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor	nd	nd	nd	nd	nd	0.310	nd	nd	nd							
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	nd	<	<	<	<	<	<	<	<							
cis-Chlordane	<	<	<	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	0.382	nd	nd	nd							
Endosulfan sulfate	0.093	nd	0.087	0.093	0.070	0.195	0.077	0.098	0.087	0.100	0.039	0.395	0.045	0.557	0.124	0.274
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	nd	nd	nd	1.18	nd	3.23	1.18	1.55	0.983	1.63	0.923	0.567		0.655	0.234	
total pesticides	**0.093**	**0.000**	**0.087**	**1.28**	**0.070**	**4.67**	**1.26**	**1.65**	**1.07**	**1.13**	**1.47**	**1.30**	**0.867**	**1.19**	**0.224**	**0.806**

Table S.9a– Measured concentrations (ng/L SWE) and CVs for PAHs, January 30, 2014

	0130UpLo1	0130UpLo2	0130UpLo3	0130Van1	0130Van2	0130Van3		event			intrasite		intersite
										UpLo	Ctr	Van	
							mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	0.966	0.816	0.844	0.842	0.786	<	0.851	0.068	0.080		0.091	0.048	
acenaphthene	<	0.826	1.24	<	1.36	<	1.14	0.283	0.247		0.288		
fluorene	nd	<	<	<	<	<							
phenanthrene	<	<	<	<	2.079	<							
anthracene	nd	nd	<	nd	nd	nd							
fluoranthene	<	0.859	<	1.81	2.02	1.64	1.08	0.737	0.678			0.104	
pyrene		1.38	1.27		1.17	1.33	1.29	0.089	0.069		0.058	0.087	
retene	<	<	<	<	<	<							
total g-p PAH	**0.966**	**3.888**	**3.369**	**2.659**	**7.43**	**2.978**	**2.30**	**1.994**	**0.867**	**0.427**	**0.569**	**0.613**	**0.596**
benzo(a)anthracene	<	<	<	<	<	<							
chrysene+triphenylene	0.739	0.556	<	0.704	0.629	0.625	0.651	0.072	0.111		0.200	0.068	
benzo(b)fluoranthene	<	<	<	<	<	<	0.257	0.182	0.706				
benzo(k)fluoranthene	2.05	1.58	1.41	2.17	1.81	1.53	1.752	0.290	0.165		0.197	0.161	
benzo(e)pyrene	<	<	<	<	<	<							
benzo(a)pyrene	nd	nd	<	<	nd	nd							
indeno(1,2,3-cd)pyrene	<	<	<	<	<	<							
dibenz(a,h)anthracene	nd	nd	nd	<	nd	nd							
benzo(ghi)perylene	<	<	<	<	0.670	<							
total p-p PAH	**2.79**	**2.14**	**1.41**	**2.82**	**3.11**	**2.15**	**1.60**	**1.00**	**0.623**	**0.558**	**0.326**	**0.182**	**0.248**
total PAH	**2.79**	**2.14**	**1.41**	**2.82**	**3.11**	**2.15**	**1.71**	**0.91**	**0.537**	**0.452**	**0.326**	**0.182**	**0.294**

Table S.9b– Measured concentrations (ng/L SWE) and CVs for pesticides, January 30, 2014

	0130UpLo1	0130UpLo2	0130UpLo3	0130Van1	0130Van2	0130Van3		event			intrasite		intersite
										UpLo	Ctr	Van	
							mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	nd	nd							
ppDDD	<	nd	nd	nd	<	nd							
opDDT	nd	nd	nd	nd	<	nd							
ppDDT	nd	1.111	<	<	<	<							
total DDT	**0.000**	**1.11**	**0.000**	**0.000**	**0.000**	**0.000**	**0.185**	**0.454**	**2.45**		**1.73**		
Hexachlorobenzene	nd	nd	nd	nd	nd	nd							
a-HCH	<	<	<	<	<	<							
b-HCH	nd	nd	nd	nd	nd	nd							
g-HCH	<	<	<	<	<	<							
d-HCH	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Trifluralin	nd	nd	nd	nd	nd	nd							
Triallate	nd	0.351	nd	nd	nd	nd	0.351						
Metribuzin	nd	nd	nd	nd	nd	nd							
Heptachlor	nd	nd	nd	nd	nd	nd							
Dacthal	<	<	<	<	<	<							
Chlorpyrifos	<	<	<	<	<	<							
cis-Chlordane	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.084	0.196	0.212	0.198	0.190	0.189	0.178	0.047	0.262	0.690	0.423	0.026	0.325
Dieldrin	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	1.28	3.65	4.15	2.63	2.89	2.75	2.89	0.987	0.341	0.671	0.507	0.048	
total pesticides	**1.3**	**4.20**	**4.37**	**2.83**	**3.08**	**2.94**	**3.13**	**1.09**	**0.348**	**0.657**	**0.510**	**0.044**	**0.329**

Table S.10a– Measured concentrations (ng/L SWE) and CVs for PAHs, February 7, 2014

	0207UpLo1	0207UpLo2	0207UpLo3	0207ctr1	0207ctr2	0207ctr3	0207Van1	0207Van2	0207Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	<	<	<	nd	<	nd	<	nd	0.668							
acenaphthene	nd	nd	<	<	<	<	<	nd	<							
fluorene	<	<	<	<	<	<	<	<	<							
phenanthrene	<	<	<	<	<	<	<	10.6	<							
anthracene	<	nd	nd	nd	<	nd	nd	<	nd							
fluoranthene	9.05	2.23	3.79	1.20	<	1.68	1.79	2.04	2.00	2.97	2.56	0.863	0.711	0.234	0.067	0.480
pyrene	0.561	1.65	1.10	0.406	0.774	<	0.010	1.01	1.25	0.847	0.520	0.614	0.494	0.441	0.869	0.597
retene	3.51	3.41	4.52	3.01	<	3.20	4.42	4.60	4.56	3.90	0.682	0.174	0.161	0.044	0.021	0.074
total g-p PAH	**13.1**	**7.30**	**9.42**	**4.62**	**0.774**	**4.89**	**6.23**	**18.2**	**8.48**	**8.13**	**5.14**	**0.632**	**0.296**	**0.672**	**0.583**	**0.478**
benzo(a)anthracene	nd	<	<	<	nd	<	<	<	<							
chrysene+triphenylene	<	0.425	0.354	<	nd	0.281	0.420	0.440	0.355	0.379	0.061	0.160	0.128		0.110	
benzo(b)fluoranthene	<	4.96	0.737	0.709	0.716	0.991	<	<	<	1.62	1.87	1.15	1.05	0.199		
benzo(k)fluoranthene	0.990	2.07	3.15	<	<	<	1.61	1.87	1.88	1.92	0.707	0.367	0.522		0.087	
benzo(e)pyrene	<	1.74	4.43	<	<	<	9.35	6.70	26.2	9.69	9.66	0.997	0.616		0.751	
benzo(a)pyrene	1.70	1.31	1.81	<	<	<	2.06	5.19	1.25	2.2	1.488	0.669	0.163		0.735	
indeno(1,2,3-cd)pyrene	nd	nd	<	nd	nd	nd	<	nd	nd							
dibenz(a,h)anthracene	1.67	2.39	2.89	<	<	0.641	2.340	3.00	1.76	2.10	0.817	0.389	0.264		0.263	
benzo(ghi)perylene	<	0.431	0.448	<	<	<	<	<	<	0.439	0.012	0.028	0.028			
total p-p PAH	**4.36**	**13.3**	**13.8**	**0.709**	**0.716**	**1.91**	**15.7**	**17.2**	**31.4**	**11.0**	**10.2**	**0.924**	**0.507**	**0.623**	**0.404**	**0.444**
total PAH	**17.4**	**20.6**	**23.2**	**5.33**	**1.49**	**6.80**	**22.0**	**35.5**	**39.9**	**19.1**	**13.1**	**0.687**	**0.141**	**0.604**	**0.287**	**0.260**

Table S.10b– Measured concentrations (ng/L SWE) and CVs for pesticides February 7, 2014

	0207UpLo1	0207UpLo2	0207UpLo3	0207ctr1	0207ctr2	0207ctr3	0207Van1	0207Van2	0207Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	<	nd	nd	nd	nd	nd	nd	nd							
opDDD	4.39	<	1.87	nd	nd	nd	<	nd	nd	3.13	1.78	0.569	0.569			
ppDDD	<	<	<	<	2.27	3.45	<	<	<	2.86	0.833	0.291		0.291		
opDDT	1.43	<	1.47	2.21	2.16	2.39	<	2.19	<	1.97	0.412	0.208	0.021	0.052		
ppDDT	2.80	<	<	2.65	1.91	2.13	<	6.03	3.47	3.17	1.50	0.476		0.172	0.382	
total DDT	**8.63**	**0.000**	**3.35**	**4.88**	**6.35**	**7.97**	**0.000**	**8.22**	**3.47**	**4.764**	**3.33**	**0.700**	**1.09**	**0.243**	**1.06**	**0.702**
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	<	<	1.17	<	<	0.480	<	<	<	0.827	0.490	0.593				
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	nd	nd	<	<	nd	nd	nd	nd	nd							
d-HCH	nd	nd	<	<	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**1.17**	**0.000**	**0.000**	**0.480**	**0.000**	**0.000**	**0.000**	**0.18**	**0.404**	**2.19**				
Trifluralin	nd	nd	0.111	<	nd	nd	nd	nd	nd							
Triallate	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Metribuzin	nd	0.377	0.374	0.327	nd	nd	0.417	<	0.389	0.376	0.033	0.087	0.006		0.051	
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	<	nd	<	<	nd	nd	nd	nd	nd							
cis-Chlordane	nd	<	<	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.174	0.182	0.173	nd	nd	0.161	0.192	0.203	0.229	0.188	0.022	0.120	0.025		0.091	
Dieldrin	3.13	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	2.28	2.66	2.49	3.80	3.60	2.71	3.15	nd	3.80	3.06	0.611	0.199	0.078	0.172	0.132	0.132
total pesticides	**5.59**	**3.22**	**3.15**	**4.13**	**3.60**	**2.88**	**3.76**	**0.203**	**4.41**	**3.44**	**1.46**	**0.425**	**0.348**	**0.178**	**0.812**	**0.415**

Table S.11a– Measured concentrations (ng/L SWE) and CVs for PAHs, February 21, 2014

	0221UpLo1	0221UpLo2	0221UpLo3	0221ctr1	0221ctr2	0221ctr3	0221Van1	0221Van2	0221Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
acenaphthylene	<	nd	nd	nd	<	<	nd	nd	nd							
acenaphthene	<	nd	<	nd	<	<	<	nd	<							
fluorene	<	nd	<	nd	<	<	<	<	<							
phenanthrene	nd	<	<	nd	nd	nd	<	nd	<							
anthracene	nd	nd	nd	nd	nd	nd	nd	<	nd							
fluoranthene	<	<	<	<	<	<	<	<	<							
pyrene		nd	nd		nd	nd		nd	<							
retene	<	<	<	nd	nd	nd	<	nd	<							
total g-p PAH	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
benzo(a)anthracene	nd	nd	nd	nd	nd	<	nd	nd	<							
chrysene+triphenylene	nd	<	nd	<	nd	<	<	nd	<							
benzo(b)fluoranthene	nd	<	nd	nd	nd	<	nd	nd	nd							
benzo(k)fluoranthene	nd	<	nd	<	<	nd	<	<	<							
benzo(e)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
benzo(ghi)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total p-p PAH	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
total PAH	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							

Table S.11b– Measured concentrations (ng/L SWE) and CVs for pesticides, February 21, 2014

	0221UpLo1	0221UpLo2	0221UpLo3	0221ctr1	0221ctr2	0221ctr3	0221Van1	0221Van2	0221Van3		event			intrasite		intersite
													UpLo	Ctr	Van	
										mean	st dev	CV	CV	CV	CV	CV
opDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDE	nd	nd	nd	nd	nd	nd	nd	nd	nd							
opDDD	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDD	nd	nd	<	nd	nd	nd	nd	<	nd							
opDDT	nd	nd	nd	nd	nd	nd	nd	nd	nd							
ppDDT	<	<	nd	nd	<	<	<	nd	<							
total DDT	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd							
a-HCH	nd	nd	nd	nd	nd	nd	<	<	nd							
b-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
g-HCH	<	<	<	<	<	<	<	nd	nd							
d-HCH	nd	nd	nd	nd	nd	nd	nd	nd	nd							
total HCH/HCB	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**							
Trifluralin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Triallate	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Metribuzin	<	<	nd	<	<	<	nd	nd	nd							
Heptachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Dacthal	<	<	<	<	<	<	<	<	<							
Chlorpyrifos	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Chlordane	<	<	<	<	<	<	<	<	<							
trans-Chlordane	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan I	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan II	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Endosulfan sulfate	0.098	0.106	0.118	0.091	0.119	0.102	0.139	0.112	0.126	0.112	0.015	0.132	0.094	0.132	0.108	0.111
Dieldrin	nd	nd	nd	nd	nd	nd	nd	nd	nd							
cis-Nonachlor	nd	nd	nd	nd	nd	nd	nd	nd	nd							
Heptachlor epoxide	nd	nd	nd	1.35	1.36	2.08	nd	nd	nd	1.59	0.418	0.262				
total pesticides	**0.098**	**0.106**	**0.118**	**1.446**	**1.48**	**2.18**	**0.139**	**0.112**	**0.126**	**0.645**	**0.820**	**1.27**	**0.094**	**0.245**	**0.108**	**0.228**

Table S.16 – n, r-critical (p>0.95) and r values for Soure Region Impact Factor Correlations

	n	r-crit for p=0.095	Aisa	Siberia	British Columbia	Washington	Oregon	urban Oregon	Willamette Valley	Eastern Or & WA
gas-phase PAH	70	0.2351	-0.199	0.234	-0.297	-0.292	0.014	0.203	0.203	
particulate-phase PAH	50	0.2784	-0.311	0.098	0.265	0.010	0.010	-0.330	-0.330	
total PAH	63	0.2479	-0.314	**0.266**	-0.140	-0.283	0.019	0.068	0.068	
phenanthrene	38	0.3197	0.054	0.226	-0.337	-0.350	-0.169	-0.188	-0.188	
floufanthene	61	0.2519	-0.115	-0.089	**0.495**	-0.350	-0.169	-0.188	-0.188	
pyrene	56	0.2630	0.054	0.226	-0.337	**0.770**	**0.501**	-0.080	-0.080	
retene	51	0.2757	-0.401	0.020	0.517	**0.513**	**0.371**	-0.084	-0.084	
total pesticides	74	0.2286	-0.252	-0.276	**0.488**	**0.293**	**0.519**	0.013	-0.084	**0.293**
endosulfan	73	0.2302	-0.401	0.020	**0.517**	**0.513**	**0.371**	-0.084	0.013	**0.513**
heptachlor epoxide	47	0.2873	-0.172	0.076	0.069	0.091	0.227	0.216	0.216	0.091

Table S.1 - Quantitation ion (Q1) and qualifier ions (Q2 and Q3) for all analytes, surrogates and internal standards - Electron Ionization.

	m/z				m/z		
target compounds	**Q1**	**Q2**	**Q3**		**Q1**	**Q2**	**Q3**
EPTC	128	132	189	benzo(k)fluoranthene	252	250	253
etridiazole	211	213	183	benzo(e)pyrene	252	250	253
acenapthylene	152	151	76	benzo(a)pyrene	252	250	253
acenaphthene	154	153	152	indeno (123-C.D)pyrene	276	274	277
fluorene	166	165	163	dibenz[a,h]anthracene	278	276	279
propachlor	120	176	93	benzo[ghi]perylene	276	274	277
atrazine desiosopropyl	173	175	158				
atrazine desethyl	172	174	187				
carbofuran	164	149	131				
simazine	201	203	186	**surrogates and**			
atrazine	200	202	215	**internal standards**	**Q1**	**Q2**	**Q3**
phenanthrene	178	176	179	EPTC-d14	142	203	201
diazinon	304	199	137	acenaphthene-d10	164	162	161
anthracene	178	176	179	fluorene-d10	1S76	174	173
triallate	268	270	272	atrazine-d5	205	220	218
acetochlor	146	162	223	phenanthrene - d10	188	189	187
methyl parathion	263	125	109	diazinon-d10	314	138	136
alachlor	188	160	237	acetochlor-d11	173	245	175
malathion	173	158	127	alachlor - d13	200	251	253
metolachlor	162	238	240	methyl parathion-d6	269	115	117
cyanazine	225	240	227	malthion-d6	174	131	133
parathion	291	155	109	parathion - d10	115	117	113
fluoranthene	202	200	203	fluoranthene-d10	212	213	211
opDDE	318	320	316	pyrene-d10	212	213	211
pyrene	202	200	203	ppDDEd8	326	324	322
ppDDE	318	316	320	ppDDT-d8	243	245	241
opDDD	235	237	165	triphenylene-d12	240	241	238
retene	219	234	204	benzo(k)fluoranthene-d12	264	265	263
ppDDD	235	237	165	benzo(a)pyrene-d12	264	265	263
opDDT	235	237	165	benzo(ghi)perylene-d12	288	289	286
ethion	231	153	384				
ppDDT	235	237	165				
benzo(a)anthracene	228	226	229				
methoxychlor	227	228	274				
chrysene and triphenylene	228	226	229				
benzo(b)fluoranthene	252	250	253				

Table S.2 -Quantitation ion (Q1) and qualifier ions (Q2 and Q3) for all analytes, surrogates and internal standards - Electron Capture Negative Ionization.

	m/z				m/z		
target compounds	**Q1**	**Q2**	**Q3**	**surrogates and internal standards**	**Q1**	**Q2**	**Q3**
trifluralin	335	336	305	PCB-138-13C	372	374	370
alpha-HCH	71	73	70	trifluralin-d14	349	350	319
HCB	284	286	282	HCB-13C	294	292	290
beta-HCH	71	73	70	Lindane-d6	72	74	263
gamma-HCH	71	73	70	chlorpyrifos-d10	322	324	214
delta-HCH	71	253	255	endosulfan I - d4	376	378	374
triallate	160	161	104	endosulfan II-d4	414	412	410
metribuzin	198	199	184				
heptachlor	268	266	300				
chlorpyrifos oxon	297	298	299				
chlorpyrifos	315	313	214				
DCPA [Dacthal]	332	333	334				
heptachlor epoxide	388	390	392				
trans-chlordane	410	408	412				
endosulfan I	404	372	370				
cis-chlordane	266	264	268				
trans-nonachlor	444	446	442				
dieldrin	346	348	380				
endrin	346	348	380				
endosulfan II	406	408	372				
cis-nonachlor	444	446	442				
endrin aldehyde	380	382	346				
endosulfan sulfate	386	388	422				

Table S.13a – ANOVA of site means of acenaphthylene

2013-02-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.157	1.052	0.066		
Column 2	3.000	2.536	0.845	0.223		
Column 3	3.000	1.739	0.580	0.048		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.337	2.000	0.168	1.499	0.296	5.143
Within Groups	0.674	6.000	0.112			
Total	1.010	8.000				

Table S.13b – ANOVA of site means of acenaphthene

2013-01-28						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	1.996	0.665	0.048		
Column 2	3.000	1.831	0.610	0.028		
Column 3	3.000	1.320	0.440	0.038		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.083	2.000	0.041	1.086	0.396	5.143
Within Groups	0.229	6.000	0.038			
Total	0.311	8.000				

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.252	1.084	0.030		
Column 2	3.000	3.638	1.213	0.114		
Column 3	3.000	2.529	0.843	0.014		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.211	2.000	0.106	2.015	0.214	5.143
Within Groups	0.315	6.000	0.052			
Total	0.526	8.000				

Table S.13b (cont.) – ANOVA of site means of acenaphthene

2013-04-15

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	3.040	1.013	0.010		
Column 2	3.000	2.855	0.952	0.004		
Column 3	3.000	1.531	0.510	0.000		

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.452	2.000	0.226	46.888	0.000	5.143
Within Groups	0.029	6.000	0.005			
Total	0.481	8.000				

Table S.13c – ANOVA of site means of fluorine

2013-01-28

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	5.247	1.749	0.116	
Column 2	3.000	5.211	1.737	0.645	
Column 3	3.000	4.142	1.381	0.087	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.262	2.000	0.131	0.465	0.649	5.143
Within Groups	1.694	6.000	0.282			
Total	1.957	8.000				

2013-02-21

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	5.985	1.995	1.055	
Column 2	3.000	4.488	1.496	1.063	
Column 3	3.000	3.140	1.047	0.428	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.350	2.000	0.675	0.795	0.494	5.143
Within Groups	5.093	6.000	0.849			
Total	6.443	8.000				

Table S.13c (cont.) – ANOVA of site means of fluorine

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	5.736	1.912	0.648		
Column 2	3.000	3.973	1.324	0.127		
Column 3	3.000	4.150	1.383	0.139		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.628	2.000	0.314	1.030	0.412	5.143
Within Groups	1.828	6.000	0.305			
Total	2.456	8.000				

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	5.150	1.717	0.402		
Column 2	3.000	3.207	1.069	0.090		
Column 3	3.000	2.426	0.809	0.235		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.312	2.000	0.656	2.704	0.145	5.143
Within Groups	1.455	6.000	0.242			
Total	2.767	8.000				

Table S.13d – ANOVA of site means of phenanthrene

2013-01-28

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	45.497	15.166	7.795	
Column 2	3.000	45.946	15.315	25.704	
Column 3	3.000	33.511	11.170	5.685	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	33.167	2.000	16.583	1.270	0.347	5.143
Within Groups	78.369	6.000	13.061			
Total	111.536	8.000				

2013-02-21

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	45.982	15.327	84.629	
Column 2	3.000	39.268	13.089	29.888	
Column 3	3.000	30.063	10.021	12.727	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	42.576	2.000	21.288	0.502	0.629	5.143
Within Groups	254.488	6.000	42.415			
Total	297.063	8.000				

Table S.13d (cont) – ANOVA of site means of phenanthrene

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	50.641	16.880	21.429		
Column 2	3.000	40.627	13.542	4.598		
Column 3	3.000	36.577	12.192	6.837		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	34.945	2.000	17.472	1.595	0.278	5.143
Within Groups	65.729	6.000	10.955			
Total	100.673	8.000				

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	44.138	14.713	3.743		
Column 2	3.000	33.520	11.173	10.378		
Column 3	3.000	21.464	7.155	0.341		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	85.802	2.000	42.901	8.899	0.016	5.143
Within Groups	28.924	6.000	4.821			
Total	114.726	8.000				

Table S.13e – ANOVA of site means of fluoranthene

2013-01-28

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	5.796	1.932	0.318	
Column 2	3.000	4.507	1.502	0.297	
Column 3	3.000	3.344	1.115	0.064	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.003	2.000	0.501	2.214	0.190	5.143
Within Groups	1.358	6.000	0.226			
Total	2.361	8.000				

2013-02-21

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	5.097	1.699	0.600	
Column 2	3.000	4.012	1.337	0.568	
Column 3	3.000	4.268	1.423	0.457	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.214	2.000	0.107	0.198	0.826	5.143
Within Groups	3.250	6.000	0.542			
Total	3.464	8.000				

Table S.13e (cont.) – ANOVA of site means of fluoranthene

2013-03-21

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	SUPPORT
Column 1	3.000	11.938	3.979	0.246	
Column 2	3.000	15.161	5.054	0.141	
Column 3	3.000	15.283	5.094	0.564	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.398	2.000	1.199	3.785	0.086	5.143
Within Groups	1.901	6.000	0.317			
Total	4.299	8.000				

2013-04-15

Anova: Single Factor

SUMMARY

Groups	Count	Sum	Average	Variance	REJECT
Column 1	3.000	8.088	2.696	0.024	
Column 2	3.000	4.982	1.661	0.258	
Column 3	3.000	3.715	1.238	0.045	

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	3.375	2.000	1.688	15.489	0.004	5.143
Within Groups	0.654	6.000	0.109			
Total	4.029	8.000				

Table S.13e (cont.) – ANOVA of site means of fluoranthene

2014-02-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	15.080	5.027	12.784		
Column 2	3.000	3.005	1.002	0.652		
Column 3	3.000	5.843	1.948	0.017		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	26.578	2.000	13.289	2.963	0.127	5.143
Within Groups	26.906	6.000	4.484			
Total	53.484	8.000				

Table S.13f – ANOVA of site means of pyrene

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.201	1.067	0.426		
Column 2	3.000	2.213	0.738	0.050		
Column 3	3.000	1.734	0.578	0.018		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.373	2.000	0.186	1.132	0.383	5.143
Within Groups	0.989	6.000	0.165			
Total	1.362	8.000				

Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	2.495	0.832	0.074		
Column 2	3.000	1.727	0.576	0.204		
Column 3	3.000	2.201	0.734	0.369		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.100	2.000	0.050	0.233	0.799	5.143
Within Groups	1.293	6.000	0.215			
Total	1.393	8.000				

Table S.13f (cont.) – ANOVA of site means of pyrene

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	7.863	2.621	0.153		
Column 2	3.000	9.625	3.208	0.128		
Column 3	3.000	9.956	3.319	0.262		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.843	2.000	0.422	2.331	0.178	5.143
Within Groups	1.085	6.000	0.181			
Total	1.929	8.000				

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	5.141	1.714	0.001		
Column 2	3.000	3.402	1.134	0.056		
Column 3	3.000	2.854	0.951	0.014		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.951	2.000	0.475	19.977	0.002	5.143
Within Groups	0.143	6.000	0.024			
Total	1.094	8.000				

Table S.13f (cont.) – ANOVA of site means of pyrene

2014-02-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.627	1.209	0.165		
Column 2	3.000	1.729	0.576	0.127		
Column 3	3.000	3.402	1.134	0.014		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.717	2.000	0.359	3.514	0.098	5.143
Within Groups	0.612	6.000	0.102			
Total	1.330	8.000				

Table S.13g– ANOVA of site means of retene

2013-01-28						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	5.841	1.947	1.084		
Column 2	3.000	2.913	0.971	0.333		
Column 3	3.000	2.292	0.764	0.132		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.394	2.000	1.197	2.318	0.179	5.143
Within Groups	3.098	6.000	0.516			
Total	5.493	8.000				

2013-02-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.366	1.122	0.516		
Column 2	3.000	3.598	1.199	0.737		
Column 3	3.000	4.237	1.412	0.757		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.136	2.000	0.068	0.101	0.905	5.143
Within Groups	4.019	6.000	0.670			
Total	4.155	8.000				

Table S.13g (cont.) – ANOVA of site means of retene

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	8.447	2.816	0.217		
Column 2	3.000	10.409	3.470	2.096		
Column 3	3.000	6.752	2.251	0.648		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	2.233	2.000	1.117	1.132	0.383	5.143
Within Groups	5.920	6.000	0.987			
Total	8.154	8.000				

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		SUPPORT
Column 1	3.000	11.386	3.795	0.226		
Column 2	3.000	6.966	2.322	0.949		
Column 3	3.000	7.086	2.362	0.932		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.228	2.000	2.114	3.009	0.124	5.143
Within Groups	4.215	6.000	0.703			
Total	8.443	8.000				

Table S.13g (cont.) – ANOVA of site means of retene

2013-12-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	26.829	8.943	23.473		
Column 2	3.000	17.909	5.970	25.246		
Column 3	3.000	21.492	7.164	57.990		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	13.432	2.000	6.716	0.189	0.833	5.143
Within Groups	213.417	6.000	35.570			
Total	226.849	8.000				

2014-02-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	11.450	3.817	0.376		
Column 2	3.000	6.581	2.194	2.529		
Column 3	3.000	13.596	4.532	0.009		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	8.615	2.000	4.308	4.434	0.066	5.143
Within Groups	5.828	6.000	0.971			
Total	14.443	8.000				

Table S.13h– ANOVA of site means of chrysene+triphenylene

2013-01-28						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.670	0.223	0.011		
Column 2	3.000	0.489	0.163	0.008		
Column 3	3.000	0.339	0.113	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.018	2.000	0.009	1.476	0.301	5.143
Within Groups	0.037	6.000	0.006			
Total	0.056	8.000				
2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	2.208	0.736	0.005		
Column 2	3.000	2.850	0.950	0.005		
Column 3	3.000	2.714	0.905	0.005		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.076	2.000	0.038	7.609	0.023	5.143
Within Groups	0.030	6.000	0.005			
Total	0.106	8.000				

Table S.13h (cont.) – ANOVA of site means of chrysene+triphenylene

2014-02-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.892	0.297	0.027		
Column 2	2.000	0.394	0.197	0.014		
Column 3	3.000	1.216	0.405	0.002		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.053	2.000	0.027	1.857	0.249	5.786
Within Groups	0.072	5.000	0.014			
Total	0.125	7.000				

Table S.13i– ANOVA of site means of heptachlor

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.773	0.258	0.013		
Column 2	3.000	1.069	0.356	0.042		
Column 3	3.000	1.263	0.421	0.001		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.041	2.000	0.020	1.092	0.394	5.143
Within Groups	0.111	6.000	0.019			
Total	0.152	8.000				

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	1.638	0.546	0.002		
Column 2	3.000	1.328	0.443	0.001		
Column 3	3.000	1.004	0.335	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.067	2.000	0.034	27.206	0.001	5.143
Within Groups	0.007	6.000	0.001			
Total	0.074	8.000				

Table S.13j– ANOVA of site means of chlorpyrifos

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		REJECT
Column 1	3.000	4.957	1.652	0.032		
Column 2	3.000	3.675	1.225	0.001		
Column 3	3.000	3.475	1.158	0.002		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.431	2.000	0.215	18.340	0.003	5.143
Within Groups	0.070	6.000	0.012			
Total	0.501	8.000				

Table S.13k– ANOVA of site means of heptachlor epoxide

2013-01-28						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	7.814	2.605	1.619		
Column 2	3.000	13.380	4.460	0.417		
Column 3	3.000	10.423	3.474	4.500		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	5.171	2.000	2.586	1.187	0.368	5.143
Within Groups	13.071	6.000	2.179			
Total	18.242	8.000				

2013-12-03						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	2.000	4.505	2.252	2.411		
Column 2	3.000	6.342	2.114	0.052		
Column 3	3.000	7.429	2.476	0.025		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.200	2.000	0.100	0.195	0.829	5.786
Within Groups	2.565	5.000	0.513			
Total	2.765	7.000				

Table S.13k (cont.) – ANOVA of site means of heptachlor epoxide

2014-02-07						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	7.444	2.481	0.038		
Column 2	3.000	10.133	3.378	0.336		
Column 3	2.000	6.956	3.478	0.210		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.657	2.000	0.828	4.329	0.081	5.786
Within Groups	0.957	5.000	0.191			
Total	2.614	7.000				

Table S.13l– ANOVA of site means of endosulfan sulfate

2013-01-28						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.456	0.152	0.000		
Column 2	3.000	0.444	0.148	0.000		
Column 3	3.000	0.411	0.137	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.000	2.000	0.000	3.100	0.119	5.143
Within Groups	0.000	6.000	0.000			
Total	0.001	8.000				

2013-03-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.467	0.156	0.000		
Column 2	3.000	0.454	0.151	0.000		
Column 3	3.000	0.418	0.139	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.000	2.000	0.000	3.552	0.096	5.143
Within Groups	0.000	6.000	0.000			
Total	0.001	8.000				

Table S.13l (cont.) – ANOVA of site means of endosulfan sulfate

2013-04-15						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	3.460	1.153	0.004		
Column 2	3.000	3.174	1.058	0.108		
Column 3	3.000	2.147	0.716	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.318	2.000	0.159	4.271	0.070	5.143
Within Groups	0.223	6.000	0.037			
Total	0.541	8.000				

2013-12-03						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	2.000	0.388	0.194	0.000		
Column 2	3.000	0.494	0.165	0.000		
Column 3	3.000	0.510	0.170	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.001	2.000	0.001	2.627	0.166	5.786
Within Groups	0.001	5.000	0.000			
Total	0.002	7.000				

Table S.13l (cont.) – ANOVA of site means of endosulfan sulfate

2014-01-13						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.268	0.089	0.000		
Column 2	3.000	0.358	0.119	0.004		
Column 3	3.000	0.261	0.087	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.002	2.000	0.001	0.642	0.559	5.143
Within Groups	0.009	6.000	0.002			
Total	0.011	8.000				

2014-02-21						
Anova: Single Factor						
SUMMARY						
Groups	Count	Sum	Average	Variance		SUPPORT
Column 1	3.000	0.322	0.107	0.000		
Column 2	3.000	0.312	0.104	0.000		
Column 3	3.000	0.376	0.125	0.000		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.001	2.000	0.000	2.524	0.160	5.143
Within Groups	0.001	6.000	0.000			
Total	0.002	8.000				

Table S.14a – ANOVA of event means of total gas-phase PAH concentration

SUMMARY					
Groups	*Count*	*Sum*	*Average*	*Variance*	REJECT
0128	9.000	175.088	19.454	30.296	
0221	9.000	167.792	18.644	77.714	
0321	9.000	243.573	27.064	19.696	
0415	9.000	167.533	18.615	40.819	
1203	9.000	59.259	6.584	159.551	
1207	9.000	91.289	10.143	87.409	
0113	9.000	7.355	0.817	0.828	
0130	6.000	21.294	3.549	4.606	
0207	9.000	73.168	8.130	26.416	

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5253.691	8.000	656.711	12.711	0.000	2.076
Within Groups	3564.872	69.000	51.665			
Total	8818.563	77.000				

Table S.14b – ANOVA of event means of total particulate-phase PAH concentration

SUMMARY					
Groups	*Count*	*Sum*	*Average*	*Variance*	REJECT
0128	9	1.635076865	0.181675207	0.030541132	
0221	9	1.780153252	0.197794806	0.057060051	
0321	9	53.20645042	5.911827825	4.038561974	
0415	9	4.298106513	0.47756739	0.283393171	
1203	9	20.54462567	2.282736186	24.98981282	
1207	9	24.23639016	2.69293224	3.172542711	
0113	9	3.912394215	0.434710468	0.155723653	
0130	6	14.43338741	2.405564569	0.38870232	
0207	9	99.36187742	11.0402086	104.0774366	

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	922.922157	8	115.3652696	7.260415111	6.04961E-07	2.075706026
Within Groups	1096.384089	69	15.88962447			
Total	2019.306246	77				

Table S.14c – ANOVA of event means of total PAH concentration

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		REJECT
0128	9	176.7235467	19.63594963	31.69536687		
0221	9	169.5724518	18.84138353	81.05607207		
0321	9	296.7794404	32.97549338	19.17117433		
0415	9	171.8310375	19.0923375	45.90147664		
1203	9	79.80347809	8.867053121	305.0103874		
1207	9	115.5258192	12.83620214	94.69598132		
0113	9	11.26784278	1.251982531	1.502587025		
0130	6	35.72784328	5.954640546	5.642420986		
0207	9	172.5296838	19.16996487	173.2669277		
ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	6068.373514	8	758.5466892	8.656041184	4.2872E-08	2.075706026
Within Groups	6046.611891	69	87.6320564			
Total	12114.9854	77				

Table S.14d – ANOVA of event means of total pesticide concentration

Anova: Single Factor						
SUMMARY						
Groups	*Count*	*Sum*	*Average*	*Variance*		REJECT
0128	9.000	31.010	3.446	3.946		
0221	9.000	27.707	3.079	5.231		
0321	9.000	22.764	2.529	3.958		
0415	9.000	33.701	3.745	2.154		
1203	7.000	17.122	2.446	0.218		
1207	9.000	22.602	2.511	4.122		
0113	9.000	10.184	1.132	2.179		
0130	6.000	18.800	3.133	1.187		
0207	9.000	30.977	3.442	2.141		
0221	9.000	5.808	0.645	0.673		
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	82.449	9.000	9.161	3.393	0.002	2.007
Within Groups	202.469	75.000	2.700			
Total	284.918	84.000				

Table S.15 – Source Region Impact Factor Boundaries

	N	S	E	W
Asia	50	15	180	100
Siberia	70	50	180	100
Alaska	70	55	-140	-170
British Columbia	60	49	-115	-132
Washington	49	46	-117	-125
Oregon	46	42	-117	-125
urban Oregon	46	44	-122	-123.5
Eastern Oregon & Washington	49	45	-117	-120.5
California Central Valley	39.5	36	-119	-123

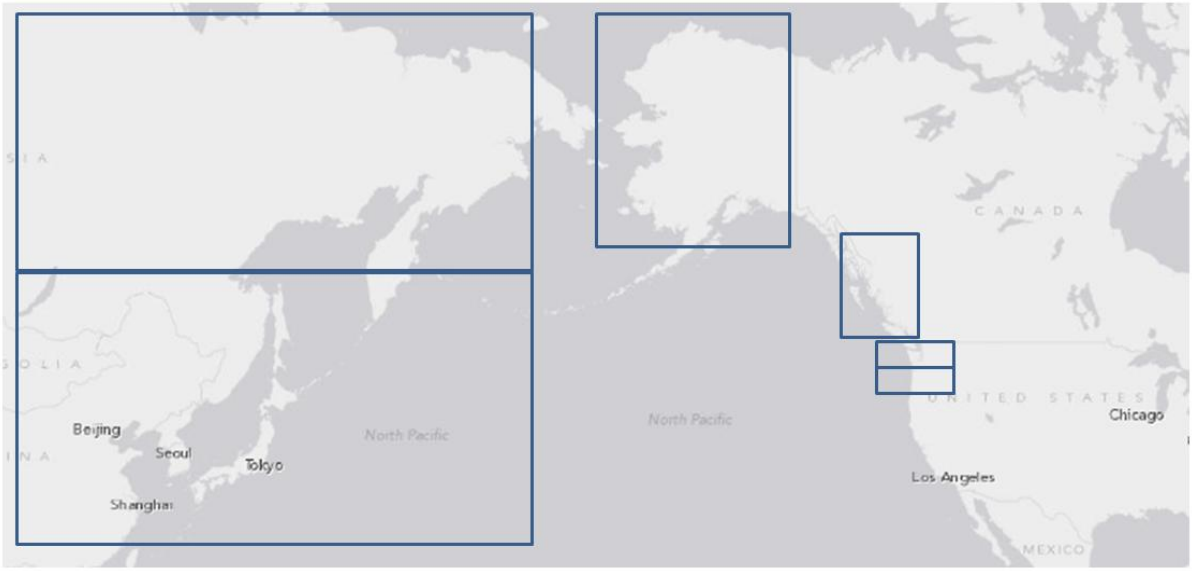

Figure S.1 – SRIF region locations.. Shown are the Asia, Siberia, Alaska, British Columbia, Washington and Oregon regions.

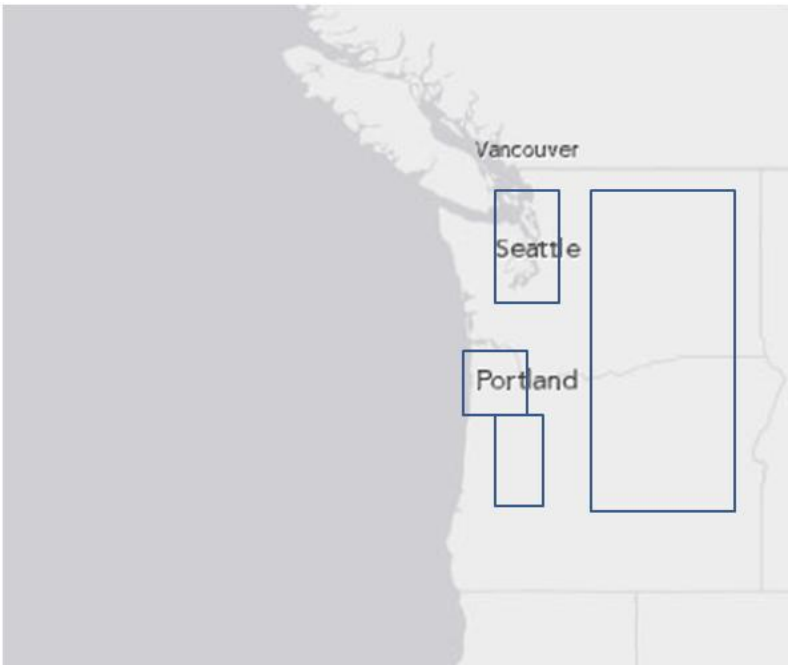

Figure S.1 – Local SRIF region locations. Shown are the urban Washington, urban Oregon, Willamette Valley and Eastern Washington-Oregon rregions.

Table S.16 – Pierson's correlation coefficients for meteorological conditions over the accumulation period.

	n	Rcrit	1/Tsnow	1/Tair	max. solar irradiance
gas-phase PAH	70	0.2351	0.0469	-0.2250	**0.4683**
particulate-phase PAH	50	0.2784	-0.1538	-0.1461	-0.0873
total PAH	63	0.2479	-0.0099	-0.2509	**0.3896**
phenanthrene	38	0.3197	**0.3784**	0.1271	0.2791
floufanthene	61	0.2519	0.0469	-0.2250	**0.4683**
pyrene	56	0.2630	0.1559	-0.1548	**0.5079**
retene	51	0.2757	-0.5306	-0.5829	0.0997
total pesticides	74	0.2286	-0.2728	-0.5069	0.0601
endosulfan	73	0.2302	0.0469	-0.2250	**0.4683**
heptachlor epoxide	47	0.2873	-0.0488	-0.2173	-0.2877