The Use of Lichen to Monitor Semivolatile Organic Compounds in High Elevation Ecosystems

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Chapter 1 – Introduction

Growing Concern for Long Range Transport of Pollutants

Semivolatile organic compounds (SOCs) are a class of organic compounds that can undergo volatilization into the atmosphere, where they can be transported by atmospheric currents and then deposited back to the Earth's surface, if they come into contact with colder environments such as high elevations or the arctic. The long range transport and deposition of SOCs to high elevation ecosystems is becoming more of a concern to the scientific community. Studies have shown that persistent organic pollutants (banned and current use), including DDTs, PCBs, endosulfans, and HCB, are found in many areas throughout the world. Many of these areas are remote with little or no direct sources of SOCs (1). The atmospheric transport and deposition of SOCs has predominantly been studied following the trend of low latitudes to high latitudes, a process known as global distillation: SOCs with higher vapor pressures are more likely to undergo global distillation than compounds with lower vapor pressures (1, 2). SOC deposition occurs through cold condensation in which SOCs precipitate and condense in colder environments, leading to elevated concentrations at deposition sites (3). A visual model of SOC sources, long range and regional transport, and their deposition to high elevation ecosystems is shown in Figure 1-1.

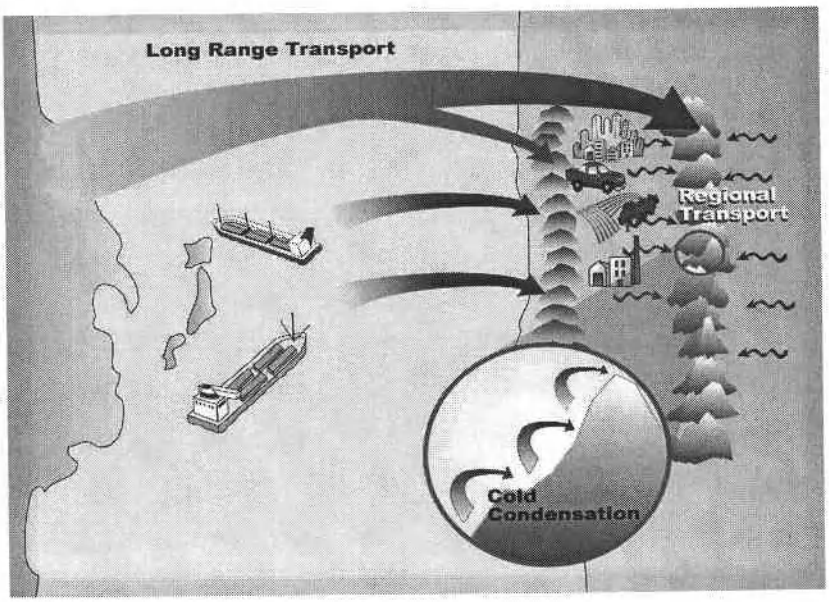


Figure 1-1: SOC sources and deposition.

Previous studies have shown accumulation of persistent organic pollutants in high elevation ecosystems. Concentrations of HCHs, PCBs, and Endosulfans were measured in conifer needles sampled from mountain areas of Alberta and British Columbia, Canada (4). Highly volatile compounds (subcooled liquid vapor pressure $P_L > 0.1$ at 25°C) showed increasing concentration with altitude and less volatile SOCs were either unrelated or inversely correlated with altitude demonstrating that alpine ecosystems accumulate these chemicals to the same degree that is observed in polar environments that are known to receive contaminants by long range transport (4). Further studies have revealed that, in the Canadian Rockies, deposition of SOCs is primarily due to long range transport and not local re-volatilization from vegetation and soil, and that air masses traveling over the Pacific Ocean and western Canada are being depleted of certain chemicals as a result of deposition onto vegetation (5). Figure 1-2 illustrates the pattern of concentrations being higher in the more western sites (5).

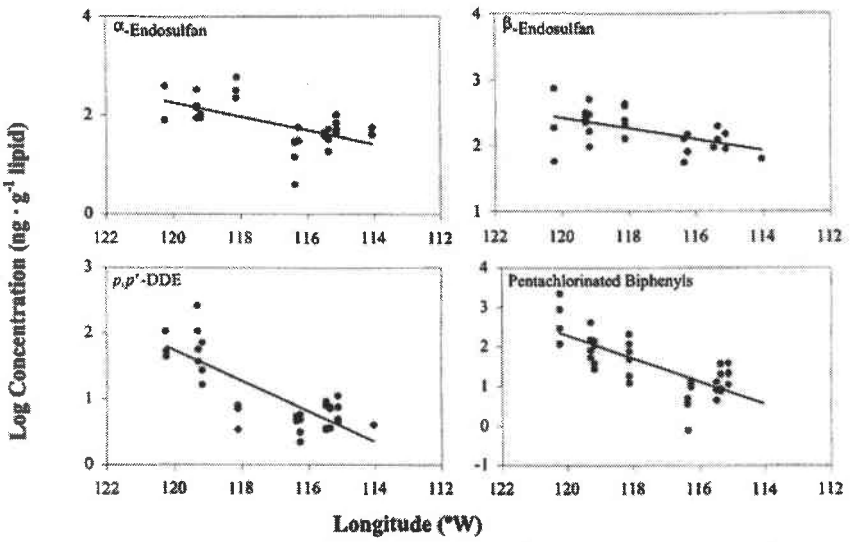


Figure 1-2: SOC concentration in conifer needles vs. longitude (Taken from reference 5)

Sources and Hazards of SOCs

The main sources of SOCs in this study, as shown above in Figure 1, are industrial, agricultural, and urban (6, 7). Industrial and urban sources contribute SOCs in the form of chlorinated flame retardants and electrical components (polychlorinated biphenyls, PCBs) and incomplete combustion products (polycyclic aromatic hydrocarbons, PAHs) (6, 7). Agricultural sources contribute SOCs in the form of banned and current use pesticides including, but not limited to, dichlorodiphenyltrichloroethane (DDT) and its degradation products, hexachlorocyclohexanes (HCHs), and endosulfans – I, II, and sulfate.

PCBs have been banned since the late 1970s, but because of their persistent nature and ability to accumulate in biological tissue (especially fatty tissue); they are still present in the environment and potentially pose some threat to humans (6-10). There are

209 different PCB congeners with varying human health effects (8, 10). Some PCBs have acute toxicity similar to dioxin, carcinogenicity, nerve toxicity, and the ability to mimic hormones (9, 10). Studies have shown that, because of the persistence of PCBs, they can be found in humans, as well as aquatic, terrestrial, and avian creatures (8).

Polycyclic aromatic hydrocarbons (PAHs) are one of the oldest known organic contaminants, because they are naturally occurring and result from the very simple process of burning organic matter. The largest anthropogenic sources of PAHs to humans are the combustion of fossil fuels in power plants, automobiles, and slash and burn agriculture (9, 10). The very act of combustion releases PAHs into the atmosphere, which makes them are large contributors to cancer and asthma in industrial and urban areas (9). PAHs like benzo[a]pyrene have some of the highest known levels of carcinogenicity (10). Although PAHs are not as persistent as other SOCs, the large volume at which they are emitted makes them of great concern.

Pesticides are always a potential risk to human health because of runoff from agricultural zones to drinking water sources. Compounds like dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), endosulfans, trifluralin, and others fall into this category (6, 10). Pesticide use is always a highly disputed issue, because of the need to balance human and ecosystem health with growing agricultural demands. Pesticide toxicity has resulted in many commonly used compounds being banned or restricted such as DDT and dieldrin (6, 10). Negative health effects from pesticides include problems associated with the digestive system, liver, nervous system, kidneys, reproductive system, and carcinogenic effects (10). Toxicity of DDT was recognized as early as 1962, and the continuing effort to identify other

persistent organic pollutants has designated some pesticides as dangerous to human and environmental health (11, 12).

Lichen as a Biomonitor

Lichens have been recognized as early as the 1860s, in Europe, as potential bio-indicators of air pollution (13). The absence of a protective cuticle layer, which can serve as a selective barrier (depending on the hydrophobicity of compound that is deposited) for higher plants, allows lichen to take in atmospheric compounds more easily. The lack of an internal transport mechanism allows compounds to be more stationary inside the lichen. The dependence on the atmosphere for nutrients, rather than the lithosphere, gives lichen a more active relationship with the environment. All of these characteristics are advantages that lichens have for monitoring airborne contaminants (14).

Historically, lichen have mostly been used to measure heavy metals and radionuclides, and have more recently been used to monitor persistent organic pollutants (14, 15). Lichen can grow to a very old age (decades to centuries) without shedding leaves or needles like higher plants (16). This gives a historical record of pollutant deposition. Lichen are also part of the diets of a variety of animals, including moose, caribou, mountain goat, grouse, wild turkey, and deer (17).

Persistent Organic Pollutants have been shown to bioaccumulate in aquatic food chains in the Great Lakes ecosystem for many years as a result of contamination (18). The recent concern of deposition of SOCs to polar and high elevation ecosystems has brought about bioaccumulation studies in these ecosystems. In Canada's central and western arctic regions, bioaccumulation of SOCs from lichen to Caribou to Wolf (Figure 1-3) has been observed, including compounds with K_{OW} values below 10^5, which were

not under consideration in management policies (15). For these reasons, measuring SOC concentrations in lichen can help one assess the potential risk these compounds pose through atmospheric transport, deposition, and potential biomagnification in the food chain (15).

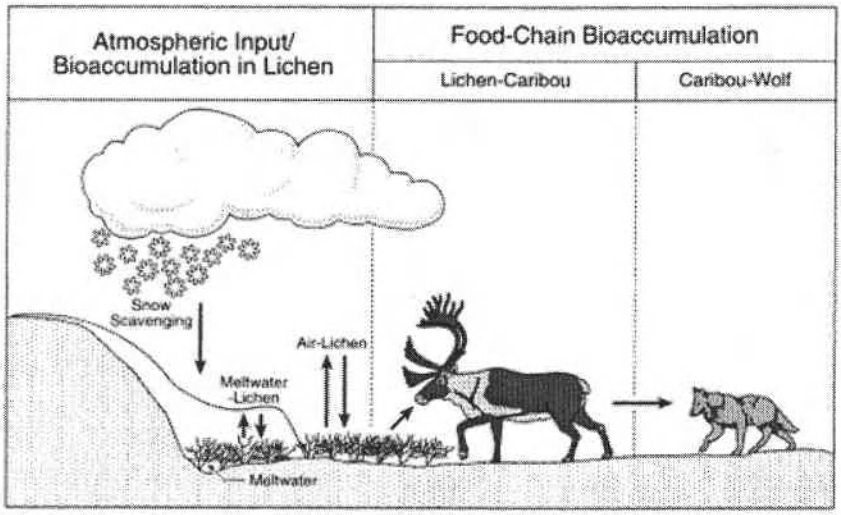


Figure 1-3: Conceptual image illustrating bioaccumulation (Taken from reference 15).

With so much interest in SOC concentrations in vegetation, the processes by which SOCs are taken into the plant have also been studied. There are three main processes by which plant uptake can occur: equilibrium partitioning between the vegetation and gas phase, kinetically limited gaseous deposition, and/or wet and dry particle bound deposition (19, 20). The process of cold condensation would fall under all three plant uptake routes. A plot illustrating each of these three processes is given in Figure 1-4 by using the SOC concentration in the gaseous phase (C_g), SOC concentration in the vegetation (C_V), and octanol-air partition coefficient (K_{OA}) (19).

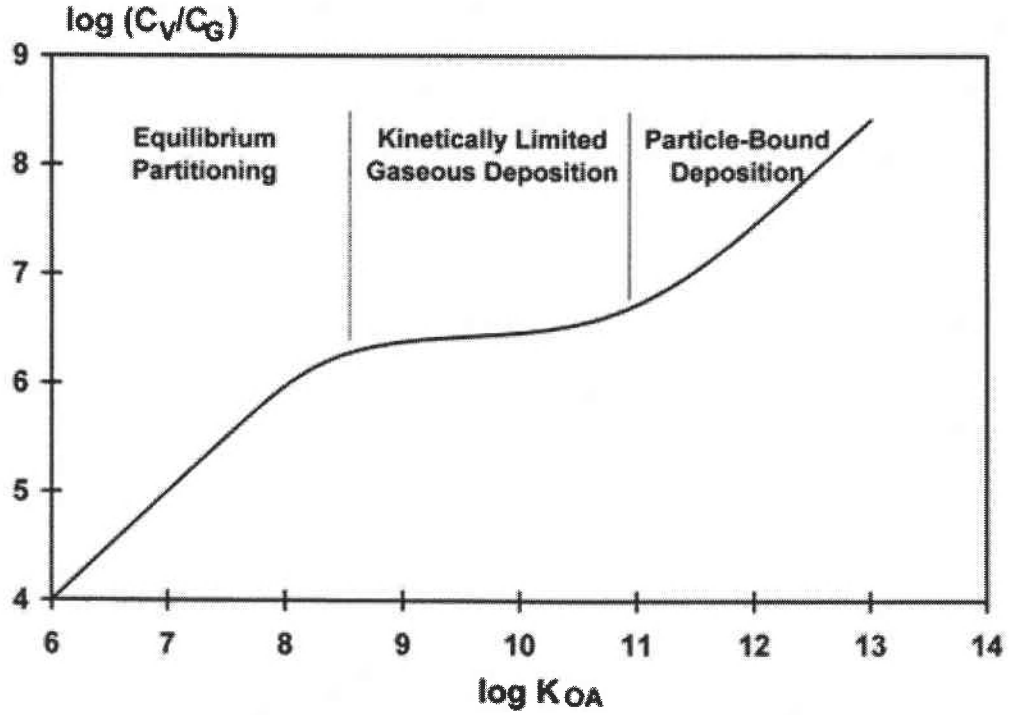


Figure 1-4: Illustrative plot of log(C_v/C_g) vs. log K_{OA} for identifying the primary process of plant uptake of more volatile SOCs (Taken from reference 19).

WACAP

The Western Airborne Contaminants Assessment Project (WACAP) has been developed to find out if a risk is posed to ecosystems and food webs in the western National Parks from long range transport of airborne contaminants (21). Airborne contaminants can pose threats to wildlife and humans through biomagnification of some compounds, described above, that can result in decreased reproductive success, stunted growth, interference with behavior, increased disease, and lower survival rates (21). Biomagnification can result in exposure of subsistence hunters and gatherers to airborne contaminants (21). Many institutions are involved in this effort, including the Environmental Protection Agency, U.S. Geological Survey, National Park Service, U.S.

Department of Agriculture - Forest Service, the University of Washington, and Oregon State University. The overall WACAP objectives are to (21):

1) Determine if contaminants are present in Western National Parks.
2) If present, determine where contaminants are accumulating (geographically and by elevation).
3) If present, determine which contaminants pose a potential ecological threat.
4) Determine which indicators appear to be the most useful to address contamination.
5) If present, determine the source of the air masses most likely to have transported contaminants to the National Parks.

Six national parks were selected in the western U.S. from Alaska to California, which are shown in Figure 1-5 (21).

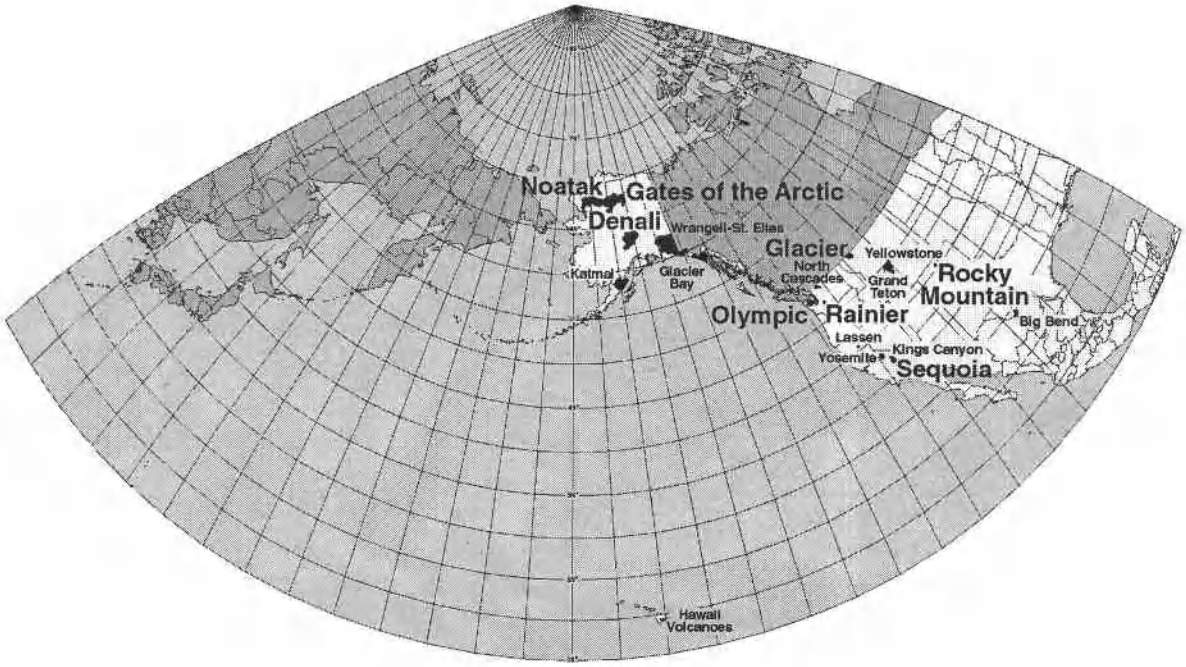


Figure 1-5: Spatial relationships among WACAP selected National Parks and other national Parks (Taken from reference 21).

A number of matrices will be analyzed from the WACAP sites, including snow, lake water, lake sediments, fish, moose, and vegetation (lichen, tree bark, and/or conifer needles). By analyzing lichen, as well as the other forms of vegetation under consideration, we hoped to determine which vegetation type(s) is best suited to meet the WACAP objectives.

Research Objectives

The specific objectives of this research were:

- To develop an analytical method to measure a wide range of SOCs in lichen.
- To measure SOCs in lichen using this analytical method.
- To determine if lichens are a suitable passive air sampler for WACAP sites.
- To compare the passive air sampling ability of lichen to conifer needles sampled in Sequoia National Park on a dry weight basis.

Chapter 2 – Manuscript I

Development of an Analytical Method for Measuring Semi-volatile Organic Compounds in Lichen

Abstract

To better understand the potential environmental impact of the long range atmospheric transport and deposition of semivolatile organic compounds (SOCs), lichen was to be used as a biomonitor in high elevation ecosystems. To effectively measure a large list of SOCs, with a wide range of physical and chemical properties a new analytical method was developed. An analytical method using accelerated solvent extraction, silica solid phase extraction clean up, and GC/MS analysis was used to measure the SOCs in lichen. We were unable to measure the more polar SOCs because of polar matrix interferences. The SOCs most likely to partition to vegetation were successfully measured using this new analytical method. In total, we were able to measure 36 out of 86 target SOCs in the lichen species *Hypogymnia inactiva*.

Introduction

The atmospheric transport and deposition of semivolatile organic compounds (SOCs) to high elevation ecosystems is becoming a potential human and ecosystem health concern in the scientific community. SOCs are a class of organic compounds that can undergo volatilization into the atmosphere and re-condense back to the surface of the earth, especially in cold climates like high elevations and polar regions (1-4). Some of these compounds are known to have many different negative human health and environmental effects (6-12). In order to assess the potential risk these compounds pose, it is important to understand their fate in the environment.

Lichen has been used as passive air samplers since the 1860s because of the absence of a cuticle layer and the ability to acquire much of their nutrition from the atmosphere (13). Historically, lichen have been primarily used to measure heavy metals (unlikely re-volatilization after deposition due to large molecular mass) and, more recently, have been used to monitor SOCs such as persistent organic pollutants (14,15). Because lichen can live to be very old, decades to centuries for some species, without shedding leaves or needles like higher plants, they provide a historical record of pollutant deposition (16). Lichen are also part of the diets of a variety of terrestrial animals. Measuring SOC concentrations in lichen can help one assess the potential risk these compounds pose through atmospheric transport, deposition, and potential biomagnification of SOCs in the terrestrial food chain (14,15).

Mary's Peak (Figure 1) was chosen as the sampling test site for the collection of lichen for analytical method development because it is the highest peak in elevation (4097 ft.) in Oregon's Coast Range and because of its close proximity of Oregon State University.

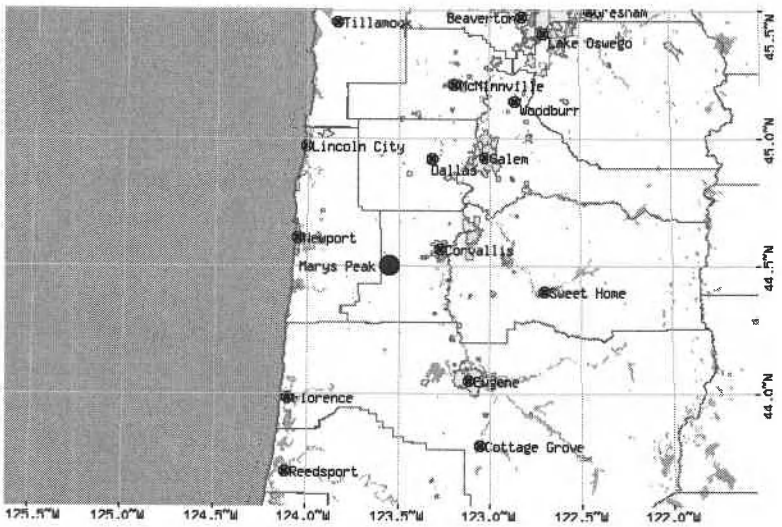


Figure 2-1: Mary's Peak Location.

Initially, the lichen species *Hypogymnia physodes* (Figure 2-2a) was expected to be present in the WACAP sampling sites in Sequoia National Park. *Hypogymnia physodes* was difficult to find in large quantities in our sampling test site at Mary's Peak. However, another species of *Hypogymnia* lichen was present in very large quantities: *Hypogymnia inactiva* (Figure 2-2b).

Figure 2-2; a: *Hypogymnia physodes*; b: *Hypogymnia inactiva*.

Because the two lichen species were very similar in thallus structure and texture (see Figure 2a,b), we decided that *Hypogymnia inactiva* would make an excellent substitute for *Hypogymnia physodes* for analytical method development. The analytical method developed using *Hypogymnia inactiva* was eventually used to measure SOCs in lichen collected from Sequoia National Park.

Materials and Methods

Samples were collected from Mary's Peak using clean nitrile gloves, clean kapak bags, the samples were transported on blue ice, and stored at the Simonich Environmental Laboratory at Oregon State University in a -20 C freezer. Twenty grams of lichen (wet weight) were loaded into a 100 ml accelerated solvent extraction (ASE) cell.

The lichen in ASE cell was spiked with target SOCs and extracted twice with dichloromethane (DCM) in the ASE at 125°C and 1500 psi. The two extracts were combined and spiked with surrogates (see Table 2-1) to give final ASE recoveries.

Initially, the goal of the target analyte spiked extractions was qualitative and not quantitative so target analytes and surrogates (Table 2-1) were spiked at high concentrations of 1 ug/20 g lichen sample. The surrogates added were stable isotope labeled analogs of the target SOCs so that we could track analyte loss during the analytical method and distinguish the surrogates from the target analytes based on their different mass to charge ratio. Following the spike, the extracts were solvent exchanged to hexane in a Zymark Turbovap II unit. The lichen extracts were never concentrated to dryness so that the SOC analytes would not volatilize.

The percent moisture was determined by drying approximately 3 g of lichen overnight at 108°C and then weighing again in the morning. The percent lipid was determined by removing 20 ml of lichen ASE extract and drying it overnight at 108°C to remove the extraction solvent and weighing the dry extracted lipid material in morning.

The lichen extracts were then extracted with water to remove polar matrix interferences by adding 100 ml Millipore water to the extracts, shaking them for 2 minutes and collecting the organic hexane layer. A second water extraction was sufficient to remove interferences and additional water extractions added little to this extract purification step. The water purified extracts were then concentrated to 3-4 ml. The remaining lichen matrix interferences were removed using Varian 20 g silica solid phase extraction (SPE) columns. Fifty mL of hexane:DCM (1:1) and fifty mL of DCM were used as elution solvents at a flow rate of 0.5 ml/second. Initially, to determine which target analytes eluted in which organic solvents from the silica SPE columns, target SOCs were spiked directly onto the SPE column and eluted with 50 mL

Hexane:DCM (4:1), Hexane:DCM (1:1), DCM, DCM:Ethyl Acetate (1:1), and Ethyl Acetate (EA) (Table 2-2).

The Hexane:DCM (1:1) and DCM SPE fractions were combined and concentrated to 300 uL and spiked with internal standards to give a concentration of 500 pg/uL in the extract. Ten microliters of the extract were taken from the concentrated fractions and diluted to 100 uL with DCM to improve the gas chromatographic separation. The diluted extracts were first analyzed on a Hewlett Packard 5890 Series II GC/FID to determine the total organic ion abundance in the sample. The diluted samples were then analyzed on an Agilent 6890 Series GC/5793 Network MS to identify and quantify the compounds present in the extract. The target analytes were measured with electron impact ionization (EI) and electron capture negative ionization (ECNI). The ECNI method was used for the halogenated, electronegative SOCs and the EI method was used for all other SOCs. Instrument parameters for the GC/EI-MS and GC/ECNI-MS methods including temperature programs and supporting information for the quantitation of each SOC using Electron Impact and Electron Capture Negative Ionization methods with selective ion monitoring (SIM) windows are given in Appendices A and B. The complete list of target SOCs, their surrogates and internal standards, and which ionization method they were measured with are given in Table 2-1.

Electron Impact Ionization	Electron Capture Negative Ionization
PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene **Pesticides and degradation products: o,p'-DDT***, p,p'DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Disulfoton, Demeton S, Ethion, Malathion*, Parathion and Parathion - methyl, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Triallate, Pebulate, EPTC, Disulfoton, Etridiazole, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine **Surrogates:** d_{10}-Fluorene, d_{10}-Phenanthrene, d_{10}-Pyrene, d_{12}-Triphenylene, d_{12}-Benzo[a]pyrene, d_{12}-Benzo[ghi]perylene, d_{14}-EPTC, d_{10}-Phorate, d_5-Atrazine, d_{10}-Diazinon, d_7-Malathion, d_{10}-Parathion, d_8-p,p'-DDE, d_8-p,p'-DDT, d_6-Methyl Parathion, d_{13}-Alachlor, d_{11}-Acetochor **Internal Standards:** d_{10}-Acenaphthene, d_{10} Fluoranthene, d_{12}-Benzo[k]fluoranthene	**PCBs**: PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5 Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5' Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5' Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6 Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6 Heptachlorobiphenyl) **Pesticides and degradation products:** Hexachlorocyclohexanes (HCH) - α*, β, γ- (lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlorepoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos, Trifluralin, Metribuzin, Mirex **Surrogates:** $^{13}C_{12}$-PCB 101 (2,2',4,5,5' Pentachlorobiphenyl), $^{13}C_{12}$-PCB 180 (2,2', 3,4,4',5,5' Heptachlorobiphenyl), d_{10} - Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ HCH, d_4-Endosulfan I, d_4-Endosulfan II **Internal Standards:** d_{14}-Trifluralin

Table 2-1: Target analytes, surrogates, and internal standards.

Results and Discussion

In general, the nonpolar analytes were eluted from the silica SPE column in nonpolar elution solvent, chlorinated analytes were eluted in the chlorinated elution solvents, and the polar compounds were eluted in polar elution solvents. Following this trend the PAHs were eluted in the Hex:DCM fraction; DDTs, HCBs, PCBs, and other chlorinated compounds eluted primarily in the DCM fraction with a few exceptions (some chlorinated analytes were eluted in the Hex:DCM and DCM:EA fractions); and the Organophosphates and other polar compounds were eluted in the DCM:EA and EA fractions. These results are given in Table 2-2. Polar lichen matrix interferences co-eluted with the polar solvents required to elute the polar analytes from the SPE column so

we were not able to measure some of the more polar target compounds that eluted in the DCM:EA (1:1) and EA fractions (Table 2-2). Ethyl acetate was used to elute all remaining lichen material and analytes from the SPE column and was collected separately and stored as an extract archive.

A. Electron Impact

Hexane:DCM 1:1 Fraction: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene
DCM Fraction: Disulfoton, Ethion, Paration, Phorate, Methoxychlor, Triallate
DCM:EA 1:1 Fraction: Diazinon and oxon, Malathion, Metalochlor, Acetochlor, Alachlor, Pebulate, EPTC, Propachlor, Atrazine
EA Fraction: Prometon, Atrazine desipropyl, Atrazine desethyl, Simazine
Not Detected: Demeton S, Carbofuran, Carbaryl, Omethoate, Cyanizine

B. Electron Capture Negative Ionization

Hexane:DCM 1:1 Fraction: Trifluralin, Hexachlorobenzene, HCH beta, Triallate, Chlorpyrifos, Chlordane, oxy, Endosulfans - I, II, and sulfate, PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 187 (2,2',3,4',5,5',6 Heptachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6 Heptachlorobiphenyl)
DCM Fraction: PCB 118 (2,3',4,4',5 Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5' Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5' Hexachlorobiphenyl), Hexachlorocyclohexanes (HCH) - α, γ- (lindane), and δ, Chlordanes – cis, trans, Nonachlor – cis, trans, Heptachlor, Heptachlorepoxide, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Dacthal, Chlorothalonil, Metribuzin, Mirex
DCM:EA 1:1 Fraction: none
EA Fraction: none
Not Detected: Chlorthalonil

Table 2-2; a: Electron Impact compounds eluted in different SPE Fractions, b: Electron Capture Negative Ionization eluted in different SPE fractions.

The compounds that eluted in the DCM:EA (1:1) and EA silica SPE fractions were not measured in the recovery experiments. The analytes that were measured eluted either in the Hex:DCM (1:1) or DCM fractions. The average recovery of SOCs from the ASE is given of three measurements in Table 2-3.

Electron Impact Ionization

Compound	*Average Recovery (%)*	*STDEV*
Acenaphthylene	53.2	14.2
Acenaphthene	77.0	22.5
Fluorene	74.5	20.6
Phenanthrene	75.5	21.8
Anthracene	67.6	14.5
Fluoranthene	72.7	15.0
Pyrene	73.3	12.2
Retene	78.9	28.0
o,p'-DDE	77.0	11.4
p,p'-DDE-	75.6	9.89
o,p'-DDD	69.9	11.1
p,p'-DDD	80.8	19.4
o,p'-DDT	78.6	12.3
p,p'-DDT	81.3	12.0
Benzo(a)anthracene	66.6	17.1
Chrysene + Triphenylene	76.3	15.6
Benzo(b)fluoranthene	84.4	21.5
Benzo(k)fluoranthene	87.7	26.7
Benzo(e)pyrene	75.9	21.8
Benzo(a)pyrene	75.2	13.4
Indeno(1,2,3-cd)pyrene	79.1	21.2
Dibenz(a,h)anthracene	80.4	23.5
Benzo(ghi)perylene	71.3	17.6

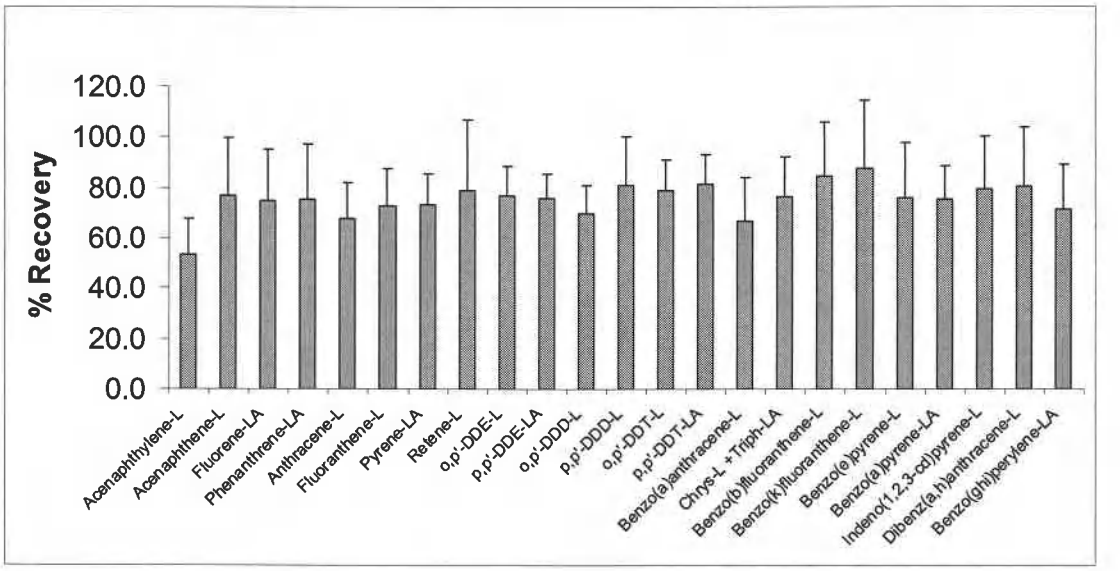
Electron Capture Negative Ionization

Compound	*% Recovery*	*STDEV*
Trifluralin	84.5	20.3
Hexachlorobenzene	81.5	19.5
HCH, beta	124	133
Triallate	59.8	95.5
Chlorpyrifos	108	22.1
Chlordane, oxy	134	58.9
Endosulfan I	55.3	21.3
PCB 74 (tetra)	93.5	32.1
PCB 101 (penta)	92.6	31.2
Endosulfan II	58.9	75.9
Endosulfan sulfate	95.1	158
PCB 187 (hepta)	124	26.9
PCB 183 (hepta)	98.0	22.4

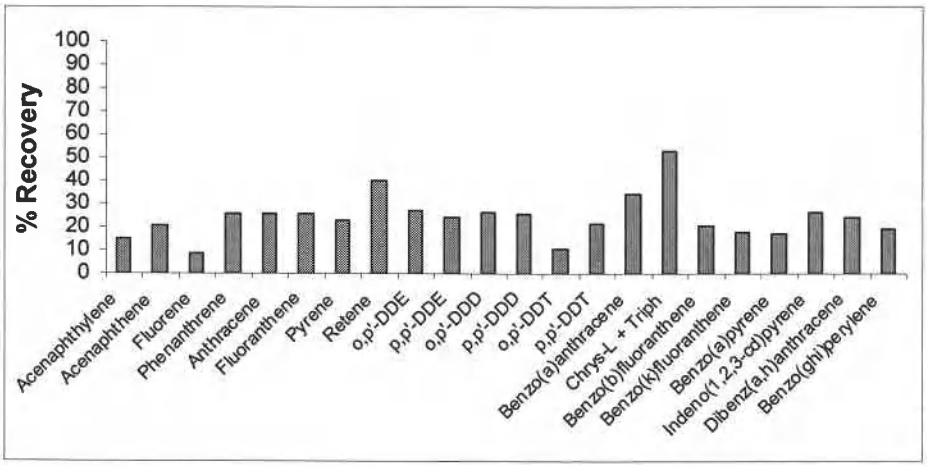
Table 2-3; a: Average recoveries of target analytes for the ASE measured with Electron impact ionization; b: Electron Capture Negative Ionization.

Ethyl acetate (EA) was also used (instead of DCM) for the ASE but it did not give recoveries as high as the ASE extractions with DCM for the EI analytes (Figure 2-3). The ASE recoveries for the DCM extractions are given in Figure 2-3 as for both the EI and ECNI analytes. Because the recoveries for the EA extractions were so low for EI compounds these extracts were not analyzed for ECNI compounds.

n = 3



n = 1



n = 3

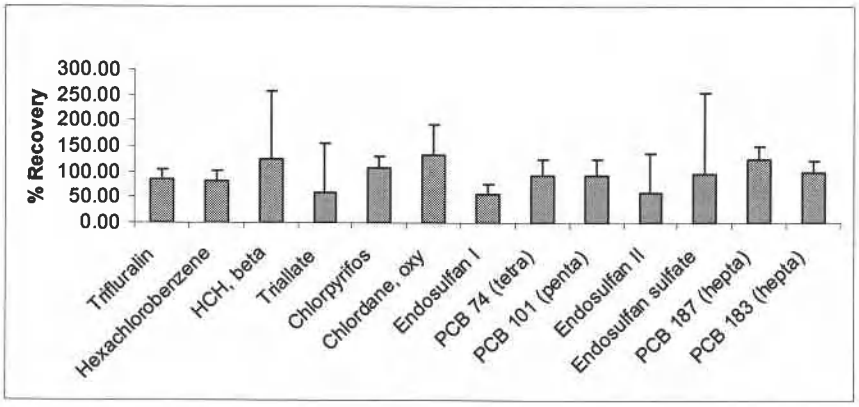


Figure 2-3; a: Recoveries of DCM extraction for EI compounds (n = 3), b: Recoveries of EA extraction for EI compounds (n = 1), c: Recoveries of DCM extraction for ECNI compounds (n = 3).

Only one EI analyte was recovered above 50% for the EA ASE extraction and 23 EI analytes were recovered above 50% for the DCM ASE extraction. The EA extraction co-extracted visibly less vegetation material, but the analyte recoveries were not high enough to use EA ASE extraction in the analytical method.

As stated above polar lichen matrix interferences co-eluted in the DCM:EA (1:1) and EA silica SPE fractions. GC/FID chromatograms, which indicate all organic material present in the lichen extracts are shown in Figure 2-3 a, b. Greater ion abundance was observed in the EA silica solid phase extraction (SPE) fraction than in the DCM silica SPE fraction.

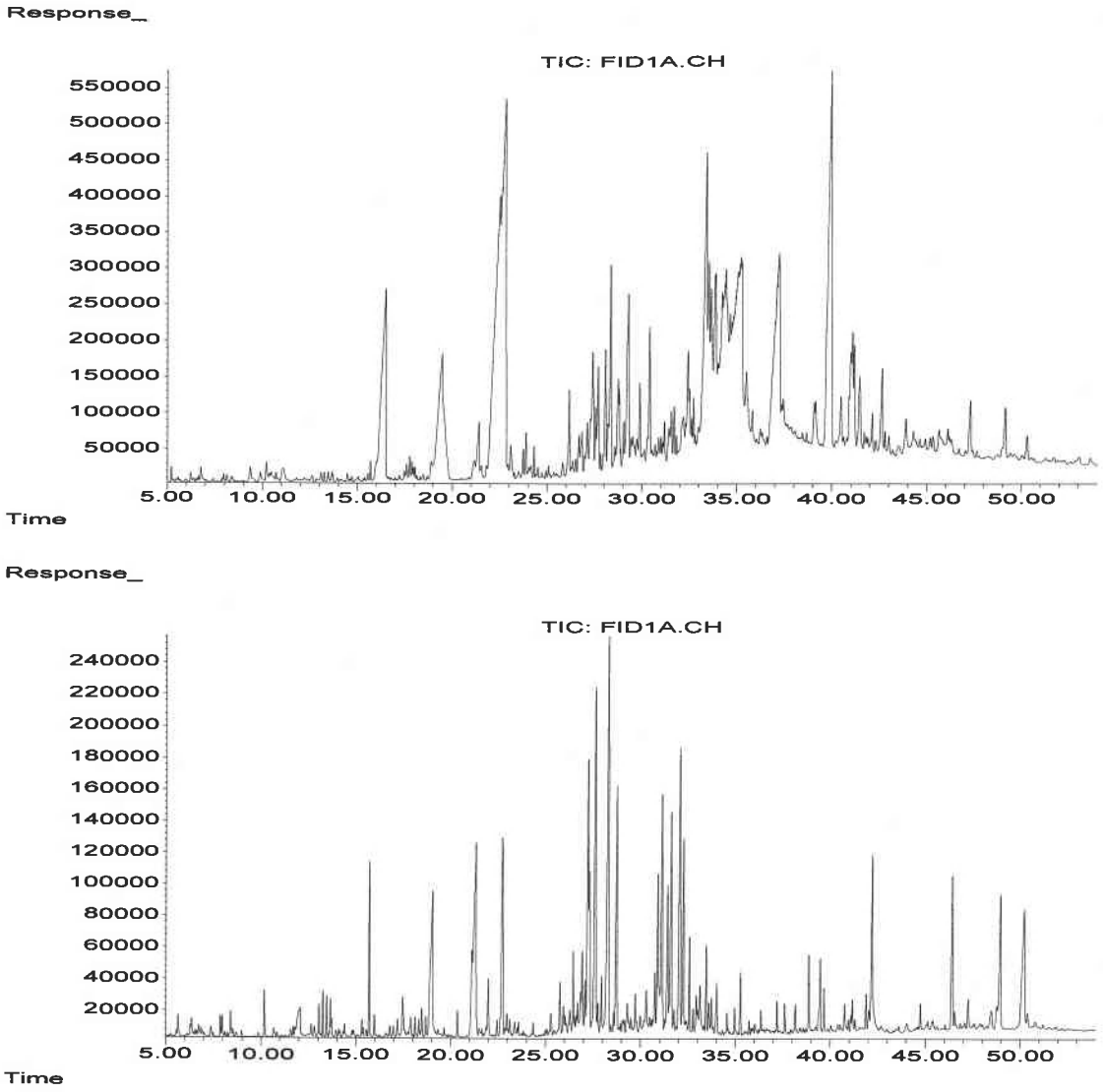


Figure 2-4; a: Ethyl acetate silica SPE fraction GC/FID chromatogram; b: DCM SPE silica fraction GC/FID chromatogram.

Although we were able to measure a large number of SOCs in the DCM SPE fraction, we were not able to measure the more polar pesticides because of co-eluting matrix interferences in the DCM:EA (1:1) and EA silica SPE fractions. This was a bit of a disappointment because many of the current use pesticides are more polar in nature. The obstacle blocking the measurement of the polar pesticides was potential loss during water extraction and to elute more polar SOCs from the silica SPE column, it was necessary to use polar solvents such as, ethyl acetate which also co-eluted a great deal of

lichen matrix interferences, causing poor chromatographic separation. A full scan EI-GC/MS chromatogram of an ethyl acetate fraction is given in Figure 2-5 illustrating the high abundance of lichen interferences that were present in the polar SPE fractions.

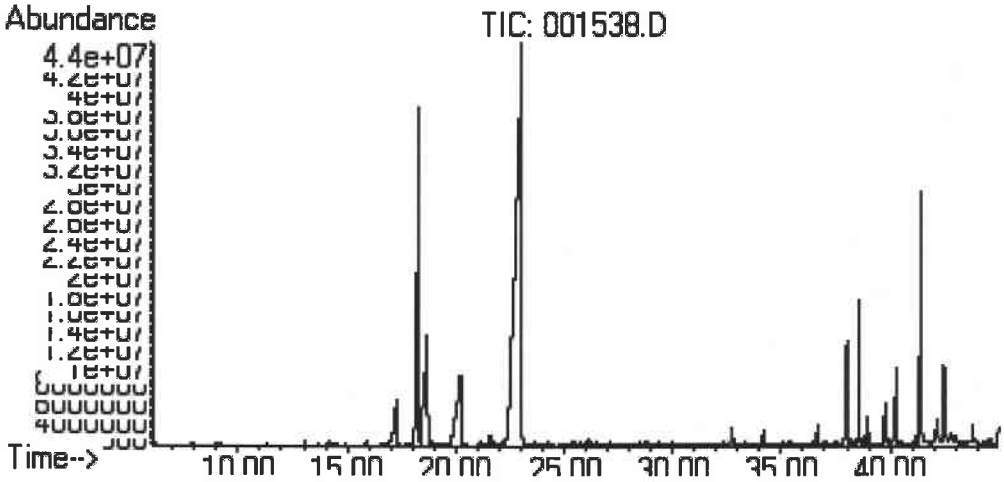


Figure 2-5: Full scan EI-GC/MS chromatogram of polar silica SPE fraction.

Various mixtures of EA and DCM were used to selectively elute the analytes and not the polar matrix interferences from the silica SPE column, but any time ethyl acetate entered the silica column lichen matrix interferences were eluted. However, the polar SOCs are less likely to partition to vegetation than the non-polar SOCs like the PAHs and organochlorines, because of their relatively low octanol-air partition coefficients. The realization that we are able to measure the SOCs that are most likely to be on lichen with this analytical method is a positive one. Furthermore, past SOC/lichen studies have measured almost exclusively, only organochlorines (14, 15, 2). The large list of SOCs for which we were able to develop an analytical method is impressive.

Chapter 3 – Manuscript II

Biomonitoring Semivolatile Organic Compounds in Sequoia National Park Using Lichen

Abstract

The Western Airborne Contaminants Assessment Project was developed to assess the potential risk posed to western North America high elevation ecosystems by atmospheric transport and deposition of pollutants. Several environmental matrices, including lichen, have been analyzed to obtain a broad understanding of the potential problem. Lichen was used as a natural passive air sampler for semivolatile organic compounds (SOCs) in this study. Lichen samples were collected from two sites with different elevations in Sequoia-Kings Canyon National Park. Polycyclic aromatic hydrocarbons (PAHs), pesticides, and PCBs were detected in lichen samples collected from the two sites, 33 SOCs in total. Of the compounds measured in relatively high concentrations, PAHs were measured in higher concentration in the lower elevation site (8040 ft.) than they were in the higher elevation site (9240 ft.). In contrast, chlorinated pesticides were measured in higher concentrations in the higher elevation site than they were in the lower elevation site. This trend appeared to be correlated with the atmospheric half-life of the SOCs measured.

Introduction

Semivolatile organic compounds (SOCs) are known to bioaccumulate in both aquatic and terrestrial food chains and may pose a potential threat to high elevation ecosystems and subsistence hunters by way of long range atmospheric transport and

deposition to these ecosystems (15, 18, 21). To asses the potential risk of airborne contaminants, including SOCs, to western North America high elevation ecosystems the Western Airborne Contaminants Assessment Project (WACAP) was developed by a number of government agencies and universities (21). Environmental samples were collected from a number of U.S. national parks as part of WACAP's objectives. The concentration of SOCs was measured in many environmental matrices, including lichen, from Sequoia-Kings Canyon National Park (SEKI), a WACAP Park. Lichen have been used as passive air samplers of different types of pollution and have recently been used to measure SOCs (13-15). Lichens are also part of the diets of a variety of animals including moose, caribou, mountain goat, grouse, wild turkey, and deer (17). These animals can live in ecosystems where SOCs are known to be deposited. In Canada's central and western arctic bioaccumulation of certain SOCs from lichen to Caribou to Wolf has been observed as mentioned in chapter one (15). Lichen was collected from two sampling sites in SEKI: Wolverton Creek (elev. 8040 ft) and Emerald Lake (elev. 9240 ft), and analyzed for a wide range of SOCs. The two sites were approximately 2.5 miles apart. The location of SEKI and the Wolverton Creek and Emerald Lake sampling sites are shown in Figure 3-1 (22).

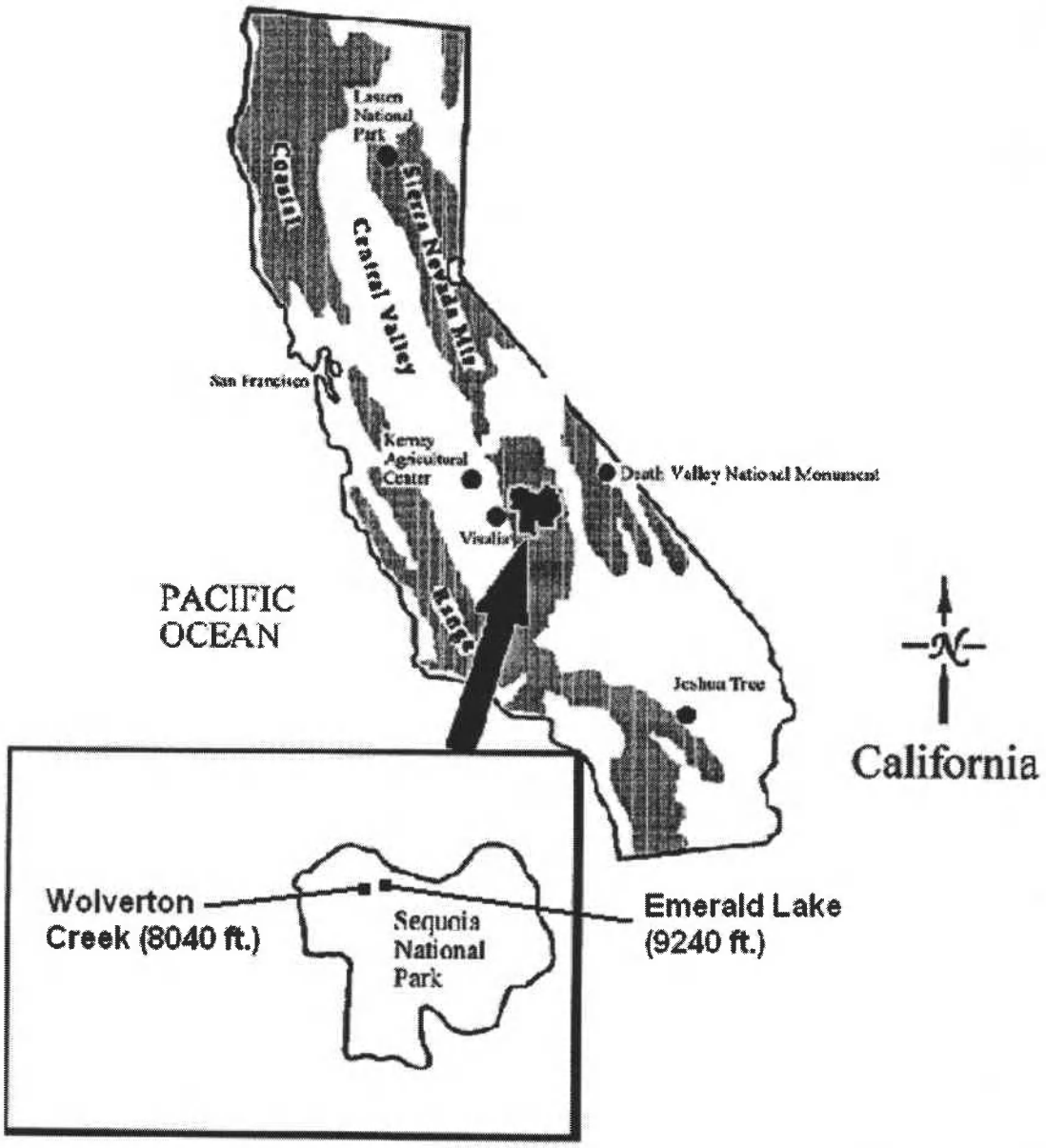


Figure 3-1: Sequoia National Park Location, Wolverton Creek and Emerald Lake sampling site locations (Taken from Reference 22).

Initially, *Hypogymnia spp.* of lichen were expected to be present in Sequoia National Park and the analytical method was developed using *Hypogymnia inactiva* as described in Chapter two. After searching the SEKI sampling sites, it was apparent that insufficient amounts of *Hypogymnia spp.* of lichen were available. The most abundant

species of lichen in SEKI was *Letharia vulpina*, a foliose lichen that grows on the bark of conifer trees (shown in Figure 3-2).

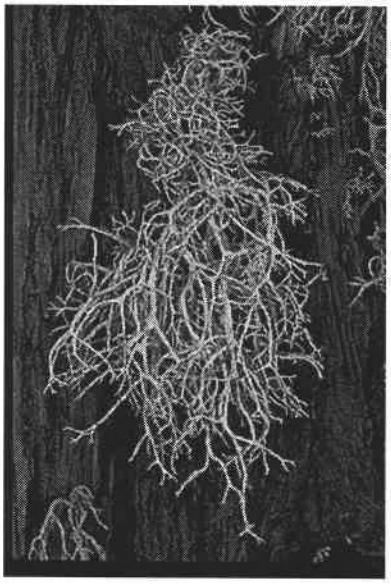


Figure 3-2: Lichen species *Letharia vulpina.*

The *Letharia spp.* lichen was collected for analysis. Two species of conifer needles (White Fir and Lodgepole Pine) were also collected and analyzed from the Emerald Lake sampling site by Lisa Deskin of the Simonich Environmental Chemistry Lab at Oregon State University. This allowed for a comparison of the two vegetation types so that it could be determined which vegetation type is most suitable passive air sampler for SOCs.

Materials and Methods

An abbreviated version of the lichen analytical method is given here. The full analytical method description is given in Chapter two. SOCs were measured in three lichen samples from each site. Approximately 20 g of lichen were packed into an accelerated solvent extraction cell, spiked with surrogates (see Table 2-1), and extracted using accelerated solvent extraction with dichloromethane (DCM) as the extraction

solvent. Extracts were solvent exchanged to hexane and extracted using water to remove polar interferences. Further purification of the lichen extracts was carried out using 20 g solid phase extraction (SPE) chromatography columns with a silica sorbent bed and Hexane:DCM (1:1) and DCM as elution solvents. Ethyl acetate was used to elute the remaining material from the SPE column for archiving. The hexane:DCM (1:1) and DCM fractions were then combined, concentrated, a 10 uL portion was diluted at a 1/10 ratio in DCM, and analyzed using gas chromatography/mass spectrometry in both the electron impact (EI) and electron capture negative ion (ECNI) ionization modes. The percent moisture and percent lipid of each lichen sample was determined.

To determine if the concentration of SOCs was statistically different between the two sites student t-tests were performed for each of the SOCs with a 5% level of significance. To determine if SOC deposition between the two sites was related to the physical properties of vapor pressure or atmospheric half life linear regressions were performed with a 5% level of significance

Results and Discussion

Site Comparison

Because the target lichen species in SEKI was changed to *Letharia vulpina* it became possible to analyze the DCM SPE fraction. *Letharia spp*. extracts had fewer polar matrix interferences in this fraction than *Hypogymnia inactiva*. This allowed us to potentially analyze a greater number of SOCs in *Letharia spp*. The average percent moisture and percent lipid values for samples collected from Wolverton Creek and Emerald Lake are given in Table 3-1.

	Percent Moisture	Percent Lipid
Wolverton Creek	14.89 ± 1.43	4.77 ± 0.75
Emerald Lake	12.21 ± 1.50	4.82 ± 0.17

Table 3-1: Percent moisture and lipid for each site, n = 3 for both sites.

Table 3-2 lists the SOCs measured in the lichen samples collected from SEKI as well as the average concentration of three samples from each site, in dry weight and lipid weight, of the compounds present in each of the lichen samples, the standard deviations, and t-values. SOCs with concentrations of 0.00 were not detected or measured below detection limits. Thirty two of the thirty six SOCs quantitated with the analytical method were measured in SEKI lichen. A t-value greater than 2.920 indicates that the analyte was found in greater concentration in Wolverton Creek (elev. 8040 ft.), a t-value less than -2.920 indicates that the analyte was found in greater concentration in Emerald Lake (elev. 9240 ft.), and t-value between -2.920 and 2.920 indicates that there is no statistical difference in the concentration of the compound between the two sites at the 5% level of significance.

	Wolverton Creek		Emerald Lake		
Name	ng/g (dw)	STDEV	ng/g (dw)	STDEV	T-value
Fluorene	0.78	0.36	0.27	0.47	1.52
Phenanthrene	7.15	1.11	5.41	0.35	2.58
Fluoranthene	3.36	0.11	2.23	0.29	6.18
Pyrene	2.05	0.09	1.89	0.25	1.10
Retene	28.28	10.29	19.20	2.69	1.48
o,p'-DDE	0.00	0.00	0.62	0.03	-33.85
p,p'-DDE	3.21	0.68	4.63	0.23	-3.41
o,p'-DDT	0.00	0.00	5.48	5.10	-1.86
p,p'-DDT	9.77	7.17	22.30	7.25	-2.13
Benzo(a)anthracene	0.29	0.12	0.24	0.11	0.48
Chrysene + Triphenylene	1.92	0.45	1.12	0.19	2.82
Benzo(ghi)perylene	0.66	0.12	0.83	0.27	-1.04
Trifluralin	0.03	0.02	0.02	0.01	1.00
HCH, alpha	0.96	0.66	0.00	0.00	2.54
HCH, beta	0.03	0.05	0.04	0.04	-0.40
HCH, gamma (Lindane)	0.76	0.19	0.94	0.50	-0.58
Dacthal	8.73	3.58	13.52	3.50	-1.66
Chlorpyrifos oxon	0.68	0.50	0.00	0.00	2.38
Chlorpyrifos	0.69	0.14	0.11	0.11	5.50
Chlordane, trans	0.40	0.19	0.00	0.00	3.62
Endosulfan I	3.17	1.32	2.32	0.54	1.03
Chlordane, cis	0.36	0.15	0.27	0.23	0.57
Nonachlor, trans	0.31	0.12	0.00	0.00	4.39
Dieldrin	0.71	0.27	0.76	0.67	-0.13
PCB 118 (penta)	0.12	0.06	0.06	0.04	1.68
Endosulfan II	3.58	0.65	7.19	0.96	-5.40
Nonachlor, cis	0.13	0.02	0.00	0.00	10.16
Endosulfan sulfate	15.10	5.54	27.14	6.33	-2.48
PCB 153 (hexa)	0.07	0.04	0.00	0.00	2.81
PCB 138 (hexa)	0.20	0.08	0.00	0.00	4.31
PCB 187 (hepta)	0.07	0.05	0.00	0.00	2.59
PCB 183 (hepta)	0.04	0.03	0.00	0.00	2.03

Table 3-2: Average analyte concentration in lichen samples (n = 3), standard deviation, and t-value from Wolverton Creek and Emerald Lake on a; a: dry weight. The t-value at the 5% level of significance is 2.920.

	Wolverton Creek		Emerald Lake		
Name	ng/g (lipid)	STDEV	ng/g (lipid)	STDEV	T-value
Fluorene	14.73	7.84	5.46	9.46	1.31
Phenanthrene	130.92	36.19	106.88	8.79	1.12
Fluoranthene	60.69	7.45	44.24	7.34	2.72
Pyrene	37.10	4.70	37.38	6.23	-0.06
Retene	518.59	236.98	380.62	67.62	0.97
o,p'-DDE	0.00	0.00	12.21	1.23	-17.20
p,p'-DDE	58.85	19.18	91.33	1.13	-2.93
o,p'-DDT	0.00	0.00	107.75	102.87	-1.81
p,p'-DDT	183.07	152.75	437.89	134.36	-2.17
Benzo(a)anthracene	5.34	2.86	4.82	2.41	0.24
Chrysene + Triphenylene	35.02	11.68	22.12	4.16	1.80
Benzo(ghi)perylene	12.05	3.64	16.55	5.87	-1.13
Trifluralin	0.48	0.30	0.31	0.27	0.74
HCH, alpha	16.45	11.02	0.00	0.00	2.59
HCH, beta	0.50	0.87	0.82	0.73	-0.48
HCH, gamma (Lindane)	13.04	4.08	18.83	10.57	-0.89
Dacthal	152.64	78.09	266.44	67.84	-1.91
Chlorpyrifos oxon	11.66	8.63	1.33	1.15	2.06
Chlorpyrifos	11.85	3.50	2.31	2.29	3.95
Chlordane, trans	6.98	3.94	0.00	0.00	3.07
Endosulfan I	55.42	28.87	45.52	8.26	0.57
Chlordane, cis	6.33	3.24	5.51	4.77	0.25
Nonachlor, trans	5.48	2.64	0.00	0.00	3.60
Dieldrin	12.30	5.57	15.54	13.61	-0.38
PCB 118 (penta)	2.17	1.13	1.14	0.71	1.34
Endosulfan II	60.72	11.88	141.50	12.07	-8.26
Nonachlor, cis	2.14	0.48	0.00	0.00	7.74
Endosulfan sulfate	255.44	91.73	531.97	93.96	-3.65
PCB 153 (hexa)	1.29	0.90	0.00	0.00	2.49
PCB 138 (hexa)	3.45	1.71	0.00	0.00	3.49
PCB 187 (hepta)	1.32	1.01	0.00	0.00	2.27
PCB 183 (hepta)	0.64	0.60	0.00	0.00	1.85

Table 3-2 continued; b: Lipid weight basis.

The majority of the compounds present in the two SEKI sites were pesticides. There were also a number of PAHs detected. A visual side by side comparison of the two sites for dry weight and lipid weight is given figure 3-2. When comparing the average

lipid content of the lichen at each site a t-value of 0.1131 was obtained indicating that there was no statistical difference in lipid content between the two sites at the 5% or 10% levels of significance.

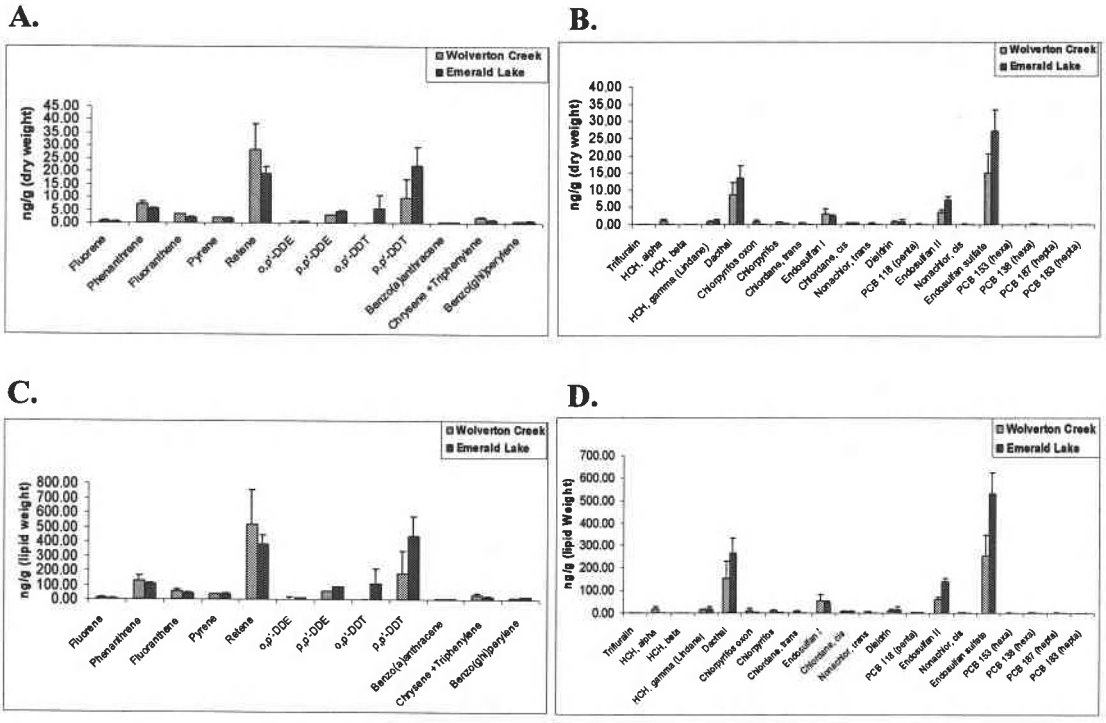


Figure 3-2; a: Dry weight comparison of SOC (compounds analyzed with electron impact, EI, ionization) concentration in lichen for Wolverton Creek and Emerald Lake, b: Dry weight comparison of SOC (compounds analyzed with electron capture negative ionization, ECNI), c: Lipid Weight comparison of SOC (compounds analyzed with electron impact, EI, ionization) concentration in lichen for Wolverton Creek and Emerald Lake, d: Lipid weight comparison of SOC (compounds analyzed with electron capture negative ionization, ECNI).

These figures illustrate that for the SOCs that were detected at relatively high concentrations, PAHs were generally detected at higher concentrations in Wolverton Creek and pesticides were generally detected at higher concentrations in Emerald Lake. Retene can originate from anthropogenic sources and natural sources which may have contributed to its concentration in lichen. The results of the t-test for the SOCs detected in lichen from SEKI (Table 3-2) did not initially show any trends between the two sites.

The SOCs with relatively low standard deviations within sites and concentrations well above instrument detection limits were selected for a site comparison to minimize uncertainty. These results are shown in Table 3-3 on a dry weight and lipid weight basis. The subcooled liquid vapor pressures and the atmospheric half lives of the SOCs are given in Table 3-3 as well to compare concentrations at the sites relative to these physical properties. Vapor pressure data was taken from the Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals volumes II and V except for retene, dacthal, and endosulfan sulfate which were calculated using EPI suite v. 3.10 (23-25). Atmospheric half life values for all SOCs in Table 3-3 were also calculated using EPI suite.

Dry Weight						
PAHs	Wolverton Creek (ng/g) dw	Emerald Lake (ng/g) dw	t-test $p < 5\%$	t-test $p < 10\%$	Vapor Pressure - Liquid (Pa)	Atmospheric Half life (hrs)
Phenanthrene	**7.15** ± 1.11	5.41 ± 0.35	no	yes	0.113	9.837
Pyrene	2.05 ± 0.09	1.89 ± 0.25	no	no	0.0119	2.567
Fluoranthene	**3.36** ± 0.11	2.23 ± 0.29	yes	yes	8.72×10^{-3}	4.392
Retene	28.28 ± 10.29	19.20 ± 2.69	no	no	3.52×10^{-4}	3.078
Chrysene + Triphenylene	**1.92** ± 0.45	1.12 ± 0.19	no	yes	1.07×10^{-4}, 1.21×10^{-4}	2.567, 2.567
Benzo(ghi)perylene	0.66 ± 0.12	0.83 ± 0.27	no	no	2.25×10^{-5}	1.478
Pesticides						
Endosulfan II	3.58 ± 0.65	**7.19** ± 0.96	yes	yes	0.394	15.716
Dieldrin	0.71 ± 0.27	0.76 ± 0.67	no	no	0.016	13.95
Endosulfan I	3.17 ± 1.32	2.32 ± 0.54	no	no	0.008	15.716
p,p'-DDE	3.21 ± 0.68	**4.63** ± 0.23	yes	yes	3.72×10^{-3}	17.275
Dacthal	8.73 ± 3.58	13.52 ± 3.50	no	no	2.73×10^{-4}	291.012
o,p'-DDT	0.00	5.48 ± 5.10	no	no	1.72×10^{-4}	37.365
p,p'-DDT	9.77 ± 7.17	**22.30** ± 7.25	no	yes	1.35×10^{-4}	37.365
Endosulfan sulfate	15.10 ± 5.54	**27.14** ± 6.33	no	yes	1.55×10^{-5}	15.716

Table 3-2; a: Average, standard deviation, and results from student's t-test of SOC concentration (ng/g) comparing compounds in high concentration from Wolverton Creek (elev. 8040 ft.) and Emerald Lake (elev. 9240 ft.) (5% level of significance = 2.920, 10% level of significance = 1.886) dry weight basis.

Lipid Weight						
PAHs	Wolverton Creek (ng/g) lipid	Emerald Lake (ng/g) lipid	t-test $p < 5\%$	t-test $p < 10\%$	Vapor Pressure - Liquid (Pa)	Atmospheric Half life (hrs)
Phenanthrene	130.92 ± 36.19	106.88 ± 8.79	no	no	0.113	9.837
Pyrene	37.10 ± 4.70	37.38 ± 6.23	no	no	0.0119	2.567
Fluoranthene	**60.69** ± 7.45	44.24 ± 7.34	no	yes	8.72×10^{-3}	4.392
Retene	518.59 ± 236.98	380.62 ± 67.62	no	no	3.52×10^{-4}	3.078
Chrysene + Triphenylene	35.02 ± 11.68	22.12 ± 4.16	no	no	1.07×10^{-4}, 1.21×10^{-4}	2.567, 2.567
Benzo(ghi)perylene	12.05 ± 3.64	16.55 ± 5.87	no	no	2.25×10^{-5}	1.478
Pesticides						
Endosulfan II	60.72 ± 11.88	**141.50** ± 12.07	yes	yes	0.394	15.716
Dieldrin	12.30 ± 5.57	15.54 ± 13.61	no	no	0.016	13.950
Endosulfan I	55.42 ± 28.87	45.52 ± 8.26	no	no	0.008	15.716
p,p'-DDE	58.85 ± 19.18	**91.33** ± 1.13	yes	yes	3.72×10^{-3}	17.275
Dacthal	152.64 ± 78.09	**266.44** ± 67.84	no	yes	2.73×10^{-4}	291.012
o,p'-DDT	0.00	107.75 ± 102.87	no	no	1.72×10^{-4}	37.365
p,p'-DDT	183.07 ± 152.75	**437.89** ± 134.36	no	yes	1.35×10^{-4}	37.365
Endosulfan sulfate	255.44 ± 91.73	**531.97** ± 93.96	yes	yes	1.55×10^{-5}	15.716

Table 3-3 continued; b: lipid weight basis. (References 23-25).

Previous studies have proposed the global distillation/cold condensation transport model in which SOCs accumulate in cold regions, high latitudes and high elevations, in which compounds with higher vapor pressures generally travel greater distances and elevations (1-4). This trend is not seen in Table 3-3. Table 3-2 suggests that SOC atmospheric half life may explain the concentration difference between the two sampling sites. As Table 3-2 indicates all PAHs that have a statistically significant difference between the two sites at either the 10% or 5% levels of significance were measured at higher dry weight and lipid weight basis concentrations in Wolverton Creek (lower elevation: 8040 ft.) than in Emerald Lake (higher elevation: 9240 ft.). Conversely, all pesticides that have a statistically significant difference at either the 10% or 5% levels of

significance were measured at higher concentrations in Emerald Lake rather than in Wolverton Creek. The remaining SOCs that did not show a statistically significant difference in dry weight and lipid weight basis concentrations between sites followed this trend except for benzo(ghi)perylene (dw, lw), endosulfan I (dw, lw), and pyrene (lw). The PAHs and pesticides, have a similar range of vapor pressures (Table 3-3) indicating that vapor pressure may not be as influential a factor as atmospheric half life, which is greater for all pesticides than PAHs (shown in Table 3-3). These results can be seen graphically in Figure 3-3. The difference in concentration on the y-axis represents the concentration of the SOCs in Emerald Lake samples minus the concentration of SOCs in Wolverton Creek. Data points above the x-axis represent SOCs that were measured at higher concentration in the higher elevation site (Emerald Lake) and data points below the x-axis represent SOCs that were measured in higher concentration in the lower elevation site (Wolverton Creek). The vapor pressures of chrysene and triphenylene were averaged because they are not chromatographically resolved.

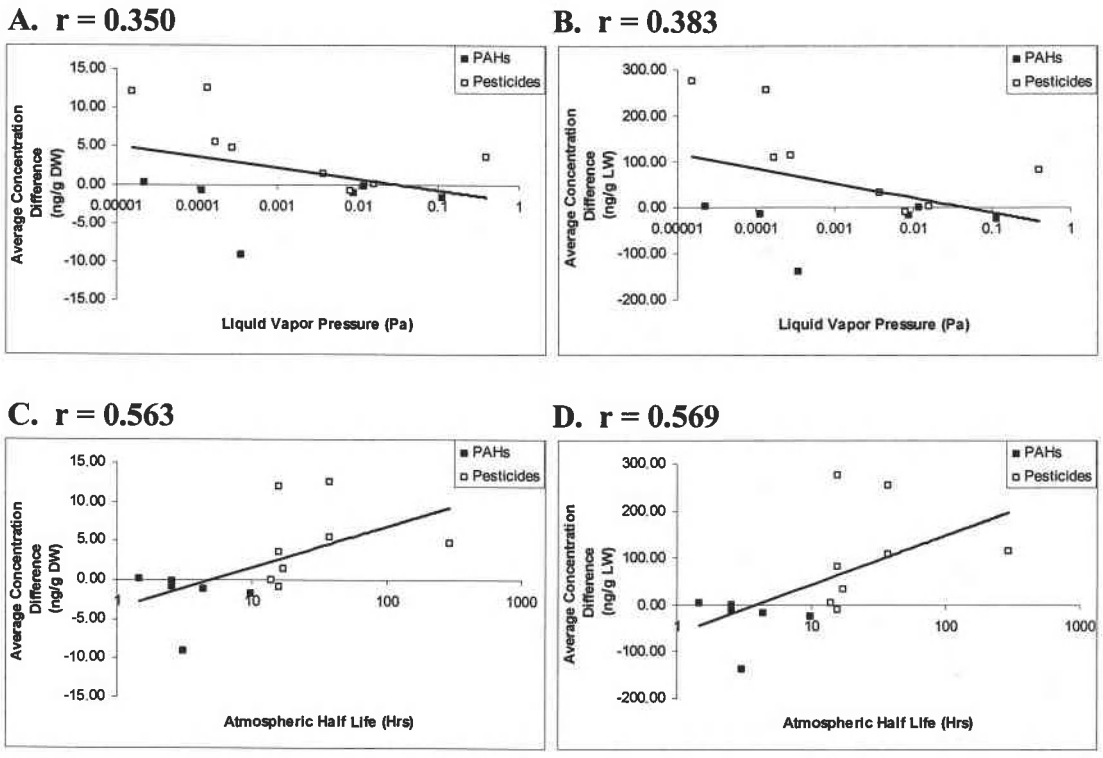


Figure 3-3; a: Comparison of the average concentration differences of SOCs between Emerald Lake and Wolverton Creek dry weight concentration vs. vapor pressure, b: Lipid weight concentration vs. vapor pressure, c: Dry weight vs. atmospheric half life, d: Lipid weight concentration vs. atmospheric half life (5% level of significance = 0.532).

No relationship was evident in the concentration difference between the two sites and vapor pressure for dry weight or lipid weight concentrations vs. vapor pressure at a 5% significance level since both of their R values were below 0.532 (Figure 3-3 a & b). A statistical relationship is observed in the concentration difference between the two sites for dry weight and lipid weight vs. atmospheric half life at a 5% significance level since both of their R values are above 0.532 (Figure 3-3 c & d). In the concentration difference vs. atmospheric half life plots all but one of the pesticides (endosulfan I) is above the x-

axis and all but one of the PAHs (benzo(ghi)perylene) is below the x-axis. This reinforces the point that pesticides were generally measured in higher concentration in the higher elevation site (Emerald Lake) and that PAHs were generally measured in higher concentration in the lower elevation site (Wolverton Creek). The site proximity to sources did not appear to play a major role in elevation distribution at SEKI since Sequoia National Park is in close proximity to both major agricultural zones (pesticide sources) and major highway, urban, and industrial zones (PAH sources) located upwind in the San Joaquin Valley.

Vegetation Type Comparison

To decide which form of vegetation was most suitable to meet the WACAP objectives for passive air sampling in national parks, lichen and conifer needles were collected and analyzed. The comparison of SOC concentration in lichen with conifer needles from Emerald Lake was done on a dry weight basis. The lichen was compared with two year old conifer needles, the oldest needles collected, to make exposure time more equal between the two forms of vegetation. The analysis and data from the conifer needles was generated by Lisa Deskin (26). These results are given in Figure 3-3 and Table 3-4. SOCs measured at concentration levels of 0.00 were either not detected or detected below detection limits. Previous studies have discovered that SOCs are usually found in higher concentrations in lichen than conifer needles due to difference in exposure time, air-side resistance of conifer needles, absence of a waxy outer cuticle in lichen, and different air-plant equilibration times (27).

Lichen (n = 3), White Fir (n = 2), Lodgepole Pine (n = 2)

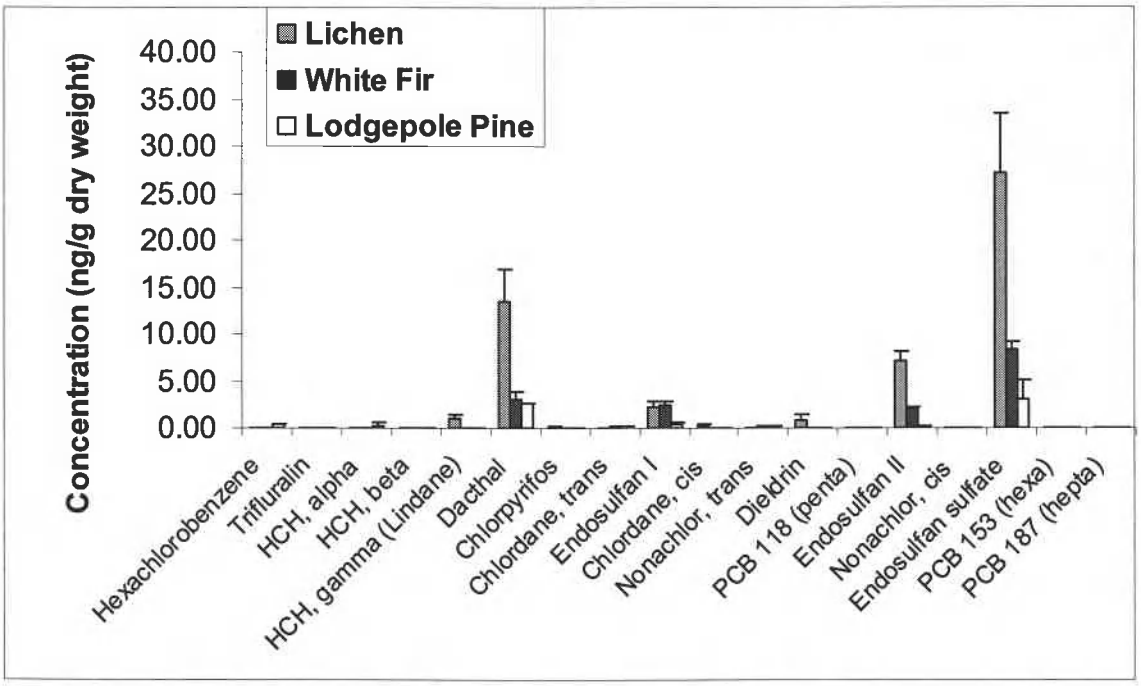


Figure 3-4: Comparison of SOC concentration in lichen (n = 3) and conifer needles (n = 2 for each species) from Emerald Lake.

Name	Lichen		White Fir		Lodgepole Pine	
	Average Conc. (ng/g dw)	STDEV	Average Conc. (ng/g dw)	STDEV	Average Conc. (ng/g dw)	STDEV
Hexachlorobenzene	0.00	0.00	0.00	0.00	0.40	0.05
Trifluralin	0.02	0.01	0.00	0.00	0.00	0.00
HCH, alpha	0.00	0.00	0.00	0.00	0.26	0.36
HCH, beta	0.04	0.04	0.00	0.00	0.00	0.00
HCH, gamma (Lindane)	0.94	0.50	0.00	0.00	0.00	0.00
Dacthal	13.52	3.50	3.00	0.91	2.57	0.07
Chlorpyrifos	0.11	0.11	0.00	0.00	0.00	0.00
Chlordane, trans	0.00	0.00	0.20	0.09	0.08	0.04
Endosulfan I	2.32	0.54	2.36	0.49	0.42	0.13
Chlordane, cis	0.27	0.23	0.00	0.00	0.00	0.00
Nonachlor, trans	0.00	0.00	0.18	0.08	0.12	0.06
Dieldrin	0.76	0.67	0.00	0.00	0.00	0.00
PCB 118 (penta)	0.06	0.04	0.00	0.00	0.00	0.00
Endosulfan II	7.19	0.96	2.11	0.16	0.25	0.02
Nonachlor, cis	0.00	0.00	0.08	0.01	0.00	0.00
Endosulfan sulfate	27.14	6.33	8.27	0.85	3.09	1.95
PCB 153 (hexa)	0.00	0.00	0.03	0.04	0.00	0.00
PCB 187 (hepta)	0.00	0.00	0.02	0.03	0.00	0.00

Table 3-3: Average SOC concentrations in lichen White Fir and Lodgepole Pine from Emerald Lake.

In total, eleven SOCs measured using GC/ENCI-MS were detected in lichen, nine in White Fir, and eight in Lodgepole Pine from Emerald Lake. Endosulfan I, an analyte measured at relatively high concentrations compared to most of the other analytes, was slightly higher in concentration in white fir than in lichen. There were also other compounds measured in the conifer needles that were not detected in lichen including chlordane (trans), nonachlor (trans), nonachlor (cis), PCB 153 (hexa), and PCB 187 (hepta) in White Fir and HCB, HCH (alpha), chlordane (trans), and nonachlor (trans) in Lodgepole Pine. The compounds trifluralin, HCH-gamma (lindane), chlorpyrifos, chlordane (cis), dieldrin, and PCB 118 were detected in lichen and not in either of the conifer needles. SOCs that were not detected in all three species were detected in relatively low concentrations. Of the four compounds measured in all the species of vegetation, they were measured in the highest concentration in lichen, except for endosulfan I, followed by White Fir, and finally Lodgepole Pine. This is most likely a function of exposure time since the lichen can be decades old and the conifer needles were two years old. It was decided that both lichen and conifer needles would be analyzed for the WACAP project because they give different and valuable information on SOC accumulation in the ecosystem over different time periods.

The detection of SOCs in snow (collected from Emerald Lake in 2003) was compared to lichen and conifer needles (28). Snow is an excellent scavenger of SOCs from air. Although snow is a hydrophilic matrix and vegetation is a hydrophobic matrix, we expect that snow and vegetation from SEKI should contain some of the same SOCs. Concentration comparisons between vegetation and snow were not done because of differences in exposure time and matrix properties. A comparison of what SOCs were

measured in each of the three matrices is given in Table 3-3 (26, 28). SOCs listed in the conifer needle column were detected in either year one or year two of White Fir and/or Lodgepole Pine. SOCs listed in bold type face were detected in all three matrices, and compounds listed in italics type face were detected in lichen and snow only.

Snow	Lichen	Conifer Needles
N.D.	Fluorene	N.A.
N.D.	Phenanthrene	N.A.
Fluoranthene	*Fluoranthene*	N.A.
Pyrene	*Pyrene*	N.A.
Retene	*Retene*	N.A.
N.D.	o,p'-DDE	N.A.
N.D.	p,p'-DDE	N.A.
N.D.	o,p'-DDT	N.A.
N.D.	p,p'-DDT	N.A.
N.D.	Benzo(a)anthracene	N.A.
N.D.	Chrysene	N.A.
N.D.	Triphenylene	N.A.
Benzo(e)pyrene	N.D.	N.A.
Benzo(a)pyrene	N.D.	N.A.
Indeno(1,2,3-cd)pyrene	N.D.	N.A.
Benzo(ghi)perylene	*Benzo(ghi)perylene*	N.A.
Trifluralin	*Trifluralin*	N.D.
Hexachlorobenzene	N.D.	Hexachlorobenzene
HCH, alpha	N.D.	HCH, alpha
N.D.	HCH, beta	N.D.
HCH, gamma (Lindane)	*HCH, gamma (Lindane)*	N.D.
Triallate	N.D.	N.D.
Dacthal	**Dacthal**	**Dacthal**
Chlorpyrifos	*Chlorpyrifos*	N.D.
Chlordane, trans	N.D.	Chlordane, trans
Endosulfan I	**Endosulfan I**	**Endosulfan I**
N.D.	Chlordane, cis	N.D.
Nonachlor, trans	N.D.	Nonachlor, trans
Dieldrin	*Dieldrin*	N.D.
PCB 118 (penta)	*PCB 118 (penta)*	N.D.
Endosulfan II	**Endosulfan II**	**Endosulfan II**
Nonachlor, cis	N.D.	Nonachlor, cis
Endosulfan sulfate	**Endosulfan sulfate**	**Endosulfan sulfate**
PCB 153 (hexa)	N.D.	PCB 153 (hexa)
PCB 138 (hexa)	N.D.	PCB 138 (hexa)
PCB 187 (hepta)	N.D.	N.D.
PCB 183 (hepta)	N.D.	N.D.

Table 3-3: SOCs measured in lichen (n = 3), conifer needles (n = 2), and snow (n = 1) from Emerald Lake (N.D. = Not Detected, N.A. = Not Analyzed For) (25, 27).

Four analytes (dacthal, Endosulfan I, II, and sulfate) were measured in all three matrices and thirteen (fluoranthene, pyrene, retene, benzo(ghi)perylene), trifluralin, γ-HCH (lindane), dacthal, chlorpyrifos, endosulfan I, dieldrin, PCB 118 (penta), endosulfan II, and endosulfan sulfate) were measured in snow and lichen. This suggests that on different exposure intervals, lichen (years-decades), conifer needles (1-2 years), and snow (weeks- months), the most common compounds undergoing atmospheric transport were current use pesticides endosulfan and dacthal.

The geographical use of dacthal and endosulfan in California in 1992 are given in Figure 3-5 (29). The endosulfan map represents endo-I and endo-II use as well as the potential for endosulfan sulfate (degradation product) formation. Although the maps in Figure 3-5 date from 1992 they give an indication of current pesticide use. Because endosulfan and dacthal have not been banned, they likely will continue to be used in large volume upwind of SEKI. The long life span of lichen makes samples collected in 2003 potential biomonitors for pollution exposure from 1992.

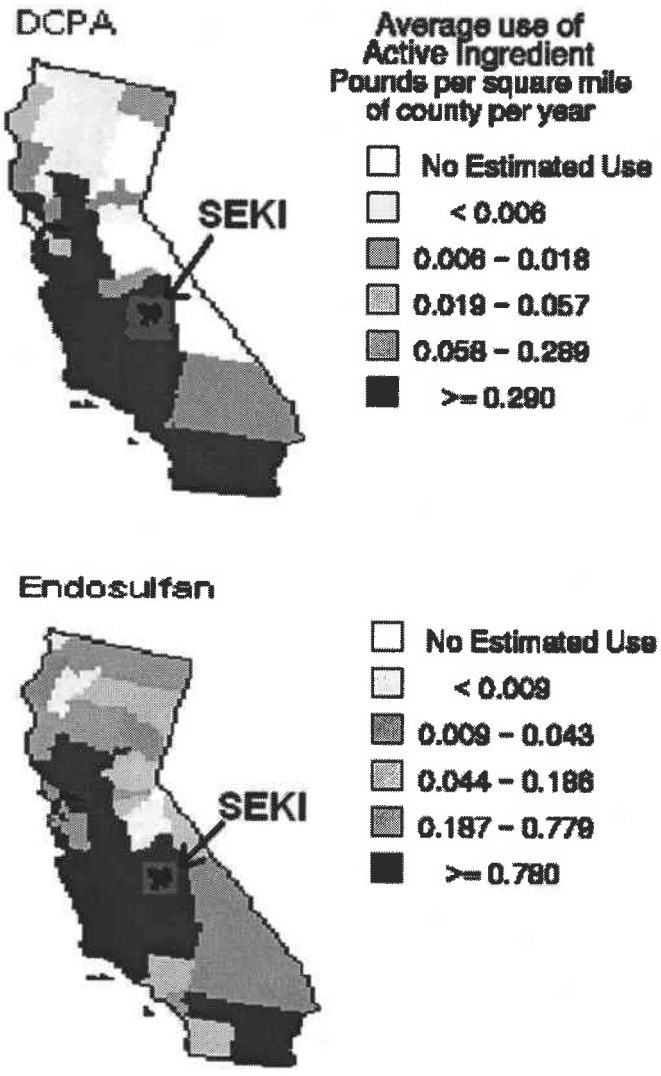


Figure 3-5: Geographical use of Dacthal (DCPA) and Endosulfan in California in 1992 (taken from reference 29).

Many of the SOCs detected in the SEKI lichen samples were pesticides. Sequoia National Park is in close proximity to the San Joaquin Valley and the high pesticide use in the central valley area of California (see Figure 3-5). The banned pesticide DDT was present in some of the highest SOC concentrations measured in lichen from this study. Various congeners of PCB were also measured indicating that recalcitrant contaminants

can persist in high elevations of Sequoia National Park even after the SOC is banned from use.

Endosulfan Comparison

Endosulfan I, endosulfan II, and endosulfan sulfate were all detected in relatively high concentrations. Of the three endosulfan forms detected, endosulfan sulfate was found in the highest concentration. In Wolverton Creek, endosulfan sulfate concentration was over four times greater than endosulfan II and almost five times greater than endosulfan I, and, in Emerald Lake, endosulfan sulfate concentration was almost four times greater than endosulfan II and almost twelve times greater than endosulfan I for dry weight concentrations. Statistical analysis showed that the degradation product endosulfan sulfate was in higher concentration than the original endosulfans used in both sites for dry weight and lipid weight (Table 3-4). Values from the t-test greater than 2.920 indicate a statistically higher concentration of endosulfan sulfate than endosulfan I or endosulfan II.

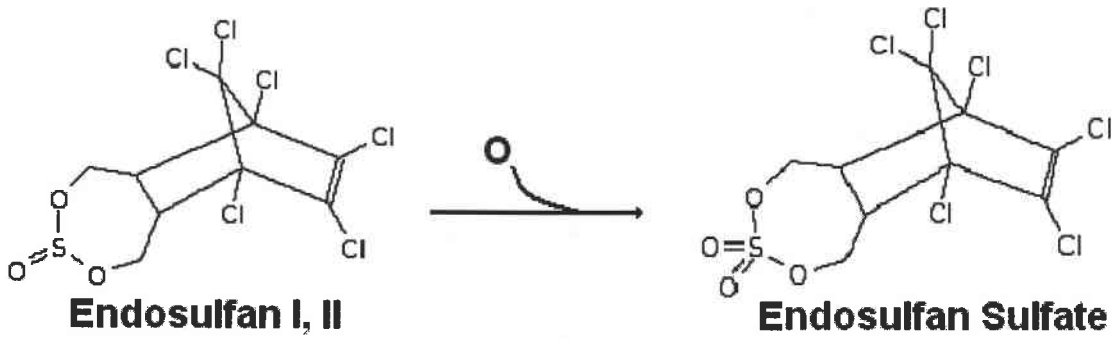
Table 3-4: Student's t-test comparing concentrations of endosulfan sulfate with endosulfan I and II in Wolverton Creek and Emerald Lake on a dry weight and lipid weight basis (95% confidence interval = 2.920).

Dry Weight			**Lipid Weight**		
Wolverton Creek	t-value	t-test $p < 5\%$	*Wolverton Creek*	t-value	t-test $p < 5\%$
Endo sulf vs. Endo I	3.62	yes	Endo sulf vs. Endo I	3.60	yes
Endo sulf vs. Endo II	3.58	yes	Endo sulf vs. Endo II	3.65	yes
Emerald Lake			*Emerald Lake*		
Endo sulf vs. Endo I	6.76	yes	Endo sulf vs. Endo I	8.93	yes
Endo sulf vs. Endo II	5.40	yes	Endo sulf vs. Endo II	7.14	yes

Endosulfan sulfate is the major product from fungal metabolism of endosulfan I and II, due to enzymatic reactions, according to Martens; 1976 (30). This is of interest because lichen is a symbiosis of fungus and algae. However, higher concentrations of

endosulfan sulfate than ensulfan I and II were measured in conifer needles from Emerald Lake as well (Figure 3-3, Table 3-3). This would indicate that endosulfan sulfate is not forming as a result of metabolism in the fungal tissue of lichen. Other studies have shown that endosulfan sulfate can form in many natural environments through biological oxidation (Figure 3-4), is more persistent than endosulfan I and II, and is less volatile than endosulfan I and II, allowing endosulfan sulfate to remain deposited and be less likely to re-volatilize after formation (31, 32). Endosulfan sulfate was also detected in snow as shown above in Table 3-3 indicating that endosulfan sulfate may be undergoing atmospheric transport after formation despite its low vapor pressure. These reasons likely explain why endosulfan sulfate was measured in significantly higher concentrations than endosulfan I and II.

Figure 3-4: Biological oxidation of endosulfan to endosulfan sulfate (30).



Previous Studies

Previous studies have measured SOCs, primarily pesticides, in the Sierra Nevada Mountains. The current use organophosphate pesticides chlorpyrifos, diazinon, diazinon-oxon, parathion, and paraoxon were measured in rain water samples from Sequoia National Park by Zabik and Seiber (33). The highest elevation site that samples were

collected was Kaweah (1920 m) making it the closest to the 2451 m and 2816 m sites where lichen was collected. Chlorpyrifos was detected at a concentration of 15 pg/mL, which roughly equals 15 pg/g (33). The chlorpyrifos concentration was most likely higher in lichen than rain due to the greatly different length of analyte exposure to atmospheric water (hours) and lichen (years), and the lipophilicity of chlorpyrifos allowing it to bioaccumulate in vegetation. The rain measurements were done in 1990-91 indicating that chlorpyrifos has been accumulating in SEKI for over a decade (33).

Further studies by Seiber's group on organophosphate pesticide deposition in the Sequoia National Park have used conifer needles as a biomonitor (34). Sample data from Kaweah is used again for elevation similarity. Samples collected during the summer of 1994 yielded chlorpyrifos and chlorpyrifos oxon concentrations of 16 and 8 ng/g dry weight respectively, values higher than observed in lichen from this study (34). In 1996 the pesticides trifluralin, chlorothalonil, chlorpyrifos, diazinon, malathion, α-HCH, γ-HCH, α-endosulfan, and β-endosulfan were measured in rain and snow from SEKI at concentrations (ng/L) as high as 1.2, 85, 4.4, 19, 24, 4.2, 1.7, 6.5, and 1.4 in rain and 2.4, 13, 13, 6.5, 6.0, 7.5, 1.87, 3.0, and 0.46 in snow respectively, showing that various pesticides are undergoing transport to and deposition in Sequoia National Park (22). Concentrations of organochlorine pesticides were generally higher in lichen, especially for endosulfans, as expected because of their relatively nonpolar nature making them more likely to partition to vegetation than water. This study supports previous studies that Sequoia National Park is exposed to SOC deposition from adjacent agricultural and industrial activities.

Chapter 4 – General Conclusion

The applications in which lichen can be used as a biomonitor continue to grow. Originally, lichen was used to monitor heavy metals, then radionuclides, and most recently SOCs (13-15). The ability to measure a relatively large list of semivolatile organic compounds has opened the possibility of using lichen as a biomonitor in other WACAP sites where lichen may play a significant role in the local food chain. Developing an analytical method to measure a wide range of SOCs in lichen completed the first research objective.

The main obstacle that shortened the list of compounds that could be measured in lichen was the co-elution of matrix interferences during silica solid phase extraction when polar elution solvents like ethyl acetate and mixtures of ethyl acetate and dichloromethane were used. However SOCs that are polar in nature are less likely to partition to vegetation than hydrophobic SOCs that we were able to measure using the analytical method developed in this study.

From this Sequoia National Park study, it can postulated that atmospheric half life may play a role in SOC deposition with elevation. This comes from the fact that SOCs (pesticides) measured in statistically greater concentrations in Emerald Lake (elev. 9240 ft.) than Wolverton Creek (elev. 8040 ft.) had longer atmospheric half lives than analytes (PAHs) measured in statistically greater concentrations in Wolverton Creek than Emerald Lake. A statistical relationship was also observed in linear regressions of concentration difference between the two sampling sites and atmospheric half life at a 5% level of significance on both a dry and lipid weight basis. SOC vapor pressure was not correlated with SOC concentration at different elevations. The SOCs that were measured in the

highest concentrations were several current use pesticides and PAHs that are currently being emitted from fossil fuel combustion. This is likely due to the close proximity of Sequoia National Park to major agricultural regions (pesticide sources) and highway, urban, and industrial regions (PAH sources). Also conifer trees may have contributed to retene concentrations because of its natural occurrence. SOCs that were measured in all matrices, lichen, conifer needles, and snow, were current use pesticides. Persistent pollutants such as DDTs were measured in both sites where lichen was collected, and PCBs were measured in Wolverton Creek. Measuring SOCs in lichen, determining that lichen is a suitable passive air sampler for WACAP sites and comparing the passive air sampling ability of lichen to conifer needles accomplished the second, third, and fourth research objectives.

Finally, the high endosulfan sulfate concentrations in lichen was most likely due to the wide range of ecosystems that endosulfan sulfate can form in, its greater persistence in the environment than endosulfan I and II, and its lower vapor pressure than endosulfan I and II, and likely not fungal metabolism within the lichen since high endosulfan sulfate concentrations were also measured in conifer needles. Previous studies have measured many current use pesticides in Sequoia National Park and other mountains in the Sierra Nevada range (22, 33, 34). This study, as well as previous studies, indicate that Sequoia National Park is potentially at risk to SOC deposition from local sources.

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APPENDIX A: GC/EI-MS parameters for target SOC analysis

INSTRUMENT CONTROL PARAMETERS

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

6890 GC METHOD

OVEN
Initial temp: 60 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	6.00	300	3.00
2	20.00	320	9.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 54.00 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 300 'C (On)
Pressure: 7.80 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.50 min
Total flow: 24.2 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 1.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 29.5 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 7.80 psi
Average velocity: 37 cm/sec

Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET)

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

BACK DETECTOR (NO DET)

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

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

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

POST RUN
Post Time: 0.00 min

TIME TABLE
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 0
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 4
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information

Tune File : MT07.U
Acquistion Mode : SIM

MS Information
-- ----------

Solvent Delay : 6.00 min

EM Absolute : True
Resulting EM Voltage : 1752.9

[Sim Parameters]

GROUP 1
Group ID : 1
Resolution : Low
Plot 1 Ion : 128.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(128.0, 30) (132.0, 30) (142.0, 30)
(189.0, 30) (203.0, 30)

GROUP 2
Group ID : 2
Resolution : Low
Group Start Time : 16.55
Plot 1 Ion : 183.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(183.0, 40) (211.0, 40) (213.0, 40)

GROUP 3
Group ID : 3
Resolution : Low
Group Start Time : 17.01
Plot 1 Ion : 76.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(76.0, 30) (128.0, 30) (151.0, 30)
(152.0, 30) (161.0, 30) (203.0, 30)

GROUP 4
Group ID : 4
Resolution : Low
Group Start Time : 17.50
Plot 1 Ion : 152.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(152.0, 30) (153.0, 30) (154.0, 30)
(162.0, 30) (164.0, 30)

GROUP 5
Group ID : 5
Resolution : Low
Group Start Time : 19.40
Plot 1 Ion : 163.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(163.0, 30) (165.0, 30) (166.0, 30)
(174.0, 30) (176.0, 30)

GROUP 6
Group ID : 6
Resolution : Low
Group Start Time : 20.02
Plot 1 Ion : 93.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(93.0, 30) (120.0, 30) (176.0, 30)

GROUP 7
Group ID : 7
Resolution : Low
Group Start Time : 20.60
Plot 1 Ion : 158.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(158.0, 30) (172.0, 30) (173.0, 30)
(174.0, 30) (175.0, 30) (187.0, 30)

GROUP 8
Group ID : 8
Resolution : Low
Group Start Time : 21.46
Plot 1 Ion : 121.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(121.0, 30) (131.0, 30) (231.0, 30)
(260.0, 30) (270.0, 30)

GROUP 9
Group ID : 9
Resolution : Low
Group Start Time : 22.15
Plot 1 Ion : 88.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(88.0, 30) (170.0, 30) (258.0, 30)

GROUP 10
Group ID : 10
Resolution : Low
Group Start Time : 22.60
Plot 1 Ion : 131.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(131.0, 10) (149.0, 10) (164.0, 10)
(183.0, 10) (186.0, 10) (200.0, 10)
(201.0, 10) (202.0, 10) (203.0, 10)
(205.0, 10) (210.0, 10) (215.0, 10)
(220.0, 10) (225.0, 10)

GROUP 11
Group ID : 11
Resolution : Low
Group Start Time : 23.20
Plot 1 Ion : 138.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(88.1, 20) (89.1, 20) (138.0, 20)
(176.0, 20) (178.0, 20) (179.0, 20)
(186.0, 20) (188.0, 20) (189.0, 20)

(199.0, 20) (304.0, 20) (314.0, 20)

GROUP 12
Group ID : 12
Resolution : Low
Group Start Time : 24.00
Plot 1 Ion : 86.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(86.0, 40) (268.0, 40) (270.0, 40)

GROUP 13
Group ID : 13
Resolution : Low
Group Start Time : 24.65
Plot 1 Ion : 146.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(146.0, 30) (162.0, 30) (173.0, 30)
(223.0, 30) (245.0, 30)

GROUP 14
Group ID : 14
Resolution : Low
Group Start Time : 25.11
Plot 1 Ion : 109.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(109.0, 15) (115.0, 15) (125.0, 15)
(160.0, 15) (188.0, 15) (200.0, 10)
(237.0, 15) (251.0, 15) (263.0, 15)
(269.0, 15)

GROUP 15
Group ID : 15
Resolution : Low
Group Start Time : 25.50
Plot 1 Ion : 115.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(115.0, 40) (116.0, 40) (144.0, 40)

GROUP 16
Group ID : 16
Resolution : Low
Group Start Time : 26.35
Plot 1 Ion : 127.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(127.0, 30) (131.0, 30) (158.0, 30)
(162.0, 30) (173.0, 30) (174.0, 30)
(238.0, 30) (240.0, 30)

GROUP 17
Group ID : 17
Resolution : Low
Group Start Time : 26.72
Plot 1 Ion : 109.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(109.0, 30) (115.0, 30) (155.0, 30)
(225.0, 30) (227.0, 30) (240.0, 30)

(291.0, 30)

GROUP 18
Group ID : 18
Resolution : Low
Group Start Time : 28.00
Plot 1 Ion : 200.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(200.0, 40) (202.0, 40) (203.0, 40)
(212.0, 40) (213.0, 40)

GROUP 19
Group ID : 19
Resolution : Low
Group Start Time : 28.60
Plot 1 Ion : 316.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(316.0, 40) (318.0, 40) (320.0, 40)

GROUP 20
Group ID : 20
Resolution : Low
Group Start Time : 28.96
Plot 1 Ion : 200.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(200.0, 40) (202.0, 40) (203.0, 40)
(212.0, 40) (213.0, 40)

GROUP 21
Group ID : 21
Resolution : Low
Group Start Time : 29.65
Plot 1 Ion : 315.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(165.1, 40) (235.0, 40) (237.0, 40)
(315.9, 40) (317.9, 40) (319.9, 40)
(324.0, 40) (326.0, 40)

GROUP 22
Group ID : 22
Resolution : Low
Group Start Time : 30.35
Plot 1 Ion : 204.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(204.0, 40) (219.0, 40) (234.0, 40)

GROUP 23
Group ID : 23
Resolution : Low
Group Start Time : 31.10
Plot 1 Ion : 165.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(153.0, 40) (165.0, 40) (231.0, 40)
(235.0, 40) (237.0, 40) (243.0, 40)
(245.0, 40) (384.0, 40)

GROUP 24
Group ID : 24
Resolution : Low
Group Start Time : 33.70
Plot 1 Ion : 226.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(226.0, 30) (227.0, 30) (228.0, 30)
(229.0, 30) (240.0, 30) (241.0, 30)
(270.0, 30)

GROUP 25
Group ID : 25
Resolution : Low
Group Start Time : 37.60
Plot 1 Ion : 250.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(250.0, 40) (252.0, 40) (253.0, 40)
(264.0, 40) (265.0, 40)

GROUP 26
Group ID : 26
Resolution : Low
Group Start Time : 42.00
Plot 1 Ion : 274.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(274.0, 40) (276.0, 40) (277.0, 40)
(278.0, 40) (279.0, 40)

GROUP 27
Group ID : 27
Resolution : Low
Group Start Time : 43.00
Plot 1 Ion : 274.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(274.0, 40) (276.0, 40) (277.0, 40)
(288.0, 40) (289.0, 40)

[MSZones]

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

Compound List Report MSD A

Method : D:\MSDCHEM\1\METHODS\OC02GSM.M (RTE Integrator)
Title : NPS analytes full scan EI
Last Update : Tue Jun 24 08:31:29 2003
Response via : Initial Calibration
Total Cpnds : 136

PK#		Compound Name	QIon	Exp_RT	Rel_RT	Cal	#Qual	A/H	ID
1	I	Acenaphthene-d10	164	18.65	1.000	L	1	A	B
2	S	EPTC-d14	142	15.75	0.844	A	1	A	B
3	S	Fluorene-d10	176	20.71	1.110	A	1	A	B
4	S	Phorate-d10	131	22.64	1.214	A	1	A	B

5	S	Atrazine-d5	205	23.76	1.274	A	1	A	B
6	S	Phenanthrene-d10	188	24.46	1.311	A	1	A	B
7	S	Diazinon-d10	314	24.45	1.311	A	1	A	B
8	I	Fluoranthene-d10	212	29.16	1.000	A	1	A	B
9	S	Acetochlor-d11	173	25.92	0.889	A	1	A	B
10	S	Methyl parathion-d6	269	26.21	0.899	A	1	A	B
11	S	Alachlor-d13	200	26.17	0.898	A	1	A	B
12	S	Malathion-d7	174	27.41	0.940	A	1	A	B
13	S	Parathion-d10	115	27.79	0.953	A	0	A	B
14	S	Pyrene-d10	212	30.00	1.029	A	1	A	B
15	S	p,p'-DDE-d8	326	30.84	1.058	A	1	A	B
16	I	Benzo(k)fluoranthene-d12	264	38.84	1.000	A	1	A	B
17	S	p,p'-DDT-d8	243	33.31	0.858	A	1	A	B
18	S	Triphenylene-d12	240	34.84	0.897	A	1	A	B
19	S	Benzo(a)pyrene-d12	264	39.79	1.024	A	1	A	B
20	S	Benzo(ghi)perylene-d12	288	44.19	1.138	A	1	A	B
21	I	Acenaphthene-d10-IS	164	18.65	1.000	L	1	A	B
22	T	EPTC	128	15.95	0.855	L	2	A	B
23	T	Etridiazole	211	17.92	0.961	L	2	A	B
24	T	Acenaphthylene	152	18.07	0.969	L	2	A	B
25	T	Pebulate	128	18.22	0.977	L	2	A	B
26	T	Acenaphthene	154	18.77	1.006	L	2	A	B
27	T	Fluorene	166	20.82	1.116	L	2	A	B
28	T	Propachlor	120	21.11	1.132	L	2	A	B
29	T	Atrazine desisopropyl	173	21.85	1.171	L	2	A	B
30	T	Atrazine desethyl	172	22.09	1.184	L	2	A	B
31	T	Phorate	260	22.78	1.221	L	2	A	B
32	T	Demeton-S	88	23.41	1.255	L	2	A	B
33	T	Carbofuran	164	23.57	1.264	L	2	A	B
34	T	Simazine	201	23.66	1.268	L	2	A	B
35	T	Prometon	210	23.70	1.270	L	2	A	B
36	T	Atrazine	200	23.83	1.278	L	2	A	B
37	T	Phenanthrene	178	24.55	1.316	L	2	A	B
38	T	Diazinon	304	24.58	1.318	L	2	A	B
39	T	Anthracene	178	24.75	1.327	L	2	A	B
40	T	Disulfoton	88	24.88	1.334	L	2	A	B
41	I	Fluoranthene-d10-IS	212	29.16	1.000	L	1	A	B
42	T	Triallate	268	25.14	0.862	L	2	A	B
43	T	Acetochlor	146	26.06	0.894	L	2	A	B
44	T	Methyl parathion	263	26.29	0.902	L	2	A	B
45	T	Alachlor	188	26.33	0.903	L	2	A	B
46	T	Carbaryl	144	26.43	0.906	L	2	A	B
47	T	Malathion	173	27.50	0.943	L	2	A	B
48	T	Metolachlor	162	27.59	0.946	L	2	A	B
49	T	Cyanazine	225	27.81	0.954	L	2	A	B
50	T	Parathion	291	27.93	0.958	L	2	A	B
51	T	Fluoranthene	202	29.23	1.002	L	2	A	B
52	T	o,p' DDE	318	29.86	1.024	L	2	A	B
53	T	Pyrene	202	30.06	1.031	L	2	A	B
54	T	p,p' DDE	318	30.90	1.060	L	2	A	B
55	T	o,p' DDD	235	31.09	1.066	L	2	A	B
56	T	Retene	219	31.49	1.080	L	2	A	B

57	T	p,p' DDD	235	32.21	1.104	L	2	A	B
58	I	Benzo(k)fluoranthene-d12-IS	264	38.84	1.000	L	1	A	B
59	T	o,p' DDT	235	32.27	0.831	L	2	A	B
60	T	Ethion	231	32.25	0.830	L	2	A	B
61	T	p,p' DDT	235	33.38	0.859	L	2	A	B
62	T	Benzo(a)anthracene	228	34.87	0.898	L	2	A	B
63	T	Chrys + Triph	228	34.99	0.901	L	2	A	B
64	T	Methoxychlor	227	35.11	0.904	L	2	A	B
65	T	Benzo(b)fluoranthene	252	38.81	0.999	L	2	A	B
66	T	Benzo(k)fluoranthene	252	38.90	1.002	L	2	A	B
67	T	Benz(e)pyrene	252	39.69	1.022	L	2	A	B
68	T	Benzo(a)pyrene	252	39.86	1.026	L	2	A	B
69	T	Indeno(1,2,3-cd)pyrene	276	43.41	1.118	L	2	A	B
70	T	Dibenz(a,h)anthracene	278	43.57	1.122	L	2	A	B
71	T	Benzo(ghi)perylene	276	44.29	1.140	L	2	A	B
72	I	EPTC-d14-LS	142	15.75	1.000	L	1	A	B
73	T	EPTC-LA	128	15.95	1.013	L	2	A	B
74	T	Etridiazole-L	211	17.92	1.138	L	2	A	B
75	T	Pebulate-L	128	18.22	1.156	L	2	A	B
76	I	Fluorene-d10-LS	176	20.71	1.000	L	1	A	B
77	T	Acenaphthylene-L	152	18.07	0.872	L	1	A	B
78	T	Acenaphthene-L	154	18.77	0.907	L	2	A	B
79	T	Fluorene-LA	166	20.82	1.005	L	2	A	B
80	I	Phorate-d10-LS	131	22.64	1.000	L	1	A	B
81	T	Phorate-LA	260	22.78	1.006	L	2	A	B
82	T	Demeton-S-L	88	23.41	1.034	L	1	A	B
83	I	Atrazine-d5-LS	205	23.76	1.000	L	1	A	B
84	T	Propachlor-L	120	21.11	0.888	L	2	A	B
85	T	Atrazine desisoproply-L	173	22.08	0.929	L	1	A	B
86	T	Atrazine desethyl-L	172	22.09	0.929	L	2	A	B
87	T	Carbofuran-L	164	23.62	0.994	L	2	A	B
88	T	Simazine-L	201	23.66	0.995	L	2	A	B
89	T	Prometon-L	210	23.70	0.997	L	2	A	B
90	T	Atrazine-LA	200	23.83	1.003	L	2	A	B
91	T	Cyanazine-L	225	27.81	1.170	L	2	A	B
92	I	Phenanthrene-d10-LS	188	24.46	1.000	L	1	A	B
93	T	Phenanthrene-LA	178	24.75	1.012	L	2	A	B
94	T	Anthracene-L	178	24.75	1.012	L	2	A	B
95	I	Diazinon-d10-LS	314	24.45	1.000	L	1	A	B
96	T	Diazinon-LA	304	24.58	1.005	L	2	A	B
97	T	Disulfoton-L	88	24.88	1.017	L	2	A	B
98	I	Acetochlor-d11-LS	173	25.92	1.000	L	1	A	B
99	T	Acetochlor-LA	146	26.06	1.005	L	2	A	B
100	I	Alachlor-d13-LS	200	26.17	1.000	L	1	A	B
101	T	Alachlor-LA	188	26.33	1.006	L	2	A	B
102	T	Metolachlor-L	162	27.59	1.054	L	2	A	B

103 I	Malathion-d7-LS	174	27.41	1.000	L	1	A	B
104 T	Triallate-L	268	25.14	0.917	L	1	A	B
105 T	Carbaryl-L	144	26.43	0.964	L	2	A	B
106 T	Malathion-LA	173	27.50	1.003	L	2	A	B
107 I	Methyl parathion-d6-LS	269	26.21	1.000	L	1	A	B
108 T	Methyl parathion-LA	263	26.29	1.003	L	2	A	B
109 I	Parathion-d10-LS	115	27.80	1.000	L	0	A	B
110 T	Parathion-LA	291	27.93	1.005	L	2	A	B
111 T	Ethion-L	231	32.25	1.160	L	2	A	B
112 I	Pyrene-d10-LS	212	30.00	1.000	L	1	A	B
113 T	Fluoranthene-L	202	29.23	0.974	L	2	A	B
114 T	Pyrene-LA	202	30.06	1.002	L	2	A	B
115 T	Retene-L	219	31.49	1.050	L	2	A	B
116 I	p,p'-DDE-d8-LS	326	30.84	1.000	L	1	A	B
117 T	o,p'-DDE-L	318	29.86	0.968	L	2	A	B
118 T	p,p'-DDE-LA	318	30.90	1.002	L	2	A	B
119 T	o,p'-DDD-L	235	31.09	1.008	L	2	A	B
120 T	p,p'-DDD-L	235	32.21	1.044	L	2	A	B
121 I	p,p'-DDT-d8-LS	243	33.31	1.000	L	1	A	B
122 T	o,p'-DDT-L	235	32.21	0.967	L	2	A	B
123 T	p,p'-DDT-LA	235	33.38	1.002	L	2	A	B
124 T	Methoxychlor-L	227	35.11	1.054	L	1	A	B
125 I	Triphenylene-d12-LS	240	34.84	1.000	L	1	A	B
126 T	Benzo(a)anthracene-L	228	34.87	1.001	L	2	A	B
127 T	Chrys-L +Triph-LA	228	34.99	1.004	L	2	A	B
128 I	Benzo(a)pyrene-d12-LS	264	39.79	1.000	L	1	A	B
129 T	Benzo(b)fluoranthene-L	252	38.90	0.978	L	2	A	B
130 T	Benzo(k)fluoranthene-L	252	38.90	0.978	L	2	A	B
131 T	Benzo(e)pyrene-L	252	39.69	0.998	L	2	A	B
132 T	Benzo(a)pyrene-LA	252	39.86	1.002	L	2	A	B
133 I	Benzo(ghi)perylene-d12-LS	288	44.19	1.000	L	1	A	B
134 T	Indeno(1,2,3-cd)pyrene-L	276	43.41	0.982	L	2	A	B
135 T	Dibenz(a,h)anthracene-L	278	43.57	0.986	L	2	A	B
136 T	Benzo(ghi)perylene-LA	276	44.29	1.002	L	2	A	B

Cal A = Average L = Linear LO = Linear w/origin Q = Quad QO = Quad w/origin
#Qual = number of qualifiers
A/H = Area or Height
ID R = R.T. B = R.T. & Q Q = Qvalue L = Largest A = All

APPENDIX B: GC/EI-MS parameters for target SOC analysis

INSTRUMENT CONTROL PARAMETERS

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

==========

6890 GC METHOD

==========

OVEN
Initial temp: 60 'C (On) Maximum temp: 325 'C
Initial time: 1.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	6.00	300	3.00
2	20.00	320	9.00
3	0.0(Off)		

Post temp: 0 'C
Post time: 0.00 min
Run time: 54.00 min

FRONT INLET (UNKNOWN) BACK INLET ()
Mode: Pulsed Splitless
Initial temp: 300 'C (On)
Pressure: 8.33 psi (On)
Pulse pressure: 20.0 psi
Pulse time: 0.60 min
Purge flow: 20.0 mL/min
Purge time: 0.50 min
Total flow: 24.1 mL/min
Gas saver: On
Saver flow: 15.0 mL/min
Saver time: 1.00 min
Gas type: Helium

COLUMN 1 COLUMN 2
Capillary Column (not installed)
Model Number: Agilent 122-5532
DB-5ms, 0.25mm * 30m * 0.25um
Max temperature: 350 'C
Nominal length: 29.9 m
Nominal diameter: 250.00 um
Nominal film thickness: 0.25 um
Mode: constant flow
Initial flow: 1.0 mL/min
Nominal init pressure: 8.44 psi
Average velocity: 37 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

FRONT DETECTOR (NO DET) BACK DETECTOR (NO DET)

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

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

COLUMN COMP 1
(No Detectors Installed)

COLUMN COMP 2
(No Detectors Installed)

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

POST RUN
Post Time: 0.00 min

TIME TABLE
Time Specifier Parameter & Setpoint

7673 Injector

Front Injector:
Sample Washes 1
Sample Pumps 4
Injection Volume 1.0 microliters
Syringe Size 10.0 microliters
PostInj Solvent A Washes 2
PostInj Solvent B Washes 2
Viscosity Delay 0 seconds
Plunger Speed Fast
PreInjection Dwell 0.00 minutes
PostInjection Dwell 0.00 minutes

Back Injector:
No parameters specified

MS ACQUISITION PARAMETERS

General Information

Tune File : NCI06.U
Acquistion Mode : SIM

MS Information

Solvent Delay : 10.00 min

EM Absolute : True
Resulting EM Voltage : 1905.9

[Sim Parameters]

GROUP 1
Group ID : Trifluralin
Resolution : Low
Plot 1 Ion : 305.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(305.1, 20) (319.2, 20) (335.1, 20)
(336.1, 20) (349.2, 20) (350.2, 20)

GROUP 2
Group ID : HCH
Resolution : Low
Group Start Time : 21.30
Plot 1 Ion : 252.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(70.0, 20) (71.0, 20) (72.0, 20)
(73.0, 20) (74.0, 20) (252.9, 20)
(262.9, 20) (281.8, 20) (283.8, 20)
(285.8, 20) (289.8, 20) (291.8, 20)
(293.8, 20)

GROUP 3
Group ID : Chlorothalonil
Resolution : Low
Group Start Time : 23.20
Plot 1 Ion : 160.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(71.0, 40) (160.1, 40) (161.1, 40)
(253.0, 40) (255.0, 40) (263.9, 40)
(265.9, 40) (267.9, 40)

GROUP 4
Group ID : Metribuzin
Resolution : Low
Group Start Time : 24.70
Plot 1 Ion : 184.1
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(184.1, 40) (198.1, 40) (199.1, 40)
(265.9, 40) (267.9, 40) (299.9, 40)

GROUP 5
Group ID : Chlorpyrifos
Resolution : Low
Group Start Time : 26.05
Plot 1 Ion : 214.0
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(214.0, 20) (237.0, 20) (239.0, 20)
(255.0, 20) (292.0, 20) (294.0, 20)
(297.0, 20) (298.0, 20) (299.0, 20)

(313.0, 20) (315.0, 20) (322.0, 20)
(324.0, 20) (329.9, 20) (331.9, 20)
(333.9, 20)

GROUP 6
Group ID : Hep Epox
Resolution : Low
Group Start Time : 27.50
Plot 1 Ion : 289.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(289.9, 20) (291.9, 20) (293.9, 20)
(351.9, 20) (387.8, 20) (389.8, 20)
(391.8, 20) (407.9, 20) (409.9, 20)
(411.9, 20) (413.9, 20) (423.9, 20)
(425.9, 20)

GROUP 7
Group ID : Endo I
Resolution : Low
Group Start Time : 28.30
Plot 1 Ion : 323.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(263.9, 20) (265.9, 20) (267.9, 20)
(323.9, 20) (325.9, 20) (327.9, 20)
(335.9, 20) (337.9, 20) (339.9, 20)
(369.9, 20) (371.9, 20) (373.9, 20)
(375.9, 20) (377.9, 20) (403.9, 20)
(407.9, 20) (409.9, 20) (411.9, 20)
(441.9, 20) (443.9, 20) (445.9, 20)

GROUP 8
Group ID : Dieldrin
Resolution : Low
Group Start Time : 29.55
Plot 1 Ion : 345.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(296.0, 40) (298.0, 40) (300.0, 40)
(345.9, 40) (347.9, 40) (379.9, 40)

GROUP 9
Group ID : Endo II
Resolution : Low
Group Start Time : 30.50
Plot 1 Ion : 323.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(323.9, 30) (325.9, 30) (327.9, 30)
(371.9, 30) (405.9, 30) (407.9, 30)
(409.9, 30) (411.9, 30) (413.9, 30)
(441.8, 30) (443.8, 30) (445.8, 30)

GROUP 10
Group ID : Endrin ald
Resolution : Low
Group Start Time : 31.00
Plot 1 Ion : 345.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)

(345.9, 40) (358.0, 40) (360.0, 40)
(362.0, 40) (379.9, 40) (381.9, 40)

GROUP 11
Group ID : Endo Sulfate
Resolution : Low
Group Start Time : 31.75
Plot 1 Ion : 357.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(357.9, 40) (359.9, 40) (361.9, 40)
(385.9, 40) (387.9, 40) (421.9, 40)

GROUP 12
Group ID : Hepta PCB
Resolution : Low
Group Start Time : 32.35
Plot 1 Ion : 393.9
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(367.8, 30) (369.8, 30) (393.9, 30)
(395.9, 30) (397.9, 30) (403.8, 30)
(405.9, 30) (407.9, 30) (409.9, 30)

[MSZones]

MS Quad : 150 C maximum 200 C
MS Source : 150 C maximum 300 C

Compound List Report MSD B

Method : C:\MSDCHEM\1\METHODS\02SA01_N.M (RTE Integrator)
Title : Calibration curve 10-20-03
Last Update : Mon Dec 22 08:06:40 2003
Response via : Initial Calibration
Total Cpnds : 53

PK#		Compound Name	QIon	Exp_RT	Rel_RT	Cal	#Qual	A/H	ID
1	I	d6-HCH, alpha-IS	72	21.42	1.000	A	2	A	B
2	S	d14-Trifluralin	349	20.84	0.973	A	2	A	B
3	S	13C-HCB	292	21.63	1.009	A	2	A	B
4	S	d6-HCH, gamma	72	22.61	1.055	A	2	A	B
5	S	d10-Chlorpyrifos	322	26.21	1.223	A	2	A	B
6	I	d6-PCB 77-IS	298	29.80	1.000	A	2	A	B
7	S	d4-Endosulfan I	378	28.71	0.964	A	2	A	B
8	S	13C-PCB 101	338	28.63	0.961	A	2	A	B
9	S	d4-Endosulfan II	412	30.61	1.027	A	2	A	B
10	S	13C-PCB 180	406	34.01	1.141	A	2	A	B
11	I	d14-Trifluralin-LS	349	20.84	1.000	A	2	A	B
12	T	Trifluralin	335	21.00	1.008	A	2	A	B
13	I	13C6-HCB-LS	292	21.63	1.000	A	2	A	B
14	T	Hexachlorobenzene	284	21.63	1.000	A	2	A	B
15	T	Chlorothalonil	266	23.46	1.085	A	2	A	B
16	T	Heptachlor	266	25.17	1.164	A	2	A	B

17	T	Dacthal	332	26.46	1.224	A	2	A	B		
18	I	d6-gamma-HCH-LS	72	22.61	1.000	A	2	A	B		
19	T	HCH, alpha	71	21.57	0.954	A	2	A	B		
20	T	HCH, beta	71	22.61	1.000	A	2	A	B		
21	T	HCH, gamma (Lindane)	71	22.75	1.006	A	2	A	B		
22	T	HCH, delta	71	23.88	1.056	A	2	A	B		
23	T	Triallate	160	23.80	1.053	A	1	A	B		
24	T	Metribuzin	198	24.85	1.099	A	2	A	B		
25	T	Aldrin	237	26.33	1.164	A	2	A	B		
26	I	d10-Chlorpyrifos-LS	322	26.21	1.000	A	2	A	B		
27	T	Chlorpyrifos oxon	297	26.18	0.999	A	2	A	B		
28	T	Chlorpyrifos	313	26.34	1.005	A	2	A	B		
29	I	d4-Endosulfan I-LS	378	28.71	1.000	A	2	A	B		
30	T	Heptachlor epoxide	390	27.62	0.962	A	2	A	B		
31	T	Chlordane, oxy	424	27.61	0.962	A	2	A	B		
32	T	Chlordane, trans	410	28.39	0.989	A	2	A	B		
33	T	Endosulfan I	404	28.79	1.003	A	2	A	B		
34	T	Chlordane, cis	266	28.79	1.002	A	2	A	B		
35	T	Nonachlor, trans	444	28.88	1.006	A	2	A	B		
36	T	Dieldrin	346	29.64	1.032	A	2	A	B		
37	I	13C-PCB 101-LS	338	28.63	1.000	A	2	A	B		
38	T	PCB 52 (tetra)	292	26.34	0.920	A	2	A	B		
39	T	PCB 74 (tetra)	292	27.69	0.967	A	2	A	B		
40	T	PCB 101 (penta)	326	28.63	1.000	A	2	A	B		
41	T	PCB 118 (penta)	326	30.57	1.068	A	2	A	B		
42	I	d4-Endosulfan II-LS	412	30.61	1.000	A	2	A	B		
43	T	Endrin	346	30.29	0.990	A	2	A	B		
44	T	Endosulfan II	406	30.67	1.002	A	2	A	B		
45	T	Nonachlor, cis	444	30.80	1.006	A	2	A	B		
46	T	Endrin aldehyde	380	31.13	1.017	A	2	A	B		
47	T	Endosulfan sulfate	386	31.87	1.041	A	2	A	B		
48	I	13C-PCB 180-LS	406	34.01	1.000	A	2	A	B		
49	T	PCB 153 (hexa)	360	31.22	0.918	A	2	A	B		
50	T	PCB 138 (hexa)	360	32.03	0.942	A	2	A	B		
51	T	PCB 187 (hepta)	394	32.45	0.954	A	2	A	B		
52	T	PCB 183 (hepta)	394	32.62	0.959	A	2	A	B		
53	T	Mirex	368	35.14	1.033	A	2	A	B		

Cal A = Average L = Linear LO = Linear w/origin Q = Quad QO = Quad w/origin
#Qual = number of qualifiers
A/H = Area or Height
ID R = R.T. B = R.T. & Q Q = Qvalue L = Largest A = All