Measurement of Semi-volatile Organic Compounds in Conifer Needles from Sequoia National Park, CA

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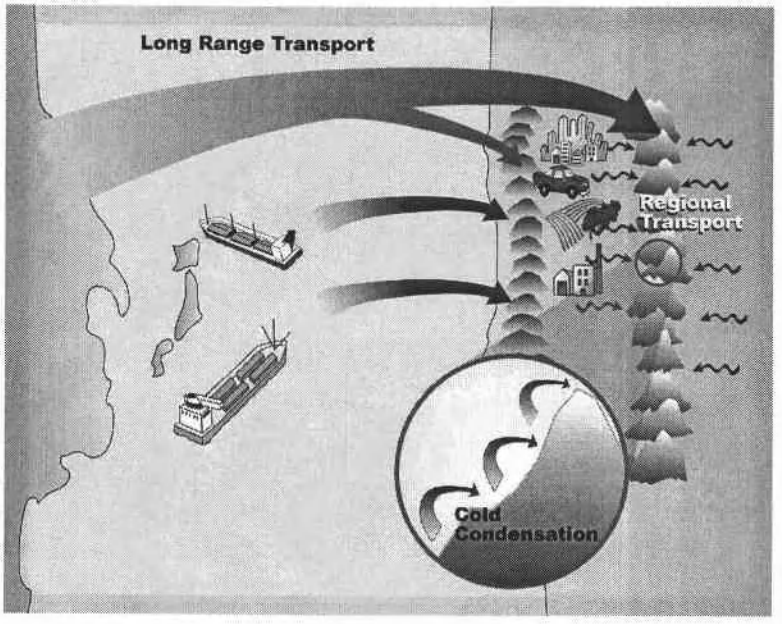
Abstract

An analytical method was adapted to extract semi-volatile organic compounds (SOCs) from conifer needles. Needles from *Abies concolor* (white fir) and *Pinus contortas* (lodgepole pine) from Sequoia National Park (SNP) were collected during the summer of 2003, and analyzed for SOCs. The goal of this research was to determine differences between one and two year old coniferous growths, differences between species, and compare deposition of SOCs in conifer needles and lichen. Eleven, primarily agricultural, SOCs were found on conifer needles from the two species, in the range of 0.0436 ng/g to 8.267 ng/g (dry weight). One year old growth generally had lower concentrations of SOCs than two year old growth, and white fir needles had generally higher concentrations of SOCs than lodgepole pine. Lichen had higher SOC concentrations than the conifer needles, but the age of the lichen samples was difficult to determine. This study demonstrates that SOC concentration on conifer needles increases with exposure time to the atmosphere, but that concentration of SOCs may vary between species.

Introduction

Semi-volatile organic compounds (SOCs) are chemicals that are capable of undergoing volatilization after release into the environment. These compounds, resulting from incomplete combustion (such as fluorene and pyrene), agriculture (such as DDT, aldrin and triallate), and industrial sources (PCBs) can volatilize from the original source area (1, 2). Atmospheric currents carry SOCs from long-range and regional sources and distill some of them to colder, high altitude and high latitude ecosystems (2, 3), making these ecosystems prone to contamination via wet or dry deposition (4). This process is shown in Figure 1.

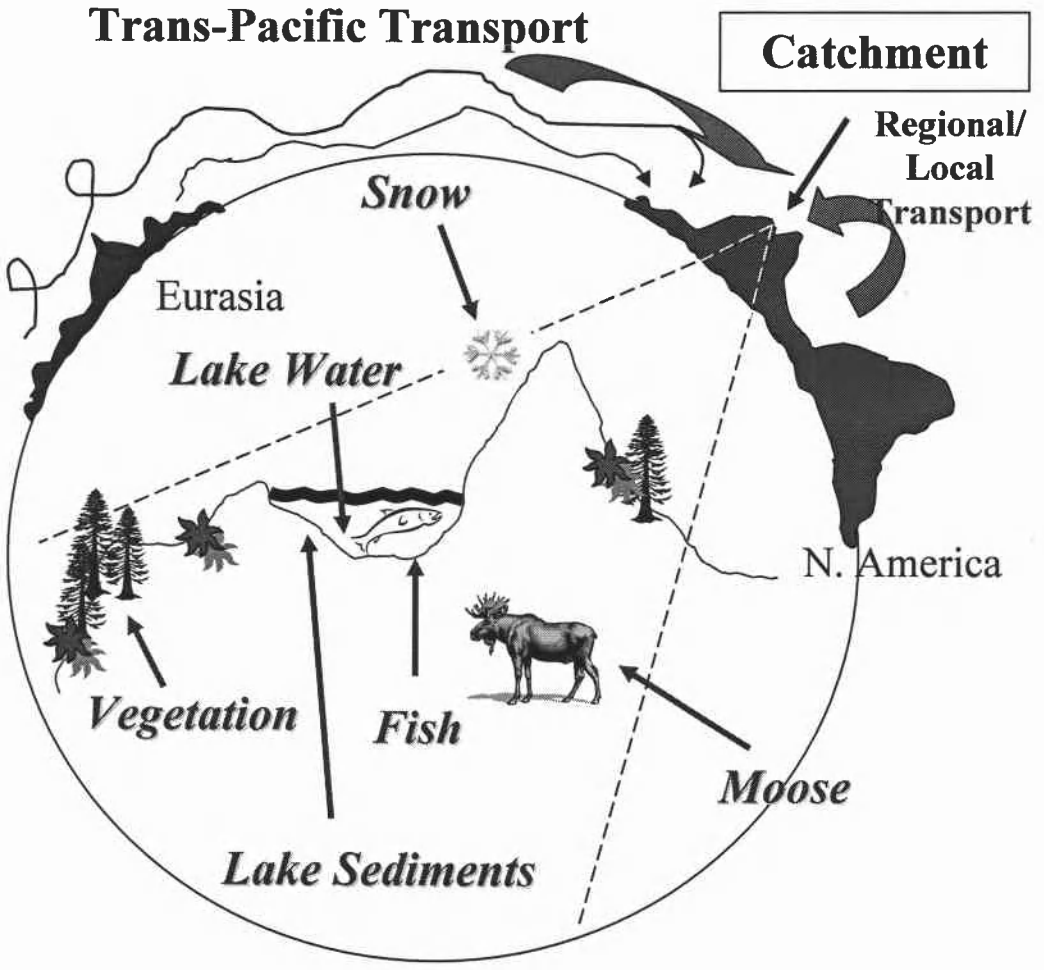
Figure 1: Long Range and Regional Transport of SOCs



Previous research has shown that some SOCs are highly lipophilic. Some are carcinogenic (5) or mimic estrogen (6, 7). For these reasons,

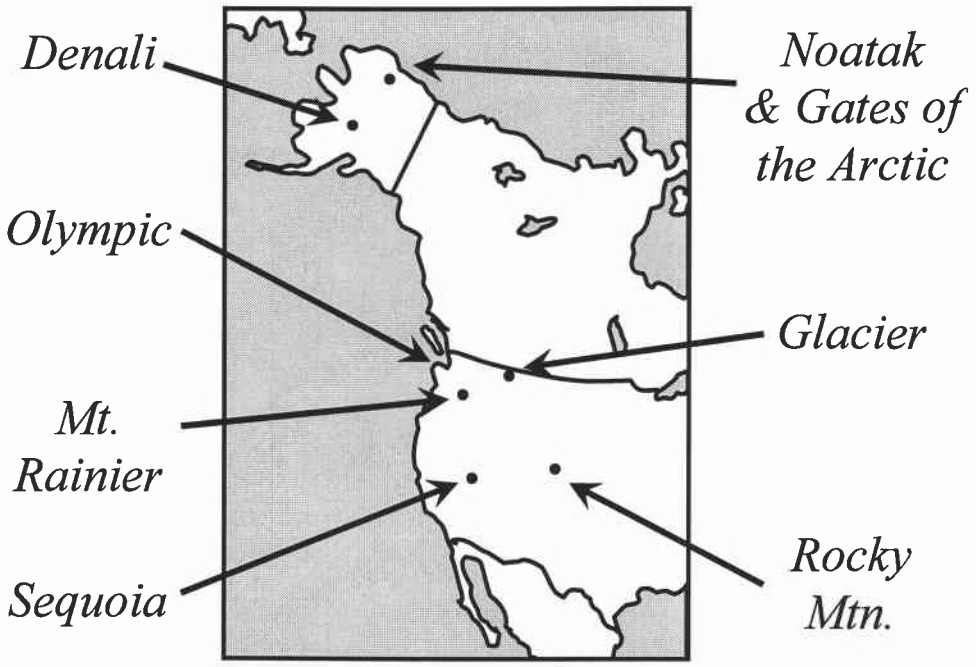
SOCs may pose potential bioaccumulation and health risks to high elevation and high latitude ecosystems (See Figure 2).

Figure 2: SOC cycling and deposition



The Western Airborne Contaminant Assessment Project (WACAP) is an investigation into the deposition of semi-volatile organic compounds (SOCs) into high-elevation ecosystems of western U.S. national parks from regional and Eurasian sources (8, 9) (Figure 3).

Figure 3: WACAP Sampling Sites



WACAP is a collaboration of scientists from National Parks Service, Environmental Protection Agency, United States Geological Service, Oregon State University, Washington State University, and the USDA Forest Service. A broad and diverse group of SOCs are under investigation in WACAP, including PAHs, PCBs, and pesticides and degradation products thereof (Table 1). Several different media are under investigation in this project, including vegetation, sediment, snow, lake water, and fish.

Table 1: Target Analytes, Surrogates, and Internal Standards

Electron Impact Ionization	Negative Chemical 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	PCBs: PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), 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: o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon, Demeton S, Ethion, Etradiazole, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine	Pesticides and degradation products: Hexachlorocyclohexanes (HCH) - α*, β, γ-(lindane), and δ, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlor Epoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorothalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Triallate, Mirex
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}-Acetochlor	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_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	Internal Standards: d_{14}-Trifluralin

Man-made passive air sampling devices, such as the USGS semi-permeable membrane devices, while eliminating variances found between natural passive air samplers, do have some drawbacks, such as cost and variations in air flow rate (10). In addition, while high-volume active air samplers are quantitative and appropriate for short-term sampling, they require a power supply not readily available at remote sites and frequent, easy access for collecting and replacing sampling media.

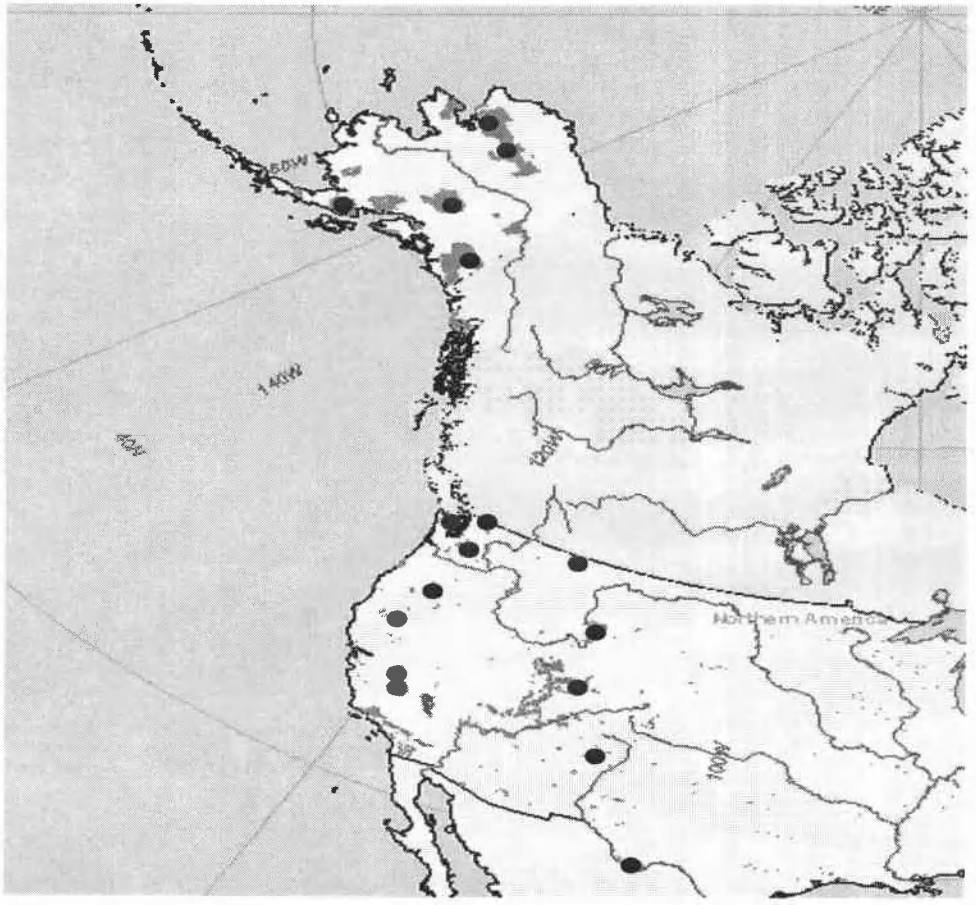
The uptake of SOCs from the atmosphere by vegetation has been shown to be proportional to the surface area and lipid content of vegetation (11, 12). The vegetation type best suited for collection and analysis from WACAP sites is under examination for use as a passive air sampler at all WACAP sites. The WACAP sampling plan is to sample different types of vegetation (conifer needles and lichen) from the primary sampling sites (Figure 4).

Figure 4: WACAP Primary and Secondary Sampling Sites

- **8 Primary Parks**
- Denali National Park & Preserve
- Gates of the Arctic National Park & Preserve
- Glacier National Park
- Mount Rainier National Park
- Noatak National Preserve
- Olympic National Park
- Rocky Mountain National Park
- Sequoia National Park

12 Secondary Parks

- Bandelier National Monument
- Big Bend National Park
- Crater Lake National Park
- Glacier Bay National Park & Preserve
- Grand Teton National Park
- Great Sand Dunes National Monument
- Katmai National Park & Preserve
- North Cascades National Park
- Petersburg District, Tongass National Forest
- Wrangell-St. Elias National Park & Preserve
- Yellowstone National Park
- Yosemite National Park



After the most appropriate vegetation type is determined, these samples will be collected from the secondary sampling sites (See Figure 4) to determine the deposition and distribution trends among collection sites and parks. The most appropriate vegetation type for use in WACAP as a passive air sampler should have the following characteristics: it should have a high lipid content for uptake of hydrophobic SOCs, easy to collect, ubiquitous at high elevations, dateable, and will allow for quantification of extracted SOCs with a reasonable analytical method. The ease with which they can be collected and dated (13), as well as their relative ubiquity at high elevations, make conifer needles worthy of further investigation for use in WACAP as a passive air sampler. Conifer needles have been identified as suitable passive air samplers due to their high lipid content and surface area (14) and SOCs have been measured in Canadian Rocky Mountain conifer needles in previous research (15). However, a direct, methodical comparison between the use of conifer needles as passive air samplers and other forms of vegetation has not been conducted.

Sequoia National Park (SNP, elevation 2816 m; Figure 3), with its proximity to agricultural and combustion SOC sources, was chosen as the investigation site for comparison between the two types of vegetation. This research examined the suitability of conifer needles as a passive air sampler, and compare results with those for lichen collected from SNP. Possible differences in SOC concentrations between the current and

previous years' conifer needles and possible species differences within a site were examined.

Determination of the source, transport route, and deposition rates of SOCs to vegetation (and into the terrestrial ecosystem) is important as it could influence international policy on the use of these chemicals and associated activities, as well as lead to a better understanding of the role of vegetation in SOC atmospheric cycling.

Experimental Methods and Materials

Collection

Analytical method development and verification was conducted on noble fir (*Abies procera*) needles collected from Mary's Peak (elevation 1249 m), Corvallis, Oregon in the fall and winter of 2003. Needles from the current growing season (Y1) and previous growing season (Y2) were collected from white fir (*Abies concolor*) and lodgepole pine (*Pinus contortas*) from Sequoia National Park, Emerald Lake (elevation 2816 m) on August 8, 2003. Scientists wore nitrile gloves while collecting needles, collected three samples of approximately 75 grams per year of growth from a height of ~1.5 m (13) from one tree from three sites within Emerald Lake, and separated the needles by year while in the field. Each year's sample was then placed into a Kapak 8" X 12" Heat Sealable Metalized Polyester Barrier Film Bag (0.0025" thick), and sealed on site. Samples were transported and stored at -20° ± 5°C.

Extraction

For extraction, ~ 30 g Y1 and ~ 30 g Y2 needles, chosen randomly from one of the three sites, were weighed in a pre-tared VWR Polystyrene weigh boat, and mixed with sufficient Na_2SO_4 (approximately 20 g/sample) for the Na_2SO_4 to form sand sized particles. Two 66 mL Accelerated Solvent Extraction (ASE) cells were prepared as follows: a 30 mm diameter, Whatman cellulose filter was placed in the bottom of the cell, and ~ 2 g of Varian Chem Tube Hydromatrix placed on top; the needles, together with Na_2SO_4, were then split and packed tightly into the cells with the packing tool provided with the instrument; ~ 2 g of Hydromatrix were added on top of the needles; 15 µL of 10 ng/µL surrogates (Table 1) were then spiked on top of the hydromatrix, and another cellulose filter placed on top. The ASE cell was then closed tightly, and needles were extracted twice at 120°C (16) and 1500 psi with 100% Optima Methylene Chloride (DCM) in a Dionex Accelerated Solvent Exchange 300 (ASE). The extracts were collected in 250 mL ICHEM clear NM BR glass bottles, capped with a solid-top Teflon resin-lined screw cap, and stored at 5°C. Two extractions were performed from Emerald Lake; error bars represent standard deviation between extractions.

Lipid determination was performed by pipetting 5.00 (± 0.01) mL of extract into a pre-weighed 75 mm aluminum weighing dish. The extract was dried for 24 hours at 110° C in a Stabil-therm Laboratory oven. The

dry weight of the needles was determined by drying ~5 g of each sample in the same manner.

Purification

Polar, matrix interferences were removed from the DCM extract by water extraction with ~ 125 mL reverse osmosis water. After addition of water, the bottle containing the extract and water was shaken for 60 s, let sit for 30 s, and then shaken for an additional 60 s. Bottles containing the water and extract were then stored overnight at 5°C. The water was pipetted off until a thin film remained above the DCM extract.

After water extraction, the conifer needle extracts in DCM were dried over Na_2SO_4 to remove any remaining water. J.T. Baker anhydrous sodium sulfate (Na_2SO_4, baked at 450°C for four hours to activate, then cooled) was added to extracts in the 250 mL bottles and shaken until the Na_2SO_4 clumped at sand sized granules. The Na_2SO_4 was left in the extract overnight, the needle extract was decanted off the Na_2SO_4, and the remaining Na_2SO_4 was rinsed with DCM a minimum of three (3) times or until DCM ran clear.

After drying over Na_2SO_4, the needle DCM extracts were transferred to a 200 mL TurboVap cell, reduced under compressed nitrogen at 12 psi in a TurboVap III, and solvent exchanged three times to hexane with a final target volume of two mL.

The needle extracts were then purified by silica gel adsorption chromatography, with increasingly polar solvents eluting increasingly polar analytes while polar matrix interferences adhered to the silica gel. Silica columns were prepared by pulling 50 mL DCM, 50 mL Optima ethyl acetate, and 100 mL hexane through the column, and discarding the rinsate. The extracts were loaded by Pasteur pipette onto a Varian 20 g / 60 mL 40 µm Bond Elution Silica Column, rinsing the TurboVap cell three times with 0.5 mL hexane. The extract was drawn into the column using a vacuum manifold until just below the frit, at which time 50 mL of hexane was added. The hexane fraction was drawn through the column at the approximate rate of one drop per second; a 125 mL brown glass bottle was used to collect this fraction, and changed out when the last of the hexane reached the frit. This process was repeated with 50 mL of 1:1 DCM:hexane, 50 mL of 100% DCM, and 50 mL ethyl acetate. The column was allowed to drain to dryness with the last fraction, the entirety of which was collected for archive. The silica gel fractions were capped, and stored at 5°C.

After silica gel clean-up, all fractions (except the 100% ethyl acetate fraction) were combined, reduced under nitrogen in the TurboVap III, and solvent exchanged three times to DCM, with a final volume of ~ 1 mL. The extracts were filtered using a 25 mm GD/X Disposable PTFE Filter with a polypropylene housing and dispensed into Waters 700 µL clear,

glass shell vials for purification via size exclusionary Gel Permeation Chromatography (GPC).

High molecular weight, non-target molecules (lipids) were separated from lower molecular weight, target analytes by GPC. A Waters 515 HPLC Pump and Waters 2487 Dual Absorbance Detector were used in combination with Waters Envirogel Size Exclusion Columns (30 x 1.5 cm and 15 x 1.5 cm). The flow rate was brought to 5 mL DCM/min, and a check standard containing target analytes run to determine current elution times of lipid fractions (F1) vs. target analytes (F2). The extracts were injected into the GPC via a Waters 717 Autosampler, with a total volume injected of 70 mL, and a 25 minute runtime. A Waters Fraction Collector III was programmed to separate collection based on these elution times. The extracts were collected in 200 mL glass TurboVap cells, with a chart recorder monitoring the elution of the extract and the chart speed set at 2 cm/min. Both F1 and F2 were collected and reduced, with F1 reduced to ~1 mL for archive, and F2 reduced to ~150 µL, both including three DCM rinses.

Analysis

A 1:3 or 1:10 dilution was performed on F2 of all extracts, and spiked with 15 uL of 10 ng/µL $^{13}C_{12}$ PCB-138. The extracts were analyzed by a 6890 Network Series Gas Chromatography (GC) Electron Capture Negative Ionization (ECNI) System and a 5973 Network Mass Selective (MS) Detector using selected ion monitoring (SIM). The GC used splitless

injection with the following temperature schedule: 60° C starting temperature, hold for 1 minute, raise by 6° C/min until temperature reaches 300° C, hold for 3 minutes, raise to 320° C over 1 minute, then hold for 9 minutes. Analytes were carried by helium gas through a J&W DB-5MS 30 m x 0.25 mm silica capillary column with a 1 µm thick silicone coat. A 75 pg/µL and 7 pg/µL check standard was analyzed prior to injection of extracts, and a 75 pg/µL check standard was analyzed between each sample to ensure that the chromatography was not affected by the remaining polar interferences. An Agilent Chem Station Data Systems with the Enviroquant option was used to quantify compounds. See Appendix I (Tables 1 and 2) for information on the quantitation and confirmation ions used to measure the target SOCs, surrogates, and internal standards (17).

Laboratory blanks, treated to the same procedure as described above with the exclusion of needles, were run with each replication and analyzed simultaneously with the corresponding samples. Analyte losses across the method were quantifyd by the addition of surrogates, directly to the needles, prior to extraction. After purification, extracts were spiked with internal standards immediately prior to analysis via GC/MS.

Results and Discussion

The initial analytical method did not include GPC, and the noble fir needle extracts were screened by GC with flame ionization detection (FID)

to qualitatively determine the purity of the extracts. Only the 1:1 DCM:hexane fraction from silica gel chromatography had low enough interference levels to analyze the extracts on GC-MS without GPC and 38 of 83 target analytes were quantitatively identified using gas chromatography coupled to mass spectrometry (GC/MS) with electron impact ionization (EI) and electron capture negative ionization (ECNI). The use of GPC removed a significant quantity of matrix interferences, lowering interference levels, allowing for the analysis of the 1:1 DCM:hexane and 100% DCM fractions from silica gel adsorption chromatography, and quantitative identification of 64 of 83 target compounds. For this reason, GPC was incorporated into the analytical method.

Analysis of SNP lodgepole pine and white fir needles samples showed that interferences were too high to quantify recoveries using EI; as a result, SNP samples were only analyzed on ECNI, reducing the target analyte list to 36 compounds. See Table 1.

The recoveries of surrogates ranged from 28.6% to 90.5% (See Figure 5). The high recovery of d14- Trifluralin is because the internal standard was d14- Trifluralin when the samples were originally analyzed, and so less was lost during the removal of interferences.

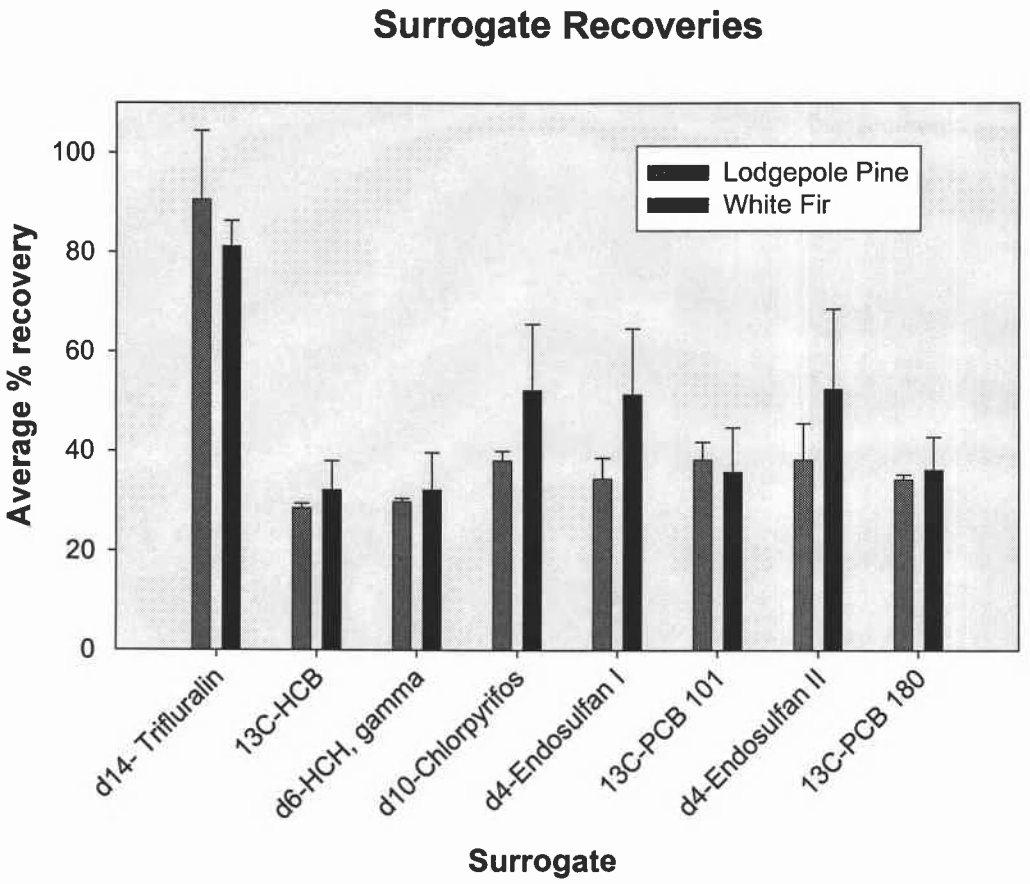
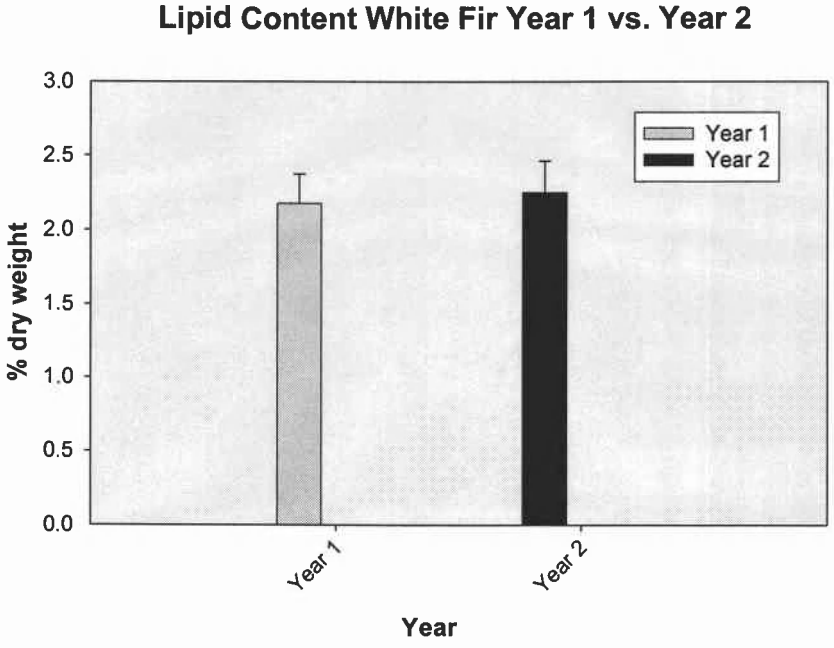


Figure 5: Surrogate recoveries: recoveries ranged from 28.6% to 90.5%. The high recovery of d14- Trifluralin is because the internal standard was d14- Trifluralin when the samples were originally analyzed, and so less was lost during the removal of interferences. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between the two extractions.

Matrix interferences proved to be somewhat more difficult to remove from lodgepole pine extracts than from white fir. One year old growth (year 1) had a higher percent lipid (dry weight) than two year old growth; the difference in % lipid between years was more pronounced in lodgepole pine. This may be due to differences in the matrix interferences and lipid content between species (Figure 6). The higher surface area of conifer needles (smaller and more abundant needles than lodgepole pine)

may have also contributed to the higher recoverable analytes on conifer than lodgepole pine.



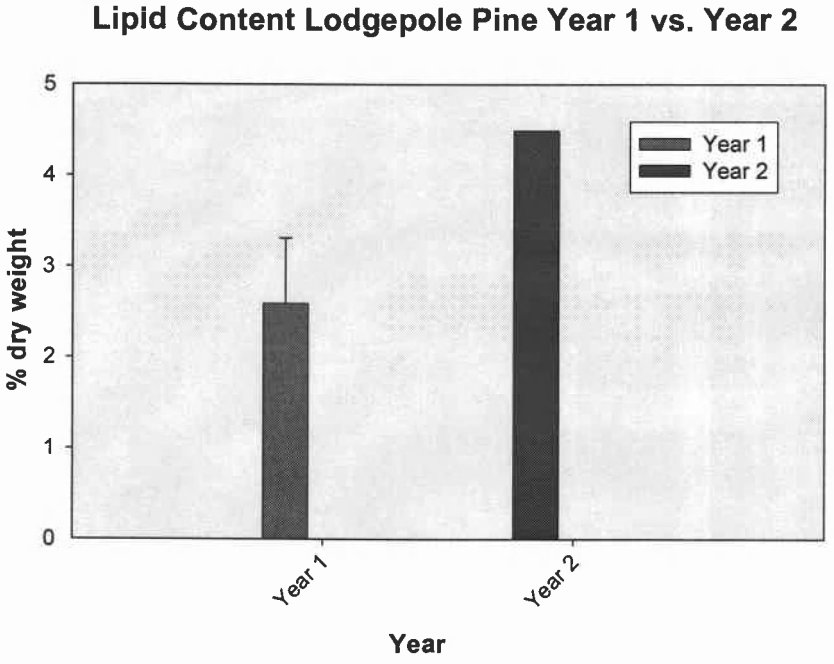


Figure 6: Percent lipid dry weight. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between two extractions.

A total of 11 compounds were measured on the conifer needles from SNP: hexachlorobenzene; dacthal; trans-chlordane; endosulfan I; trans-nonachlor; endosulfan II; cis-nonachlor; endosulfan sulfate; PCB 153; PCB 138; and PCB 187. The concentrations of SOCs measured in SNP were higher than concentrations found in previous research on conifer needles in the Canadian Rockies (15). Those measured by Davidson et al had only 0.5-1.5 ng/g β-endosulfan, .050-.350 ng/g HCB, whereas SNP conifer needle samples had concentrations in the range of 0.39/0.41 ng/g HCB and 0.7-8.2 ng/g endosulfan (on a ng/g dry weight basis). The number and concentration of SOCs measured increased with the length of time the needles were exposed to the atmosphere, as shown by the general increase in concentration of SOCs between Year 1 and Year 2 samples for both species, more so with white fir than for lodgepole pine (Figure 7 and 8).

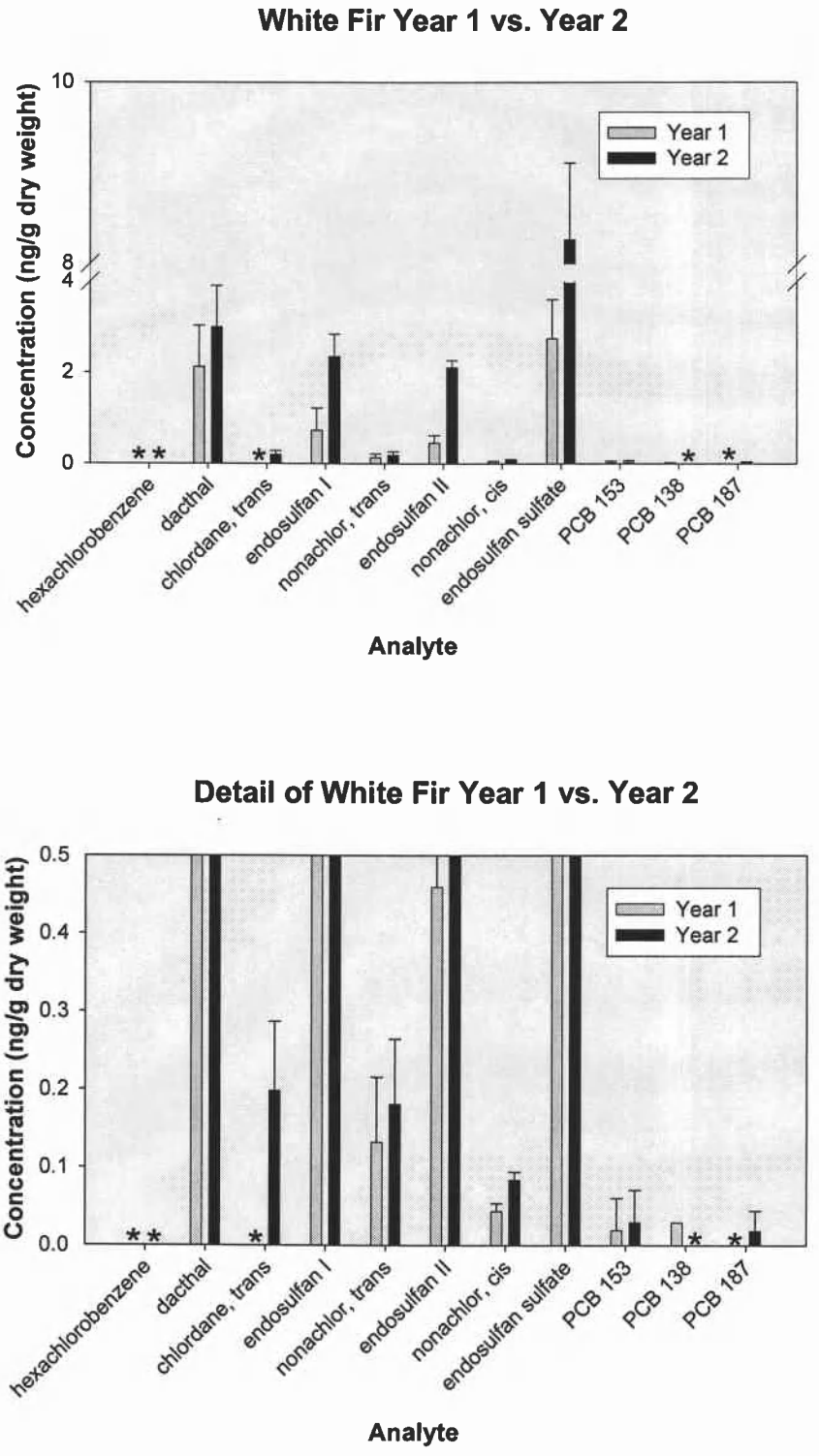


Figure 7: Comparison of concentration of SOCs found in white fir year 1 and 2, with detail. ** indicates SOCs below quantitation limits. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between two extractions.

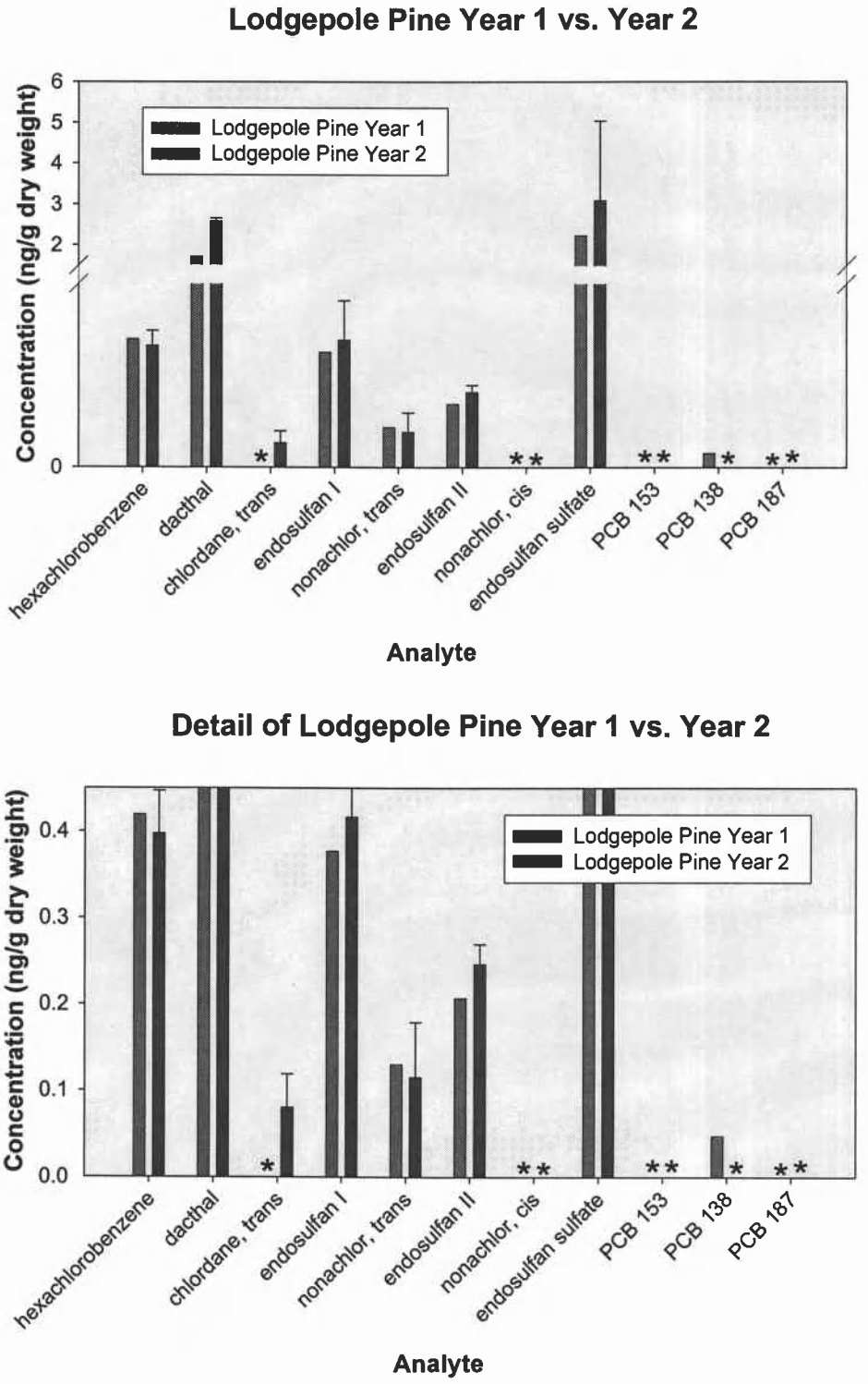


Figure 8: Comparison of concentration of SOCs found in lodgepole pine year 1 and 2, with detail. ** indicates SOCs below quantitation limits. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between two extractions.

Deposition of SOCs varied between species regardless of sample age, with white fir generally containing higher concentrations than lodgepole pine (Figures 9 and 10). This data opposes the hypothesis that deposition of SOCs increases with lipid content, as lodgepole pine needles had a higher measured lipid content (Figure 6).

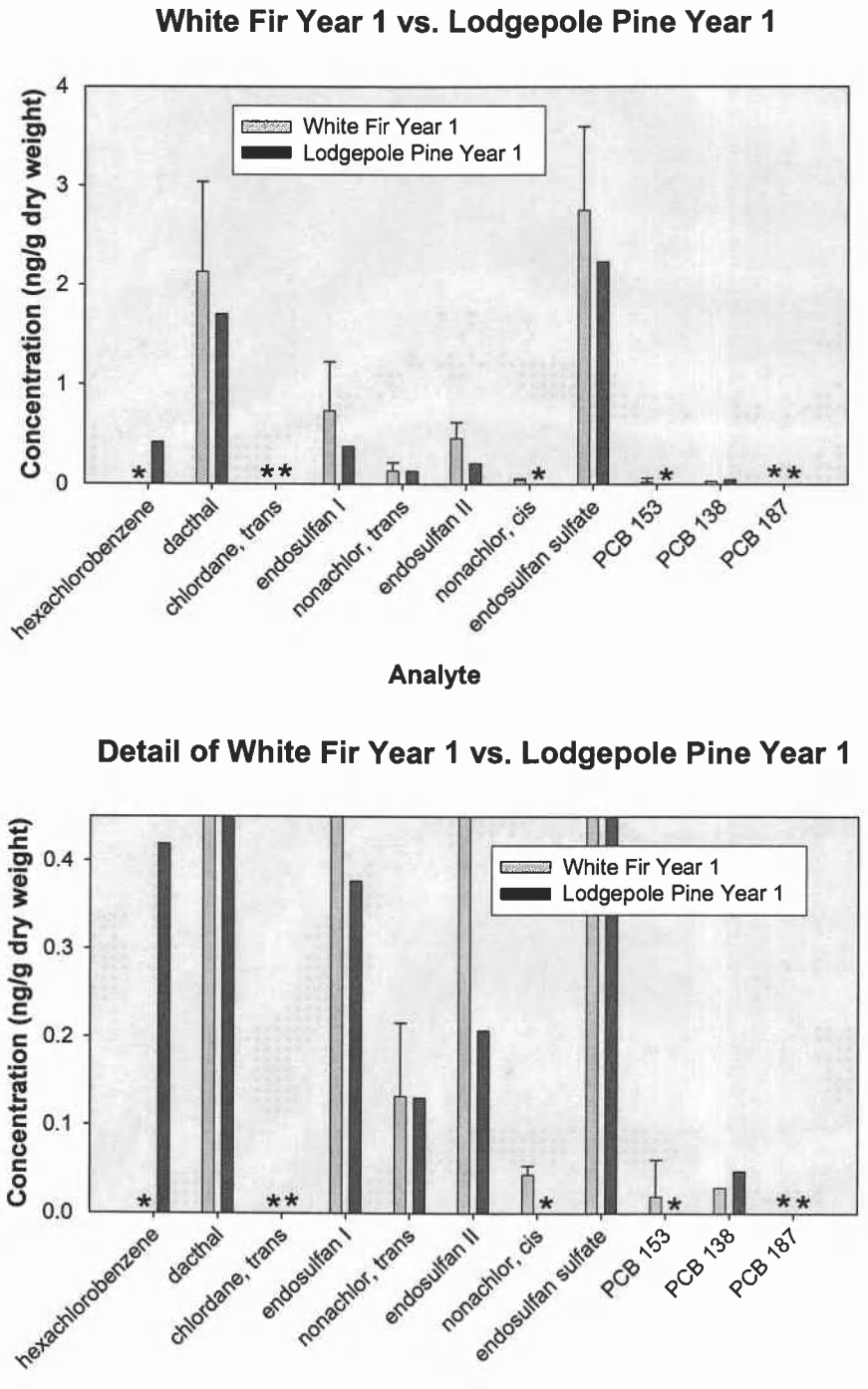
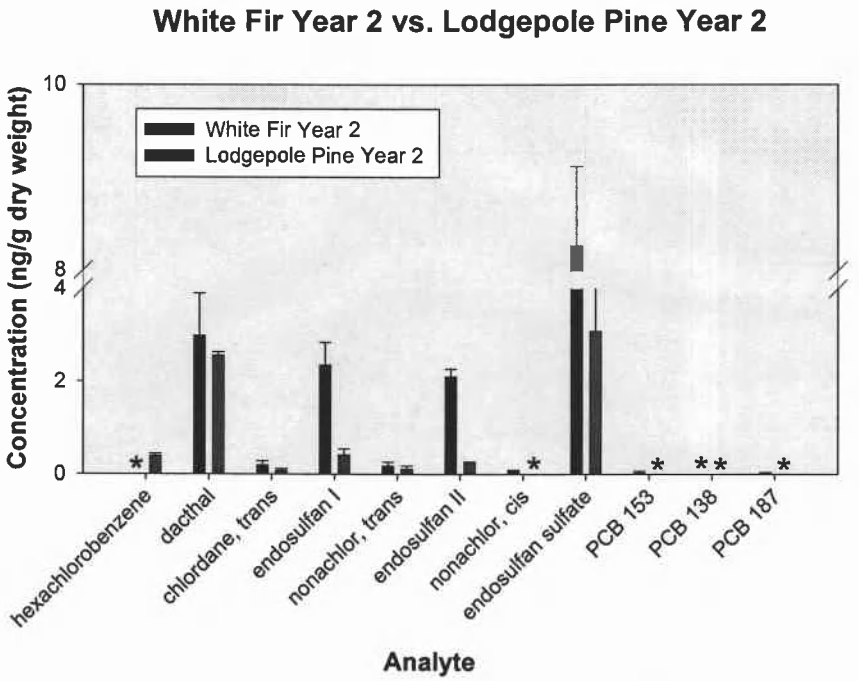


Figure 9: Comparison of concentration of SOCs found in lodgepole pine year 1 and white fir year 1, with detail. ** indicates SOCs below quantitation limits. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between two extractions.



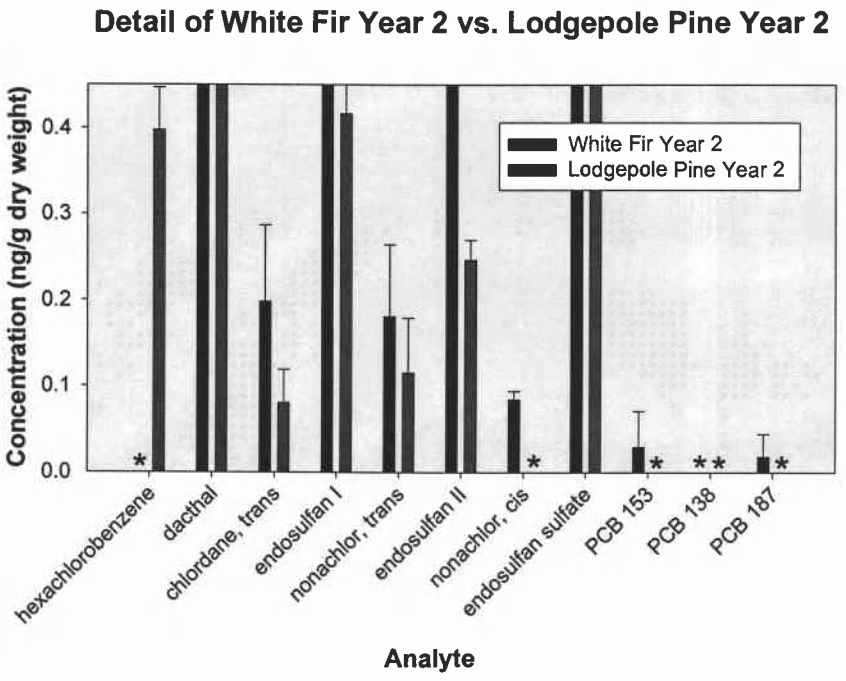
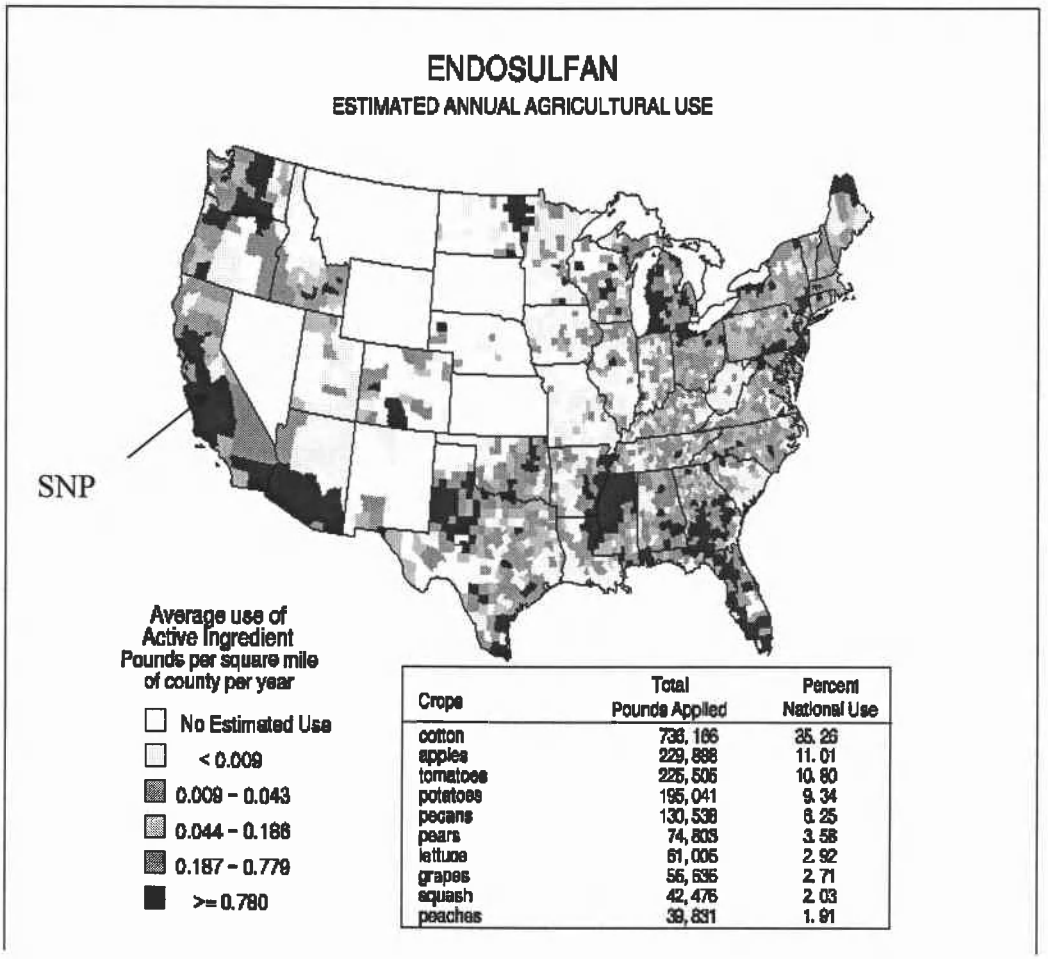


Figure 10: Comparison of concentration of SOCs found in white fir year 2 and lodgepole pine year 2, with detail. ** indicates SOCs below quantitation limits. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2. Concentrations are averaged between two extractions.

The comparatively high concentration of the current use pesticides endosulfan and dacthal (DCPA) in both species, and in both age categories, is not surprising due to the close proximity of SNP to agricultural areas (Figures 11 and 12).



Crops	Total Pounds Applied	Percent National Use
cotton	736,166	35.26
apples	229,898	11.01
tomatoes	225,505	10.80
potatoes	195,041	9.34
pecans	130,538	6.25
pears	74,803	3.58
lettuce	61,005	2.92
grapes	56,535	2.71
squash	42,476	2.03
peaches	39,831	1.91

Figure 11: Annual agricultural endosulfan usage for the continental United States. http://ca.water.usgs.gov/pnsp/use92/endoslfn.html

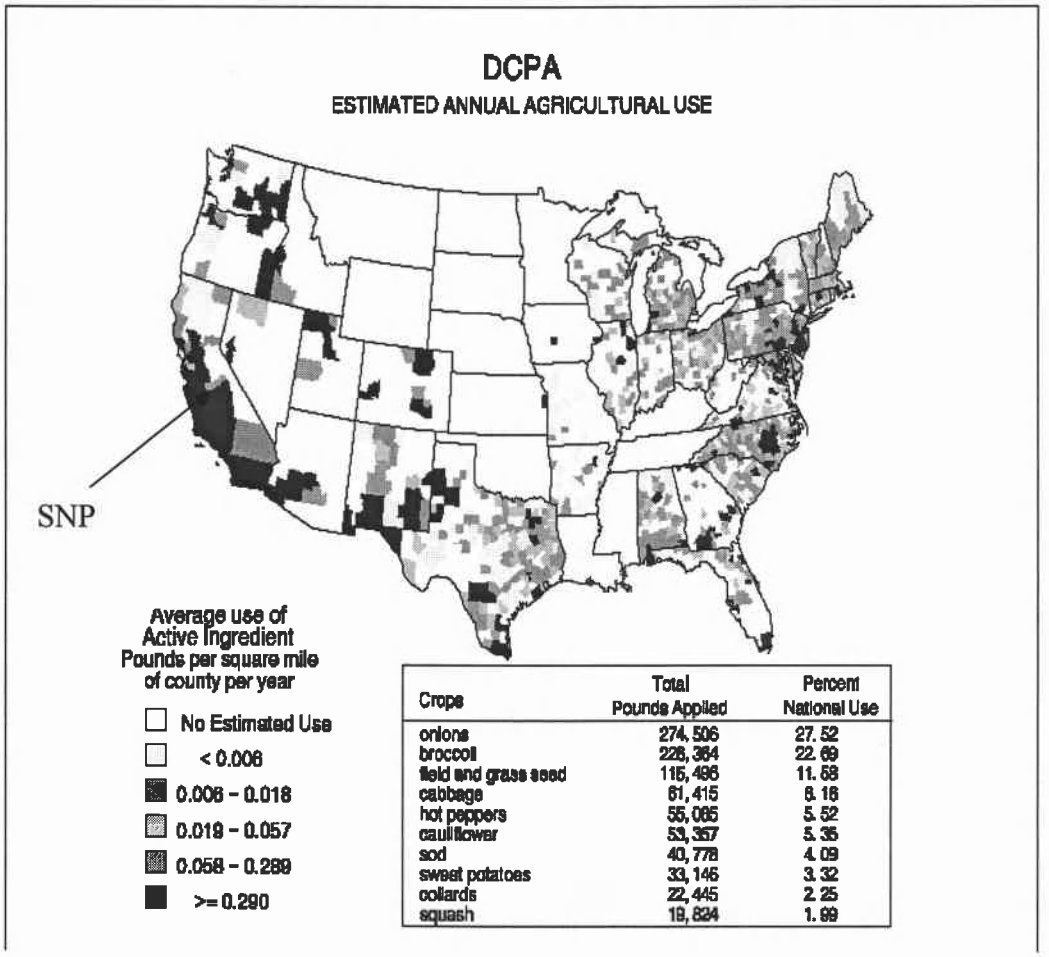
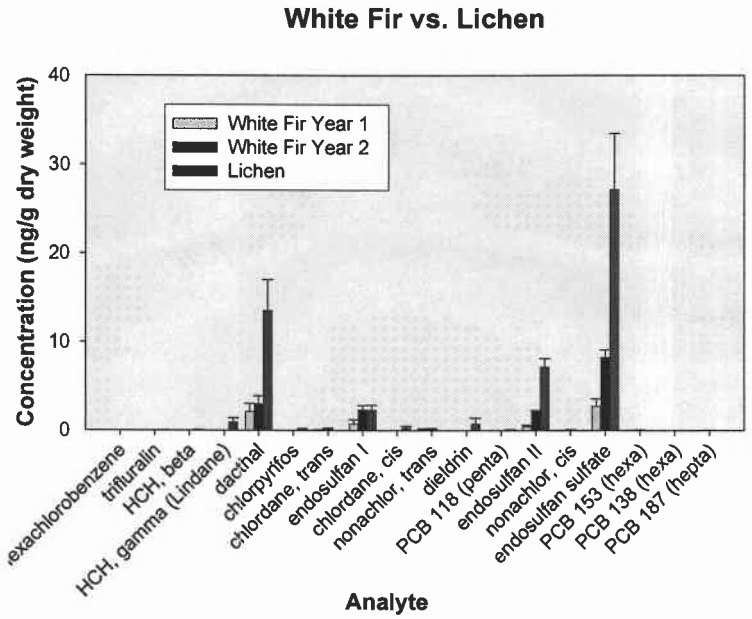


Figure 12: Annual agricultural DCPA (dacthal) usage for the continental United States. http://ca.water.usgs.gov/pnsp/use92/endoslfn.html

When comparing lichen to both white fir and lodgepole pine collected from the same site in SNP, it is clear that a higher concentration and number of SOCs were measured in lichen (Figures 13 and 14). This is likely due to the greater length of exposure time of lichen to the atmosphere (several years vs. one to two years). Although lichen had a larger number and concentration of SOCs present, it is difficult to determine the age of lichens, making them suitable only for indication of total exposure of the ecosystem to the SOCs in question over the last 10-20 years. In contrast, while the conifer needles contained fewer SOCs,

they are a good indicator of what the ecosystem has been exposed to in recent years.



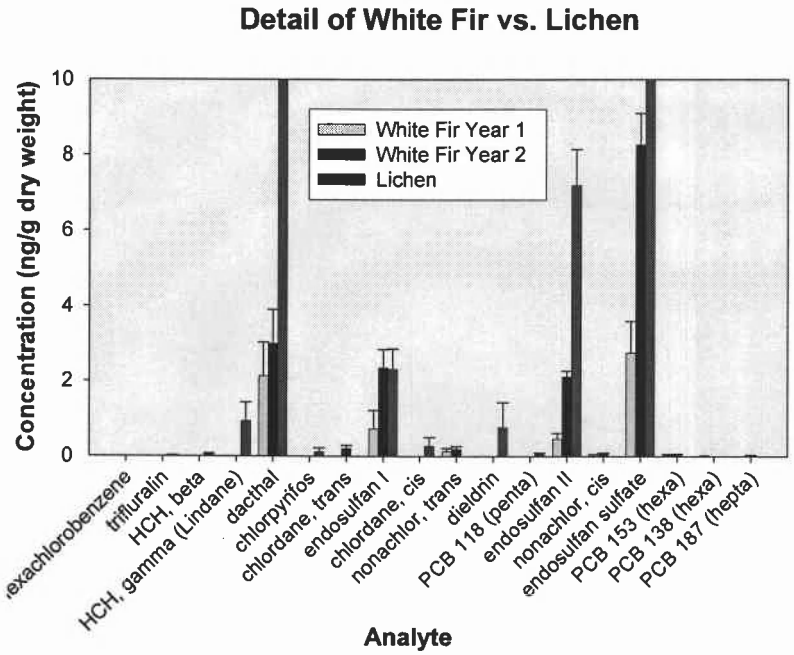
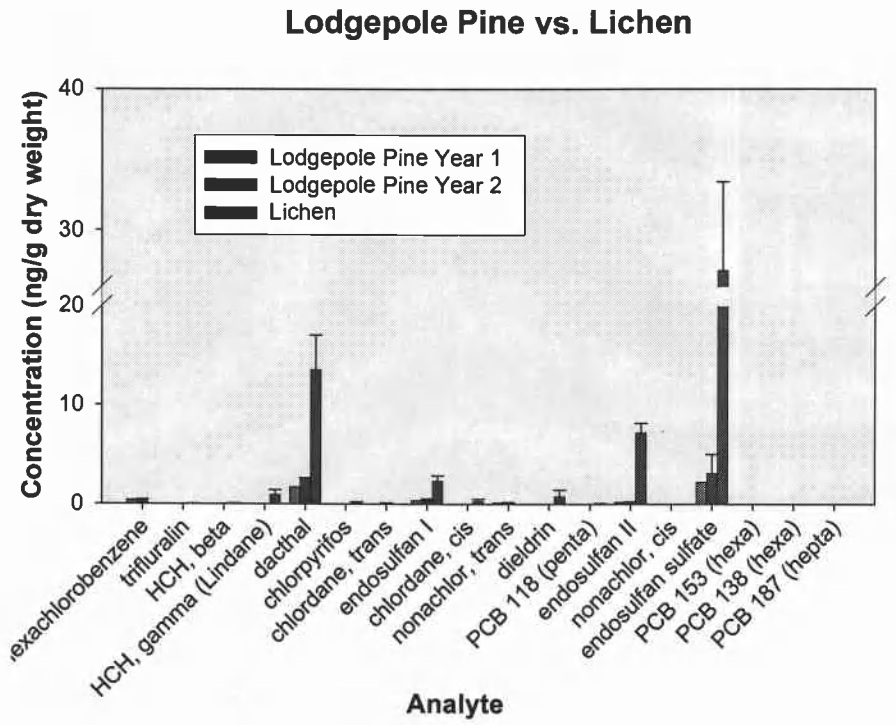


Figure 13: White fir year 1 and year 2 vs. lichen, with detail. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2.



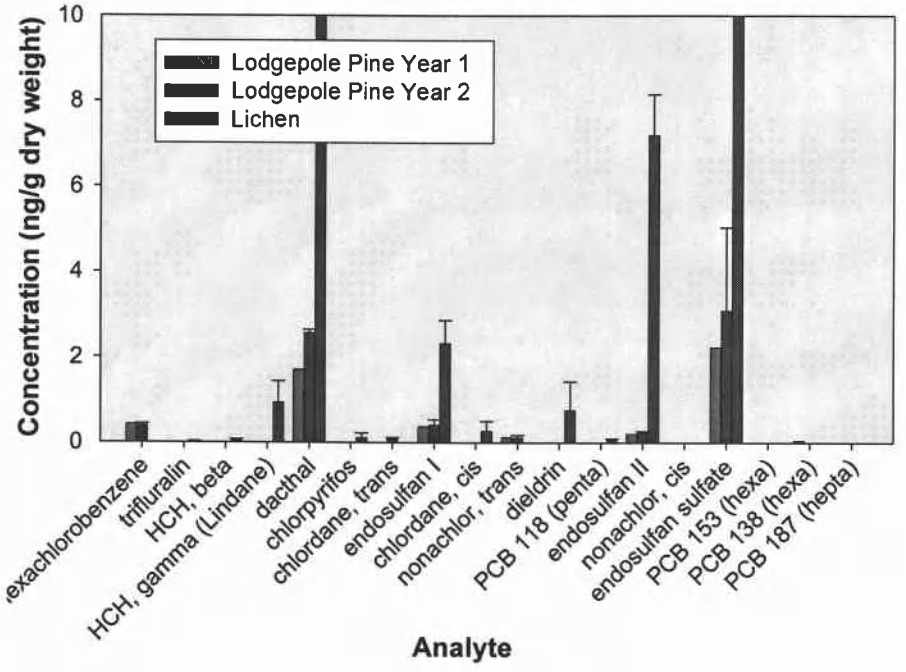


Figure 14: Lodgepole pine year 1 and year 2 vs. lichen, with detail. Error bars represent standard deviation between extractions; n=2 for white fir year 1 and 2; n=2 for lodgepole pine year 1, n=1 for lodgepole pine year 2.

In conclusion, the conifer needles from SNP used for this study contained 11 SOCs. Two year old samples generally had higher concentrations of SOCs than one year old samples, and white fir samples had higher concentrations than those found in lodgepole pine. The conifer needle samples were easier to collect and date than lichen, but lichen did give a better indication of site exposure to SOCs over the last 10-20 years. Our data indicates that high elevation ecosystems in SNP are impacted by both historic and current use pesticides used in the surrounding agricultural areas.

Acknowledgements

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Appendix I

TABLE 1. Quantitation information for each SOC analyzed using Electron Impact Ionization including selective ion monitoring (SIM) windows.

Analyte	Retention Time (min)	Quantitation Ion (m/z)	Confirmation Ion (m/z)	Confirmation Ion (m/z)	Quantitation Compound
SIM Window 1					
d_{14}-EPTC	15.13	142	203		d_{10}-Acenaphthene
EPTC	15.33	128.1	132.1	189.1	d_{14}-EPTC
SIM Window 2					
Etridiazole	17.37	210.9	212.9	182.9	d_{14}-EPTC
SIM Window 3					
Acenaphthylene	17.50	152.1	151.1	76	d_{10}-Fluorene
Pebulate	17.58	128.1	203.1	161.1	d_{14}-EPTC
SIM Window 4					
d_{10}-Acenaphthene	18.06	164	162		Internal Standard
Acenaphthene	18.18	154.1	153.1	152.1	d_{10}-Fluorene

SIM Window 5					
Fluorene-$_{d10}$	20.12	176	174		d_{10}-Acenaphthene
Fluorene	20.22	166.1	165.1	163.1	d_{10}-Fluorene
SIM Window 6					
Propachlor	20.55	120.1	176.1	93.1	d_5-Atrazine
SIM Window 7					
Atrazine desisopropyl	21.59	173	175	158	d_5-Atrazine
Atrazine desethyl	21.74	172	174	187.1	d_5-Atrazine
SIM Window 8					
d_{10}-Phorate	22.00	131	270		d_{10}-Acenaphthene
Phorate	22.14	260.1	231	121.1	d_{10}-Phorate
SIM Window 9					
Demeton-S	22.79	88	170	258.1	d_{10}-Phorate
SIM Window 10					
Prometon	23.12	210.1	225.2	183.1	d_5-Atrazine
Carbofuran	23.13	164.1	149.1	131	d_5-Atrazine
Simazine	23.19	201.1	203.1	186.1	d_5-Atrazine

d_5-Atrazine	23.24	205	220		d_{10}-Acenaphthene
Atrazine	23.31	200.1	202.1	215.1	d_5-Atrazine
SIM Window 11					
d_{10}-Diazinon	23.80	314	138		d_{10}-Acenaphthene
d_{10}-Phenanthrene	23.86	188	189		d_{10}-Acenaphthene
Phenanthrene	23.93	178.1	176.1	179.1	d_{10}-Phenanthrene
Diazinon	23.93	179.1	199.1	304.1	d_{10}-Diazinon
Anthracene	24.14	178.1	176.1	179.1	d_{10}-Phenanthrene
Disulfoton	24.20	88.1	89.1	186	d_{10}-Diazinon
SIM Window 12					
Triallate	24.45	268	270	86.1	d_7-Malathion
SIM Window 13					
d_{11}-Acetochlor	25.27	173	245		d_{10}-Fluoranthene
Acetochlor	25.40	146.1	162.1	223.1	d_{11}-Acetochlor
SIM Window 14					
d_{13}-Alachlor	25.53	200	251		d_{10}-Fluoranthene
d_6-Methyl parathion	25.65	269	115		d_{10}-Fluoranthene
Alachlor	25.69	188.1	160.1	237.1	d_{13}-Alachlor
Methyl parathion	25.72	263	125	109	d_6-Methyl parathion

SIM Window 15					
Carbaryl	25.99	144.1	115.1	116.1	d_7-Malathion
SIM Window 16					
d_7-Malathion	26.77	174	131		d_{10}-Fluoranthene
Malathion	26.85	173.1	158	127	d_7-Malathion
Metolachlor	26.91	162.1	238.1	240.1	d_{13}-Alachlor
SIM Window 17					
d_{10}-Parathion	27.16	115			d_{10}-Fluoranthene
Parathion	27.29	291	155	109	d_{10}-Parathion
Cyanazine	27.36	225.1	227.1	240.1	d_5-Atrazine
SIM Window 18					
d_{10}-Fluoranthene	28.52	212	213		Internal Standard
Fluoranthene	28.59	202.1	200.1	203.1	d_{10}-Pyrene
SIM Window 19					
o,p' DDE[1]	29.18	318	316	320	d_8-p,p'-DDE
SIM Window 20					
d_{10}-Pyrene	29.36	212	213		d_{10}-Fluoranthene

Pyrene	29.43	202.1	203.1	200.1	d_{10}-Pyrene
SIM Window 21					
d_8-p,p'-DDE	30.13	326	324		d_{10}-Fluoranthene
p,p' DDE	30.18	317.9	315.9	319.9	d_8-p,p'-DDE
o,p' DDD[2]	30.41	235	237	165.1	d_8-p,p'-DDE
SIM Window 22					
Retene	30.76	219.1	234.2	204.1	d_{10}-Pyrene
SIM Window 23					
Ethion	31.51	231	384	153	d_{10}-Parathion
p,p' DDD	31.52	235	237	165.1	d_8-p,p'-DDE
o,p' DDT[3]	31.58	235	237	165.1	d_8-p,p'-DDT
d_8-p,p'-DDT	32.58	243	245		d_{12}-Benzo(k)fluoranthene
p,p' DDT	32.65	235	237	165.1	d_8-p,p'-DDT
SIM Window 24					
d_{12}-Triphenylene	34.17	240	241		d_{12}-Benzo(k)fluoranthene

Benzo(a)anthracene	34.19	228.1	226.1	229.1	d_{12}-Triphenylene
Chrysene+Triphenylene	34.28	228.1	226.1	229.1	d_{12}-Triphenylene
Methoxychlor	34.39	227.1	228.1	274.1	d_8-p,p'-DDT
SIM Window 25					
Benzo(b)fluoranthene	38.11	252.1	250.1	253.1	d_{12}-Benzo(a)pyrene
d_{12}-Benzo(k)fluoranthene	38.13	264	265		Internal Standard
Benzo(k)fluoranthene	38.20	252.1	250.1	253.1	d_{12}-Benzo(a)pyrene
Benz(e)pyrene	39.00	252.1	250.1	253.1	d_{12}-Benzo(a)pyrene
d_{12}-Benzo(a)pyrene	39.10	264	265		d_{12}-Benzo(k)fluoranthene
Benzo(a)pyrene	39.18	252.1	250.1	253.1	d_{12}-Benzo(a)pyrene
SIM Window 26					
Indeno(1,2,3-cd)pyrene	42.62	276.1	274.1	277.1	d_{12}-Benzo(ghi)perylene
Dibenz(a,h)anthracene	42.75	278.1	276.1	279.1	d_{12}-Benzo(ghi)perylene
SIM Window 27					
d_{12}-Benzo(ghi)perylene	43.34	288	289		d_{12}-Benzo(k)fluoranthene

Benzo(ghi)perylene	43.42	276.1	274.1	277.1	d_{12}-Benzo(ghi)perylene

[1]Dichlorodiphenyldichloroethylene

[2]Dichlorodiphenyldichloroethane

[3]Dichlorodiphenyltrichloroethane

TABLE 2. Quantitation information for each SOC analyzed using Electron Capture Negative Ionization including selective ion monitoring (SIM) windows.

Analyte	Retention Time (min)	Quantitation Ion (m/z)	Confirmation Ion (m/z)	Confirmation Ion (m/z)	Quantitation Compound
SIM Window 1					
d_6-Trifluralin	13.69	349.2	350.2	319.2	$^{13}C_{12}$-PCB #138
Trifluralin	13.90	335.1	336.1	305.1	d_6-Trifluralin
SIM Window 2					
HCH, alpha[1]	14.61	71.0	73.0	70.0	d_6-gamma-HCH
$^{13}C_6$-Hexachlorobenzene	14.69	291.8	293.8	289.9	$^{13}C_{12}$-PCB #138
Hexachlorobenzene	14.70	283.8	285.8	281.8	$^{13}C_6$-Hexachlorobenze
HCH, beta	15.94	71.0	73.0	70.0	d_6-gamma-HCH
d_6-gamma-HCH	16.01	72.0	74.0	263.0	$^{13}C_{12}$-PCB #138
HCH, gamma	16.19	71.0	73.0	70.0	d_6-gamma-HCH
SIM Window 3					

Chlorothalonil	17.18	266.0	268.0	264.0	d_6-gamma-HCH
HCH, delta	17.70	71.0	252.9	254.9	d_6-gamma-HCH
Triallate	17.72	160.0	161.1		d_6-gamma-HCH
SIM Window 4					
Metribuzin	19.15	198.0	199.1	184.0	d_6-gamma-HCH
Heptachlor	19.61	266.0	268.0	299.9	d_6-gamma-HCH
SIM Window 5					
Chlorpyrifos oxon	21.14	297.0	298.0	299.0	d_{10}-Chlorpyrifos
d_{10}-Chlorpyrifos	21.19	322.0	324.0	213.9	$^{13}C_{12}$-PCB #138
Aldrin	21.24	237.0	238.8	329.9	d_6-gamma-HCH
Chlorpyrifos	21.37	313.0	315.0	213.9	d_{10}-Chlorpyrifos
Dacthal	21.54	332.0	330.0	334.0	d_6-gamma-HCH
SIM Window 6					
Chlordane, oxy	23.12	424.0	426.0	352.0	d_4-Endosulfan I
Heptachlor epoxide	23.13	390.0	388.0	392.0	d_4-Endosulfan I
PCB # 74[2]	23.28	292.0	294.0	290.0	$^{13}C_{12}$-PCB #101
SIM Window 7					
Chlordane, trans	24.26	409.9	407.9	411.8	d_4-Endosulfan I
$^{13}C_{12}$-PCB #101	24.68	338.0	336.0	340.0	$^{13}C_{12}$-PCB #138

PCB # 101	24.69	326.0	328.0	324.0	$^{13}C_{12}$-PCB #101
d_4-Endosulfan I	24.72	378.0	376.0	374.0	$^{13}C_{12}$-PCB #138
Endosulfan I	24.82	403.9	371.9	369.9	d_4-Endosulfan I
Chlordane, cis	24.83	266.0	264.0	268.0	d_4-Endosulfan I
Nonachlor, trans	24.98	443.8	445.8	441.8	d_4-Endosulfan I
SIM Window 8					
Dieldrin	26.07	345.9	347.9	379.9	d_4-Endosulfan I
Endrin	27.00	345.9	347.9	379.9	d_4-Endosulfan II
SIM Window 9					
PCB # 118	27.51	326.0	328.0	324.0	$^{13}C_{12}$-PCB #101
d_4-Endosulfan II	27.48	412.0	414.0	410.0	$^{13}C_{12}$-PCB #138
Endosulfan II	27.56	405.9	407.9	371.9	d_4-Endosulfan II
Nonachlor, cis	27.79	443.8	445.8	441.8	d_4-Endosulfan II
SIM Window 10					
Endrin aldehyde	28.24	379.9	381.9	345.9	d_4-Endosulfan II
PCB # 153	28.48	360.0	362.0	358.0	$^{13}C_{12}$-PCB #180
SIM Window 11					
Endosulfan sulfate	29.33	385.9	387.9	421.8	d_4-Endosulfan II
PCB # 138	29.65	360.0	362.0	358.0	$^{13}C_{12}$-PCB #180

$^{13}C_{12}$-PCB #138	29.65	372.0	374.0	370.0	Internal Standard
SIM Window 12					
PCB # 187	30.29	393.9	359.9	397.9	$^{13}C_{12}$-PCB #180
PCB # 183	30.54	393.9	359.9	397.9	$^{13}C_{12}$-PCB #180
$^{13}C_{12}$-PCB #180	32.60	405.9	407.9	409.9	$^{13}C_{12}$-PCB #138
Mirex	34.10	367.8	369.8	403.8	$^{13}C_{12}$-PCB #180

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[1]Hexachlorocyclohexane

[2]Polychlorinated Biphenyls

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