AN ABSTRACT OF THE THESIS OF

Yunzhu Wang for the degree of Master of Science in Chemistry presented on June 2, 2005

Title: Analysis of Semi-Volatile Organic Compounds in High Elevation Lake Sediments.

Abstract approved:

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Staci Simonich

The transport and deposition of airborne contaminants, including semi-volatile organic compounds (SOCs), to high elevation ecosystems is recognized as a potential threat to these ecosystems. The objectives of this research were to develop an analytical method to measure a wide range of SOCs in high elevation lake sediment and to evaluate decennial to century trends in SOC contaminant flux to a high elevation lake catchment, by dating and analyzing the sediment core. The new analytical method and its validation for the measurement of SOCs in high elevation lake sediments are described. The target compounds are 74 SOCs, including organochlorines, polycyclic aromatic hydrocarbons (PAHs),

polychlorinated biphenyls (PCBs), carbamates, organophosphates, and s-triazines. Pressurized Liquid Extraction was used to extract SOCs from sediment. Gel Permeation Chromatography and silica gel adsorption chromatography were used to purify the sediment extract. Finally, GC/MS, with Electron Impact and Electron Capture Negative Ionization mass spectrometry, was used for the measurement and quantitation of SOCs in the sediment.

The percent recovery of target SOCs in sediment using our analytical method was 30 to 95%. The method estimated detection limit was 5 to 570 pg/g (wet weight). Analysis of NIST Standard Reference Material 1944, a New York/New Jersey marine sediment, using our analytical method showed that the measured mean concentration of 23 out of the 24 target SOCs with certified values had a percent difference less than 30% from the certified value. Using our analytical method, we measured SOCs in a sediment core collected from Pear Lake, Sequoia National Park, CA. By measuring the concentrations of SOCs in the different sediment layers, we were able to determine the historical deposition of SOCs to Sequoia National Park. Some PCBs, PAHs, chlordanes, endosulfans, dieldrin, and DDTs were measured in the sediment core from Pear Lake. The flux of historical use pesticide decreased after they were banned in the US, while the flux of current use pesticide has increased in recent years. SOC

deposition to the sediment depends on the use volume and magnitude of their respective K_{ow} and K_{oc} value.

Analysis of Semi-Volatile Organic Compounds in High Elevation Lake Sediments

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APPROVED:

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Major Professor, representing Chemistry

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Chair of the Department of Chemistry

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Yunzhu Wang, Author

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This document has been subjected to appropriate institutional peer review and/or administrative review and approved for publication.

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1. Introduction

1.1 Semi-Volatile organic compound deposition to high elevation ecosystem

Recently, semi-volatile organic compounds (SOCs) have been measured in air, water and biota from high elevation sites due to the long-range atmospheric transport and deposition of these compounds *[1-3]*. This topic has become a major area of research in environmental chemistry *[4]*.

Atmospheric contaminant transport and deposition has been recognized as a potential threat to aquatic and terrestrial ecosystems for several decades. Initially, the long-range transport of the acidic precursors of acidic deposition was identified *[5]*. After the trans-boundary transport of these airborne contaminants was demonstrated, other airborne contaminant threats to ecosystems and human health were identified *[6]*. SOCs have the potential to be transported globally by the atmosphere *[7]*. Most SOCs are anthropogenic and have relatively long half-lives (>2 days) in atmosphere *[8,9]*.

Previous research has shown the presence of SOCs in high elevation ecosystems, including European high altitude mountain lake sediments *[10-12]*, snow *[13,14]*, and lake water *[15]*. SOCs have also been measured in snow *[1]* and sediment *[16]* from the Canadian Rocky Mountains and in snow and rain samples collected from the Sierra

Nevada Mountain range *[17]*. However, there is no data on SOC deposition to high elevation ecosystems in other parts of the Western US.

SOCs are chemicals with intermediate vapor pressures between 10^{-5} to 10^{-2} Pa. SOCs are present in both the atmospheric gas and particle phases, with liquid-phase vapor pressures less than 10^{-4} Pa existing primarily in the particle phase. SOCs with vapor pressures greater than 10^{-4} Pa exist primarily in the gas phase in the atmosphere. There are various sources of SOCs, including industrial sources (polychlorinated biphenyls, PCBs), incomplete combustion sources (polycyclic aromatic hydrocarbons, PAHs), and agricultural sources (DDT and other pesticides).

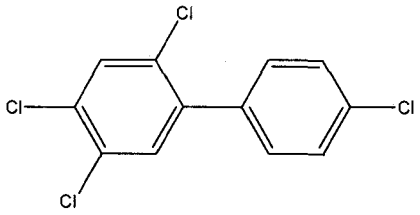
PCBs are mixtures of up to 209 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs *[18]*. PCBs were used as coolants and lubricants in transformers, capacitors, and other electrical equipment because they are thermal stable and are were good insulators *[18]*. The manufacture of PCBs was banned in the U.S. in 1977 because of evidence they build up in the environment and can cause harmful health effects *[18]*. Even though PCB production was banned, there are still historical sources of PCBs and PCBs are still emitted to the atmosphere from these sources. PCBs do not readily breakdown in the environment and, therefore, can remain

in lake catchments for very long periods of time, such as the Great Lakes *[19]* and Lake Tahoe *[17]*. PCBs can travel globally via the atmosphere and be deposited in areas far away from their source *[20]*. In water, a small amount of PCBs may remain dissolved, but most sorb to organic particulate matter and are buried in sediments *[21]*. PCB-74 (2,4,4',5-Tetrachlorobiphenyl), PCB-101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB-118 (2,3',4,4',5-Pentachlorobiphenyl), PCB-153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB-138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB-187 (2,2',3,4',5,5',6-Heptachlorobiphenyl), and PCB-183 (2,2',3,4,4',5',6-Heptachlorobiphenyl) are the PCBs we chose to study in this research project (see Figure 1.1), because of their toxicity and range of physical chemical properties. PCBs have been measured in lake water *[3]*, lake sediment *[16]*, and soil *[22]* from high elevation ecosystem.

PAHs are produced by biomass burning and the incomplete combustion of fossil fuels. PAHs continue to be emitted today from these sources, and have been identified as hazardous to humans *[23]*. Some PAHs may cause cancer and may affect the eyes, kidneys and liver *[23]*. They have been measured in high concentrations in air close to urban or industrial areas *[24-26]* and in low concentrations in rural or remote areas *[27-29]*. There are seventeen PAHs in this research project (see Figure 1.2), such as phenanthrene, fluorene, fluoranthene

and pyrene. PAHs have been measured in lake water, lake sediment, and snow in high elevation sites throughout Europe *[10,14]*.

The structures of some of the pesticides studied in this research are given in Figure 1.3. Several pesticides are currently banned in the US, including DDT, dieldrin, chlordane, and hexachlorobenzene (HCB) *[30]*. After being widely used in farming and forestry, the DDTs and HCB were measured in water from high mountain areas in Europe *[3]*, and in snow from the Sierra Nevada mountain range *[17]*. Endosulfan is still widely use as an insecticide in Canada, the US, and Europe.



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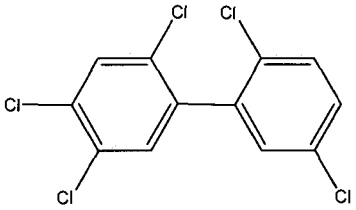

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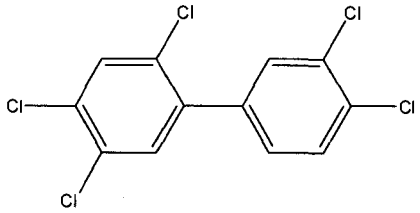

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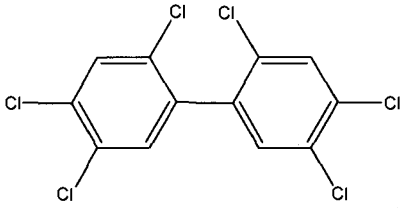

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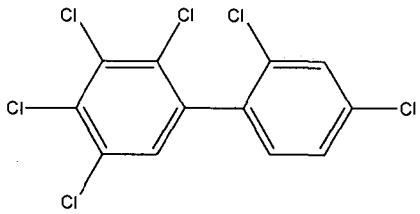

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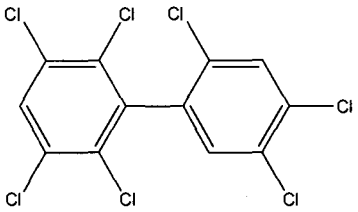

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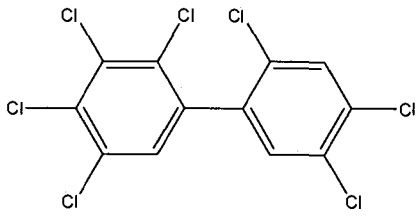


PCB-183

Figure 1.1 Structures of PCBs studied in this research

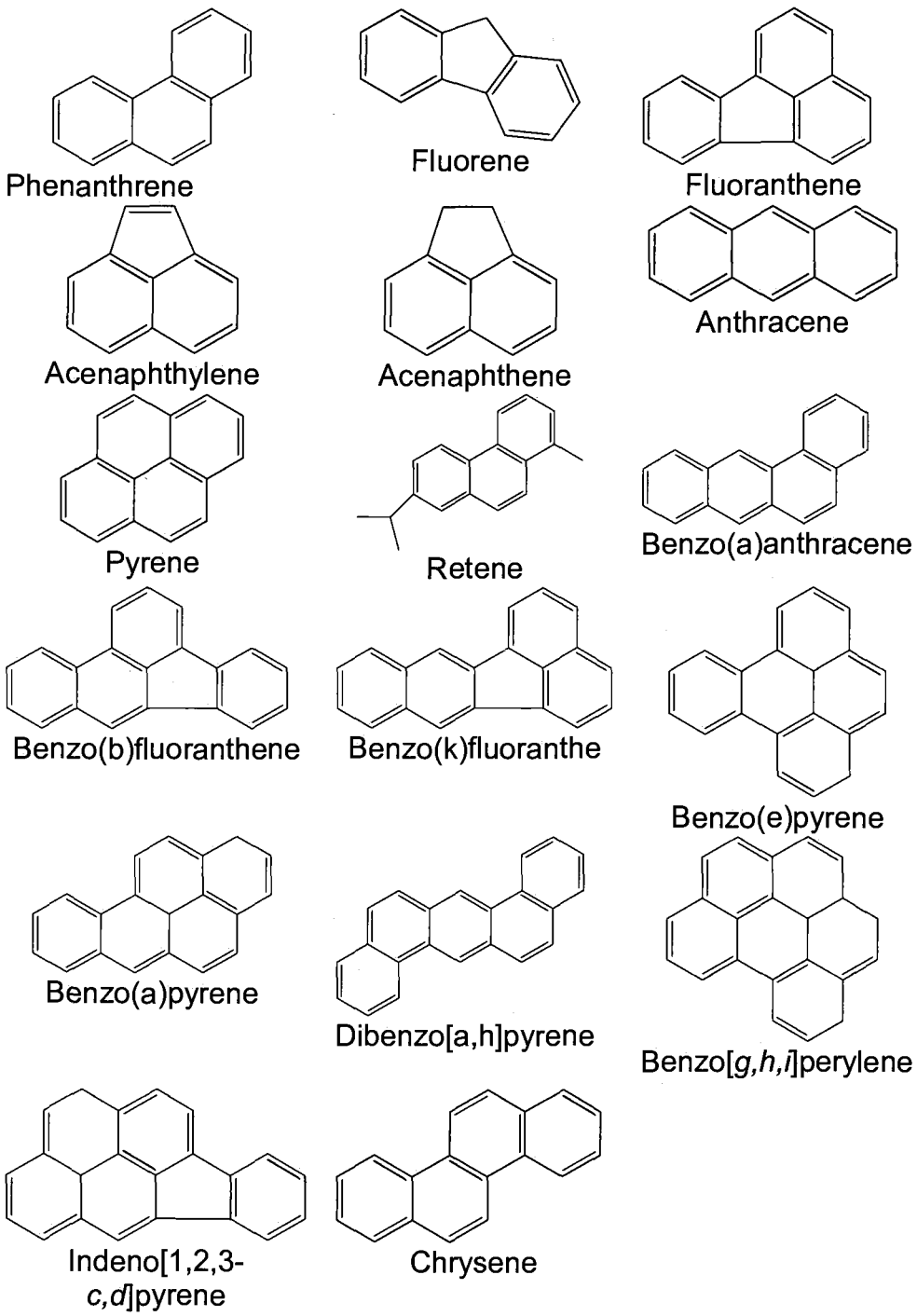
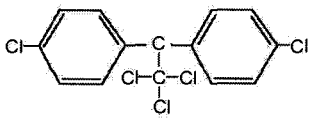
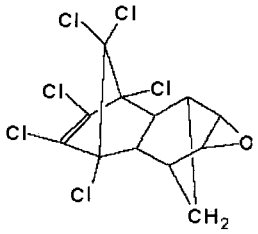


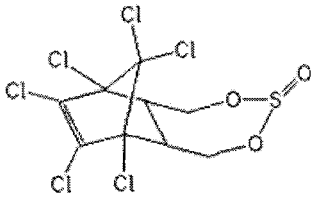
Figure 1.2 Structures of PAHs studied in this research



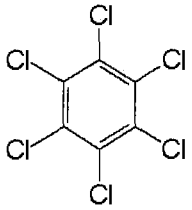
p,p'-DDT



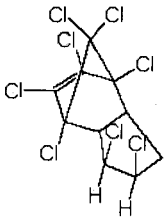
Dieldrin



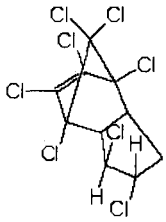
Endosulfan



HCB



Cis



Trans

Chlordane

Figure 1.3 Structures of some of the pesticides studied in this research

1.2 Western Airborne Contaminants Assessment Project (WACAP)

Currently, there is insufficient evidence to determine if high elevation ecosystems in the Western United States are threatened by regional and long-range atmospheric contamination of SOCs. The goal of WACAP is to assess the deposition of airborne contaminants in western national parks, providing regional and local information on exposure, accumulation, impacts, and probable sources *[31]*. In addition, the following specific objectives were identified: (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 Park sites *[31]*.

Eight parks have been selected for WACAP study sites based on their locations. In each park, two lake catchments were chosen for the collection of different samples, including snow, lake water, lake sediment, fish, and vegetation. Figure 1.4 shows a diagram of the lake catchment approach. SOCs undergo long-range and regional transport and cold condense in the cold high elevation regions. Figure 1.5 shows the locations of the eight National Parks and the corresponding lake

catchments being studied by WACAP. Figure 1.5 also lists the elevation and mean annual temperature of the lake catchments.

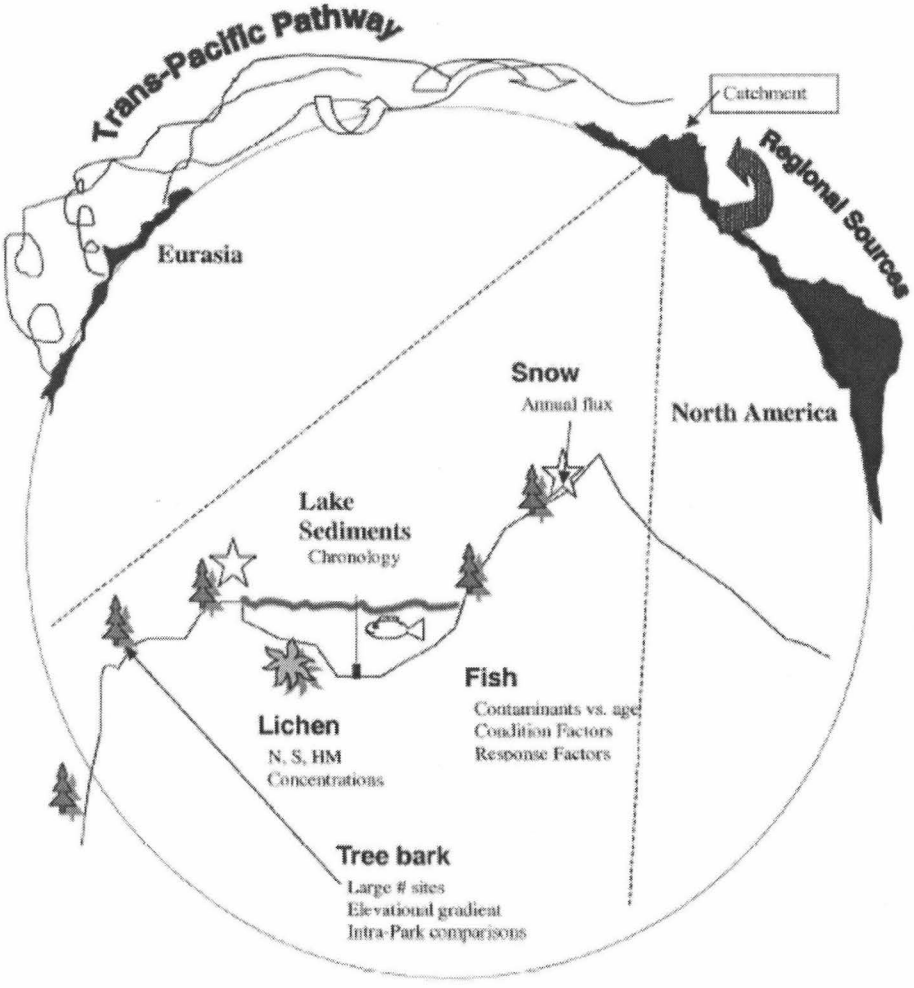


Figure 1.4 WACAP Conceptual Diagram of Airborne Contaminant Assessment Approach *[31]*.

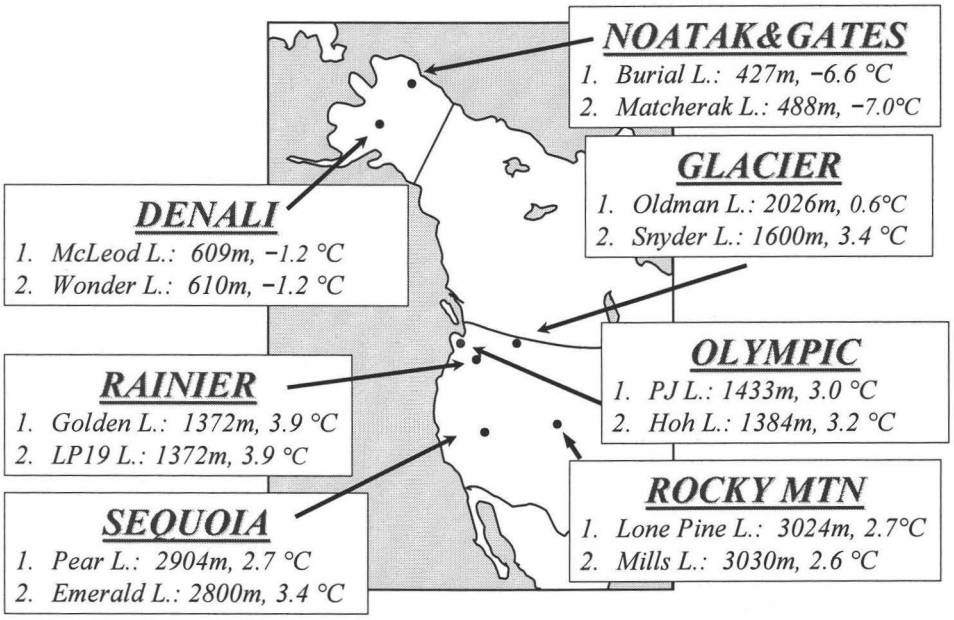


Figure 1.5 Selected National Parks in the Western US showing elevations and mean annual temperature of the lake catchments.

1.3 Lake Sediment

Lake sediments are widely used in environmental chemistry because of their chronological history of contaminant deposition. Since anthropogenic SOCs were first produced and released into the atmosphere, they have undergone long-range transport and deposition to lake sediment. Therefore, the sediment chronology of SOC deposition in each of the 14 WACAP lake catchments will provide time trend information of the pre- and post-industrial SOC flux to these ecosystems.

In order to determine the SOC flux in sediment cores, we need to understand two pieces of information about the cores. First, we need to know if the sediment layers were deposited in chronological order and if they have been disturbed with time or during sediment core collection. Second, we need to determine the sedimentation rate or the rate of particulate material deposition to the sediment surface. The most widely used dating techniques involve the natural radioactive isotope of ^{210}Pb (half life of 22.3 yr), ^{238}U and ^{137}Cs (half life of 30 yr). ^{210}Pb forms naturally in sediments and soils containing ^{238}U. ^{210}Pb is one of the elements formed from the radioactive decay of ^{238}U. This ^{210}Pb is called supported ^{210}Pb, because it is constantly being replenished from local ^{238}U. ^{210}Pb also forms naturally from ^{222}Rn gas and quickly deposits back to the earth as unsupported ^{210}Pb. Supported and unsupported ^{210}Pb make up the total ^{210}Pb measured in sediment.

$$^{238}U \xrightarrow{4.51\times10^{9}\,y} {}^{226}Ra \xrightarrow{1602\,y} {}^{222}Rn \xrightarrow{3.82\,d} {}^{210}Pb \xrightarrow{22.26\,y} {}^{210}Po \xrightarrow{138.4\,d} {}^{206}Pb$$

The newest sediment (top layer) contains the highest concentration of ^{210}Pb. Older sediments (deeper layers) contain the same amount of supported ^{210}Pb as the top layer, but less unsupported ^{210}Pb. The supported ^{210}Pb concentration is constant over time and depth, while the unsupported ^{210}Pb diminishes over time and depth. ^{137}Cs is a good indicator of the years 1954 and 1963. Because of atomic weapon testing, the ^{137}Cs has extremely high concentrations in sediment deposited during these two years *[32]*.

We assume the supply of unsupported ^{210}Pb to the sediment is the same for each time interval, the initial concentration $C_0(t)$ of unsupported ^{210}Pb in sediment of age t years must satisfy:

$$C_0(t)*r(t) = \text{const} \qquad \text{(Eqt 1-1)}$$

Where r(t) g/cm^{2}yr is the dry mass sedimentation rate at time t. So the present concentration of unsupported ^{210}Pb at depth x is:

$$C(x) = C_0(t)*e^{-kt} \qquad \text{(Eqt 1-2)}$$

Where

$$k=\log 2/22.3=0.3114$$

is the radioactive decay constant of ^{210}Pb*[32]*.

Dating using ^{210}Pb and ^{137}Cs has been used very reliably where the sedimentation rate is relatively constant and the sediment stratigraphy is unambiguous *[32]*.

The sedimentation rate varies from lake to lake. The sediment flux for any lake depends on land cover, climate, topography, geology, basin configuration and lake productivity *[31]*. Considering all of these factors, the sedimentation rates for high elevation lakes range from 0.02 to 2 cm/yr *[31]*. Therefore, a one cm thick layer of sediment may represent 0.5 years to decades of SOC deposition. The WACAP sediment sampling sites were chosen from lakes with small catchments, low productivity, and minimal catchment disturbance *[31]*.

The objectives of this research were to develop a new analytical method for measuring a wide range of SOCs in sediment, to measure SOCs in a sediment core collected from Pear Lake in Sequoia National Park, CA, and to determine the historical deposition of SOCs to this lake catchment.

2. Measurement of semi-volatile organic compounds in high elevation lake sediments

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2.1 Introduction

Semi-volatile organic compounds (SOCs), such as polycyclic aromatic hydrocarbons (PAHs), DDTs, hexachlorocyclohexanes (HCHs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs), are relatively persistent in high elevation ecosystems *[2,4,33,34]*. Because of their persistance, bioaccumulation, and toxicity, some SOCs are no longer used in developed countries. These properties also enhance the deposition of some SOCs to cold sites, such as the artic and high elevation ecosystems. Once they are released into the atmosphere, some SOCs transfer and condense to these cold regions. This mechanism is called global distillation or orographic cold trapping *[4,7,35]*.

High elevation lake sediments are repositories of SOCs. Based on the chronology of sediments, the long-term temporal deposition trends of SOCs can be reconstructed by analyzing different layers of the sediment samples. The concentrations of SOCs in the undisturbed sediment layers can show the historical deposition inventories.

The following techniques were used to determine the concentration and flux of SOCs in sediment cores. First, the stratigraphy of the core was determined. Second, the sedimentation rate of each layer of sediment was determined by measuring the natural radioactive isotope of unsupported ^{210}Pb (half life of 22.3 yr) and ^{137}Cs (half life of 30 yr).

An analytical method was developed to measure a wide range of SOCs in sediment. Pressurized liquid extraction (PLE) was used for the extraction of SOCs from sediment. In this research project, a conventional solvent, methylene chloride, was used at a high temperature (100°C) and high pressure (1500 psi) to extract SOCs from sediment samples quickly, with a small solvent volume. With PLE, it is possible to pressurize the sample cell while keep the solvent as a liquid at a high temperature *[36-38]*. The higher extraction temperature results in higher solubility of SOCs, faster diffusion rates, larger mass transfer coefficients, and lower solvent viscosity and surface tension *[39]*. PLE has been previously used to extract different SOCs from sediment *[40]*. One of the major shortcomings of those methods is the co-extraction of large amounts of lipid *[40]*. These lipid interferences must be separated from the target SOCs or the chromatographic performance will be severely affected.

Gel permeation chromatography (GPC) has been used on biological extracts *[40]* to remove lipid. The cross-linked polymer used in the GPC column separates low molecular weight compounds (SOCs) from the high molecular weight interferrants with molecular weights up to 250,000. Because sediment is a good sink for anthropogenic contaminants, as well as dead biota, there is a significant portion of high molecular weight material left over in sediment. In order to do a fast and

efficient purification to remove high molecular weight interferences and sulfur from sediment extractions, GPC was used on sediment extracts. Sulfur can interfere with PCB measurements as a co-eluting chromatographic peak *[41]*.

The objective of this research was to develop a new and efficient analytical method to measure a wide range of SOCs (see Table 2.1) in sediment. The analytical method was validated using a National Institute of Standards and Technology (NIST) standard reference material sediment. Finally, the new analytical method was used to measure SOCs in Pear lake (Sequoia National Park, CA) sediments to calculate the concentration and flux of SOCs in each sediment layer and determine the long-term temporal trends of SOC deposition to this high elevation ecosystem.

2.2 Materials and Methods

2.2.1 Standards and Reagents

The SOC standards (Table 2.1) were acquired from the EPA repository or purchased from Chem Services Inc (West Chester, PA), Restek (Bellefonte, PA), Sigma-Aldrich Corp (St. Louis, MO), or AccuStandard (New Haven, CT). The standard spike solution concentrations for each surrogate and internal standard were approximately 10 ng/uL.

Solvents (methylene chloride, ethyl acetate, and hexane) for extraction and purification were purchased from Fisher Scientific (Fairlawn, NJ) optima grade. Mega bonded silica columns were purchased from Varian (Palo Alto, CA). Sodium sulfate (Pesticide grade) for drying was purchased from J.T. Baker.

Standard Reference Material (SRM) 1944 was purchased from the NIST, USA. It is New York/New Jersey waterway sediment collected in 1976 from six sites in the vicinity of New York Bay and Newark Bay and mixed and freeze dried before storage.

2.2.2 Field Sampling

The sampling location was Pear Lake, Sequoia National Park, California (Figure 2.1), located 2904 m above sea level (36.60° N, 118.67° W). Two sediment cores were collected in Pear Lake on August 23rd, 2003.

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	**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: o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, Ethion, Malathion, Parathion and Parathion -methyl, Methoxychlor, Acetochlor, Alachlor, Prometon, Triallate, EPTC, Etridiazole, Propachlor, Metolachlor, Diazinon, Pebulate, Atrazine desisopropyl, Atrazine desethyl, Simazine, Cyanazine, Atrazine	**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: 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	**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

Table 2.1 System Monitored Target Compounds, Isotope Labeled Surrogate Compounds, and Internal Standards

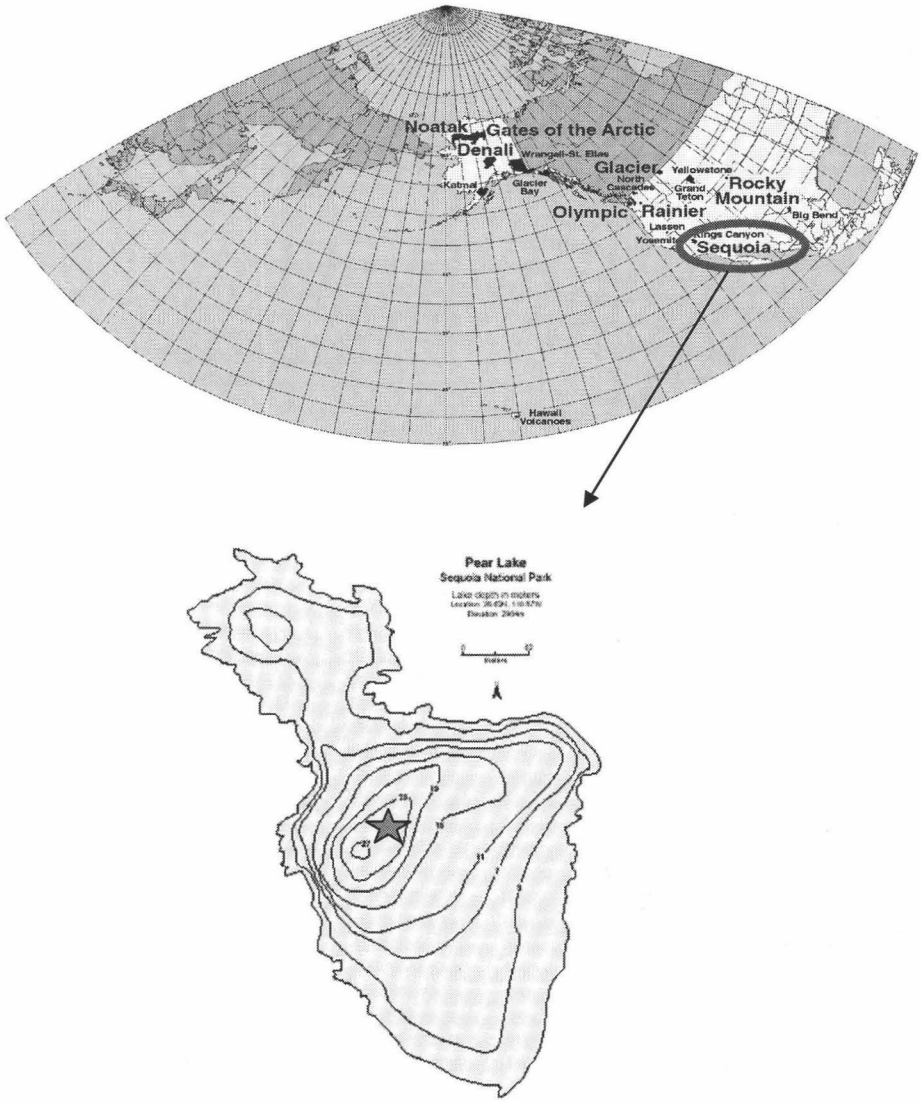

Figure 2.1 Map of Pear Lake, Sequoia National Park (*the approximate sampling location of the sediment core)

Using an Uwitec gravity corer with an 8.6 cm internal diameter, sediment cores between 25 and 50 cm in depth were obtained. The sediment cores were examined to insure an intact surface layer. An acceptable sediment core was undisturbed by invertebrate tubes. Each acceptable core was sectioned by precisely slicing it into 0.5 cm or 1.0 cm increments with a clean stainless steel appliance. The cores were sliced into 0.5 cm increments for the first 10 cm, and 1.0 cm increments for the remainder of the core depth. Each sediment slice was stored in a solvent rinsed glass jar, with a cleaned aluminum foil cap liner and stored at -20°C until processing.

2.2.3 Radiometric Dating Procedure

Slices of each core were homogenized and sub-sampled and dated by analyzing ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay at the Liverpool University Environmental Radioactivity Laboratory, using an Ortec HPGe GWL series well-type coaxial low background intrinsic gernanium detectors*[32]*. ^{210}Pb was determined by its gamma emissions at 46.5keV, and ^{226}Ra by the 295keV and 352keV γ-rays emitted by its daughter radionuclide ^{204}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration *[32]*. ^{137}Cs and ^{241}Am were measured by their emissions at 662keV and 59.5keV respectively *[32]*. The absolute efficiencies of the detectors were determined using

calibrated sources and sediment samples of known activity *[32]*. Corrections were made for the effect of self absorption of low energy-rays within the sample *[32]*.

2.2.4 Measurement of Percent Moisture and Total Organic Carbon

The measurement of moisture and total organic carbon on the Pear Lake sediment layers was done by Willamette Research Station (Corvallis, OR).

Each sediment sample was homogenized, and a portion (~ 1 g to 5 g dry weight) of the sample was removed for freeze-drying. A sediment sample was weighed before and after freeze drying and the difference in the mass was used to determine the percent moisture.

To measure the total organic carbon (TOC), 10 mg to 30 mg aliquots of dried sediment were transferred to silver (Ag) capsules. 50 mL of reverse osmosis water was added to each capsule to wet the sediment and the sediment capsules were exposed to HCl fumes for 18-hours to removal carbonates. After removal from the acid vapor environment, the capsules were dried for 4 hours at 60°C in a forced air oven. The Ag capsules were sealed and all samples were analyzed using a Carlo Erba EA1108 CN analyzer. The Ag capsules were sealed, placed in an auto-sampler, and subsequently dropped individually into the vertical quartz combustion tube of the Carlo Erba 1108A elemental analyzer.

The samples were flash-combusted to produce CO_2 that was separated from other gases on a porous polymer column (Porapak Q). After separation, the CO_2 peak was detected by thermal conductivity and the concentration determined by comparison to known standards.

2.2.5 Pressurized Liquid Extraction (PLE)

Frozen sliced sediment samples were thawed and ground with baked and cooled Na_2SO_4 to remove excess water. Each 66mL cell was filled with the sediment and Na_2SO_4 (1:8 ratio of wet sediment to Na_2SO_4) mixture and a 1 um cellulose filter placed in the bottom of the cell. Approximately 17g of wet sediment was extracted for each sediment layer. Before extraction, 15uL of the 10 ng/uL surrogate solution was added on top of each sediment filled cell. The cell was extracted using an Accelerated Solvent Extraction (ASE) 300 instrument (Dionex Corp., Sunnyvale, CA) in 2 extraction steps, using methylene chloride, under a cell pressure of 1500 psi and temperature of 100°C for 10 minutes, with 100% flushing volume.

2.2.6 Extract Purification and Measurements of Percent Lipid

After extraction by PLE, the sediment extracts were subjected to two purification steps. First, a 20 g silica SPE cartridge was conditioned with 50 mL ethyl acetate, 50 mL methylene chloride, and 50 mL hexane to

remove the very polar interferences. The extract volume was reduced to ~1 mL and solvent exchanged to hexane by TurboVap (Zymark Inc). The concentrated extracts were loaded on to the pre-conditioned silica SPE cartridges. The silica gel elution step involved 100 mL ethyl acetate-methylene chloride (1:1). The silica purified extracts were then concentrated to ~0.7 mL and solvent exchanged to methylene chloride. Gel Permeation Chromatography (GPC) clean up system (Waters Inc, Milford, MA) was used to remove high molecular weight interference and sulfur. This GPC is equipped with a guard column, a 15 cm (dia 1.9 cm) and 30 cm (dia 1.9 cm) Waters Envirogel analytical column, in series, and a DCM mobile phase with a flow rate of ~5 mL/min. The analyte fraction eluted from 12.25-21.00 min and was collected. The purified extracts were concentrated down to ~300 uL, and spiked with 15 uL of the 10 ng/uL internal standard (see Table 2.1) prior to the analysis by GC-MS.

To determine the percent lipid for the sediment samples, the lipid portion from GPC fraction was collected and concentrated to ~1 mL. The lipid extract was dried in an oven at 102 °C for 1 hour. After the lipid fraction had cooled, the remaining weight was recorded as the mass of lipid.

2.2.7 Extract Analysis

The purified sediment extracts were analyzed by gas chromatography (Agilent 6890) with a mass spectrometer (Aglient 5973N MSD) (GC-MS), using both electron impact (EI) and electron capture negative ionization (ECNI) mode. A DB-5MS column (J&W Scientific, 30 m x 0.25 mm i.d.; 0.25 um film thickness) was used for analyzing different target compounds (see Table 2.1). The GC/EI-MS oven temperature program was 60°C (held for 1 min), and ramped at 6 °C/min to get 300 °C (held for 3 min), ramped 20 °C to 320 °C (held 9 min). The entire cycle run time was 54 min. The GC/ECNI-MS oven temperature program was 120 °C for 1 min, ramped at 4 °C /min to 275 °C, ramped at 6 °C/min to 320 °C (held 5 min). The analytes were quantified using selected ion monitoring (SIM). The monitored ions for each of the target compounds, the isotopically labeled surrogates, and internal standards are given in Appendix 1 and 2 *[42]*.

2.2.8 Quality Assurance/Quality Control (QA/QC)

In order to determine the precision and accuracy of our measurements, we measured lab blanks at a 5% frequency, Standard Reference Material at a 10% frequency, replicate injections at a 10% frequency, and at least one instrument performance check standard per batch.

All of the results reported in this thesis are lab blank subtracted. The lab blanks were prepared using the same steps, and at the same time, as the samples. Lab blanks were spiked with the same amount of surrogate standards and internal standards as the sediment samples. It is impossible to take a clean blank sediment matrix to the sampling field and treat it the same way as we treated the sediment cores. So there is no field blank for this sediment study.

Based on the WACAP QA/QC plan, the concentrations reported in this thesis are lab blank subtracted. All surrogate recoveries were within 30 to 130% for the entire procedure. Duplicate injection was done for the layer from year 1963, and the relative standard difference was less than 25% for the two injections.

2.3 Results and Discussion

2.3.1 Method Development

Sediment samples obtained from Cottage Grove Reservoir, Oregon (in August 2002) were used for analytical method development and validation. Before following the steps in 2.2.4, 2.2.5, and 2.2.6, triplicate sediment samples were spiked with 1.5 ng of each the of target SOCs (see Table 2.1) prior to PLE, and the surrogate and internal standard SOCs were spiked after the final concentration step but prior to GC/MS

analysis. This was done in order to determine the recovery of analytes for the entire analytical method.

These sediment samples were also used for determining the sample-specific estimated method detection limits (EDL). The EDLs were calculated using the approach described in EPA Method 8280A, "The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)." The EDL is an estimate of the concentration of a given target analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. The following equation was used to calculate the EDL:

$$EDL = \frac{2.5 \times C_{is,s} \times H_{n,s} \times D}{H_{is,s} \times RF} \qquad \text{(Eqt 2-1)}$$

Where

$C_{is,s}$ = the concentration of the internal standard in the sample.

$H_{n,s}$ = the peakheight of the noise for the quantitation ion at the target analyte's retention time if the target analyte is absent from the sample or near the target analyte's retention time if the target analyte is present in the sample.

S= sample

D = the dilution factor, or the final volume of the sample divided by the initial sample wet weight.

H_{is} = the peak height of the internal standard in the sample.

RF = the response factor, or the ratio of the area of the target analyte to that of the internal standard multiplied by the ratio of the concentration of the internal standard to that of the target analyte. Because RF can vary with concentration, the RF used in this equation was determined from the lowest concentration calibration standard in which the target analyte was still detected *[31]*.

Table 2.2 shows the percent recovery of each of the target compounds for the entire analytical method, the percent relative standard deviation of the recovery for the triplicate samples, and the estimated method detection limit of the analytical method.

2.3.2 Method Validation

SRM 1944 was purchased from NIST, USA. It is New York/New Jersey waterway sediment, collected from six sites in the vicinity of New York Bay and Newark Bay. There are certified concentrations for: 24 PAHs, 35 PCB congeners, and 4 chlorinated pesticides. Replicate (n=6) 0.5 g (dry weight) samples of SRM 1944 were spiked with 15 uL of the 10 ng/uL surrogate standard and were individually extracted, followed by the silica gel SPE and GPC purification. The purified extracts were concentrated to ~300 uL and then spiked with 15 uL of the 10 ug/uL internal standard solution. We measured 37 of our target SOCs (see

Table 2.3) in SRM 1944, even though some of them (including dacthal, chlorpyrifos, dieldrin, and mirex) did not have certified concentrations. Table 2.3 shows the comparison of the mean concentrations we measured and the certified concentrations.

The following equation was used to compare our measured concentration to the certified concentration:

$$PD\% = \frac{\overline{C}_m - (\overline{C}_c \pm SE)}{\overline{C}_c} \times 100\% \qquad \text{(Eqt 2-2)}$$

Where

PD = Percent difference.

$\overline{C}_m$ = Our measured mean concentration.

$\overline{C}_c$ = The mean certified concentration from SRM 1944 certificate.

SE = Standard error for each certified concentration.

Figure 2.2 shows the comparison of the measured mean concentration to the SRM certified value mean. The results from ECNI have six replicate samples (n=6) and the results from EI have triplicate samples (n=3). The measured mean concentration of cis-chlordane is significantly lower than the SRM certified mean value. In the SRM certificate, there are only reference values, not certified values, for acenaphthene and fluorene. Our measured mean concentration of 23 out of the 24 target SOCs with certified values had a percent difference less than 30% from the certified value.

Chemical Class / Compounds	Avg. % Rec	Avg. % RSD	EDL[1]. pg/g (wet wt)
Amide Pesticides			
Propachlor	71.1	27.1	9.9
Alachlor	101.5	8.9	245.5
Acetochlor	48.0	8.9	20.4
Metolachlor	58.6	13.5	33.2
Organochlorines Pesticides and Metabolites			
HCH, gamma	56.2	21.6	496.3
HCH, alpha	52.2	24.5	388.8
HCH, beta	62.6	16.6	569.0
HCH, delta	60.4	17.0	379.4
Methoxychlor	100.9	10.0	12.2
Heptachlor epoxide	71.6	18.8	692.3
Endrin aldehyde	65.2	16.1	302.9
Endrin	57.9	10.0	667.2
Heptachlor	43.6	16.8	264.4
o,p'-DDE	60.1	16.8	36.5
Chlordane, oxy	66.0	19.3	197.6
Dieldrin	50.1	21.5	327.3
Chlordane, cis	69.7	16.7	120.0
p,p'-DDD	52.2	16.1	22.4
Nonachlor, trans	72.4	15.1	87.5
o,p'-DDD	64.3	19.5	8.2
Chlordane, trans	74.4	17.9	89.3
Nonachlor, cis	66.4	5.8	77.9
Aldrin	56.6	23.4	263.7
o,p'-DDT	95.7	6.2	25.5
p,p'-DDE	58.2	18.0	61.7
Mirex	60.5	14.6	221.5
p,p'-DDT	63.5	8.9	41.1
Organochlorine Sulfide Pesticides and Metabolites			
Endosulfan sulfate	57.6	1.6	105.6
Endosulfan I	67.0	17.9	218.8
Endosulfan II	60.7	4.2	82.4
Phosphorothioate Pesticides			
Methyl parathion	33.7	7.7	74.5
Malathion	40.5	6.1	115.3
Diazinon	49.5	12.0	34.2
Chlorpyrifos	63.1	22.0	314.0
Thiocarbamate Pesticides			
EPTC	24.1	5.5	17.4
Pebulate	33.0	12.4	16.1
Triallate	75.5	3.9	42.7
Triazine Herbicides and Metabolites			
Atrazine desisopropyl	114.5	15.3	90.0
Atrazine desethyl	6.4	29.5	26.1
Simazine	4.5	60.1	128.1
Cyanazine	52.9	17.3	267.5
Atrazine	25.6	77.4	11.7
Prometon	12.9	10.0	176.3
Miscellaneous Pesticides			
Metribuzin	61.7	14.0	231.0
Etridiazole	22.2	1.4	12.1
Dacthal	41.2	11.7	27.9
Trifluralin	42.2	17.6	13.7
Hexachlorobenzene	37.2	17.2	10.8
Polycyclic Aromatic Hydrocarbons			
Acenaphthylene	44.0	36.3	5.1
Acenaphthene	48.0	31.3	13.4
Fluorene	51.6	20.9	7.3
Anthracene	52.9	27.1	7.5
Phenanthrene	54.6	13.1	12.5
Pyrene	52.3	6.0	58.4
Fluoranthene	56.5	6.4	5.0
Chrysene + Triphenylene	66.7	17.1	37.8
Benzo(a)anthracene	56.6	10.3	61.4
Retene	72.7	8.9	76.4
Benzo(k)fluoranthene	77.7	13.5	51.2
Benzo(a)pyrene	62.1	16.7	16.3
Benzo(b)fluoranthene	70.6	7.1	49.8
Indeno(1,2,3-cd)pyrene	63.9	8.2	38.3
Dibenz(a,h)anthracene	74.7	8.8	20.8
Benzo(e)pyrene	84.2	9.3	28.5
Benzo(ghi)perylene	63.4	11.2	8.7
Polychlorinated Biphenyls			
PCB 74	57.0	17.6	565.0
PCB 101	56.8	17.7	242.8
PCB 138	60.0	14.3	41.7
PCB 153	57.8	15.3	30.2
PCB 118	57.0	15.5	46.2
PCB 187	61.8	15.3	4.3
PCB 183	62.9	14.0	37.9
Average Recoveries and %RSD	57.7	16.1	127.0
Max	114.5	77.4	692.3
Min	4.5	1.4	4.3

[1]Sample-specific Estimated Method Detection Limits

Table 2.2 Target Compounds Percent Recoveries for the entire analytical method, Percent RSD and Estimated Method Detection Limits

ECNI Target Comounds	Meas Conc (ug/kg)	SE (ug/kg)	Certi Conc (ug/kg)	SE (ug/kg)	% PD
Hexachlorobenzene	4.30	0.75	6.03	0.35	-22.9
HCH, alpha	1.53	0.69	2.00	0.30	-8.69
Chlordane, trans	8.87	2.07	8.00	2.00	0.00
Chlordane, cis	6.06	1.36	16.51	0.83	-58.2*
Nonachlor, trans	5.95	0.37	8.20	0.51	-21.1
PCB 101 (penta)	48.7	1.62	73.4	2.50	-30.2
PCB 118 (penta)	37.6	1.30	58.0	4.30	-27.6
Nonachlor, cis	2.95	0.14	3.70	0.70	0.00
PCB 153 (hexa)	49.6	2.60	74.0	2.90	-29.0
PCB 138 (hexa)	58.8	3.30	62.1	3.00	-0.422
PCB 187 (hepta)	20.3	1.60	25.1	1.00	-15.1
PCB 183 (hepta)	9.99	0.57	12.19	0.57	-13.3
Dacthal	0.185	0.07	NA		
Chlorpyrifos	0.779	0.13	NA		
Dieldrin	13.6	1.23	NA		
PCB 74 (tetra)	28.5	1.14	NA		
Mirex	0.839	0.03	NA		

EI Target Compounds	Meas Conc (ug/g)	SE (ug/g)	Certi Conc (ug/g)	SE (ug/g)	% PD
Acenaphthene	0.211	0.002	0.57	0.03	57.65*
Fluorene	0.309	0.007	0.85	0.03	60.08*
Phenanthrene	4.84	0.05	5.27	0.22	-3.99
Anthracene	1.25	0.02	1.77	0.33	0.00
Fluoranthene	7.09	0.18	8.92	0.32	-16.9
Pyrene	6.61	0.21	9.70	0.42	-27.5
p,p'-DDE	0.072	0.00	0.086	0.012	-2.48
o,p'-DDD	0.041	0.00	0.038	0.008	0.00
p,p'-DDT	0.120	0.00	0.119	0.011	0.00
Benzo(a)anthracene	4.87	0.22	4.72	0.11	0.00
Benzo(b)fluoranthene	4.77	0.314	5.96	0.42	-12.9
Benzo(k)fluoranthene	1.95	0.08	2.30	0.20	-6.58
Benzo(a)pyrene	3.57	0.19	4.30	0.13	-14.1
Benzo(ghi)perylene	2.68	0.13	2.84	0.10	-1.99
EPTC	0.012	0.00	NA		
Acenaphthylene	0.825	0.002	NA		
Phorate	0.010	0.00	NA		
Retene	1.13	0.007	NA		
Methoxychlor	1.74	0.01	NA		
Chrys-L +Triph	2.94	0.11	NA		

Table 2.3 Comparison of our mean Measured Concentration and Certified Concentration for SRM 1944 (*Not within the 30 percent differences range). Certificate values for acenaphthene and fluorene are reference values and not certified values.

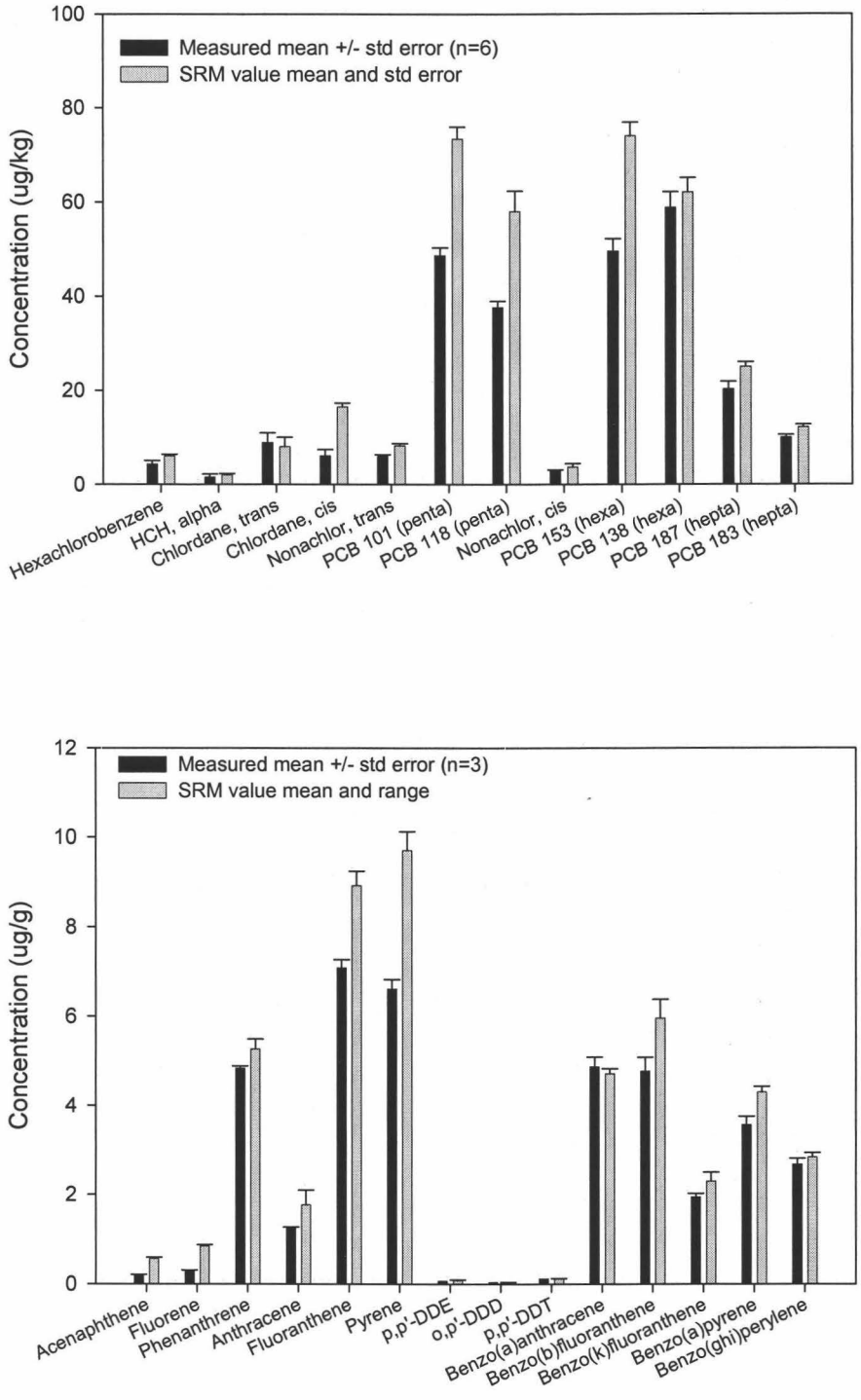

Figure 2.2 Method Validation Results—Comparison of Measured Mean Concentration with Certified Value of SRM 1944

2.3.3 Radiometric Dating

Table 2.4 provides specific information on the Pear Lake sediment cumulative dry mass (g/cm^2), mean age of each layer (year), and the sedimentation rate (g/cm^2y). The sedimentation rate varies between 0.006 and 0.014 g/cm^2y. This confirms that Eqt 1-2 is appropriate for determining the age of the sediment layers. Figure 2.3 is the plot of sediment core depth verses the year. ^{137}Cs indicates the year 1963.

Depth		Chronology			Sedimentation Rate		
		Date	Age				
cm	g cm^{-2}	AD	y	±	g cm^{-2} y^{-1}	cm y^{-1}	± (%)
*0.00	0.00	2003	0				
*0.50	0.03	2001	2	1	0.012	0.19	3.4
*1.00	0.06	1998	5	2	0.012	0.18	3.5
1.50	0.09	1995	8	3	0.012	0.17	3.7
*2.00	0.13	1992	11	4	0.012	0.17	4.1
2.50	0.16	1989	14	5	0.011	0.15	4.4
3.00	0.20	1986	17	6	0.011	0.14	4.8
*3.50	0.24	1982	21	7	0.011	0.13	5.1
4.00	0.28	1978	25	8	0.010	0.13	5.4
4.50	0.32	1974	29	9	0.010	0.13	5.6
*5.00	0.36	1970	33	10	0.011	0.13	6.2
5.50	0.41	1967	36	11	0.012	0.13	7.1
*6.00	0.46	1963	40	12	0.014	0.13	8.1
*6.50	0.50	1959	44	13	0.014	0.13	8.7
7.00	0.55	1955	48	14	0.012	0.13	9.0
7.50	0.59	1951	52	15	0.011	0.13	9.3
8.00	0.64	1947	56	16	0.010	0.13	9.6
8.50	0.68	1943	60	17	0.011	0.13	9.8
9.00	0.72	1939	64	18	0.011	0.13	10.0
9.50	0.76	1935	68	19	0.011	0.12	10.8
*10.00	0.80	1931	72	20	0.010	0.12	12.1
10.50	0.83	1926	77	21	0.008	0.11	13.4
11.00	0.87	1922	81	22	0.007	0.10	14.8
11.50	0.91	1917	86	23	0.006	0.08	16.1
12.00	0.95	1910	93	24	0.006	0.07	20.4
12.50	1.00	1902	101	25	0.006	0.07	24.7
13.00	1.04	1895	108	26	0.006	0.06	29.0
13.50	1.09	1887	116	27	0.006	0.07	33.2
*14.00	1.13	1879	124	28	0.006	0.07	37.5
14.50	1.17	1872	131	29	0.006	0.07	41.8

Table 2.4 ^{210}Pb chronology of the Pear Lake sediment core *[43]*
(*Layers selected for SOC analysis)

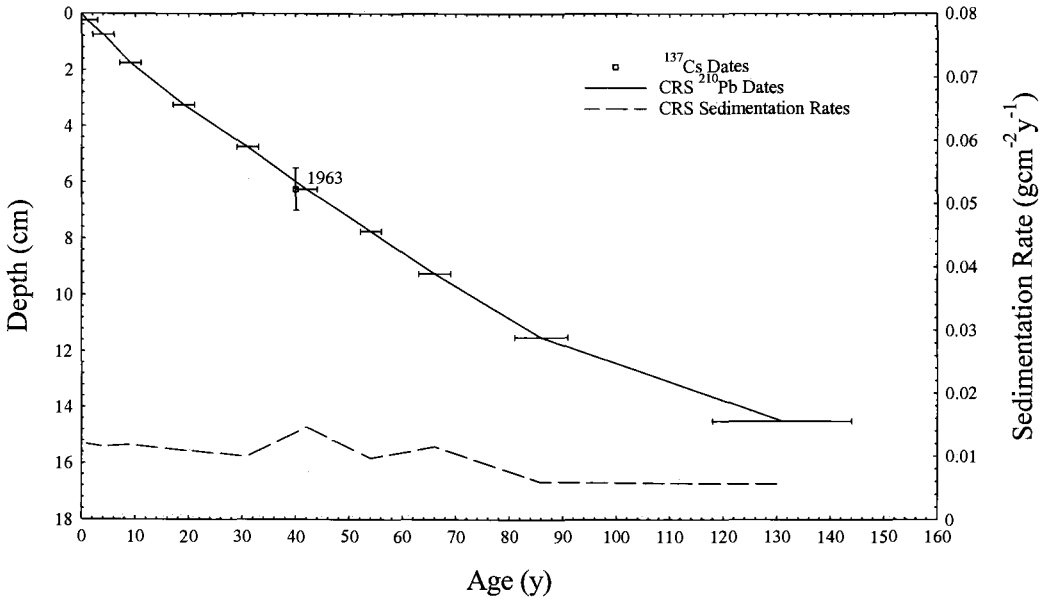

Figure 2.3 Radiometric chronology of Pear Lake core showing the CRS model dates and sedimentation rates and also the 1963 depth determined from the ^{137}Cs record *[43]*.

2.3.4 SOC Accumulation and Flux

Figure 2.4 shows the percent moisture, percent TOC, and percent lipid content of the sediment layers selected from Pear Lake, Sequoia National Park for SOC analysis. The percent moisture is almost constant in these sediment layers, from 89.9% to 95.3%. There is not much TOC difference of this lake sediment. The top layer has the highest TOC content (15.3%) and the selected bottom layer has the lowest TOC content (11.2%). There is a wide range in the lipid content of this lake sediment, from 0.173% to 3.14%. The lipid in the sediment was from detritus and likely degrades more rapidly than SOCs over time. This is why the top layer of sediment has the highest lipid content.

Because SOCs may have higher concentrations because of their association with organic carbon and lipids, Figure 2.5, 2.6, 2.7, 2.8, 2.9 and 2.10 show the dry weight flux, total organic carbon normalized flux and lipid normalized flux of SOCs measured in the Pear Lake sediment core. We are the first to examine the lipid normalized flux of SOCs in lake sediment.

PCBs were banned in the US in 1977 *[30]*, but continue to be released from old sources. Four PCB congeners were measured in these selected sediment layers, PCB 153, PCB 138, PCB 187, and PCB 183. Fig 2.5 shows that the highest total PCB dry weight flux was in 2003 (the top sediment layer) but the highest lipid normalized flux was in

1963, which is when PCBs were widely used. For each congener, the sediment flux varies from layer to layer. Only the total PCB flux has a time trend that could track sediment chronology (see Figure 2.5).

The total PCB flux in the top layer is 175 ng/cm^{2}y. PCBs have been measured in Canadian Mid-latitude and Arctic Lake sediments *[16]*. The total PCB flux ranged from 0.0111 ng/cm^{2}y to 0.42 ng/cm^{2}y for different lakes in that region *[16]*. Because of Pear Lakes proximity to urban sources (San Francisco and Los Angeles), the PCB sediment flux is much higher in Pear Lake than in Canada.

PAHs are currently released from incomplete combustion sources. The layer from 1970 has the highest PAH flux and, after that decade, the flux of PAHs to Pear Lake sediment decreased (see Figure 2.6). Since Pear Lake is downwind of urban areas (including I-5), the PAH flux in Pear Lake is quite high. Compared to the total PAH flux in European high altitude mountain lakes (0.0044 to 0.17 ug/cm^{2}y) *[10]*, the total PAH flux in Pear Lake is about 100 ug/cm^{2}y for the top layer.

Chlordane was used as a pesticide on crops, lawns, and gardens, and to control termites in US from 1948 to 1978 *[30]*. Chlordane was banned for use in the US in 1988 *[30]*. In this study, the highest flux of chlordanes was measured in the sediment layer corresponding to 1982 (950 ng/cm^{2}y) (see Figure 2.7). Due to the persistence of the chlordanes, they continue to be released to the atmosphere and cold

condense in high elevation ecosystem. This is the first time chlordanes have been measured in high elevation lake sediments.

Endosulfan is a currently used pesticide to control insects on food and non-food crops, including wood. The measured dry weight flux is from 13.7 ng/cm^{2}y to 688 ng/cm^{2}y. Figure 2.8 shows that the flux of endosulfans to Pear Lake has been highest in recent years. This is the first time endosulfans have been measured in high elevation lake sediments.

Figure 2.9 shows the dieldrin flux over time. From the 1950s until 1970, dieldrin was a widely used pesticide for crops like corn and cotton. In 1974, because of concerns about damage to the environment and potentially to human health, EPA banned all uses of dieldrin *[30]*. Our data suggest that the flux of dieldrin to Pear Lake peaked around 1963. Although the dry weight flux indicates a high dieldrin flux in recent years (2003), the lipid normalized flux suggests that the dieldrin flux to Pear Lake is leveling off.

DDT is a pesticide once widely used to control insects in agriculture and insects that carry diseases such as malaria. Its use in the U.S. was banned in 1972 because of damage to wildlife *[30]*. Figure 2.10 shows that the flux of DDT to Pear Lake sediment peaked in the early 1960's (82 ug/cm^{2}y). After it was banned, the flux dropped to about 10 ug/cm^{2}y in 2003. We detected primarily fresh DDT (o,p'-DDT) in sediment layers

corresponding to 1959 and 1963, which is when DDT was widely used. We primarily detected the degradation products of DDT in layers from recent years.

There are other system monitored target compounds (listed in Table 2.1) that were not detected in the Pear Lake sediment. This maybe because they have either very low usage (or emissions) in California, or have very low $\log K_{ow}$ and $\log K_{oc}$ values.

K_{ow} estimates the log octanol-water partition coefficient, which is ratio of the concentration of a chemical in the octanol and aqueous phases at equilibrium. The organic carbon normalized partition coefficient (K_{oc}) describes the partitioning of a chemical between the aqueous phase and soil or sediment in contact with water. Table 2.5 gives the estimated $\log K_{ow}$ and $\log K_{oc}$ values for our target SOCs. The SOCs detected in Pear Lake sediments have $\log K_{ow}$ and $\log K_{oc}$ values greater than 3.5. Target SOCs with values below 3.5 were not detected in Pear Lake sediment

2.4 Conclusions

PCBs, PAHs and some high logKoc pesticides were measured in high elevation lake sediments collected from Pear Lake, Sequoia National Park, CA. Based on the predominance of atmospheric mechanism for the transport of these compounds to the high elevation ecosystem, their

dry weight flux (or lipid normalized flux) shows the historic time trend of deposition. The highest flux of each historic use SOC was measured in the year of their wide spread use and low fluxes were measured after they were banned. Endosulfan, a current use pesticide, has the highest flux in recent years due to its wide spread continued use.

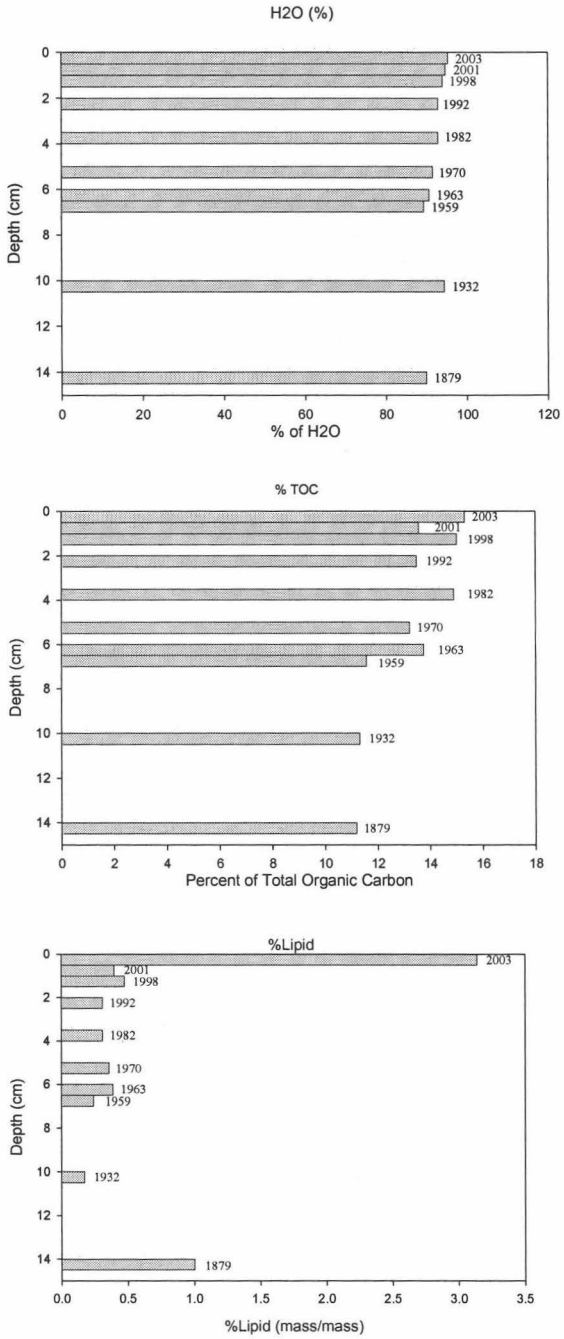

Figure 2.4 H_2O, total organic carbon (TOC), and lipid content (percent) in selected layers from Pear Lake, Sequoia National Park

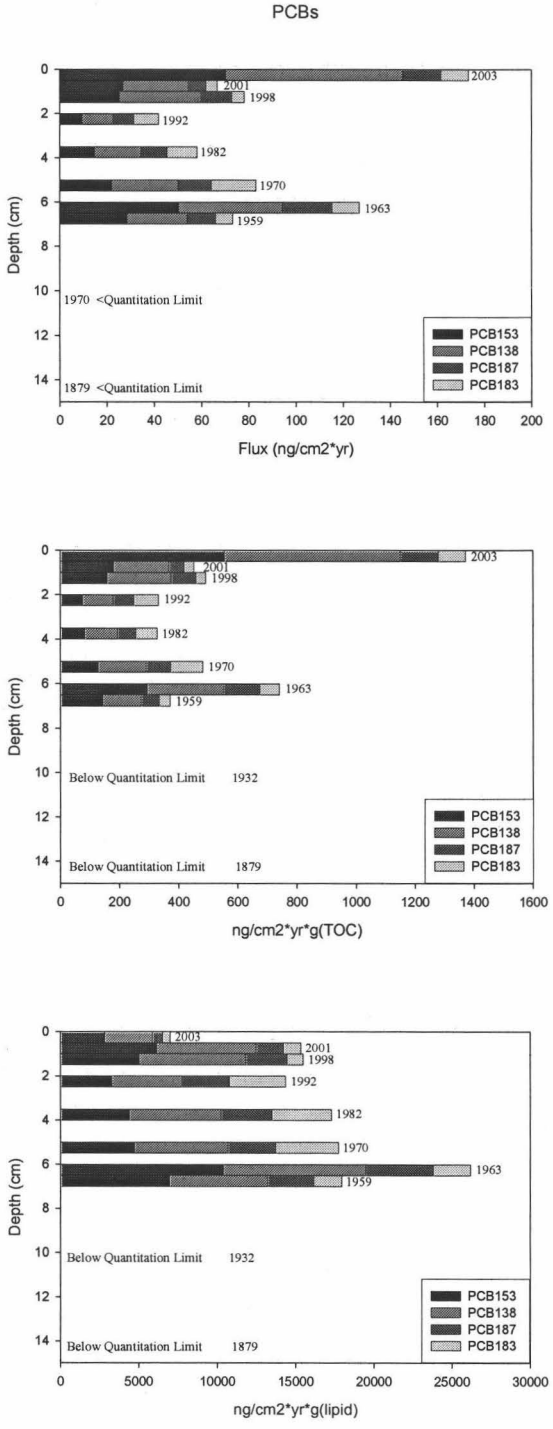

Figure 2.5 Comparison of flux, TOC normalized flux and lipid normalized flux of PCBs in selected layers from Pear Lake, Sequoia National Park

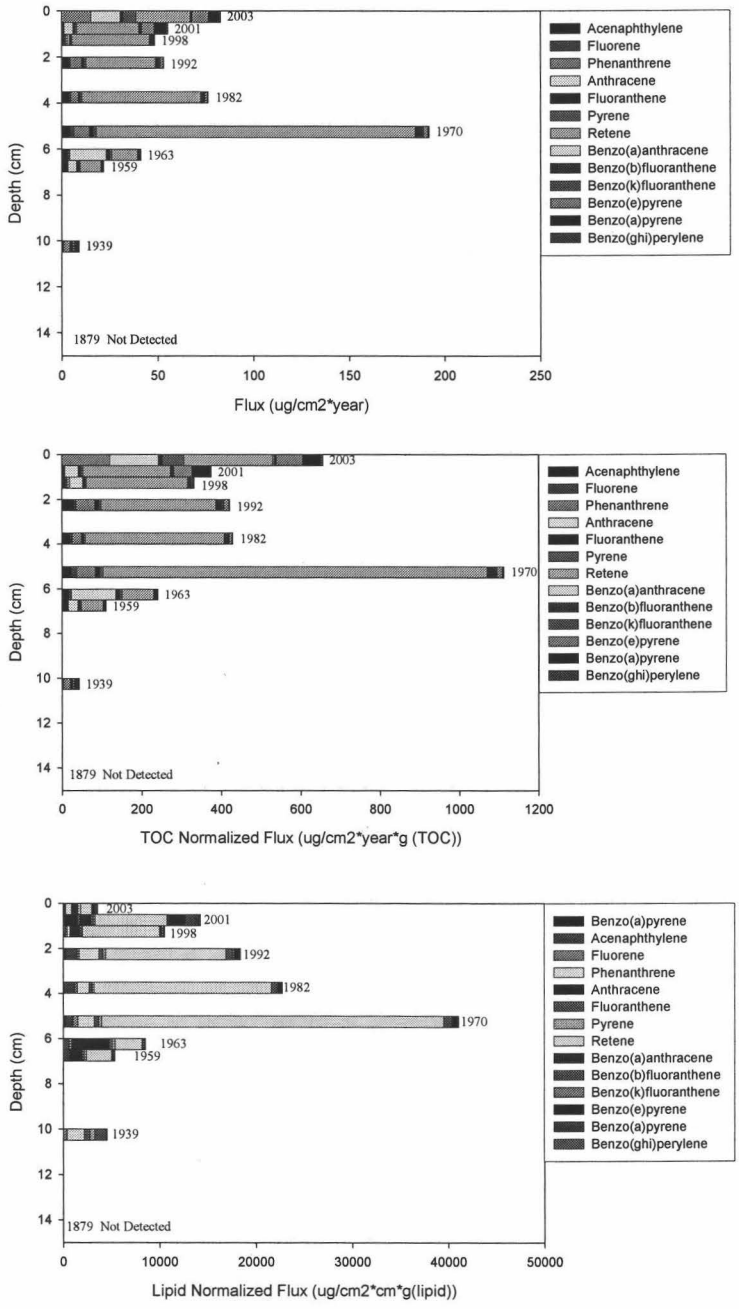

Figure 2.6 Comparison of flux, TOC normalized flux and lipid normalized flux of PAHs in selected layers from Pear Lake, Sequoia National Park

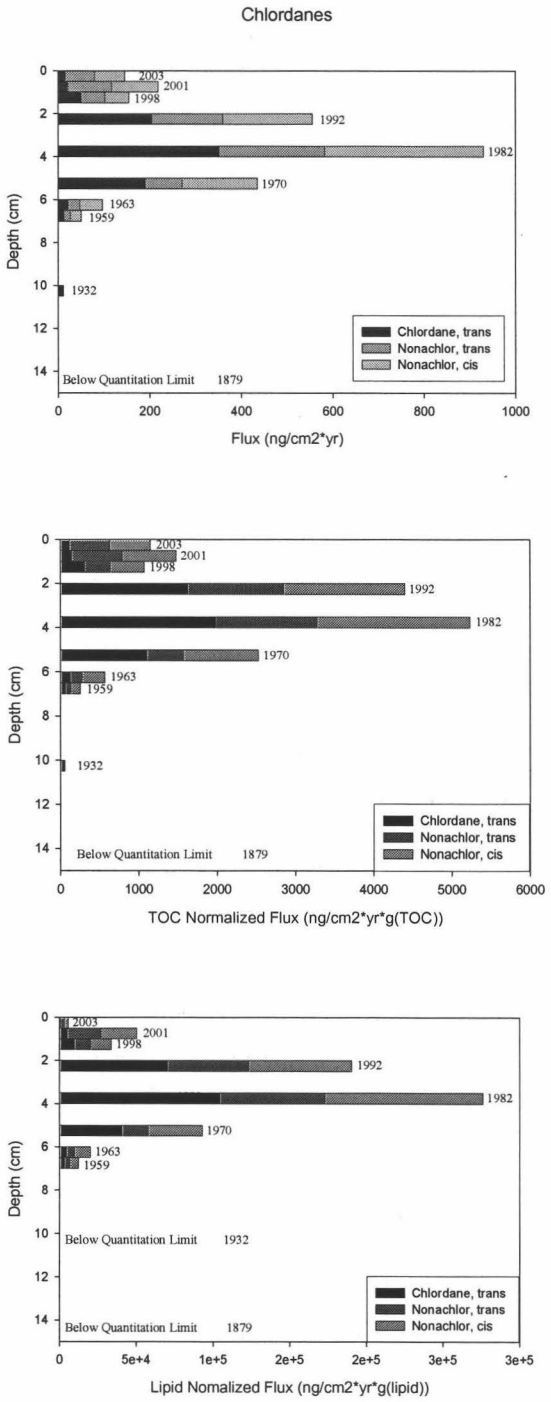

Figure 2.7 Comparison of flux, TOC normalized flux and lipid normalized flux of Chlordanes in selected layers from Pear Lake, Sequoia National Park

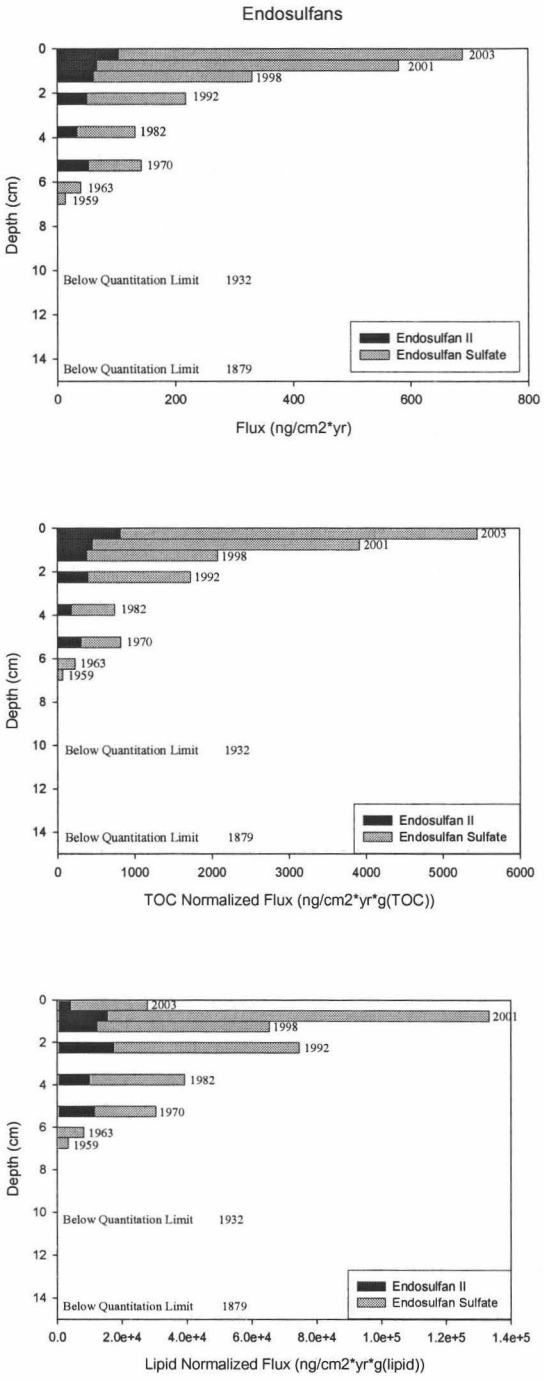

Figure 2.8 Comparison of flux, TOC normalized flux and lipid normalized flux of Endosulfans in selected layers from Pear Lake, Sequoia National Park

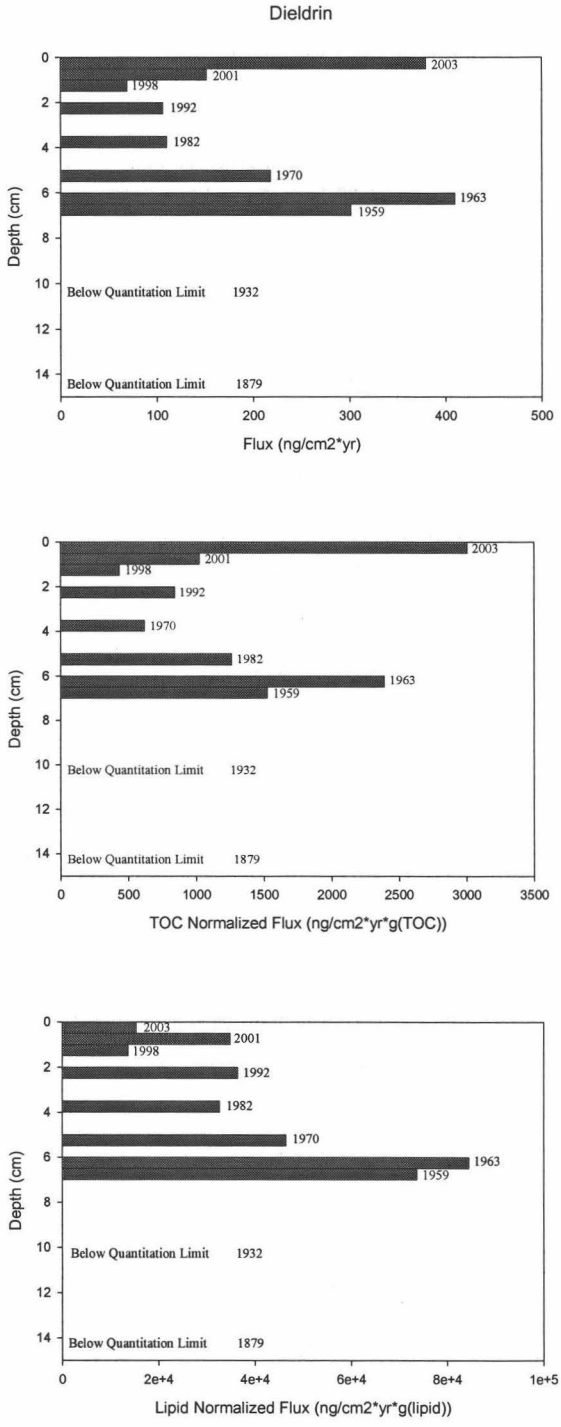

Figure 2.9 Comparison of flux, TOC normalized flux and lipid normalized flux of Dieldrin in selected layers from Pear Lake, Sequoia National Park

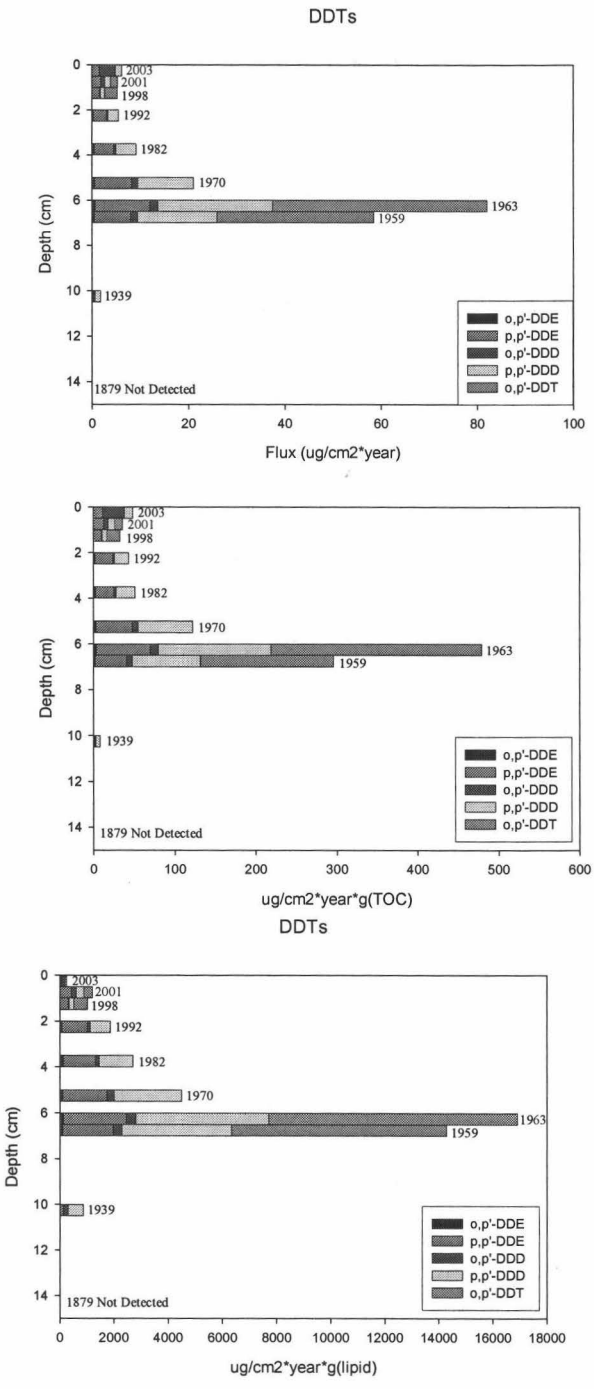

Figure 2.10 Comparison of flux, TOC normalized flux and lipid normalized flux of DDTs in selected layers from Pear Lake, Sequoia National Park

Chemical Class / Compounds	log K_{ow}	log K_{oc}[2]
Amide Pesticides		
Propachlor	2.4	2.5
Alachlor	2.6	2.3
Acetochlor	3.03[1]	2.2
Metolachlor	3.1	2.5
Organochlorines Pesticides and Metabolites		
HCH, gamma	3.8	3.5
HCH, alpha	3.8	3.5
HCH, beta	4.0	3.5
HCH, delta	4.1	3.5
Methoxychlor	4.5	4.6
Heptachlor epoxide	4.6	3.7
Endrin aldehyde	4.8	4.0
Endrin	5.2	4.0
Heptachlor	5.2	4.7
o,p'-DDE	5.5	5.2
Chlordane, oxy	5.5	3.9
Dieldrin	5.5	4.0
Chlordane, cis	5.9	4.9
p,p'-DDD	5.9	5.2
Nonachlor, trans	6.1	5.2
o,p'-DDD	6.1	5.2
Chlordane, trans	6.1	4.9
Nonachlor, cis	6.4	5.2
Aldrin	6.5	5.0
o,p'-DDT	6.8	5.4
p,p'-DDE	6.9	5.2
Mirex	6.9	5.7
p,p'-DDT	6.9	5.3
Organochlorine Sulfide Pesticides and Metabolites		
Endosulfan sulfate	3.7	4.5
Endosulfan I	4.7	4.3
Endosulfan II	4.8	4.3
Phosphorothioate Pesticides		
Methyl parathion	2.7	2.7
Malathion	2.9	1.5
Diazinon	3.7	3.1
Chlorpyrifos	5.1	3.8
Thiocarbamate Pesticides		
EPTC	3.2	2.4
Pebulate	3.8	2.7
Triallate	4.6	3.2
Triazine Herbicides and Metabolites		
Atrazine desisopropyl	1.36[1]	1.8
Atrazine desethyl	1.78[1]	1.9
Simazine	2.2	2.2
Cyanazine	2.2	2.1
Atrazine	2.3	2.4
Prometon	2.7	2.2
Miscellaneous Pesticides		
Metribuzin	1.70[1]	3.1
Etridiazole	2.6	1.9
Dacthal	4.3	2.5
Trifluralin	5.3	4
Hexachlorobenzene	5.5	3.5
Polycyclic Aromatic Hydrocarbons		
Acenaphthylene	3.9	3.8
Acenaphthene	4.0	3.8
Fluorene	4.2	4.1
Anthracene	4.5	4.3
Phenanthrene	4.5	4.3
Pyrene	5.1	4.8
Fluoranthene	5.2	4.9
Chrysene + Triphenylene	5.7	5.4
Benzo(a)anthracene	5.9	5.4
Retene	6.4	5.2
Benzo(k)fluoranthene	6.5	5.9
Benzo(a)pyrene	6.5	5.9
Benzo(b)fluoranthene	6.6	5.9
Indeno(1,2,3-cd)pyrene	6.7	6.4
Dibenz(a,h)anthracene	6.8	6.4
Benzo(e)pyrene	6.9	5.9
Benzo(ghi)perylene	7.0	6.4
Polychlorinated Biphenyls		
PCB 74	6.3	4.7
PCB 101	6.4	4.9
PCB 138	6.7	5.1
PCB 153	6.9	5.1
PCB 118	7.0	4.9
PCB 187	7.2	5.3
PCB 183	8.3	5.3

[1]log K_{ow} estimated by Estimation Program Interface Suite. Note: All other log K_{ow} values were selected from reference *[44]*.
[2]All log K_{oc} are estimated by Estimation Program Interface Suite.

Table 2.5 Estimated logK_{ow} and logK_{oc} values for target SOCs

3. Conclusions

Research has been done on the deposition of SOCs to high elevation ecosystem in Europe *[10-12]*, the Canadian Rocky Mountains *[12,16]*, and the Sierra Nevada Mountain range *[17]*. However, there is no data on the deposition of SOCs to high elevation ecosystems throughout the Western US. This research is part of WACAP and developed a new analytical method for the measurement of SOCs in lake sediments collected from high elevation ecosystems. The percent recovery of target SOCs in sediment, using the new analytical method, was 30 to 95%. The method estimated detection limit was 5 to 570 pg/g (wet weight). By applying the new analytical method to measure NIST SRM 1944, 23 out of the 24 target SOCs with certified values had a percent difference less than 30% from the certified value.

Sediment samples from Pear Lake, Sequoia National Park were analyzed using the new analytical method. The SOC dry weight flux, total organic carbon (TOC) normalized flux, and lipid normalized flux were determined. The SOCs that were banned in US showed decreasing fluxes with time after the ban. Some hydrophobic current use pesticides, such as endosulfan, showed increasing fluxes with time to recent years. PAHs continue to be deposited to Pear Lake sediment.

Due to the geological location of Pear Lake, it is adjacent to urban areas (San Francisco and Los Angeles) and agricultural areas (San

Joaquin Valley). Because of the large number of cars in California, the incomplete combustion emissions from vehicles deposit in Pear Lake.

The SOC deposition to lake sediment depends on both the use volume (or emissions) and the K_{ow}/K_{oc} value. Compared to the results from other high elevation sediment research, the flux of SOCs to Pear Lake is relatively high.

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Appendix 1

Electron Impact

Analyte	Retention Time (min)	Quantiation Ion m/z	Confirmation Ion m/z	2nd Confirmation Ion m/z	Quantitation Compound
SIM Window 1					
EPTC-$_{d14}$	15.13	142	203		*Acenaphthene-$_{d10}$
EPTC	15.33	128.1	132.1	189.1	EPTC-$_{d14}$
SIM Window 2					
Etridiazole	17.37	210.9	212.9	182.9	EPTC-$_{d14}$
SIM Window 3					
Acenaphthylene	17.50	152.1	151.1	76	Fluorene-$_{d10}$
Pebulate	17.58	128.1	203.1	161.1	EPTC-$_{d14}$
SIM Window 4					
*Acenaphthene-$_{d10}$	18.06	164	162		Internal Standard
Acenaphthene	18.18	154.1	153.1	152.1	Fluorene-$_{d10}$
SIM Window 5					
Fluorene-$_{d10}$	20.12	176	174		*Acenaphthene-$_{d10}$
Fluorene	20.22	166.1	165.1	163.1	Fluorene-$_{d10}$
SIM Window 6					
Propachlor	20.55	120.1	176.1	93.1	Atrazine-$_{d5}$
SIM Window 7					
Atrazine desisopropyl	21.59	173	175	158	Atrazine-$_{d5}$
Atrazine desethyl	21.74	172	174	187.1	Atrazine-$_{d5}$
SIM Window 8					
Phorate-$_{d10}$	22.00	131	270		*Acenaphthene-$_{d10}$
Phorate	22.14	260.1	231	121.1	Phorate-$_{d10}$
SIM Window 9					
Demeton-S	22.79	88	170	258.1	Phorate-$_{d10}$
SIM Window 10					

* Internal Standard

Prometon	23.12	210.1	225.2	183.1	Atrazine-$_{d5}$
Carbofuran	23.13	164.1	149.1	131	Atrazine-$_{d5}$
Simazine	23.19	201.1	203.1	186.1	Atrazine-$_{d5}$
Atrazine-$_{d5}$	23.24	205	220		*Acenaphthene-$_{d10}$
Atrazine	23.31	200.1	202.1	215.1	Atrazine-$_{d5}$
SIM Window 11					
Diazinon-$_{d10}$	23.80	314	138		*Acenaphthene-$_{d10}$
Phenanthrene-$_{d10}$	23.86	188	189		*Acenaphthene-$_{d10}$
Phenanthrene	23.93	178.1	176.1	179.1	Phenanthrene-$_{d10}$
Diazinon	23.93	179.1	199.1	304.1	Diazinon-$_{d10}$
Anthracene	24.14	178.1	176.1	179.1	Phenanthrene-$_{d10}$
Disulfoton	24.20	88.1	89.1	186	Diazinon-$_{d10}$
SIM Window 12					
Triallate	24.45	268	270	86.1	Malathion-$_{d7}$
SIM Window 13					
Acetochlor-$_{d11}$	25.27	173	245		*Fluoranthene-$_{d10}$
Acetochlor	25.40	146.1	162.1	223.1	Acetochlor-$_{d11}$
SIM Window 14					
Alachlor-$_{d13}$	25.53	200	251		*Fluoranthene-$_{d10}$
Methyl parathion-$_{d6}$	25.65	269	115		*Fluoranthene-$_{d10}$
Alachlor	25.69	188.1	160.1	237.1	Alachlor-$_{d13}$
Methyl parathion	25.72	263	125	109	Methyl parathion-$_{d6}$
SIM Window 15					
Carbaryl	25.99	144.1	115.1	116.1	Malathion-$_{d7}$
SIM Window 16					
Malathion-$_{d7}$	26.77	174	131		*Fluoranthene-$_{d10}$
Malathion	26.85	173.1	158	127	Malathion-$_{d7}$
Metolachlor	26.91	162.1	238.1	240.1	Alachlor-$_{d13}$
SIM Window 17					
Parathion-$_{d10}$	27.16	115			*Fluoranthene-$_{d10}$
Parathion	27.29	291	155	109	Parathion-$_{d10}$
Cyanazine	27.36	225.1	227.1	240.1	Atrazine-$_{d5}$

* Internal Standard

SIM Window 18					
*Fluoranthene-$_{d10}$	28.52	212	213		Internal Standard
Fluoranthene	28.59	202.1	200.1	203.1	Pyrene-$_{d10}$
SIM Window 19					
o,p' DDE	29.18	318	316	320	p,p'-DDE-$_{d8}$
SIM Window 20					
Pyrene-$_{d10}$	29.36	212	213		*Fluoranthene-$_{d10}$
Pyrene	29.43	202.1	203.1	200.1	Pyrene-$_{d10}$
SIM Window 21					
p,p'-DDE-$_{d8}$	30.13	326	324		*Fluoranthene-$_{d10}$
p,p' DDE	30.18	317.9	315.9	319.9	p,p'-DDE-$_{d8}$
o,p' DDD	30.41	235	237	165.1	p,p'-DDE-$_{d8}$
SIM Window 22					
Retene	30.76	219.1	234.2	204.1	Pyrene-$_{d10}$
SIM Window 23					
Ethion	31.51	231	384	153	Parathion-$_{d10}$
p,p' DDD	31.52	235	237	165.1	p,p'-DDE-$_{d8}$
o,p' DDT	31.58	235	237	165.1	p,p'-DDT-$_{d8}$
p,p'-DDT-$_{d8}$	32.58	243	245		*Benzo(k)fluoranthene-$_{d12}$
p,p' DDT	32.65	235	237	165.1	p,p'-DDT-$_{d8}$
SIM Window 24					
Triphenylene-$_{d12}$	34.17	240	241		*Benzo(k)fluoranthene-$_{d12}$
Benzo(a)anthracene	34.19	228.1	226.1	229.1	Triphenylene-$_{d12}$
Chrys+Triph	34.28	228.1	226.1	229.1	Triphenylene-$_{d12}$
Methoxychlor	34.39	227.1	228.1	274.1	p,p'-DDT-$_{d8}$
SIM Window 25					
Benzo(b)fluoranthene	38.11	252.1	250.1	253.1	Benzo(a)pyrene-$_{d12}$
*Benzo(k)fluoranthene-$_{d12}$	38.13	264	265		Internal Standard
Benzo(k)fluoranthene	38.20	252.1	250.1	253.1	Benzo(a)pyrene-$_{d12}$
Benz(e)pyrene	39.00	252.1	250.1	253.1	Benzo(a)pyrene-$_{d12}$
Benzo(a)pyrene-$_{d12}$	39.10	264	265		*Benzo(k)fluoranthene-$_{d12}$
Benzo(a)pyrene	39.18	252.1	250.1	253.1	Benzo(a)pyrene-$_{d12}$

* Internal Standard

SIM Window 26					
Indeno(1,2,3-cd)pyrene	42.62	276.1	274.1	277.1	Benzo(ghi)perylene-$_{d12}$
Dibenz(a,h)anthracene	42.75	278.1	276.1	279.1	Benzo(ghi)perylene-$_{d12}$
SIM Window 27					
Benzo(ghi)perylene-$_{d12}$	43.34	288	289		*Benzo(k)fluoranthene-$_{d12}$
Benzo(ghi)perylene	43.42	276.1	274.1	277.1	Benzo(ghi)perylene-$_{d12}$

Appendix 2

Electron Capture Negative Ionization

Analyte	Retention Time (min)	Quantiation Ion m/z	Confirmation Ion m/z	2nd Confirmation Ion m/z	Quantitation Compound
SIM Window 1					
*Trifluralin-$_{d14}$	13.69	349.2	350.2	319.2	Internal Standard
Trifluralin	13.90	335.1	336.1	305.1	Hexachlorobenzene-$^{13}C_6$
SIM Window 2					
HCH, alpha	14.61	71.0	73.0	70.0	gamma-HCH-$_{d6}$
$^{13}C_6$-Hexachlorobenzene	14.69	291.8	293.8	289.9	*Trifluralin-$_{d14}$
Hexachlorobenzene	14.70	283.8	285.8	281.8	Hexachlorobenzene-$^{13}C_6$
HCH, beta	15.94	71.0	73.0	70.0	gamma-HCH-$_{d6}$
d_6-gamma-HCH	16.01	72.0	74.0	263.0	*Trifluralin-$_{d14}$
HCH, gamma	16.19	71.0	73.0	70.0	gamma-HCH-$_{d6}$
SIM Window 3					
Chlorothalonil	17.18	266.0	268.0	264.0	Hexachlorobenzene-$^{13}C_6$
HCH, delta	17.70	71.0	252.9	254.9	gamma-HCH-$_{d6}$
Triallate	17.72	160.0	161.1		gamma-HCH-$_{d6}$
SIM Window 4					
Metribuzin	19.15	198.0	199.1	184.0	gamma-HCH-$_{d6}$
Heptachlor	19.61	266.0	268.0	299.9	Hexachlorobenzene-$^{13}C_6$
SIM Window 5					
Chlorpyrifos oxon	21.14	297.0	298.0	299.0	Chlorpyrifos-d_{10}
d_{10}-Chlorpyrifos	21.19	322.0	324.0	213.9	*Trifluralin-$_{d14}$
Aldrin	21.24	237.0	238.8	329.9	gamma-HCH-$_{d6}$
Chlorpyrifos	21.37	313.0	315.0	213.9	Chlorpyrifos-d_{10}
Dacthal	21.54	332.0	330.0	334.0	Hexachlorobenzene-$^{13}C_6$
SIM Window 6					
Chlordane, oxy	23.12	424.0	426.0	352.0	Endosulfan I-d_4
Heptachlor epoxide	23.13	390.0	388.0	392.0	Endosulfan I-d_4
PCB # 74	23.28	292.0	294.0	290.0	PCB #101 $^{13}C_{12}$

* Internal Standard

SIM Window 7					
Chlordane, trans	24.26	409.9	407.9	411.8	Endosulfan I-d_4
PCB #101 $^{13}C_{12}$	24.68	338.0	336.0	340.0	*Trifluralin-$_{d14}$
PCB # 101	24.69	326.0	328.0	324.0	PCB #101 $^{13}C_{12}$
Endosulfan I-d_4	24.72	378.0	376.0	374.0	*Trifluralin-$_{d14}$
Endosulfan I	24.82	403.9	371.9	369.9	Endosulfan I-d_4
Chlordane, cis	24.83	266.0	264.0	268.0	Endosulfan I-d_4
Nonachlor, trans	24.98	443.8	445.8	441.8	Endosulfan I-d_4
SIM Window 8					
Dieldrin	26.07	345.9	347.9	379.9	Endosulfan I-d_4
Endrin	27.00	345.9	347.9	379.9	Endosulfan II-d_4
SIM Window 9					
PCB # 118	27.51	326.0	328.0	324.0	PCB #101 $^{13}C_{12}$
Endosulfan II-d_4	27.48	412.0	414.0	410.0	*Trifluralin-$_{d14}$
Endosulfan II	27.56	405.9	407.9	371.9	Endosulfan II-d_4
Nonachlor, cis	27.79	443.8	445.8	441.8	Endosulfan II-d_4
SIM Window 10					
Endrin aldehyde	28.24	379.9	381.9	345.9	Endosulfan II-d_4
PCB # 153	28.48	360.0	362.0	358.0	PCB #180 $^{13}C_{12}$
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	PCB #180 $^{13}C_{12}$
SIM Window 12					
PCB # 187	30.29	393.9	359.9	397.9	PCB #180 $^{13}C_{12}$
PCB # 183	30.54	393.9	359.9	397.9	PCB #180 $^{13}C_{12}$
PCB #180 $^{13}C_{12}$	32.60	405.9	407.9	409.9	*Trifluralin-$_{d14}$
Mirex	34.10	367.8	369.8	403.8	PCB #180 $^{13}C_{12}$

* Internal Standard