Current and Historical Deposition of Persistent Organic Pollutants to High Elevation Ecosystems in the Western U.S.

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Introduction

Previous studies suggest that some persistent organic pollutants (POPs), and other anthropogenic semi-volatile organic compounds (SOCs), undergo long-range atmospheric transport and redeposition to colder areas such as high-elevations[1] and high-latitudes[2]. SOCs may redeposit to the earth's surface by air-surface exchange, dry deposition, and wet deposition[1,3-4]. Snow is an efficient scavenger of SOCs from the atmosphere[5] and is the dominant form of precipitation for some high-elevation ecosystems in North America[6]. During annual snowmelt, SOCs may be released from the snow pack into high-elevation and high-latitude perched lakes[4]. Each year, hydrophobic SOCs deposit to the high elevation lake sediments and, if the sediment core is undisturbed, provide a historical record of the deposition of these SOCs to the high elevation ecosystem.[7]

Although the deposition of SOCs to high elevation ecosystems has been studied in the Canadian Rockies[3-4] and in the European High Mountains[7], there is limited data on the deposition of SOCs to high elevation ecosystems in the Western U.S.[8-9] The Western Airborne Contaminant Assessment Project (WACAP) was developed to study the atmospheric deposition of SOCs to, and their environmental fate in, high-elevation and high-latitude ecosystems located in national parks in the Western U.S., from 2003-2005.[6] These national parks, their general locations, and the elevation and average mean temperature of each of the lake catchments under study are given in Figure 1. The objective of the research described was to determine the current and historical flux of persistent organic pollutants, and other anthropogenic semi-volatile organic compounds, to these high elevation lake catchments using snow and sediment core data.

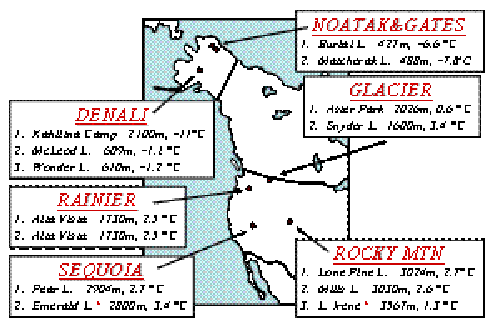

Figure 1. Location, elevation, and mean annual temperature of WACAP lake catchments.

Materials and Methods

Annual snow pack samples were collected during the time of maximum accumulation from north facing open areas at each of the WACAP lake catchments (see Figure 1) from 2003-2005. A vertical face of the snow pit was shaved using a clean Lexan shovel. 50-kg samples where collected over the entire vertical column and stored in 60 X 60 cm solvent rinsed PTFE bags. The snow samples were placed in a black low density polyethylene bags to protect them from ultra-violate light. Finally, the snow samples were placed in high density polypropylene bags for increased protection and shipped in 94.6-L coolers with dry ice overnight to the laboratory. Once in the laboratory, the snow samples were stored at -20 °C until extraction. The 50 kg snow samples were melted without additional heat, spiked with isotopically labeled surrogates (see Figure 2) and extracted using a hydrophobicly and hydrophilicly modified Speedisk.[10] The snow extracts were purified using silica gel chromatography and gel permeation chromatography.[10]

The sediment cores were collected using an Uwitec gravity corer with an 8.6 cm internal diameter and were collected to a depth of 25 to 50 cm. The core was sliced at 0.5 cm intervals to a depth of 10 cm and 1.0 cm intervals for the remainder of the core. The sediment slices were stored in clean glass jars and kept frozen until analysis. Each sediment layer was dated using ^{137}Cs and ^{210}Pb. The sediment slices were thawed, ground with Na_2SO_4, packed into a cell, spiked with isotopically labeled surrogates (see Figure 2) and extracted at 1500 psi and 100 °C with dichloromethane using accelerated solvent extraction. The sediment extracts were purified using silica gel chromatography and gel permeation chromatography.[10]

The purified snow and sediment extracts were spiked with isotopically labeled internal standards (see Figure 2) and analyzed by GC/EI-MS and GC/ECNI-MS (using selected ion monitoring) for the SOCs listed in Figure 2.[10]

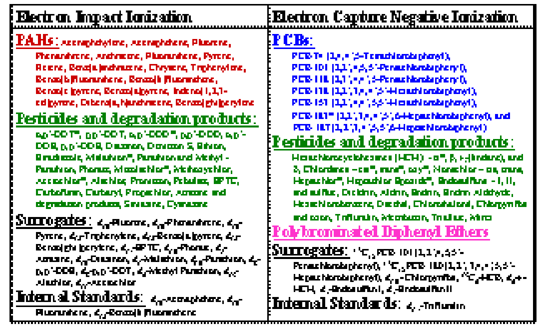

Figure 2. Target SOCs, surrogates, and internal standards

Results and Discussion

To date, the 2003 WACAP snow samples have been analyzed for the target SOCs listed in Figure 2. These data can be used to understand the current deposition of SOCs to the respective WACAP parks and lake catchments. These data suggest that historic use SOCs, as well as current use SOCs, are being deposited to the high elevation lake catchments within the Parks via snow.

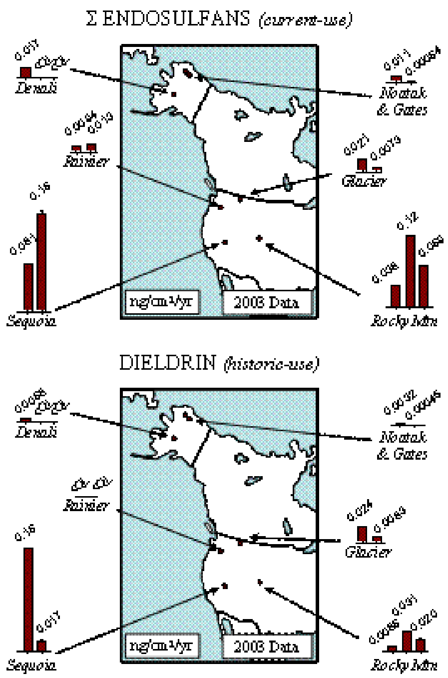

Figure 3. 2003 snow flux to WACAP lake catchments for representative pesticides

Figure 3 shows the 2003 snow flux of two representative pesticides to the WACAP lake catchments (described in Figure 1). Endosulfan continues to be used as a pesticide in the U.S., while dieldrin use in the U.S. was discontinued in 1974. In general, our 2003 snow data suggests that current use pesticides (such as endosulfan, dacthal, and chlorpyrifos) have higher snow fluxes to the WACAP lake catchments located in Sequoia and Rocky Mountain National Parks because of the Park's proximity to U.S. agriculture. More volatile historic use pesticides (such as the hexachlorocyclohexanes - HCHs) show a more even distribution of snow flux to all of the WACAP lake catchments, regardless of proximity to U.S. agriculture. However, less volatile historic use pesticides (such as dieldrin – Figure 3) have elevated snow fluxes in Sequoia and Rocky Mountain National Parks because of their continued slow volatilization from U.S. agricultural soils historically contaminated from their use. In addition, the a-HCH to g-HCH ratio in 2003 snow suggests that Glacier National Park is influenced by the use of g-HCH (Lindane) in the near by Canadian Prairies. These data can be used to estimate the current input of SOCs into the WACAP lake catchments via snow deposition.

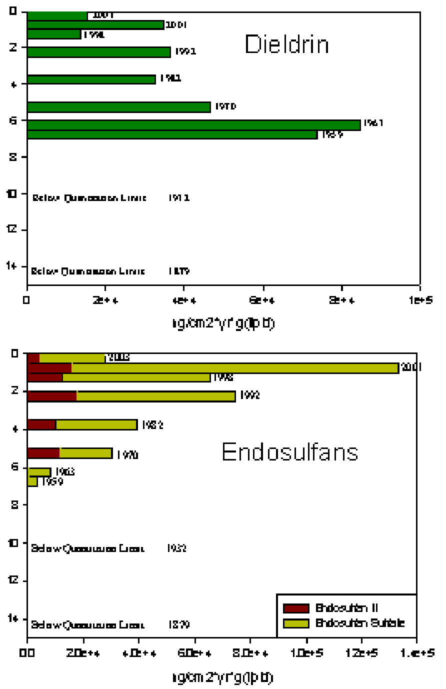

Figure 4. Pear Lake (Sequoia National Park) sediment flux since 1879 for representative pesticides.

Dated sediment cores collected from the respective WACAP lake catchments provide a historical perspective on the flux of SOCs to the lake catchment over the past 100-150 years. For example, the Pear Lake sediment core (Sequoia National Park) flux data (shown in Figure 4) for representative pesticides (dieldrin and endosulfan) suggest that the flux of banned pesticides (such as dieldrin and the DDTs) to the high elevation lake catchments is decreasing from high fluxes in the 1950s-1960s, while the flux of current use pesticides (such as endosulfan) has been highest in recent years. The sediment core flux data shown in Figure 4 is consistent with the initial use of these representative pesticides (dieldrin was first used in 1948 and endosulfan was first used in 1956) as well as their current status (dieldrin was banned in 1974 and endosulfan continues to be used in the U.S.). The sediment core data confirms that both historic and current use pesticides continue to be deposited to high elevation ecosystems located in western U.S. national parks.

Acknowledgements

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