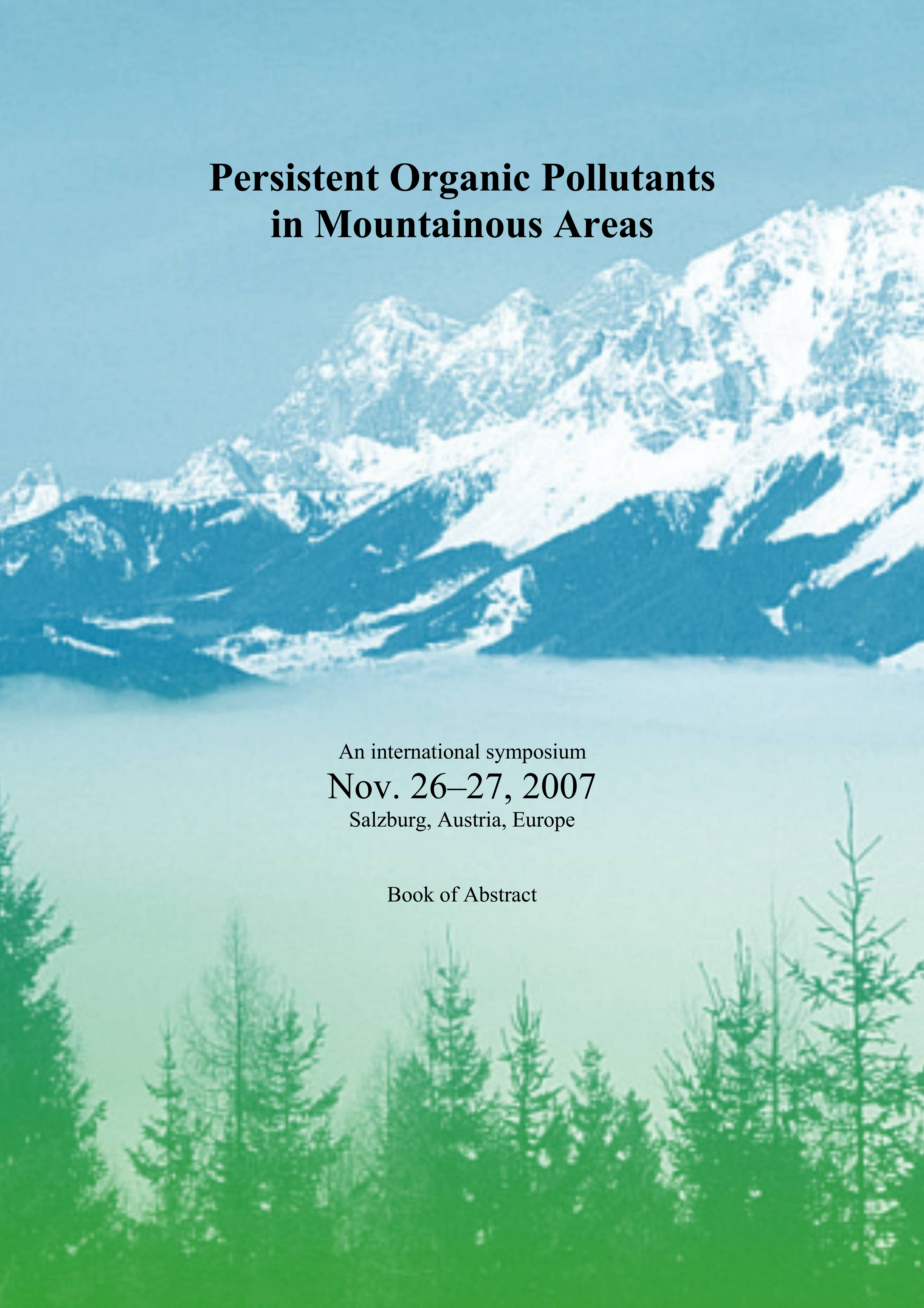

Persistent Organic Pollutants in Mountainous Areas

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Book of Abstract

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Understanding Air and Soil Concentration Changes with Altitude in Mountains at Different Latitude

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Introduction. Air and soil samples have been, or are currently being, taken along 13 elevational gradients along the Western American Cordillera and are being analysed for the concentrations of organochlorine pesticides in past and present use, polychlorinated biphenyls, as well as polycyclic aromatic hydrocarbons. The sampling transects range from Patagonia in Southern Chile to Southern Alaska, and encompass a wide variety of mountain systems in boreal, temperate, subtropical and tropical climates. The mountains vary in terms of altitudinal range, vegetation cover, temperature gradients, precipitation gradients, exposure to large scale and local wind systems, and proximity to organic contaminant sources. Ultimate aim of the interpretation of the concentration gradients is to understand the mechanism of organic contaminant accumulation at high altitudes in particular, and the factors controlling spatial concentration differences along environmental gradients in general (Daly and Wania, 2005).

Results and Discussion. In the absence of local contaminant sources, annual mean air concentrations measured with XAD-resin based passive air samplers generally displayed relatively minor differences along an altitudinal transect. This indicates relatively efficient atmospheric mixing on the scale of a mountain slope. However, even relatively minor local sources, such as vehicular traffic, can dominate concentration gradients in otherwise remote regions. For example, PAH concentrations in air and soil from Western Canadian mountains are strongly correlated with the proximity to major roadways.

In contrast to the atmosphere, soil concentrations can display considerable variability along an elevational gradient even in the absence of local sources, and often increase with altitude. For example, soil concentrations of endosulfan-I and II, dacthal, lindane and dieldrin increased significantly with altitude along the westfacing slope of Mount Revelstoke in the Selkirk Mountains (Daly et al. 2007a). Similarly, in Costa Rica, highest concentrations of the fungicides chlorothalonil, and the insecticide metabolite endosulfan sulphate were detected in soils sampled in montane cloud forests at high altitude (Daly et al. 2007b), despite being further removed from agricultural use areas than many other sampling sites at lower elevations.

Preliminary conclusions drawn from a selected number of concentration gradients are:

- Changes in the amount and temperature of the precipitation falling along a mountain slope appear to be important factors in determining variations in atmospheric deposition rates with altitude.
- In tropical mountains, rain is the dominant mode of precipitation up to very high altitudes, and highest orographic cold-trapping appears to occur for substances with an air-water partition coefficient log K_{AW} between -3 and -5. Such substances are not efficiently rain scavenged at the temperature prevailing in tropical lowlands, but are subject to efficient rain-out at the lower temperature of tropical mountains (Daly et al. 2007b).
- In temperate mountains, the relative efficiency of rain and snow scavenging (Lei and Wania, 2004) will influence changes in the rate of atmospheric deposition with altitude, and high deposition at high altitudes is expected for substances that are efficiently scavenged by snow. In such mountains, temperature and often also the precipitation rate undergoes seasonal changes, leading to complex temporal and spatial variations of atmospheric deposition with altitude.
- Not all of the atmospherically deposited contaminants will be retained on the surface. Some snow-scavenged contaminants will already evaporate during snow metamorphosis (Herbert et al., 2005), and further volatilisation losses will occur during snow-free period from alpine areas with little vegetation cover and low organic matter soils. Dense vegetation cover extending to high elevations within tropical mountains suggests that the retentive capacity of tropical soils only drops substantially at very high altitudes.
- Whereas the deposition rates are generally hypothesised to increase with elevation (because temperatures drop and precipitation rates increase), the soil organic matter content in mountains at medium and high latitudes tends to decrease with elevation and in particular will drop strongly above the tree line. Accordingly, temperate mountain soils from intermediate elevations may often display the highest concentrations of organic contaminants (Daly et al., 2007a).

Acknowledgements. This work was and is funded through a Canon National Parks fellowship, the Canadian Natural Sciences and Engineering Research Council, the United Nations Environmental Program (UNEP Chemicals), and Environment Canada.

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Ambient Air and Deposition sampling - A New Approach for Alpine Sites

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Abstract

A novel ambient air sampling technique has been developed within the project MONARPOP, which affords the opportunity to attribute measured concentrations of different POPs to four predefined source regions which are important for the alpine area. Such ambient air samplers and in addition bulk deposition samplers have been installed at three high altitude sampling sites Weissfluhjoch (CH; 2663 m), Zugspitze (D; 2650 m) and Sonnblick (A; 3106 m). Since the start of the project sampling was done for five trimonthly periods. For most of the analysed POPs no predominant source region could be detected so far, but clear seasonal differences were obvious. The concentration levels for ambient air and deposition as well were in the same range as those measured in the rural lowlands indicating long-range transport of PCDD/F and PCBs to these sites.

1. Introduction

The project Interreg III B Project MONARPOP was initiated to get a more detailed picture of the fate of POPs within the alpine region. Needle, SPMD (semi permeable membrane devices), humus and soil samples have been taken at 40 sites and seven height profiles across the alpine region to get more information about regional and altitudinal concentration gradients for those toxic substances. Ambient air, deposition and SPMD samples at three high altitude sites have been taken to get information about long range transport of POPs, predominant source regions and the impact on the alpine region. This paper gives information with the thematic priority on the ambient air and the deposition part of the project, in particular the novel sampling approach for source region depending sampling.

2. Material and Methods

One aim of the project was to look for source regions of POPs which are predominant for the Alps. For this reason it was planned to carry out ambient air measurements for various POPs with the additional requirement to attribute the measured concentrations to source regions. This means the sampled air masses have to correlated with their way to the sampling sites and possible influences by POP emissions during this way.

In contrast to gaseous pollutants like NO_x for which the attribution to air masses can be done after the onsite and online monitoring, this is not possible for POPs. Long lasting sampling periods are necessary for POPs due to their typical low concentration ranges. Using traditional sampling methods in most of the cases weather situations will change during sampling, deleting all source region related information.

A possible way out is the predefinition of possible source regions and the separated, source region specific sampling of air masses arriving at the sampling site. This means the correlation of measured concentrations to source regions at the sampling stage.

Three source regions have been selected which are known as important for the Alps from NO_x investigations.

Existing sampling techniques for POPs have been modified for the planned investigations. Ambient air samplers have been equipped with four filter cartridges. Three are attributed to one of the predefined source regions, the fourth was chosen for undefined weather situations. The selection of the corresponding filter cartridge was done by remote control based on meteorological trajectory forecasts. All filter cartridges and moving parts have to be heated due to the hard weather conditions at the selected sites. In addition to the ambient air samplers also deposition samplers for bulk deposition have been installed at the three high altitude sites. The deposition samplers are built according to DIN 19739-1, "Measurement of atmospheric deposition of organic trace substances – funnel adsorber method", but necessarily in a heated version.

Three high altitude measurement sites have been installed at three mountain summits which provide well equipped infrastructures of meteorological stations necessary for the operation of POP samplers. The three sites are Weissfluhjoch (CH; 2663 m), Zugspitze (D; 2650 m) and Sonnblick (A; 3106 m). All these three sites are well staffed all around the year to ensure a daily support of the sampling equipment and short reaction times in the case of malfunctions.

At all three high altitude sites an array of samplers has been installed. As an example the arrangement at the sampling site at "Zugspitze", is shown in the picture above:

(1) a low volume sampler for the collection of organochloropesticides (OCP) and polyaromatic hydrocarbons (PAH)

(2) a high volume sampler for the collection of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) and polybrominated diphenylethers (PBDE)

(3) 7 identical deposition samplers, each used for the collection of one of these four groups of pollutants completed by chlorinated paraffins (CP), Nitrophenols and trichloroacetic acid.

(4) A meteorological cabin for SPMD sampling

3. Results and Discussion

Since the start of the project sampling was done for five trimonthly periods. For most of the analysed POPs no source region which was predominant in all sampling periods could be detected so far, but clear seasonal differences were obvious. A continuation of these measurements is planned to clarify if these detected seasonal differences are periodical.

The concentration levels for ambient air and deposition as well are in the same range as those measured in the rural lowlands indicating clearly a long-range transport of POPs to these sites and to the whole alpine region.

Determination of Organochlorine Pesticides, Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons in the Free Troposphere Over Europe

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Introduction Persistent organic pollutants (POPs), i.e. organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), are a concern for the ecosystems of remote areas (such as alpine and polar regions) and human health as they are bioaccumulative, resist degradation and cycle for long time in the environment. Most POPs are considered to be ubiquitous in the global atmosphere (e.g. Holoubek et al., 2002) and concentrations expected to decrease with height, which, however, has hardly been addressed so far. Samples with free tropospheric only have been collected in the Himalayans and have been analysed for PAHs (Ciccioli et al., 1996). Recent model results suggest transport of OCPs and PAHs in the upper troposphere and lower stratosphere (Semeena et al., 2006).

Methods High volume (Digitel) air samples were taken 19.-29.6.2007 on the terrace of the UFS Observatory, which is located on a steep, southern slope some 300 m below Mt. Zugspitze summit, Bavarian Alps, 2650 m a.s.l.. Gas and particulate phases were collected separately (glass fibre filters and polyurethane foam plugs in series). Using pollution level (visibility > 5 km, particle number concentration $N_{3\text{-}800nm} < 2000$ cm^{-3}) and meteorological criteria (wind, negative evening atmospheric relative humidity trend $\Delta rh_{evening} < -3\%$) we identified episodes of advection of free tropospheric (FT) air, 2-7 h, during several nights. 2 FT samples have been collected (by combining several such episodes) and 6 samples of mostly BL air (eventually mixed with free tropospheric air to some, though limited extent). BL air samples were collected during day-time. In addition, each 5 PUF and GFF field blanks were taken. The samples were extracted (dichloromethane), fractionated (silica gel columns) and analyzed (GC-ECD or GC-MS). Limits of quantification after consideration of field blanks were 0.02-0.35 pg m^{-3}.

Results and discussion Concentration levels were orders of magnitude below typical polluted air levels. Surprisingly, samples of FT air and BL air did not differ significantly with regard to POP concentrations (Table 1) or other indicators for pollution: The concentration ranges of most OCPs (including DDT) and PCBs, as well as $N_{3\text{-}800nm}$ were lower in tropospheric air but the concentration ranges of the FT and BL air sample subsets were overlapping. HCHs and most PAHs were even higher concentrated in FT air. Pollutant ratios indicate less influence of primary emissions of DDT and HCH in FT air and faster degradation of PAHs in BL air (Table 1). The latter can be explained by photochemistry (day-time vs. night-time sample subsets). OCPs, most PCBs and 3-ring PAHs were higher concentrated in the gas-phase, while PCB 180 and the more heavy PAHs were predominantly associated with particulate matter. Further data analysis will encompass air mass origin and trace compound patterns.

Table 1: OCP, PCB and PAH total (gas and particulate) concentrations in the FT and BL sample subsets, as time-weighted mean (min-max).

	Free tropospheric air (night-time)	**Boundary layer or mixed air (day-time)**
HCB	0.7 (0.4-1.6)	1.8 (1.1-4.3)
HCHs (sum of 3)	5.0 (3.7-8.4)	3.3 (1.2-10.2)
PCBs (sum of 7)	1.1 (1.0-1.3)	1.8 (0.9-4.4)
DDTs (sum of 6)	1.2 (1.1-1.3)	1.5 (0.4-7.0)
α-HCH/γ-HCH	0.96 (0.7-1.3)	0.54 (<0.02-12)
$C_6Cl_6 + C_6HCl_5$	0.75 (0.36-1.9)	2.4 (1.3-2.6)
DDT/total DDTs	0.31 (<0.2-0.41)	0.56 (<0.2-0.69)
PAHs (sum of 27)	99 (85-235)	79 (62-289)
ANT/(PHE+ANT)	0.027 (0.023-0.029)	0.015 (0.004-0.11)
BAA/(CHR+BAA)	0.83 (0.76-0.86)	0.74 (0.68-0.90)

unit: pg m^{-3}

Acknowledgements

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SEASONAL AND ALTITUDINAL TRENDS OF CHLORINATED PESTICIDES IN THE CENTRAL HIMALAYAN ATMOSPHERE

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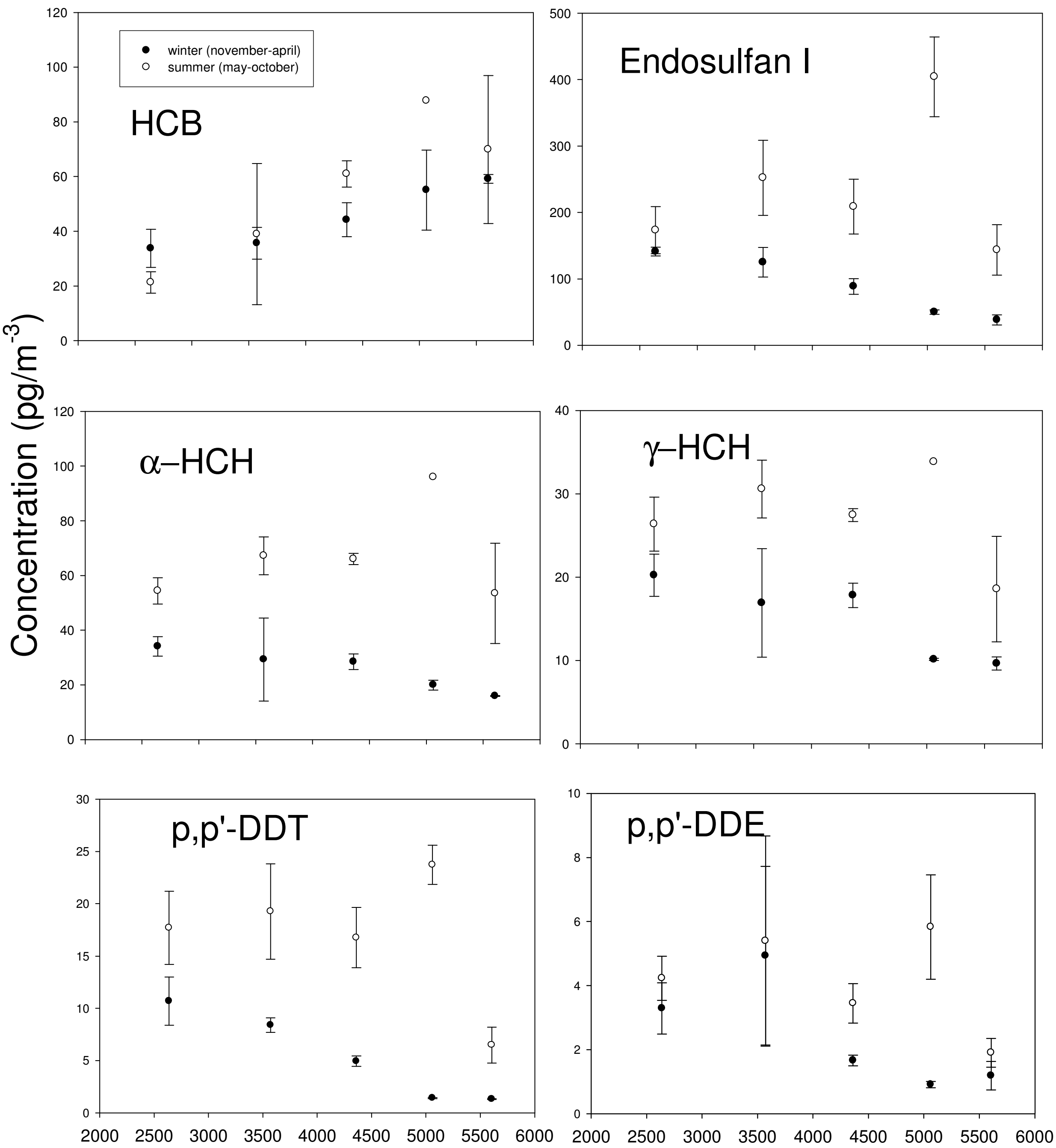
Abstract

XAD-resin based passive air samplers were used to measure the concentrations of hexachlorobenzene (HCB), endosulfan I, α-hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (γ-HCH), p,p'-DDE and p,p'-DDT over an altitudinal transect from 2638 to 5605m a.s.l in the Central Himalaya (27°44'-27°60'N, 86°43'-86°50'E). Whereas there is no known usage of these chemicals in this high altitude region, they are used extensively on the Indian Subcontinent. Air concentrations were similar to those found in North American mountains[1]. Concentration gradients with altitude displayed large differences between summer (May to October) and winter (November to April). In summer concentrations of all the chemicals increased with elevation up to a maximum at 5000 m a.s.l and then declined above that elevation. Winter time concentration of all chemicals declined with altitude, except for HCB which had similar elevational trends year-round. This indicates that during the summer monsoon lower tropospheric air contaminated with pesticides is being driven by thermal and mechanical forcing from the Indian subcontinent into the central Himalaya[2]. During winter high altitude sites are well above the boundary layer. For HCB global sources appear to be more important than regional transport with the monsoon.

1) Daly, G.L., et al. Environ. Sci. Technol. 2007, 41, 6020-6025.

2) Arndt, R.L., et al. Atmos. Environ. 1998, 32, 1398–1406.

Figure 1: Seasonal atmospheric concentrations of chlorinated pesticides in the Central Himalaya as a function of altitude. Air concentrations were corrected for changes in sampler uptake rate due to atmospheric pressure and temperature changes caused by increasing altitude.



WHAT GOES UP MUST COME DOWN: THE ATMOSPHERIC TRANSPORT AND DEPOSITION OF SEMI-VOLATILE ORGANIC COMPOUNDS TO HIGH ELEVATION ECOSYSTEMS IN THE WESTERN U.S.

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Introduction Previous studies suggest that some anthropogenic semi-volatile organic compounds (SOCs) undergo long-range atmospheric transport and redeposition to colder areas such as high-elevations and high-latitudes. Snow is an efficient scavenger of SOCs from the atmosphere and is the dominant form of precipitation for some high-elevation ecosystems in North America. During annual snowmelt, SOCs may be released from the snow pack into high-elevation and high-latitude perched lakes.

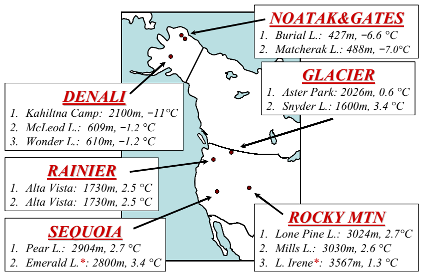

Figure 1. Location, elevation, and mean annual temperature of WACAP lake catchments.

Although the deposition of SOCs to high elevation ecosystems has been studied in the Canadian Rockies and in the European High Mountains, there is limited data on the deposition of SOCs to high elevation ecosystems in the Western U.S. 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. 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.

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, 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	**Polybrominated Diphenyl Ethers**
Internal Standards: d_{10}-Acenaphthene, d_{10}-Fluoranthene, d_{12}-Benzo[k]fluoranthene	**Surrogates:** $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2', 3,4,4',5,5'-Heptachlorobiphenyl), d_{10} - Chlorpyrifos, $^{13}C_6$-HCB, d_6-γ-HCH, d_4-Endosulfan I, d_4-Endosulfan II **Internal Standards:** d_{14}-Trifluralin

Figure 2. Target SOCs, surrogates, and internal standards

Results and discussion To date, the 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 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.

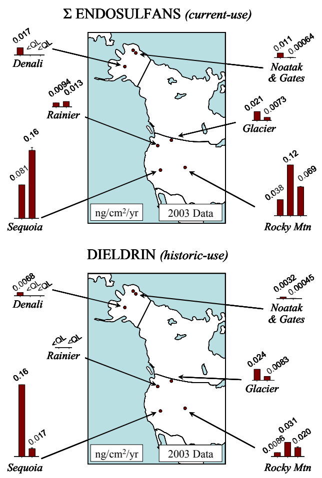

Figure 3. 2003 snow flux to WACAP lake catchments for representative pesticides

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.

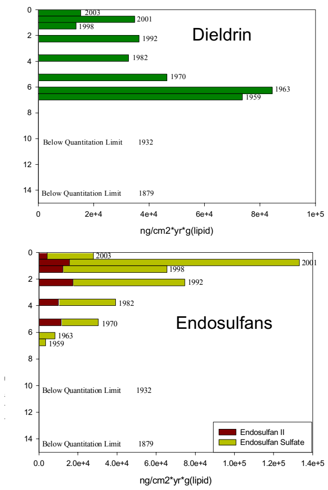

Figure 4. Pear Lake (Sequoia National Park) sediment flux since 1879 for representative pesticides.

LONG-TERM STUDIES WITH SEMIPERMEABLE MEMBRANE DEVICES (SPMD) IN MOUNTANEOUS AREAS

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Introduction

Semipermeable Membrane Devices (SPMD) were initially designed as passive samplers to operate in aquatic environments but lately their use was extended as passive air samplers[1]. This device consists of a membrane in this case composed of a low density polyethylene (LDPE) that encloses a lipophilic solvent: triolein. SPMDs are integrative samplers, accumulating compounds during the exposure time until reaching equilibrium. The device - air exchange of compounds obeys first order kinetics and can be divided into three stages a) linear uptake where the uptake is proportional to the concentration of the compound in the device surroundings b) curvilinear stage where the elimination of the absorbed compound achieves importance and c) equilibrium stage where the uptake and release of the analyte in the device are equiparable[3,4]. When the device is operating in the linear uptake stage, the sampler is called kinetic sampler. In the current work, SPMD were deployed at remote mountain areas in different exposure periods. Organochlorine pesticides characterised by their different properties were quantitatively analysed by means of HRGC-HRMS.

Materials and Methods

Analysis Membrane devices were cut into slices and spiked with ^{13}C-Chloropesticides standards (Cambridge Isotope Laboratories, USA), extracted for 24 hours with 100 ml cyclohexane, cleaned by mixed columns filled with silica gel, Al_2O_3 and Na_2SO_4 and eluted with a mixture *n*-hexane/dichloromethane 1:1. and further eluted through a C18 modified silica column with acetonitrile followed by separation with HRGC on a Rtx-Dioxin2 column (Restek, Germany) and detection with HRMS.

Results and Discussion

SPMD exposure in Period 1 finishes before winter, thus higher compound concentrations are expected and period 2 finished in early summer. Analyzing the results obtained at the different altitudes for altitude profiles, a very similar pattern is observed at the profile in the periods 1 and 2 for the compounds 2,4´DDT, 4,4´DDT, cyclodiene pesticides cis-Chlordane, Dieldrin and α-Endosulfan and β-Endosulfan. It is also remarkable that the sum of compounds accumulated in Period 1 and Period 2 assembles the amount of these chemicals accumulated in the whole year (Period 3). We can infer for these compounds that the membrane devices are still working as