Profiles and Levels of POPs and SOCs in Fish from Alpine Lakes of US National Parks

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Introduction

Persistent organic pollutants (POPs) and semi-volatile organic compounds (SOCs) have been shown to deposit from the atmosphere[1] and accumulate at low levels in remote locations[2, 3]. Globally, a theory of temperature dependant enhancement of POPs in cold, polar regions has been proposed to explain latitudinal concentration differences[4, 5]. Recently, researchers have demonstrated that less volatile compounds tend to become trapped in cold, high elevations ecosystems of the mid-lattitude[6]. Precipitation, and snow in particular[7], has been shown to be an effective scavenger of POPs to cold, high elevations[8]. Mid latitude alpine areas, with significant precipitation rates and relative proximity to sources for some POPs have been shown to receive significant fluxs (300-400 ng/m^2/mo)[1].

Concern has grown surrounding potential unanticipated effects of POP and SOC accumulation in apparently remote, high elevation ecosystems[9]. Monitoring programs have been undertaken in several regions to better understand POP and SOC deposition and fate, as well as to assess the potential for ecosystem and health effects from these anthropogenic compounds in alpine ecosystems[8, 9]. To date, researchers have documented the atmospheric deposition, altitudinal enhancement, and food-chain magnification of POPs and SOCs in European high mountain lakes[1, 6, 10]. Some data has been made available regarding similar processes in N. America especially in the Canadian Rockies[11]. Altitudinal enhancement of POPs in Canadian snow has been demonstrated[12], and atmospheric deposition of some organochlorine (OC) pesticides has been documented to high lakes of the Sierra Nevada's in the US[13]. Out of the documented potential for enhancement of atmospherically deposited POPs in high elevation ecosystems, the US Park Service has directed studies to assess the deposition of airborne contaminants in high elevation parks to provide regional and local information on exposure, accumulation, impacts, and probable sources[9]. Fish, often at the highest trophic level of these alpine ecosystems, are also a good measure of potential human exposure to POPs and SOCs from these alpine ecosystems. To this end, fish from alpine lakes of US National Parks (NP) in Colorado (Rocky Mountain NP) and California (Sequoia/Kings Canyon NP) (Figure 1) have been collected and analyzed for a suite of more than 60 POPs and SOCs (Table 1).

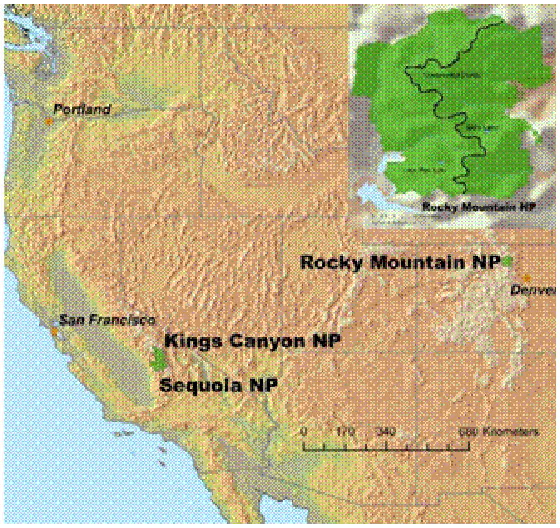


Figure 1 - 2003 Sampling Sites

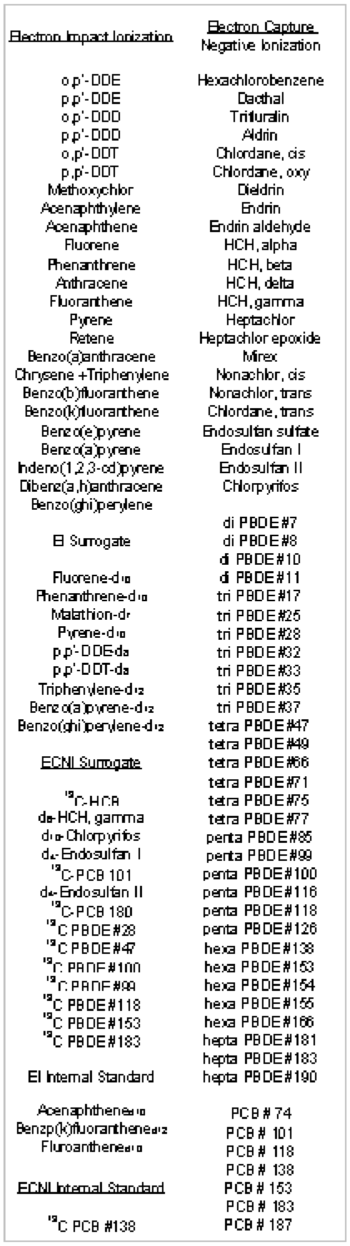
Materials & Methods

Our method development and analysis utilized native stable isotope labeled analogs of many of our analytes as recovery surrogates and internal standards (Table 1) (CIL, ChemService, AccuStandard, CDN, RESTEK), Optima grade solvents (Fischer, Pittsburgh, PA), UHP Helium, Methane, and Nitrogen (BOC, Murray Hill, NJ), and pesticide grade Na_2SO_4 (JT Baker, Phillipsburg, NJ). All glassware, foil, (and Na_2SO_4) were baked at 345(400°C for Na_2SO_4) for 12 (5) hours and solvent rinsed prior to use. Fish (weighed, measured, identified by sex and species, and dissected for histology, pathology, and serum biomarker and hormone analysis) were caught by hook and line between 8/24/2003-9/13/2003, packed in foil, and sealed in polyethylene bags on dry ice or -20°C freezer until homogenized under liquid N_2. A subset of 9 fish from each of the 4 lakes of Rocky Mountain (CO) and Sequoia/Kings Canyon NP (CA) (n=36) were selected for SOC analysis to best represent the age and gender profile of the lake. Fish homogenate was spiked with isotope labeled recovery surrogates, ground with Na_2SO_4 until powdered, and solvent extracted at high temperature and pressure (Dionex ASE-300). Percent lipid was determined gravimetrically, and interferences were removed from the extract using size exclusion and silica chromatography. Final extracts were reduced under N_2 to ~300 µL and internal standards added. Analysis was by gas chromatography-mass spectrometry using electron impact (EI) and electron capture negative ionization (ECNI) in the selected ion monitoring (SIM) mode.

Results & Discussions

POPs and SOCs measured ranged between 39 ng/g ww (pp-DDE) and 2.7 pg/g ww (triBDE #28) for compounds detected at a frequency of >33% (Figure 1). The values of nearly all analytes measured were comparable to similar remote or high elevation samples from the literature[6, 10, 13-18]. Values from US NP alpine fish were higher than reported elsewhere for dieldrin and benzo(b)fluoranthene. Similarly, values for the following compounds ranged lower in US NP alpine fish than in the literature: p,p'-DDE, trans-Chlordane, Heptachlor-epoxide, Endrin, PCB 118, PCB 183, PCB 101, Fluoranthene, and Anthracene. SOC profiles of US NP Alpine fish were usually dominated by either dieldrin or p,p-DDE, averaging 4.7 and 10.4 ng/g ww respectively. SOC and POPs profiles in fish from Sequoia/Kings Canyon NP consistently were dominated by the DDTs. In general historical use organochlorine pesticides (POPs) were present in higher concentrations (average 3.7 ng/g ww) followed by PBDEs and current use pesticides (1.3 and 1.2 ng/g ww) followed by PCBs (0.93 ng/g ww). This trend changed somewhat for Rocky Mountain NP, where a few PAHs were present at surprising levels (0.04-6.0 ng/g ww), and dominated the profile after dieldrin (Figure 1). PAHs were not present in Sequoia/Kings Canyon NP fish. Sequoia/Kings Canyon NP fish, (immediately adjacent to the intensely agricultural San Jocquin valley of California) when compared to fish from Rocky Mountain NP in Colorado, had significantly higher concentrations of: Dacthal, Endosulfans, DDT's, and PCBs (p<0.001, 0.05, 0.05, 0.05 respectively). However, when only fish of the same species were compared (brook trout), only Dacthal remained significantly higher in the California fish. These differences are not likely covariance since we found no other significant differences between the two populations (elevation, age, sex-ratio, mass, length, condition factor, p>0.05).

Table 1 – Analytes & Internal Standards



Electron Impact Ionization	Electron Capture Negative Ionization
o,p'-DDE	Hexachlorobenzene
p,p'-DDE	Dacthal
o,p'-DDD	Trifluralin
p,p'-DDD	Aldrin
o,p'-DDT	Chlordane, cis
p,p'-DDT	Chlordane, oxy
Methoxychlor	Dieldrin
Acenaphthylene	Endrin
Acenaphthene	Endrin aldehyde
Fluorene	HCH, alpha
Phenanthrene	HCH, beta
Anthracene	HCH, delta
Fluoranthene	HCH, gamma
Pyrene	Heptachlor
Retene	Heptachlor epoxide
Benzo(a)anthracene	Mirex
Chrysene +Triphenylene	Nonachlor, cis
Benzo(b)fluoranthene	Nonachlor, trans
Benzo(k)fluoranthene	Chlordane, trans
Benzo(e)pyrene	Endosulfan sulfate
Benzo(a)pyrene	Endosulfan I
Indeno(1,2,3-cd)pyrene	Endosulfan II
Dibenz(a,h)anthracene	Chlorpyrifos
Benzo(ghi)perylene	
	di PBDE #7
EI Surrogate	di PBDE #8
	di PBDE #10
Fluorene-d_{10}	di PBDE #11
Phenanthrene-d_{10}	tri PBDE #17
Malathion-d_7	tri PBDE #25
Pyrene-d_{10}	tri PBDE #28
p,p'-DDE-d_8	tri PBDE #32
p,p'-DDT-d_8	tri PBDE #33
Triphenylene-d_{12}	tri PBDE #35
Benzo(a)pyrene-d_{12}	tri PBDE #37
Benzo(ghi)perylene-d_{12}	tetra PBDE #47
	tetra PBDE #49
ECNI Surrogate	tetra PBDE #66
	tetra PBDE #71
^{13}C-HCB	tetra PBDE #75
d_6-HCH, gamma	tetra PBDE #77
d_{10}-Chlorpyrifos	penta PBDE #85
d_4-Endosulfan I	penta PBDE #99
^{13}C-PCB 101	penta PBDE #100
d_4-Endosulfan II	penta PBDE #116
^{13}C-PCB 180	penta PBDE #118
^{13}C PBDE #28	penta PBDE #126
^{13}C PBDE #47	hexa PBDE #138
^{13}C PBDE #100	hexa PBDE #153
^{13}C PBDE #99	hexa PBDE #154
^{13}C PBDE #118	hexa PBDE #155
^{13}C PBDE #153	hexa PBDE #166
^{13}C PBDE #183	hepta PBDE #181
	hepta PBDE #183
EI Internal Standard	hepta PBDE #190
Acenaphthene d_{10}	PCB # 74
Benzp(k)fluoranthene d_{12}	PCB # 101
Fluroanthene d_{10}	PCB # 118
	PCB # 138
ECNI Internal Standard	PCB # 153
	PCB # 183
^{13}C PCB #138	PCB # 187

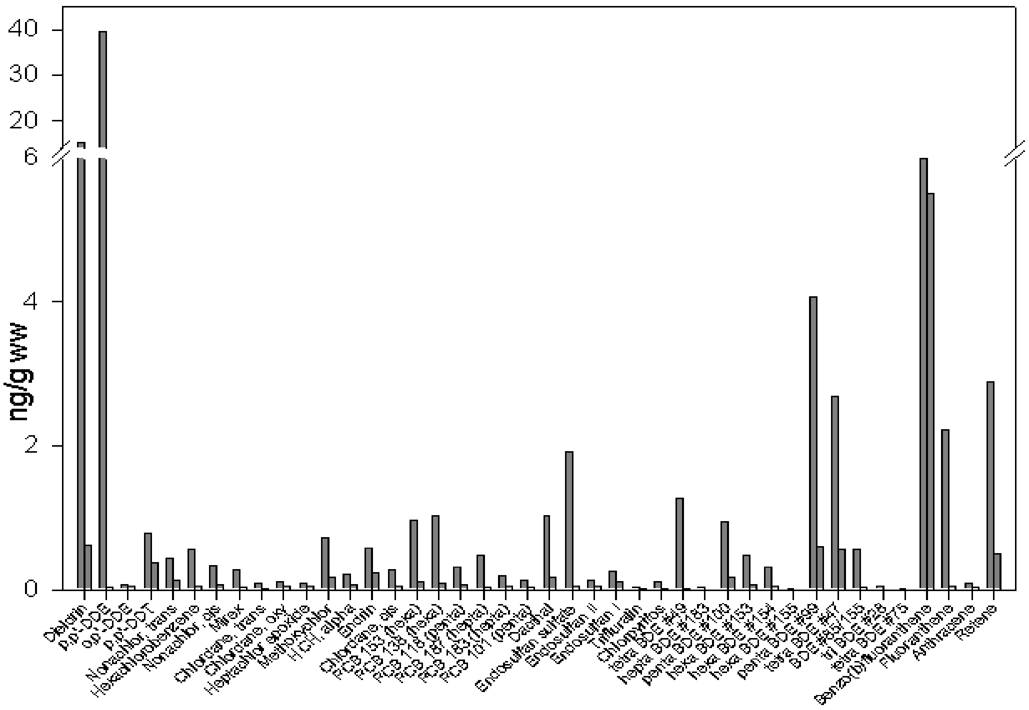


Figure 2 - Ranges of POPs and SOCs in Fish from Alpine US National Parks

The lack of difference in POPs' levels for fish from different western N. American alpine parks suggests that a global background is atmospherically depositing at these locations. A difference between the two parks' fishs' current use compound profiles and levels (current use pesticides, PAHs) suggests regional agricultural and or industrial sources are over-layed on global deposition. Tests for correlations between compounds concentration and histology and pathology indicies are needed to determine if the POPs and SOCs might be posing a threat to fish health. Further consumption/risk analysis is needed to understand if these levels of POPs and SOCs pose any significant risk to human health.

Acknowledgments

This is part of the Western Airborne Contaminants Assessment Project, a collaboration of the National Park Service, the Environmental Protection Agency, the U.S. Geological Survey, Oregon State University, University of Washington, and the U.S.D.A. Forest Service. It was funded through cooperative and interagency agreements with the National Park Service, and in-kind contributions from all project partners. More about WACAP can be found on the web site: http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.htm. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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