WESTERN AIRBORNE CONTAMINANTS ASSESSMENT PROJECT FINAL REPORT: VOLUME I

The Fate, Transport, and Ecological Impacts of Airborne Contaminants in Western National Parks (USA)

Burial Lake, Noatak National Preserve
Photo: Adam Schwindt

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Abbreviations, Acronyms, and Symbols

ºC	degrees Celsius
µeq/L	microequivalencies per liter
µL	microliter
µm	micrometer
^{137}Cs	radionuclide of cesium
^{210}Pb	radionuclide of lead
^{226}Ra	radionuclide of radium
^{241}Am	americium, radioactive decay product of ^{241}Pu (plutonium)
a-HCH	hexachlorocyclohexane-alpha (also α-HCH)
Al	aluminum
ANOVA	analysis of variance test
ARD	Air Resources Division (of the National Park Service)
As	arsenic
B	boron
Ba	barium
BAND	Bandelier National Monument
BDL	below detection limit
Be	beryllium
BeP	benzo[e]pyrene
Bi	bismuth
BIBE	Big Bend National Park
C	carbon
Ca	calcium
CAAS	combustion atomic absorption spectrophotometry
CBL	Chesapeake Bay Laboratory
Cd	cadmium
Ce	cerium
CI	confidence interval
CIC	constant initial concentration

Cl^-	chloride
CLDN	chlordane
CLPYR	chlorpyrifos
cm	centimeter
cm^3	cubic centimeter
Co	cobalt
Cr	chromium
CRLA	Crater Lake National Park
CRS	constant rate of supply
Cs	cesium
Cu	copper
CUP	current-use pesticide
CWSC	Colorado Water Science Center Laboratory (USGS)
DCM	dichloromethane
DCPA	dacthal
DENA	Denali National Park and Preserve
DL	detection limit
DOC	dissolved organic carbon
dw	dry weight
Dy	dysprosium
EA	ethyl acetate
ECNI	electron capture negative ionization
ECRC	Environmental Change Research Centre
ECSMTP	Standards, Measurements, and Testing Program of the European Commission
EDL	estimated detection limit
EI	electron impact
EMAP-SW	Environmental Monitoring and Assessment Program – Surface Water
ENDO	endosulfan
EPA	Environmental Protection Agency
EPA-ORD	EPA Office of Research and Development
Er	erbium
ERRC	Environmental Radioactivity Research Centre
Eu	europium

FF	focusing factor
g	gram
GAAR	Gates of the Arctic National Park and Preserve
GC/MS	gas chromatography mass spectrometry
Gd	gadolinium
GFF	glass fiber filter
g-HCH	hexachlorocyclohexane-gamma, or lindane (also γ-HCH)
GIS	geographic information system
GLAC	Glacier National Park
GLBA	Glacier Bay National Park and Preserve
GPC	gel permeation chromatography
GRSA	Great Sand Dunes National Park and Preserve
GRTE	Grand Teton National Park
ha	hectare
HCB	hexachlorobenzene
HCl	hydrochloric acid
He	helium
HF	hydrofluoric acid
Hg	mercury
HgS	mercury sulfide
Hg_{tot}	total mercury
HNO_3	nitric acid
Ho	holmium
HUP	historic-use pesticide
IAS	inorganic ash spheres
IBC	industrial/urban use compounds
IcdP	indeno[1,2,3-cd]pyrene
ICP-AES	inductively coupled plasma-atomic emission spectrophotometry
ICP-MS	inductively coupled plasma-mass spectrometry
IMPROVE	Interagency Monitoring of Protected Visual Environments Program
JMP	statistical software package (SAS Institute, Cary, North Carolina)
K	potassium
KATM	Katmai National Park and Preserve

kg	kilogram
kg/ha/yr	kilogram per hectare per year
K_{ow}	octanol-water coefficient
kV	kilovolt
L	liter
La	lanthanum
LAVO	Lassen Volcanic National Park
Li	lithium
m	meter
MA	macrophage aggregate
MDL	method detection limit
MeHg	methyl mercury
Mg	magnesium
mg/kg	milligram per kilogram
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
Mn	manganese
Mo	molybdenum
MORA	Mount Rainier National Park
N	nitrogen
N_2	dinitrogen (or nitrogen gas)
Na	not applicable (also NA)
Na	sodium
NCEP	National Centers for Environmental Prediction
NCLR	nonachlor
Nd	neodymium
ng/g	nanogram per gram
ng/L	nanograms per liter
ng/µL	nanogram per microliter
NH_4^+	ammonium
NHEERL	National Health and Environmental Effects Research Laboratory
Ni	nickel

NIST	National Institute of Standards and Technology
nm	nanometer
NO_3^-	nitrate
NOAA	National Oceanic and Atmospheric Administration
NOAT	Noatak National Preserve
NOCA	North Cascades National Park
NO_x	nitrogen dioxide
NPS	National Park Service
NRC	National Research Council
NRCC	National Research Council of Canada
O_2	oxygen
OC	organochlorines
OLYM	Olympic National Park
ORNL	Oak Ridge National Laboratory
OSU	Oregon State University
PAH	polycyclic aromatic hydrocarbon
PASD	passive air sampling device
Pb	lead
PBDE	polybrominated diphenyl ether
PBT	persistent, bioaccumulative, and toxic
PC	particulate carbon
PCB	polychlorinated biphenyl
PE	percent enrichment
Pg	picogram
pg/g ww	picogram per gram wet weight
POP	persistent organic pollutant
Pr	praseodymium
PRISM	Parameter-elevation regressions on independent slopes model
PTFE	polytetrafluoroethylene
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
Rb	rubidium
Re	rhenium

RIA	radioimmunoassay
RO	reverse osmosis
ROMO	Rocky Mountain National Park
RSD	relative standard deviation
S	sulfur
Sb	antimony
SCP	spheroidal carbonaceous particle
SD	standard deviation
Se	selenium
SE	standard error
SEC	Simonich Environmental Chemistry Laboratory
SEKI	Sequoia and Kings Canyon National Parks
SiO_2	silica (silicon dioxide)
Sm	samarium
SO_4^{2-}	sulfate
SOC	semi-volatile organic compound
Sr	strontium
SRM	standard reference material
STLE	Stikine-LeConte Wilderness, Tongass National Forest
SWE	snow water equivalent
Tb	terbium
TC	total carbon
Te	tellurium
TIC	total inorganic carbon
Tl	thallium
Tm	thulium
TOC	total organic carbon
U	uranium
UMNRAL	University of Minnesota Research Analytical Laboratory
USEPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
USGS-BRD	USGS Biological Resource Division

USGS-CWSC	USGS Colorado Water Science Center
USGS-NRP	USGS National Research Program (Trace Element Environmental Analytical Chemistry Project)
USGS-WWSC	USGS Wisconsin Water Science Center
V	vanadium
Vtg	vitellogenin
W	tungsten
WACAP	Western Airborne Contaminants Assessment Project
WRS	Willamette Research Station (U.S. EPA Analytical Laboratory in Corvallis)
WRST	Wrangell-St. Elias National Park and Preserve
ww	wet weight
XAD	resin (Amberlite XAD) for passive air sampling devices
y	year
yr	yr
Y	yttrium
Yb	ytterbium
YOSE	Yosemite National Park
Zn	zinc
Zr	zirconium

Executive Summary

Chapter 1. Introduction

The Western Airborne Contaminants Assessment Project (WACAP) was initiated to determine the risk from airborne contaminants to ecosystems and food webs in western national parks of the United States. From 2002 through 2007, WACAP researchers conducted analysis of the concentrations and biological effects of airborne contaminants in air, snow, water, sediments, lichens, conifer needles, and fish in watersheds in each of eight core parks in the western United States, including Alaska (Figure 1):

1. Noatak National Preserve (NOAT)
2. Gates of the Arctic National Park and Preserve (GAAR)
3. Denali National Park and Preserve (DENA)
4. Olympic National Park (OLYM)
5. Mount Rainier National Park (MORA)
6. Glacier National Park (GLAC)
7. Rocky Mountain National Park (ROMO)
8. Sequoia and Kings Canyon National Parks (SEKI)

The parks included 6 west coast and Alaska parks (NOAT, GAAR, DENA, OLYM, MORA, and SEKI) and 2 parks in the Rocky Mountains (ROMO and GLAC). We selected two sites/lakes for sampling in each park—with the exception of NOAT and GAAR, where we sampled one site in each, as the parks are adjacent—for a total of 14 sites.

Semi-volatile organic compounds (SOCs) and heavy metals were the primary focus of the study. The SOCs fall into four general classes: current-use pesticides (CUPs), North American historic-use pesticides (HUPs), industrial/urban use compounds (IUCs), and combustion byproducts. The primary heavy metal of concern is mercury (Hg).

The seven ecosystem components selected for analysis (air, snow, water, sediments, lichens, conifer needles, and fish) were chosen for several reasons. Concentrations of contaminants in air can readily be compared among sites both within this study and with sites from other studies. In many of the high altitude and high latitude sites studied, snow represents a potentially major pathway for input of contaminants to ecosystems. Lake water samples provide an overview of watershed chemical and physical characteristics that help interpret the contaminants data. Lake bottom sediments show historical patterns of change over time in contaminant deposition. Vegetation samples are used to determine spatial gradients of contaminants, and also provide data on direct uptake of contaminants that accumulate in ecosystems through litterfall. Fish bioaccumulate contaminants in their tissues, resulting in toxic effects in the fish themselves, and in birds, animals, and humans who consume the fish.

WACAP researchers evaluated selected contaminant concentrations in samples from multiple ecosystem components specifically to determine the origin of airborne contaminants and whether these sources are local, regional, or global. In addition, air flow patterns to parks were analyzed

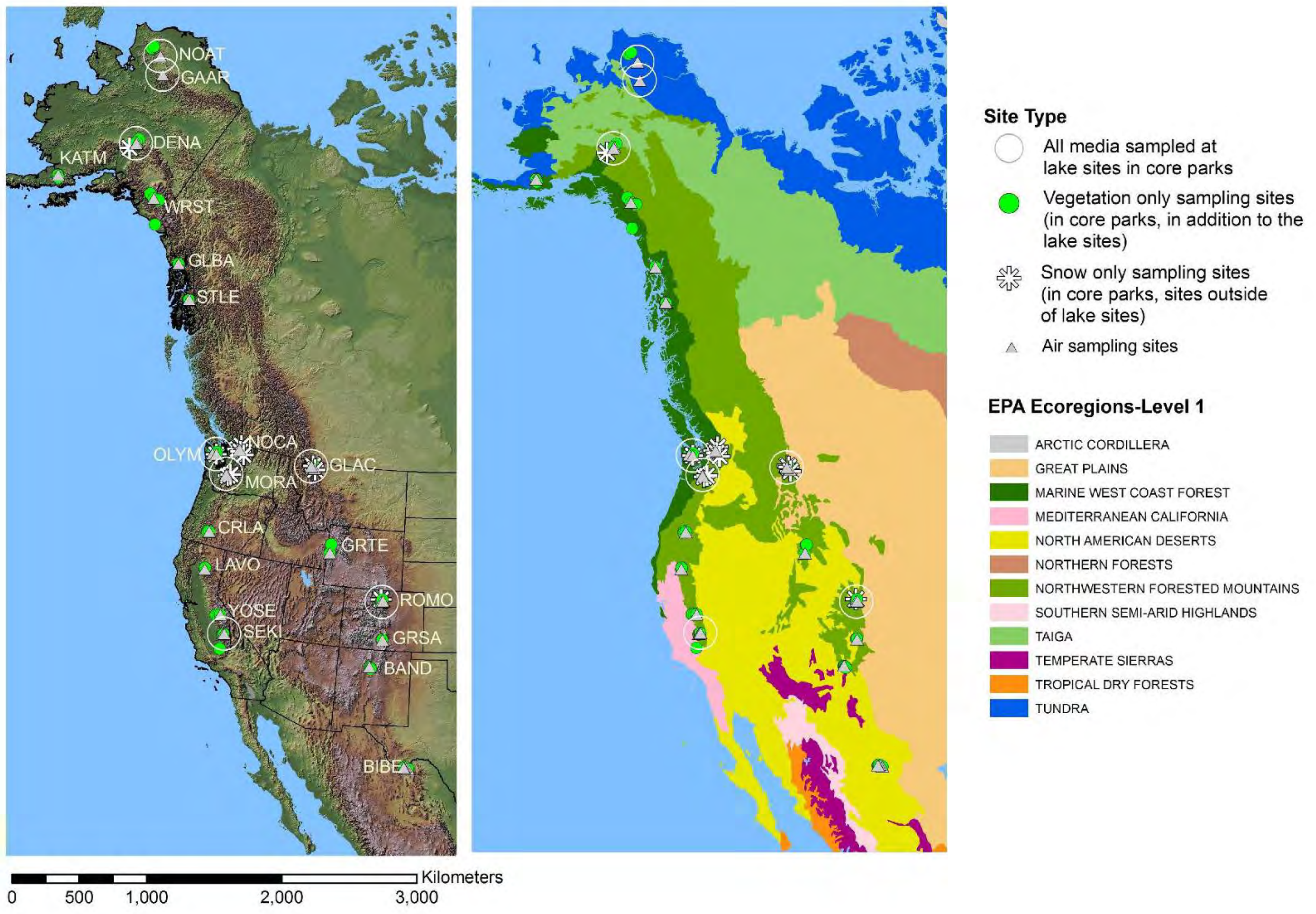

Figure 1. WACAP Sites Mapped on North American Shaded Relief Map and EPA Level 1 Ecoregions (Biomes). See Table 1-4 for key to national park abbreviations. Vegetation-only sampling sites in core parks designate sites used in elevational transect in addition to lake sites. Snow-only sampling sites in core parks designate alternate sampling locations when lake sites could not be reached safely.

through a process known as back-trajectory analysis, to assist in understanding potential sources of contaminants to parks.

The specific objectives that guided the development of WACAP were:

1. Determine if contaminants are present in western national parks.
2. If contaminants are present, determine where they are accumulating (geographically and by elevation).
3. If contaminants are present, determine which ones pose an ecological threat.
4. Determine which indicators appear to be the most useful for assessing contamination.
5. If contaminants are present, determine the source of the air masses most likely to have transported contaminants to the national park sites.

In addition to the 8 core parks sampled, WACAP identified 12 secondary parks (or monuments, preserves, or forests) for expanded spatial and environmental assessment (Figure 1). These locations were identified for collection of samples from three ecosystem components: air, lichens, and conifer needles.

1. Bandelier National Monument (BAND)
2. Big Bend National Park (BIBE)
3. Crater Lake National Park (CRLA)
4. Glacier Bay National Park and Preserve (GLBA)
5. Great Sand Dunes National Park and Preserve (GRSA)
6. Grand Teton National Park (GRTE)
7. Katmai National Park and Preserve (KATM)
8. Lassen Volcanic National Park (LAVO)
9. North Cascades National Park (NOCA)
10. Stikine-LeConte Wilderness, Tongass National Forest (STLE)
11. Wrangell-St.Elias National Park and Preserve (WRST)
12. Yosemite National Park (YOSE)

At all core and secondary parks, vegetation was sampled over an elevational gradient (including core park target watersheds), and passive air sampling devices (PASDs) were deployed for one year.

The WACAP study was designed as a screening study to assess contaminant concentrations across large-scale spatial gradients and temporal scales relevant to western national parks. Future related work, if conducted, might address additional concerns, for example, clarifying the various temporal and spatial dimensions of contaminant pathways and defining and documenting the extent and magnitude of specific ecological effects.

The US Environmental Protection Agency (USEPA), US Geological Survey (USGS), US Forest Service (USFS), Oregon State University, and University of Washington worked in partnership with the National Park Service (NPS) on this assessment. Information acquired through this project is intended to enhance scientific understanding of the global fate, transport, and associated ecological impacts on sensitive ecosystems of airborne contaminants in western parks. It will also help the NPS determine what actions are needed to further understand, mitigate, or communicate impacts of potential effects of contaminants in national parks.

Chapter 2. Park Summaries

Park-specific summaries for the 8 core WACAP parks and the 12 secondary parks provide a quick but in-depth graphical and written overview of the key results from the sites within the parks and show how key variables associated with these sites compare with each other and among results from other parks. Summaries identify key findings specific to each park.

Chapter 3. Contaminants Studied and Methods Used

WACAP researchers measured over 100 different SOCs spanning a wide range of volatility, water solubility, and hydrophobicity, as well as persistence in the environment (Figure 2). Table 3-3 in the body of the report lists the SOCs, including abbreviation, chemical class, and regulatory status. Figure 3-1 provides a summary of the 70 SOCs (excluding PBDEs in fish and sediment) found at detectable levels in WACAP snow, water, vegetation, lake sediment, and/or fish. The SOC physio-chemical properties have been used to interpret the atmospheric transport, deposition, and accumulation of these compounds to the ecosystems assessed in WACAP. Finally, some of the SOCs measured in WACAP have been classified as persistent, bioaccumulative, and toxic (PBT) chemicals by the USEPA. These PBT chemicals include benzo(a)pyrene, aldrin, dieldrin, chlordane, DDT, DDD, DDE, hexachlorobenzene, mirex, and polychlorinated biphenyls (PCBs). As with SOCs, the metals chosen for measurement in WACAP media were selected because they serve as markers for a variety of different sources. These include anthropogenic sources such as coal combustion, petroleum combustion, industrial emissions, agriculture, medical waste, incineration, and automotive sources, as well as natural sources such as sea aerosols, volcanic deposits, and minerals. Mercury is a metal of particular concern because of its detrimental neurological effects, as well as other effects, on humans, fish, and other organisms, and it is classified by USEPA as a PBT chemical.

Because of the remote locations of the WACAP sites, atmospheric transport modeling was an integral part of understanding how the contaminants were transported to the sites. We modeled atmospheric transport via back-trajectory cluster analysis on three different time scales for each of the WACAP core parks. A back-trajectory represents a meteorological calculation of the path that an individual air particle has traveled over a specific time period. By grouping similar trajectories into clusters, we obtained information about the routes of contaminant transport, as well as the climatology for each park.

WACAP researchers assessed snowpack contaminants by sampling the seasonal snowpack from at least 1 site in or near the 14 WACAP core park watersheds during each of the 3 years of the study, in order to analyze inter-annual variability of contaminant loading.

We used PASDs to (1) obtain a measure of SOCs in ambient air by means of a simple, standardized technology to compare loadings between parks and across geographic and elevational gradients, (2) compare PASD and vegetation concentrations, and (3) compare ambient air SOC concentrations in WACAP parks to ambient air concentrations at other national and international locations measured with the same PASD design. In total, 37 PASDs were strategically deployed

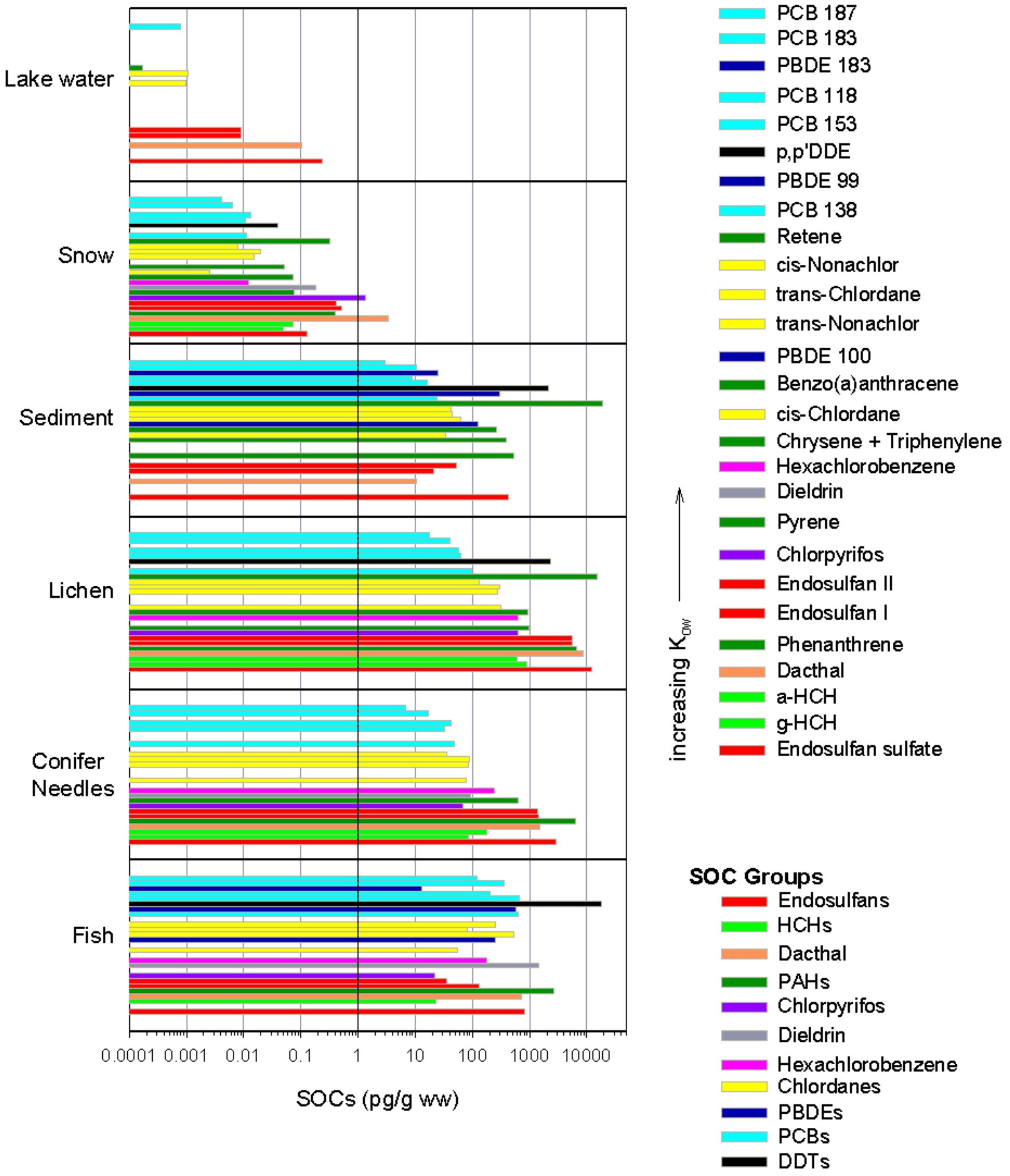

Figure 2. Mean SOC Concentrations (pg/g ww) in Lake Water, Snow, Sediments, Lichens, Conifer Needles, and Fish from Emerald Lake (SEKI). SOCs are ordered by increasing K_{ow}, or decreasing polarity and solubility in water, color-coded by group. SOC concentrations were 3 to 7 orders of magnitude higher in sediments and biota relative to snow and water. SOC concentrations in water, snow, and vegetation, but not sediments and fish, generally decreased with decreasing polarity. Compared to vegetation, fish were better accumulators of PCBs and dieldrin and poorer accumulators of PAHs, endosulfans, HCHs, dacthal, and chlorpyrifos. If no data are shown, all samples were below detection limits; PBDEs were measured in sediments and fish only.

in core and secondary WACAP parks. Multiple PASDs were deployed in the eight core WACAP parks and two of the secondary parks to sample target watersheds and to obtain data along elevational gradients.

We conducted vegetation sampling to (1) determine types and concentrations of SOCs that accumulate in vegetation in each WACAP park, (2) compare individual SOC concentrations within and across parks, especially along latitudinal and elevational gradients, to test for a cold fractionation effect, (3) evaluate metal and nutrient concentrations in lichens in relation to known ranges for lichens at other sites across the western United States, (4) determine the relationship between environmental factors such as geographical location, proximity to urban-industrial and agricultural areas, nitrogen concentrations in ambient particulates, and lichen nitrogen and sulfur content with SOC concentrations in vegetation, and (5) estimate total concentrations of SOCs in conifer needles at WACAP sites as a way of evaluating potential SOC inputs to watersheds via litterfall.

We collected lake water samples from each catchment during the ice-free summer season to characterize the condition of the WACAP lakes by assessing the chemical and physical characteristics of water quality, including trophic state, chemical contamination, and acidification status. Analytes included pH, alkalinity, specific conductance, dissolved organic carbon, dissolved inorganic carbon, chlorophyll-*a*, total nitrogen, total phosphorus, and major cations and anions.

We collected lake sediment cores to provide information about the accumulation and sources of contaminants in the 14 WACAP catchments during the last ~150 years. We dated cores and analyzed sections for SOCs, mercury, metals, total carbon, total organic carbon, and total inorganic carbon. In addition, we assessed spheroidal carbonaceous particles (SCPs) in sediment because they serve as unambiguous indicators of deposition from industrial combustion of fossil fuels, and offer clues as to the source fuel type.

Fish were used as the key bioaccumulators of SOC, Hg, and metal exposure because they are continually immersed in the lake and provide an indication of impacts to the food web. Fish, particularly top predators, are bioindicators of contaminant exposure because they accumulate organic and metal contaminants through their diet. Piscivorous birds and mammals, including humans, bioaccumulate contaminants when they consume fish. Selected biomarkers analyzed for effects on fish condition and health included macrophage aggregates (MA), plasma vitellogenin (Vtg), 11-ketotestosterone, testosterone, estradiol, and gonad, kidney, liver, spleen, and gill histopathology. Contaminant concentrations and fish health analyses were assessed for each fish, allowing a direct correlation of SOC, Hg, and metal concentrations to fish health parameters.

A small number of samples from moose liver and muscle tissue were collected in order to explore the potential for the bioaccumulation of contaminants through the terrestrial food web. Tissues from a total of three moose donated by hunters in Denali National Park and Preserve in 2004 and 2005 were analyzed for mercury, other metals, and SOCs.

Chapter 4. Contaminant Distribution

Spatial patterns of the contaminants found in greatest general abundance within each contaminant category (SOCs, mercury, trace metals, SCPs, nutrients) are as follows.

Total SOC concentrations in snow were highest in the Rocky Mountains (GLAC and ROMO) and California (SEKI) parks. This general pattern was often repeated for other ecosystem components. The highest SOC concentrations in vegetation were measured at SEKI, GLAC, YOSE, and GRSA. At parks with the highest SOC concentrations in vegetation, the total SOC concentration was dominated by CUP residues, notably endosulfans and dacthal.

Lichen concentrations of PCBs and many pesticides increased with elevation at most of the WACAP parks for which there were sufficient data, suggesting that these compounds are undergoing cold fractionation. Concentrations of polycyclic aromatic hydrocarbons (PAHs) decreased with increasing elevation at most parks, suggesting an association with wildfires at lower, more heavily wooded elevations. Nitrogen concentrations in lichens from SEKI, GLAC, BAND, and BIBE were elevated, indicating enhanced nitrogen deposition in these parks. Lichen sulfur concentrations indicated enhanced sulfur deposition at SEKI and GLAC.

Fish whole-body lake mean and individual fish concentrations for dieldrin and Sum DDTs (DDT, DDD, and DDE) are shown in Figure 3, along with contaminant health thresholds for humans and piscivorous wildlife. Concentrations of dieldrin in fish (notably at ROMO, SEKI, and GLAC) were significantly elevated compared with those in fish from similar Canadian studies. DDT concentrations in fish from SEKI, GLAC, and ROMO were higher than those reported for many fish elsewhere in the world, including fish from sites in Africa, where DDT is used for mosquito control. Concentrations of the industrial flame retardant compound poly-brominated diphenyl ether (PBDE) in WACAP fish were approximately 3 times higher than concentrations in fish from similar alpine environments in Europe, and concentrations of CUPS in WACAP fish were 2-9 times lower. All WACAP fish had lower PCB, HCH, and HCB concentrations than fish in some recent surveys conducted in other locations of atmospheric contaminants and reported in the literature. Mercury concentrations in fish (Figure 4) from this study were compared with concentrations published in the literature for fish in other areas. In general, mercury concentrations in trout from the parks in this study were lower than those reported for trout in lakes in the Midwest and Northeast United States. However, mercury concentrations were higher in WACAP fish than in some species of fish from northern lakes in Canada and from mountain and sub-Arctic ecosystems in Europe. See Table 5-1 (pages 5-6 through 5-10) in the body of the WACAP report for comparisons of WACAP fish contaminant concentrations to those found in other studies.

At WACAP parks in the conterminous 48 states, strong correlations were found between CUP concentrations in snow and vegetation and percent cropland within 150 km. Concentrations of the CUPs chlordanes, dacthal, and endosulfans in lichens and conifer needles, DDTs in conifer needles, and PAHs in lichens correlated well with agricultural intensity, indicating that most CUP concentrations in these parks are probably attributable to regional agricultural sources. Pesticide deposition in the Alaska parks is attributed to long-range trans-Pacific transport, because there are no significant regional pesticide sources nearby (Figure 5).

Where banned (historic-use) contaminants are found in park ecosystems, concentrations significantly higher than those found in the Alaska parks probably indicate that re-volatilization of persistent compounds is occurring from regional or local soils. Information about probable sources or source areas of atmospherically transported contaminants into parks was assessed from many varied types of data, including atmospheric transport pathways, contaminant spatial patterns, and groupings of types of contaminants.

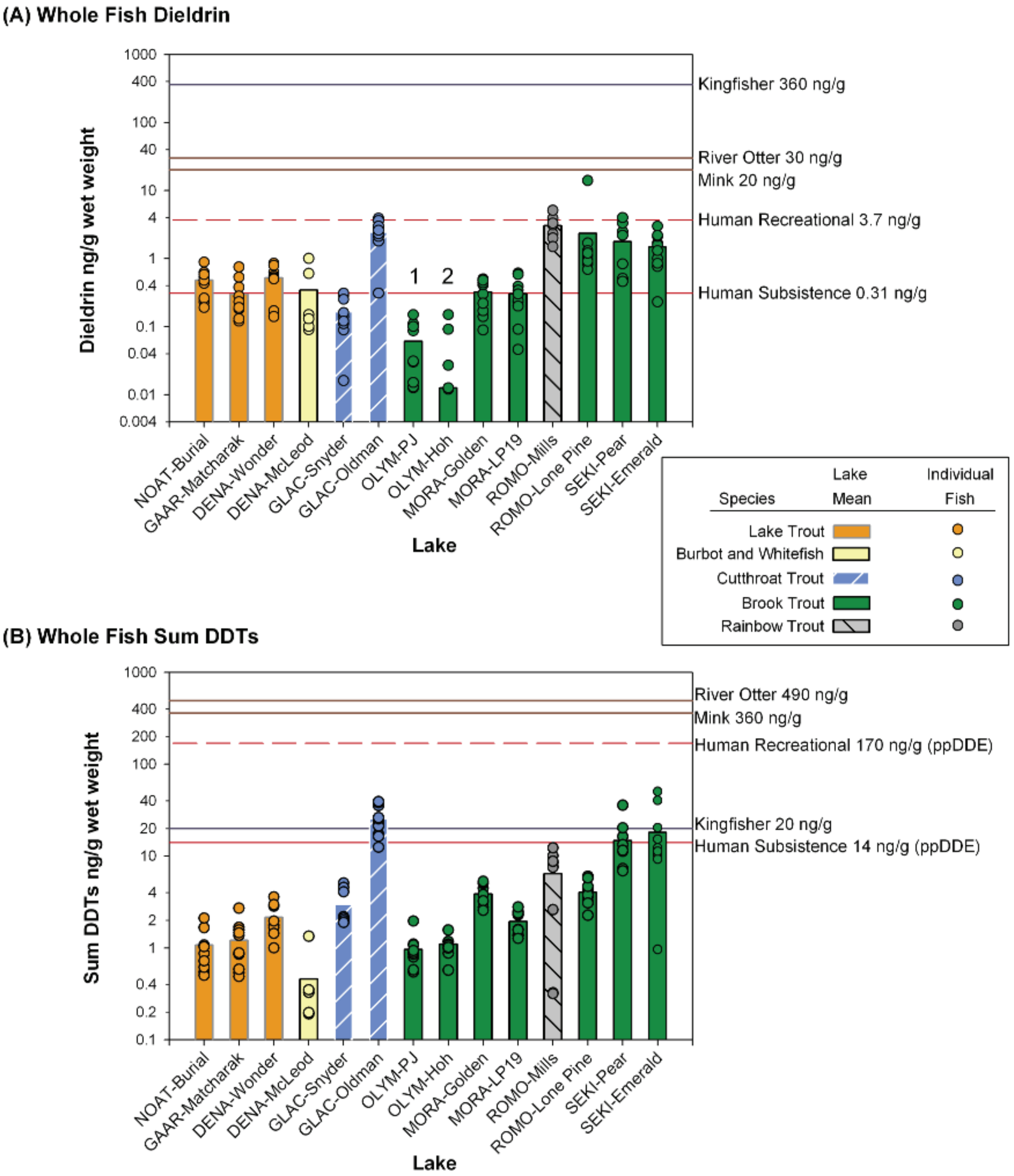

Figure 3. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) (A) Dieldrin and (B) Sum DDTs (DDT, DDD, and DDE) Concentrations with Contaminant Health Thresholds for Wildlife and Humans. Mean dieldrin concentrations in fish (A) exceeded human contaminant health thresholds for subsistence fishers in 9 WACAP lakes, and some fish in 4 lakes exceeded the thresholds for recreational fishers; no lakes exceeded health thresholds for piscivorous wildlife. Mean concentrations of sum DDTs (B) in 3 lakes exceeded human contaminant health thresholds for subsistence fishers for p,p′-DDE, which was the form of DDT most frequently detected in the fish; thresholds for recreational fishers were not exceeded. Some fish in SEKI and the mean concentration of fish in Oldman Lake (GLAC) also exceeded the threshold for kingfishers. If no label is present at the top of a bar, the analyte was detected in at least 70% of the samples. “1” indicates that the analyte was detected in 50-70% of the samples, and “2” indicates that the analyte was detected in less than 50% of the samples. Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet as determined by Lazorchak et al. (2003). See Section 5.4.3 for a description of the human contaminant health thresholds. Data are plotted on a $\log_{10}$ scale and below detection limit values are reported as ½ the EDL.

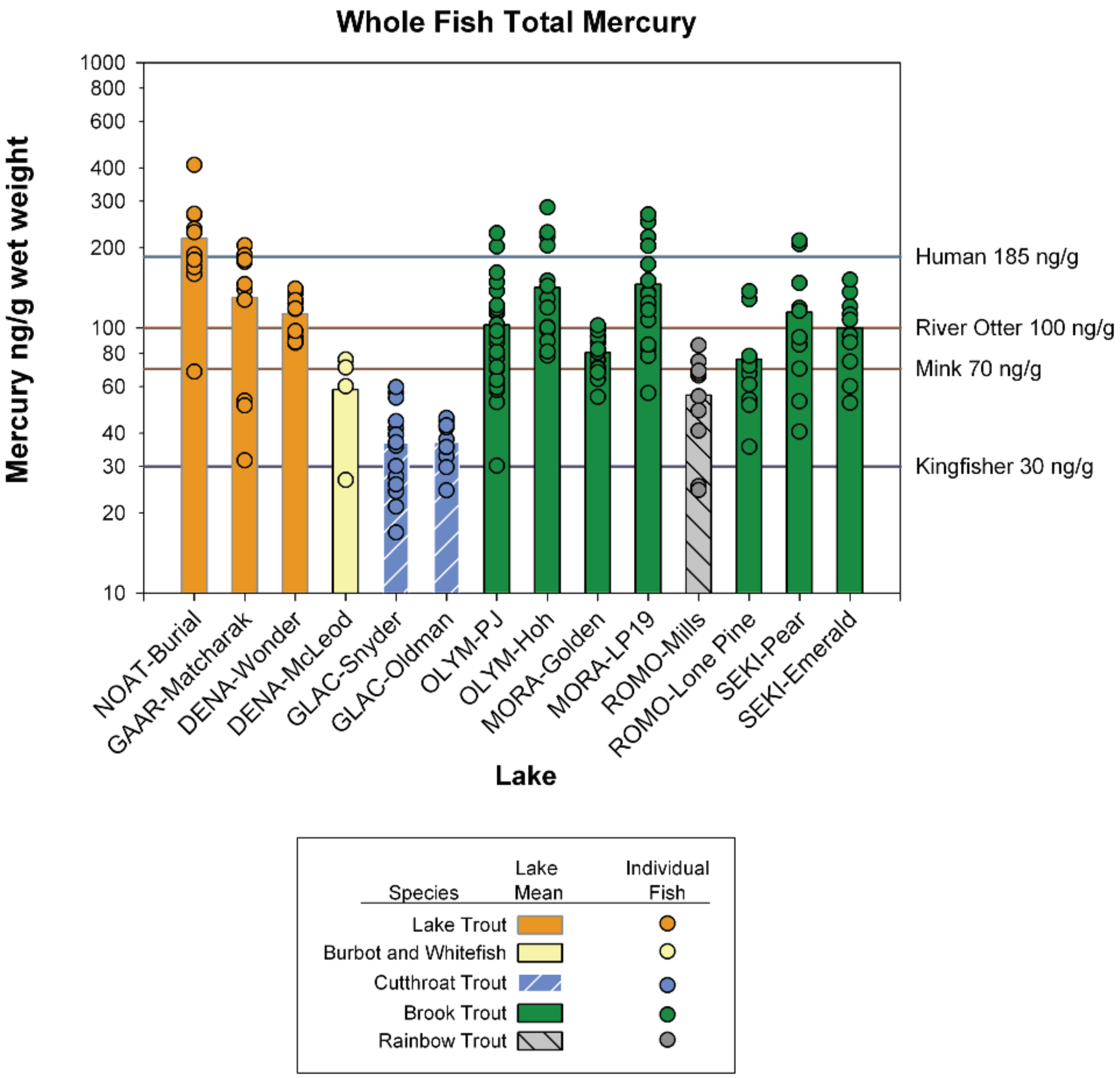

Figure 4. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Total Mercury and Contaminant Health Thresholds for Various Biota. The mean ng/g total Hg in fish at NOAT exceeds the human contaminant threshold, while some fish at Matcharak Lake (GAAR), PJ and Hoh Lakes (OLYM), LP19 (MORA), and Pear Lake (SEKI) exceed the human contaminant threshold. The mean ng/g Hg concentration in fish at all parks exceeds the kingfisher contaminant threshold, and the mean at 7 lakes exceeds all wildlife thresholds—Burial Lake (NOAT), Matcharak Lake (GAAR), Wonder Lake (DENA), PJ and Hoh Lakes (OLYM), LP19 (MORA), and Pear Lake (SEKI). The human threshold is 300 ng/g wet weight (USEPA, 2001), and is based on methyl-Hg in the fillet for a general population of adults with a body weight of 70 kg and 0.0175 kg fish intake per day. 95-100% of Hg in fish is methyl-Hg (Bloom, 1992), and 300 ng/g in the fillet is equivalent to 185 ng/g ww whole body methyl-Hg (Peterson et al., 2007). Contaminant health thresholds in piscivorous animals (wildlife) are based on 100% fish in the diet for whole body total Hg, as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale; the y-axis starts at 10 ng/g.

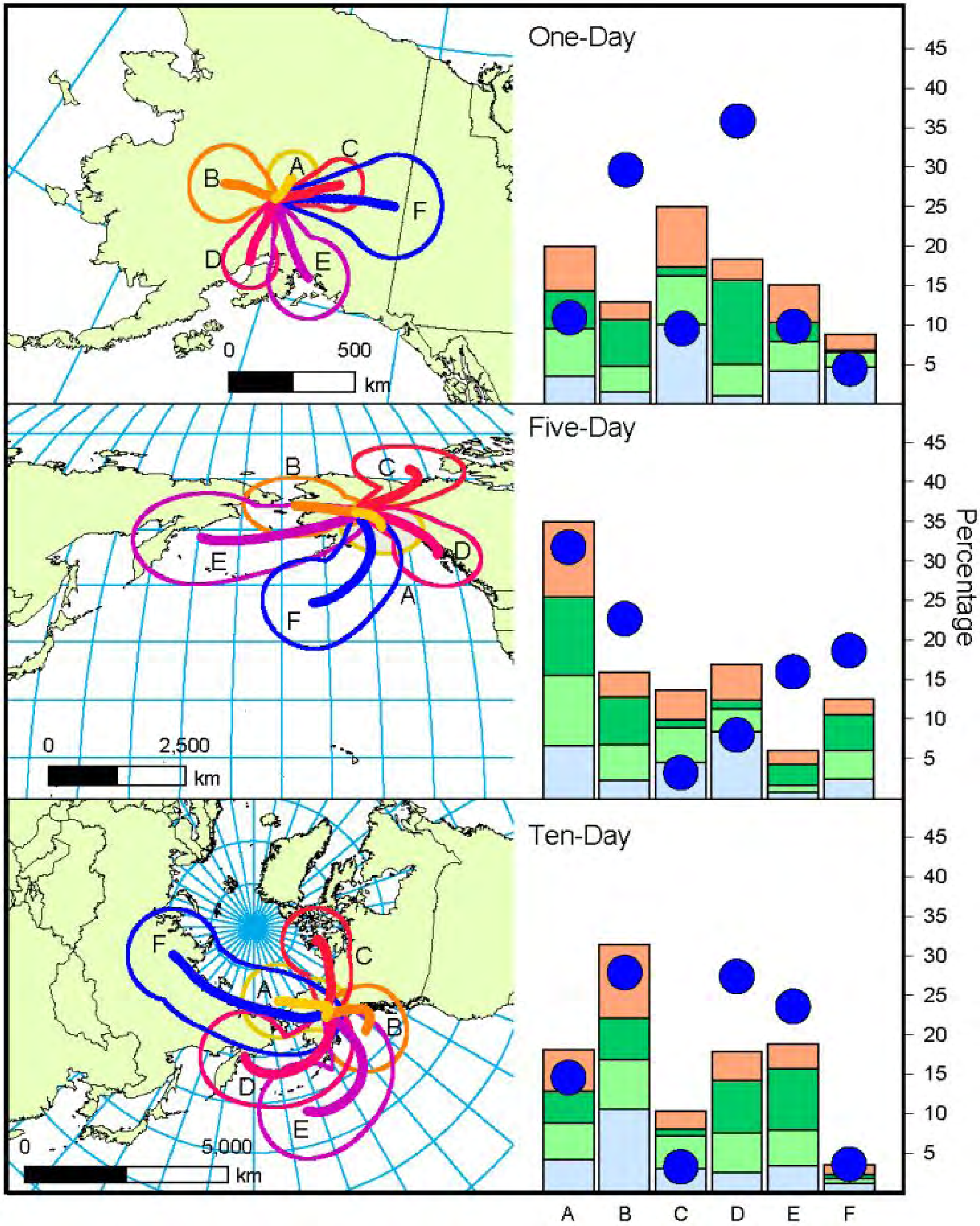

Figure 5. 1-, 5-, and 10-Day Cluster Plots for DENA. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

In GLAC, PAH concentrations in snow, sediment, and vegetation in the Snyder Lake watershed were higher than those in the Oldman Lake watershed and 10 to 100 times higher than those in all other WACAP parks. Several lines of evidence point to the aluminum smelter in Columbia Falls, Montana, as the most likely major source of these elevated PAHs to Snyder Lake.

At ROMO, higher SOC and Hg deposition in snow was found in the Mills Lake watershed (on the east side of the Continental Divide), than in Lone Pine Lake (on the west side), possibly because the Continental Divide serves as a topographic barrier for transport of SOCs and Hg from agricultural and populated areas on the east side of ROMO to the west side. SOC concentrations in air (PASDs), conifer needles, and fish show no clear evidence of an east side enhancement.

Sediment cores provide a historical record of contaminant deposition over the past ~150 years. The temporal records from sediment cores indicate that in nearly all parks, Hg deposition increased in the twentieth century because of anthropogenic sources. In many parks, mercury deposition fluxes have declined somewhat, although in other parks the Hg flux appears to still be increasing. This finding reflects a complex array of decreasing regional sources, combined with increasing global contributions and watershed influences on sediment records.

Lead (Pb), cadmium (Cd), and SCPs in sediment indicate regional fossil fuel combustion sources. SCPs clearly show the build-up from industrial sources in lakes in the conterminous 48 states during the late twentieth century. In recent decades, Pb, Cd, and SCPs have declined substantially, reflecting source reductions related to the Clean Air Act and regulation of lead in gasoline. Lead concentrations in lichens at SEKI and MORA have decreased 5- to 6-fold since the 1980s.

In the Alaska lakes, SCPs in sediment were non-detectable and Pb and Cd showed little sign of a twentieth century increase. Only the Hg flux showed a consistent increase in the Alaska lake sediments, reflecting a primary contribution from global sources.

Chapter 5. Biological and Ecological Effects

WACAP assessed the impacts and/or effects of contaminants on biota and ecosystems in a variety of ways. Key results include the following.

Bioaccumulation of SOCs in vegetation appears to occur over time. Second-year needles contained approximately triple the concentrations of contaminants in first-year needles. The amount of contaminant stored in vegetation that eventually contributes to accumulation of SOCs in forest litter-fall and soils is likely to be dependent upon forest productivity (annual above-ground biomass production), tree species, and proximity to contaminant sources.

We observed biomagnification throughout park ecosystems. Concentrations of SOCs were 5 to 7 orders of magnitude higher in fish than in snow, water, and the PASD monitors indicating air concentrations. Concentrations of SOCs were 3 to 5 orders of magnitude higher in fish tissue than in sediments. Vegetation tended to accumulate more PAHs, CUPs, and HCHs, whereas fish accumulated more PCBs, chlordanes, DDTs, and dieldrin. SOCs in vegetation and air (PASD monitors) were expected to show similar patterns; however, this was not the case, possibly because each medium absorbs different types of SOCs with varying efficiencies.

In this study, WACAP researchers assessed both fish-condition biomarkers and concentrations of contaminants in fish tissue. Most fish appeared normal during field necropsies. Macrophage aggregates (MAs; an immune system response, Figure 6) generally increased with mercury concentrations and age in brook, rainbow, and cutthroat trout. Vitellogenin (Vtg) concentrations in male fish are widely used as a biomarker for environmental estrogen exposure. Compounds such as dieldrin, DDT, PDBEs, PCBs, PAHs, endosulfan, and methoxychlor (among others) are known or suspected endocrine disrupting contaminants. Although sample sizes in this study were very small, significant correlations between contaminants in fish tissue and Vtg concentrations in male fish were found in the two core WACAP lakes sampled in ROMO in 2003. Two additional lakes in ROMO, sampled as part of a separate study, contained fish with high concentrations of Vtg; however, contaminants analysis of these fish has not yet been conducted. Two male fish from GLAC and one male fish from MORA also displayed elevated concentrations of Vtg. The fish from Oldman Lake (GLAC) with high Vtg concentrations also contained the highest concentrations of DDT of any of the fish sampled in the project.

Intersex, the presence of both male and female reproductive structures in the same animal, is also a commonly used biomarker of estrogen-like chemical exposure. Intersex fish were found in ROMO and GLAC lakes. In this study, four levels of intersex condition were characterized, both for current samples collected in WACAP, and for historic samples obtained for comparison from museums. The data show that the number of sites with intersex fish has increased since the late 1800s. In the current WACAP samples, 8 of 117 fish in the Rocky Mountains were identified as intersex and none of the 90 samples collected at other parks in the west were intersex. Six of 11 water bodies sampled in ROMO contained intersex fish. Sample size in the project was low, and WACAP was not designed to fully characterize the extent and range of intersex fish in remote sites in the west. However, based on the initial sampling conducted here, it appears that intersex condition in fish from remote areas might be concentrated in the Rocky Mountains. Further investigation is warranted (a variety of potential hypotheses are discussed in the report).

In addition, the severity of abnormalities observed in the intersex fish from ROMO was greater than in any historical samples, displaying category 4 gonad abnormalities, low androgen and estrogen levels, and elevated levels of Vtg. The three intersex fish that were also sampled for contaminants contained high levels of endocrine disrupting contaminants such as dieldrin, DDT, chlordanes, and PCBs. However, whether contaminants are causing the intersex condition in fish cannot be definitively determined with this small dataset.

Mercury concentrations increased with fish age in all fish species up to approximately 15 years of age. Fish older than 15 years had less mercury. Several hypotheses could account for this finding and are discussed in more detail in Chapter 5 of the report. Fish mercury concentrations in WACAP were highest in Burial Lake (NOAT), with the mean Hg concentration exceeding the USEPA contaminant health threshold for human consumption (see Figure 4). The other Arctic lake in this study, Matcharak (GAAR), also contains fish with elevated concentrations, with some fish exceeding human contaminant health thresholds. Because mercury concentrations in snow, sediment, and vegetation were found to be low in these two parks, it is likely that in-lake biological processes, including fish age, Hg methylation rate, watershed biogeochemical characteristics, and food web efficiency influence the higher rates of bioaccumulation in Alaska lakes.

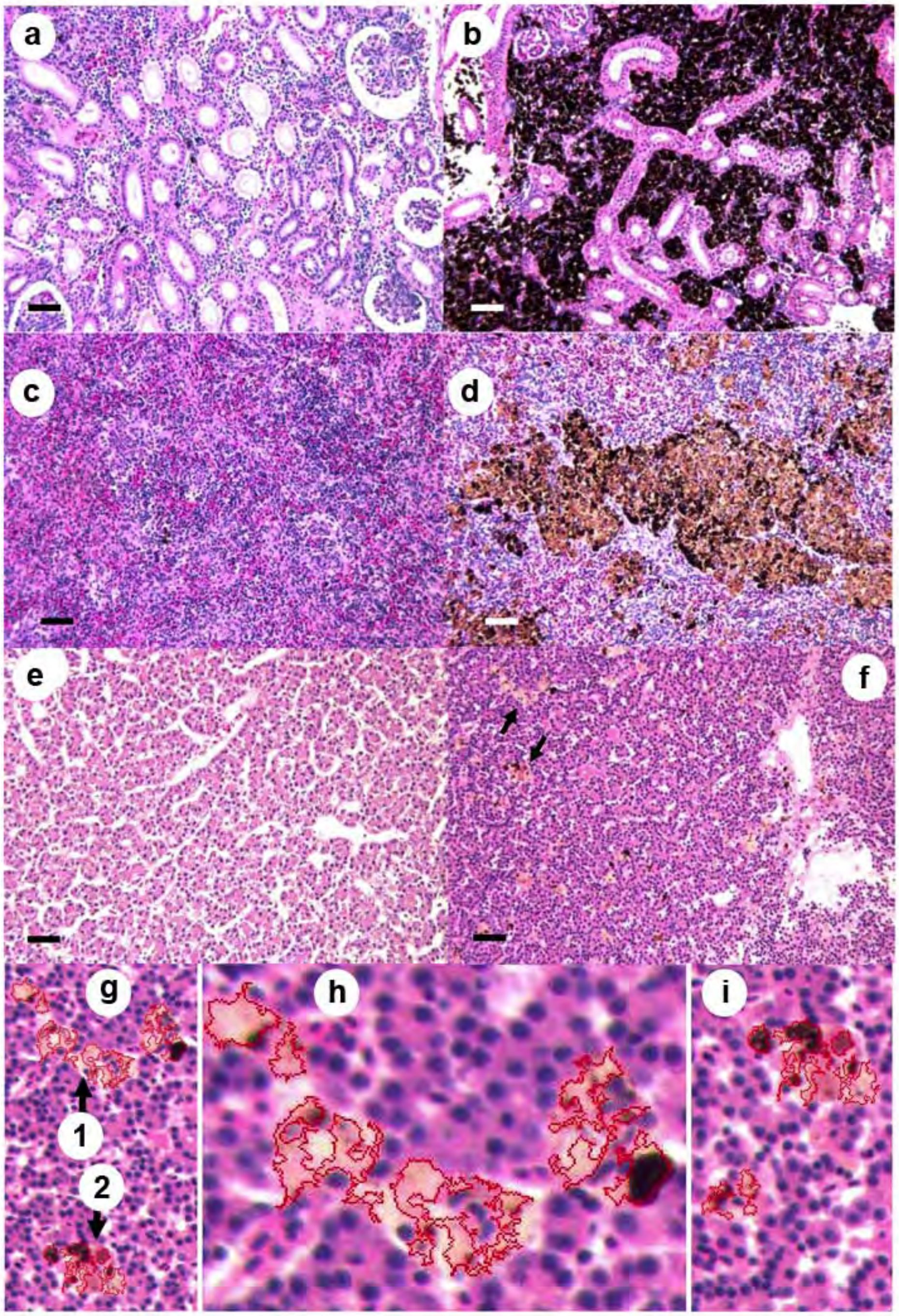

Figure 6. Representative Hematoxylin-Eosin Stained Brook Trout Organs Showing the Relative Difference between Fish with Very Few or No Macrophage Aggregates (MAs) and Extensive Accumulations of MAs (a-f) and Outlined High Magnification Hepatic MAs (g-i). Bars = 50 µm. (a) Kidney with a few MAs; (b) Kidney with extensive MAs; (c) Spleen with a few MAs; (d) Spleen with extensive MAs; (e) Liver with no MAs; (f) Liver with extensive MAs; (g) High magnification of liver MAs corresponding to MAs (arrows) in (f); (h) 2X magnification of the MA corresponding to arrow 1 in (g); (i) 2X magnification of the MA corresponding to arrow 2 in (g). The outlined areas in (g) through (i) are the computer output of delineated MAs in the liver based on pigment selection by the computer program. Modified from Schwindt et al. (2006).

Current contaminant concentrations in 136 fish from 14 lakes in the 8 core WACAP parks were compared to the USEPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories*. The contaminant health threshold is the point at which a 70-kg person who consumes 17.5 g of fish per day (2.3 servings per month; recreational fish consumption) or 142 g per day (19 servings per month; subsistence fish consumption) increases lifetime risk of developing cancer by 1 in 100,000, or significantly increases risk of chronic (non-cancer) disease. Most contaminant concentrations in fish fell below these thresholds. However over half (77 of 136) of the individual fish from 11 of the 14 lakes analyzed carried concentrations of dieldrin and/or p,p,′-DDE that exceeded contaminant health thresholds for subsistence fishing (Figure 3). The lake average fish dieldrin and/or p,p,′-DDE concentrations exceeded subsistence fishing thresholds in nine of the lakes and recreational fishing thresholds in none of the lakes, although five individual fish exceeded dieldrin thresholds for recreational fish consumption in Mills and Lone Pine lakes (ROMO), Pear Lake (SEKI), and Oldman Lake (GLAC). No other SOC concentrations measured in fish from the eight core WACAP parks exceeded human contaminant health thresholds. Of the other compounds detected in >50% of fish (chlorpyrofos, dacthal, endosulfans, methoxychlor, mirex, HCB, a-HCH, g-HCH, chlordanes, heptachlor epoxide, and PBDEs), all were 1 to 7 orders of magnitude below the human contaminant health thresholds.

We assessed impacts of contaminants on aquatic food chains by comparing fish contaminant concentrations with published contaminant health threshold for impacts to mink, river otter, and belted kingfishers. At numerous sites, mean concentrations for mercury in WACAP fish were above thresholds for potential negative health effects on the aforementioned wildlife (Figure 4). Contaminant health thresholds for PCBs for wildlife (banned from production and use in the United States in 1979) were not exceeded. DDT production ceased in the United States in 1972. Some fish at the two sites in SEKI, and the mean concentration of fish in Oldman Lake in GLAC, had concentrations of the sum of DDTs above the threshold for negative health effects for kingfishers (Figure 3B). The concentrations of chlordane, once a broad-use pesticide used to control underground termites, were below thresholds for wildlife, except that one fish in Oldman Lake in GLAC exceeded the threshold for kingfishers. A suspected carcinogen and endocrine disruptor, chlordane was banned in the United States in 1983. The acutely toxic pesticide dieldrin was banned for agricultural use in the United States in 1974 and for most other uses in 1987. The highest dieldrin concentrations in fish in this study were found in ROMO. Dieldrin was produced in nearby Denver, Colorado, from 1952 to 1973. Mean concentrations of dieldrin in fish at all WACAP sites were below the contaminant health thresholds for wildlife (Figure 3A).

We analyzed moose tissue samples for SOCs and metals in Alaska parks with the intent of exploring linkages between the Alaska food web and humans engaging in subsistence hunting. However, tissue samples from only three animals were collected, all in DENA. Few of the target SOC compounds were detected in the moose liver or muscle tissues analyzed. The generally low detection frequencies and the absence of any major patterns among SOC compound groups, among individual moose, or between moose tissue types suggest that these moose were not biomagnifying SOCs to a concentration of concern. Metals concentrations were low, and at the deficiency level for copper, which decrease adsorption of iron in the blood. Compared to the sparse data available from other studies for metals in moose tissue, the WACAP samples were generally lower in cadmium, copper, and zinc.

Chapter 6. Recommendations and Conclusions

The report concludes with recommendations to the National Park Service that respond to the question, “What did you learn in this project that could help guide or focus future work within the NPS on contaminants in parks in the western United States?” These recommendations are specific to the original five project objectives. Also included is a list of additional research questions posed by WACAP scientists. These questions define fertile areas for future research into processes, mechanisms, and ecological interactions of contaminants in western ecosystems. In addition, broad conclusions answering the questions posed by the five project objectives are discussed.

Contaminants were found in all WACAP lakes. In some cases, the concentrations in fish were found to exceed important human and wildlife thresholds. It might be perceived that the two lakes per park that WACAP examined are somehow outliers and that they do not represent the total population of lakes within parks. From a strictly statistical perspective, these lakes are not representative of the population of lakes. However, the lakes were selected to provide “clean” and unambiguous signals of atmospherically deposited contaminants and in no way were they selected to provide the highest or lowest contaminant concentrations. For future work, researchers might choose to consider implementing a robust statistical sampling design for specific parks that would provide a quantitative estimate of the contaminant condition of all lakes in the population.

CHAPTER 1

Introduction

1.1 Background

Transport and deposition of atmospheric contaminants has been recognized as a possible threat to aquatic and terrestrial ecosystems for several decades. However, it was not until the 1970s and 1980s that the potential for significant regional-scale ecological impacts of long-range transport of contaminants, particularly the acidic precursors of acidic deposition, was recognized (Likens et al., 1979) and later documented and quantified across multiple spatial scales (Linthurst et al., 1986). In this case, it was demonstrated that SO_x and NO_x, byproducts of combustion, were transported thousands of kilometers in the atmosphere, transformed to acids, and deposited via precipitation on sensitive ecosystems that lacked sufficient buffering capacity to neutralize the acid (Galloway and Cowling, 1978). In addition, metals were recognized as another class of contaminants associated with the combustion of fossil fuels that could be transported great distances in the atmosphere (Galloway et al., 1982).

Once the concept of trans-boundary airborne contaminants had been demonstrated with acidic precipitation, numerous other airborne contaminant threats to ecosystems and the humans that depend upon them were identified (Perry et al., 1999). The lack of local or watershed sources of contaminants confirmed that the impacts of long-range atmospheric transport of contaminants threatened many remote ecosystems (Barrie et al., 1992; MacDonald et al., 2000). It is now well known that metals, particularly mercury and lead, are emitted by human activities and can be transported short and long distances from their sources to be deposited, retained, and, in some instances, bioaccumulated within distant ecosystems. Similarly, a vast array of persistent organic pollutants (POPs) and semi-volatile organic compounds (SOCs) are recognized as having the potential to be transported by the atmosphere (Simonich and Hites, 1995; Muir et al., 1996; Li et al., 1998; Van Drooge et al., 2002). These compounds are derived *only* from human activities and many persist in the environment for long periods of time (Gubala et al., 1995; Fernandez et al., 2000; Helm et al., 2002).

Recent studies have pointed out the atmospheric linkage between air masses traversing Eurasia and arriving in North America (Welch et al., 1991; Wania and Mackay, 1996; Jaffe et al., 1999). Although few studies have measured persistent and bioaccumulating toxics in these air masses, model output suggests that they are likely to contain a variety of contaminants (Perry et al., 1999; Koziol and Pudykiewicz, 2001). Recent studies by authors of this report (Jaffe, Simonich, and others) have demonstrated some key linkages between air masses arriving on the west coast of North America and Eurasian industrial and agricultural sources (Jaffe et al., 2005; Weiss-Penzias et al., in press). Many of the tracers used by air monitors to identify trans-Pacific air masses (e.g., CO, aerosols, O_3) are directly related to human activities and combustion sources. However, from an ecological perspective, it is very complicated to track these short lived and/or highly reactive tracers through ecosystem compartments where they are not retained as SOCs and metals are. This is particularly true in remote locations.

There is ample evidence of regional as well as long-range sources of atmospheric contamination to remote ecosystems in the western United States, but there is scant evidence in any published source that a threat to ecosystems is being realized. This is particularly true over large spatial scales. One of the major problems is that the atmospheric scientists who have identified the long-range transport across the Pacific Ocean from Eurasia have little information about deposition of inorganic and organic contaminants in these air masses. One of the few and most convincing publications regarding this issue describes the concentration of POPs in snow sampled in the Canadian Rocky Mountains during the spring of 1995 and 1996 (Blais et al., 1998). The data in this publication suggest that there is good evidence that high-elevation ecosystems are at risk with respect to SOCs for two primary reasons: (1) long-range transport of contaminants possibly being deposited with the annual snow pack and (2) cold fractionation of the lighter SOCs, resulting in migrations of these and other compounds to the higher (i.e., colder) alpine areas (Wania and Mackay, 1996). Cold fractionation appears to function at latitudinal as well as elevational gradients, putting northern ecosystems are risk. A recent publication documents the cold-trapping of POPs by vegetation in mountains in western Canada (Davidson et al., 2003).

Certainly there is sufficient scientific evidence to ponder the question of risk to high-latitude ecosystems from airborne contaminants in the western United States. The information to date, from various disciplines, published and reported independently, has generated considerable concern regarding the risk to western ecosystems, prompting the US Environmental Protection Agency (USEPA) to convene the First International Conference on Trans-Pacific Transport of Atmospheric Contaminants in Seattle, Washington, in July 2000. The meeting was attended by over 100 experts, representing disciplines that included energy and emissions, atmospheric sciences, marine sciences, biogeochemistry, biological sciences, and international environmental policy. This workshop culminated in a consensus statement published in *Science* (Wilkening et al., 2000). Three of the conclusions from this conference most pertinent to this undertaking are worth noting here:

- The nature, magnitude, and spatial distribution of the effects of airborne chemicals transported in the Pacific region, including changes in variability, are largely unknown.

- Long-range transport could have significant impacts on the chemistry of the troposphere above the Pacific Ocean, and of the ocean itself, and on contaminant concentrations in terrestrial and aquatic ecosystems.
- Some airborne chemicals, especially organochlorines and mercury, have the potential to enter food webs and biomagnify, thereby increasing the toxicological risk to top predators, including humans.

These conclusions were applied to a broad suite of contaminants, including organic contaminants, heavy metals (including mercury), and radionuclides.

1.2 Approach

In 2001, the National Park Service (NPS) convened the first of two workshops at which experts discussed how to identify a scientific approach that could be followed to quantify the risk from airborne contaminants to the national parks in the western United States. This action followed the legal mandate described in the National Park Service Organic Act (1916) that created the NPS. This federal legislation required protection of the national parks for perpetuity, "…unimpaired for the enjoyment of future generations." The Clean Air Act augmented this responsibility in 1977 by defining specific goals, objectives, and mechanisms for protecting air quality in major parks and preventing "significant deterioration" of air quality. Not only are the national parks widely distributed, but many of them have considerable elevation ranges, possibly predisposing these high-elevation locations, because of their cold alpine climates, to become long-term sinks for some classes of contaminants. Moreover, high-latitude national parks in Alaska are also perceived to be at risk of becoming sinks for air pollution, given their cold climates and the trans-continental air masses to which they are exposed.

The Western Airborne Contaminants Assessment Project (WACAP) was initiated by the NPS as a direct result of these workshops. In communication with a broad range of NPS personnel, the WACAP goal was finalized:

> To assess the deposition of airborne contaminants in western national parks, providing regional and local information on exposure, accumulation, impacts, and probable sources.

At this early stage, WACAP conceptually incorporated an integrated, interdisciplinary, multi-scalar scientific approach to the problem (Figure 1-1). The project was initiated, and principal investigators with expertise in a broad range of disciplines were organized to develop a research plan that was peer reviewed by an international scientific review panel, revised, published (USEPA, 2003), and implemented in 2003. The WACAP report authors are shown in Table 1-1.

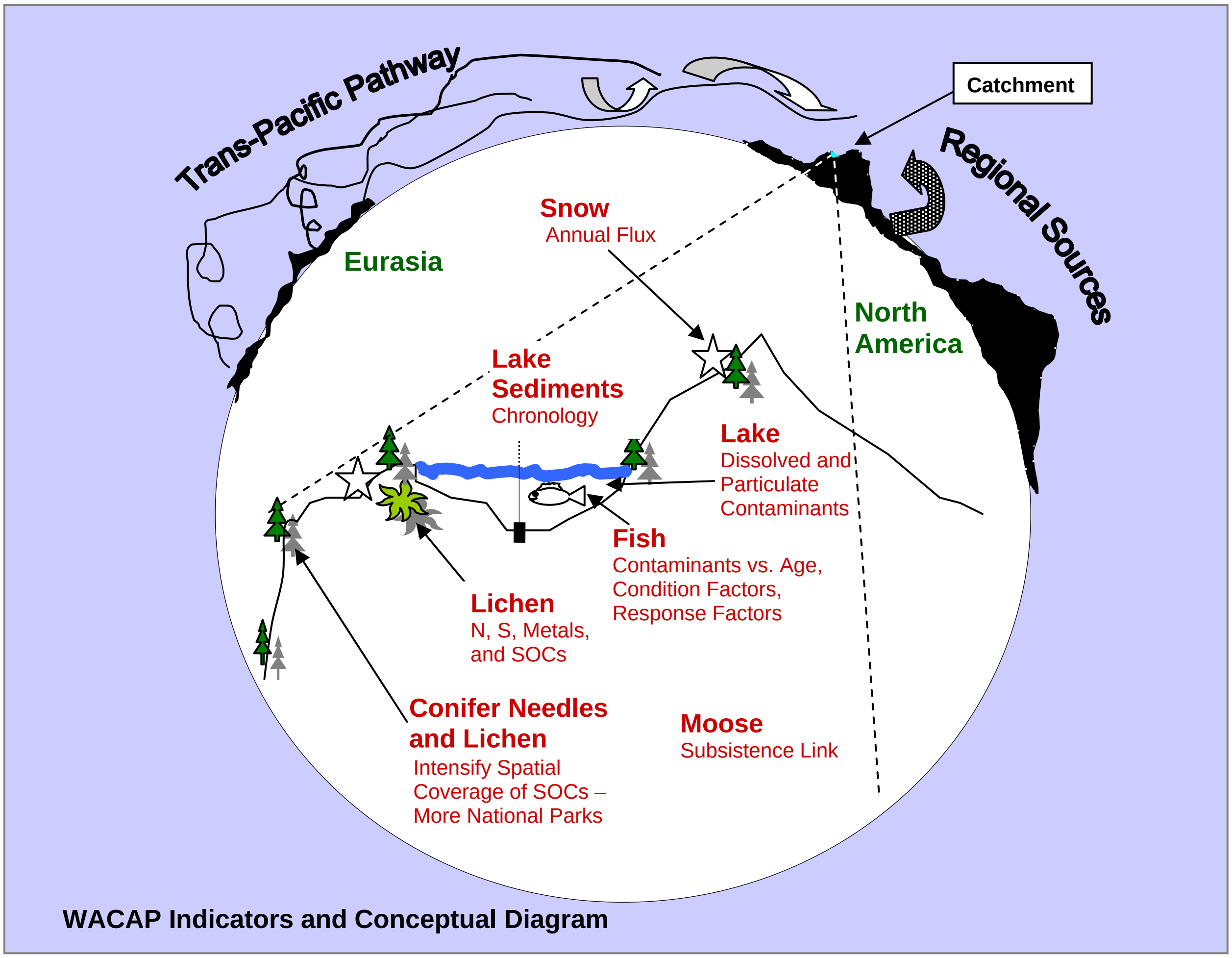

Figure 1-1. WACAP Conceptual Diagram of Airborne Contaminant Assessment Approach

Because very little was known about the contaminant concentrations and potential impacts in any of the western national parks at that time, an inventory of baseline SOCs, metals, and nutrient contaminants across various ecosystem components (i.e., snow, water, vegetation, fish, and sediment) was selected as the approach to be taken (Table 1-2). "Impacts" in the goal statement refers to evidence of accumulation in the food web—particularly animals—and does not go so far as to attempt to establish "effects," such as reproductive or lethal responses.

The specific objectives that guided the development of WACAP were also thoroughly examined and approved by both the scientific team and the NPS:

1. Determine if contaminants are present in western national parks.
2. If contaminants are present, determine where they are accumulating (geographically and by elevation).
3. If contaminants are present, determine which ones pose a potential ecological threat.
4. Determine which indicators appear to be the most useful to assess contamination.
5. If contaminants are present, determine the source of the air masses most likely to have transported contaminants to the national parks sites.

Table 1-1. WACAP Report Authors

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[1] NPS = National Park Service, USGS = US Geological Survey, USDA-FS = US Dept. of Agriculture Forest Service, OSU = Oregon State University, USEPA = US Environmental Protection Agency

Table 1-2. Ecosystem Components Sampled for WACAP

Media	Frequency of Sampling	Purpose
Snow	Annually in the spring in each of the 14 sites in the 8 core parks	Direct measure of annual atmospheric loading; snow is 90% of annual precipitation in many alpine sites
Fish	Once in each of the 14 sites in the 8 core parks	Direct measure of food web impacts and food web bioaccumulation/biomagnification
Water	Once in each of the 14 sites in the 8 core parks	Measure of hydrophilic current-use chemicals and baseline water chemistry
Lake Sediment	Once in each of the 14 sites in the 8 core parks	Provides historic trends (~150 yrs) of contaminant loading to watershed
Vegetation	Once as elevation transects in the 8 core parks and 12 secondary parks	Direct measure (conifer and lichens) of food web bioaccumulation of nitrogen, sulfur, mercury and other metals Measure (lichens at core parks) of ecosystem exposure for SOCs; large number for statistical comparisons within and among sites, parks and elevations at a broad spatial scale
Air	Deployed PASDs (passive air sampling devices) for approximately one year in most core and secondary parks	Estimate of airborne exposure of SOCs at a site over a period of time
Moose	Once from several Alaska sites	Direct measure of subsistence food resources
Atmospheric Transport	Models developed based on 5 years of data for each park	Back trajectory models identify likely sources of contaminants

1.3 Park Selection

One of the most difficult issues was identifying which national parks should be included in the spatial design. We initially determined that we could include six parks, based on the estimated budget available for the effort, assuming that each park would have two intensive sites (i.e., lakes). However, with additional funding committed from “fee demo” sources, we were able to include 8 parks and 14 core sites. These sites, and the lakes in particular, were perceived to be natural precipitation/deposition collectors, representing some of the most remote, undisturbed remaining landscapes in the western United States. Contaminants collected at these sites were presumed not to be derived from local sources or historic land uses within the parks, given their National Park designation. However, we recognized the potential for the proximal influence of local and regional atmospheric contaminant sources and planned to interpret results with this in mind. We decided which parks to include based on the physical locations and characteristics of the parks rather than any other criteria. Through an iterative process, we identified indicators of interest, determined the number of sites in each park, set criteria for the attributes of sites within parks, and consulted with experts at each park, all with consideration for the overall spatial design and acknowledgment of budget realities.

It was clear from the outset that a strong spatial design containing enough sites to provide ample statistical power for hypothesis testing was outside the budget and scope of this project. Moreover, given the absolute lack of information of any kind regarding the impacts of airborne contaminants on the systems of interest, it seemed unwarranted and premature to pursue such a design, even if funding had been available. Rather, we decided that the first question that needed to be answered across large-scale spatial gradients appropriate to the western national parks was, “Is there a problem with respect to contaminants in the parks?” It was decided that if this policy question could be answered in a rigorous way by WACAP, then future work, if warranted, could be designed to deal with a more detailed secondary set of objectives based on the results of WACAP. These secondary objectives might include resolving the various temporal and spatial dimensions of contaminant pathways and defining and documenting specific ecological effects.

Because trans-Pacific air masses moving generally from west to east affect the west coast of the North American mainland from Alaska to California (Bailey et al., 2000; Husar et al., 2001), we selected a series of national parks ranging from Arctic Alaska south to California. Our intent was to identify a core set of western national parks along a north-south latitudinal gradient that could be affected by air masses moving across the Pacific Ocean. We wanted to accomplish this while recognizing that air masses originating in North America are also of potential interest and should be considered. We also wanted to include some parks in the interior of the western United States that could be affected by trans-Pacific air masses but that might be influenced more by regional air masses. We selected six west coast parks (NOAT, GAAR, DENA, OLYM, MORA, and SEKI) and two interior parks (GLAC and ROMO), for a total of eight core parks where all media would be sampled and evaluated. GAAR is juxtaposed to NOAT, thus we selected one site in each. As a result, 14 sites/lakes are associated with the core parks. Table 1-3 lists the locations of the lake sites in the core parks.

To provide better coverage, we identified 12 additional (secondary) parks where vegetation samples for SOC analyses would be collected. Vegetation samples from multiple sites representing a range of elevations were taken from both the core and secondary parks (Table 1-4) to provide a better understanding of contaminant deposition in the west. In 2005, we also deployed passive air sampling devices (PASDs) for one year in both core parks and secondary parks as a means of further linking our spatial interpretations.

Table 1-3. WACAP Sites in Core Parks. All media were sampled, including water, snow, air (PASDs), vegetation (conifer needles and lichens), fish, and sediments. Parks are listed alphabetically by park code.

Park Code	Park[1]	State	Lake Site	Latitude[2] (dd)	Longitude[2] (dd)	Lake Elevation[3] (m)	Year Sampled
DENA	Denali NP and Preserve	Alaska	McLeod	63.38	-151.07	564	2004
DENA	Denali NP and Preserve	Alaska	Wonder	63.48	-150.88	605	2004
GAAR	Gates of the Arctic NP and Preserve	Alaska	Matcharak	67.75	-156.21	502	2004
GLAC	Glacier NP	Montana	Oldman	48.50	-113.46	2026	2005
GLAC	Glacier NP	Montana	Snyder	48.62	-113.79	1597	2005
MORA	Mt. Rainier NP	Washington	Golden	46.89	-121.90	1369	2005
MORA	Mt. Rainier NP	Washington	LP19	46.82	-121.89	1372	2005
NOAT	Noatak National Preserve	Alaska	Burial	68.43	-159.18	430	2004
OLYM	Olympic NP	Washington	Hoh	47.90	-123.79	1380	2005
OLYM	Olympic NP	Washington	PJ	47.95	-123.42	1384	2005
ROMO	Rocky Mountain NP	Colorado	Lone Pine	40.22	-105.73	3018	2003
ROMO	Rocky Mountain NP	Colorado	Mills	40.29	-105.64	3030	2003
SEKI	Sequoia and Kings Canyon NP	California	Emerald	36.58	-118.67	2810	2003
SEKI	Sequoia and Kings Canyon NP	California	Pear	36.60	-118.67	2908	2003

[1]NP = National Park, [2]dd= decimal degrees; [3] from drg (digital raster graphic), m = meter

The selection of the core set of national parks provides a group of 8 parks ranging over 30 degrees of latitude with 2 pairs of parks (one coastal and one interior) rather closely linked at about the same latitude (OLYM and GLAC; SEKI and ROMO). This spatial arrangement, along with the location of the secondary parks, is depicted in Figure 1-2, in association with EPA Level 1 Ecoregions (http://www.epa.gov/bioiweb1/html/usecoregions.html).

The dominant factor influencing the deposition and accumulation of SOCs in the ecosystem is temperature. This is especially true for those contaminants that demonstrate cold fractionation. Figure 1-3 depicts the mean annual air temperature one could expect at each of the WACAP sites in the eight core national parks. Temperature data were estimated from the nearest and most representative locations with long-term meteorological data. In some cases, a small correction was made to account for the difference in altitude between the meteorological and lake site (D. Jaffe, pers. comm., University of Washington, Bothel). It is useful to notice that there is general agreement in temperature for all of the sites in the conterminous United States, and that the four sites in Alaska, although lower in elevation, are significantly colder.

Table 1-4. Vegetation WACAP Sites in Core and Secondary Parks (SOCs in conifer needles, lichens, and PASDs[1]). Parks are listed alphabetically by park code, with core parks in bold.

Park Code	Park[2]	State	No. of Vegetation Sampling Sites	Minimum Elevation of Sites (m)	Maximum Elevation of Sites (m)	No. of Air Sampling Sites	Year Sampled
BAND	Bandelier National Monument	New Mexico	5	1854	2926	1	2005
BIBE	Big Bend NP	Texas	5	560	2316	4	2005
CRLA	Crater Lake NP	Oregon	5	1798	2713	1	2005
DENA	**Denali NPP**	**Alaska**	**6**	**221**	**1753**	**2**	**2004**
GAAR	**Gates of the Arctic NPP**	**Alaska**	**1**	**505**	**505**	**1**	**2004**
GLAC	**Glacier NP**	**Montana**	**5**	**961**	**2024**	**2**	**2004**
GLBA	Glacier Bay NPP	Alaska	4	8	625	1	2005
GRSA	Great Sand Dunes NPP	Colorado	5	2469	3338	1	2005
GRTE	Grand Teton NP	Wyoming	5	2073	3048	1	2005
KATM	Katmai NPP	Alaska	6	36	1112	1	2005
LAVO	Lassen Volcanic NP	California	5	1829	2713	1	2005
MORA	**Mt. Rainier NP**	**Washington**	**5**	**654**	**1809**	**2**	**2004**
NOAT	**Noatak National Preserve**	**Alaska**	**3**	**227**	**675**	**1**	**2004**
NOCA	North Cascades NP	Washington	5	198	1600	1	2005
OLYM	**Olympic NP**	**Washington**	**5**	**137**	**1850**	**2**	**2004**
ROMO	**Rocky Mountain NP**	**Colorado**	**6**	**2560**	**3451**	**5**	**2004**
SEKI	**Sequoia & Kings Canyon NPs**	**California**	**11**	**427**	**2911**	**4**	**2003 & 2004**
STLE	Stikine-LeConte Wilderness, Tongass NF	Alaska	5	1	1064	4	2005
WRST	Wrangell-St. Elias NPP	Alaska	6	7	1421	1	2005
YOSE	Yosemite NP	California	5	661	3048	1	2005

[1] PASDs = passive air sampling devices, [2]NP = National Park, NF = National Forest, NPP = National Park and Preserve

1.4 Site Selection Within Parks

Within each of the core national parks, we selected two catchments containing lakes (i.e., sites) that met the following pre-established criteria.

- Catchment is small, typical of the catchments found in the park (elevation, soils, vegetation, aspect, etc.).
- Catchment contains a lake (≥5 m deep; larger than ~0.8 hectares in surface area).
- Lake contains reproducing fish populations (preferably salmonids).
- No anadromous fish reach the lake.
- Lake is without major inlets, outlets, or glaciers in the catchment.
- Lake bathymetry is acceptable for sediment core analysis.

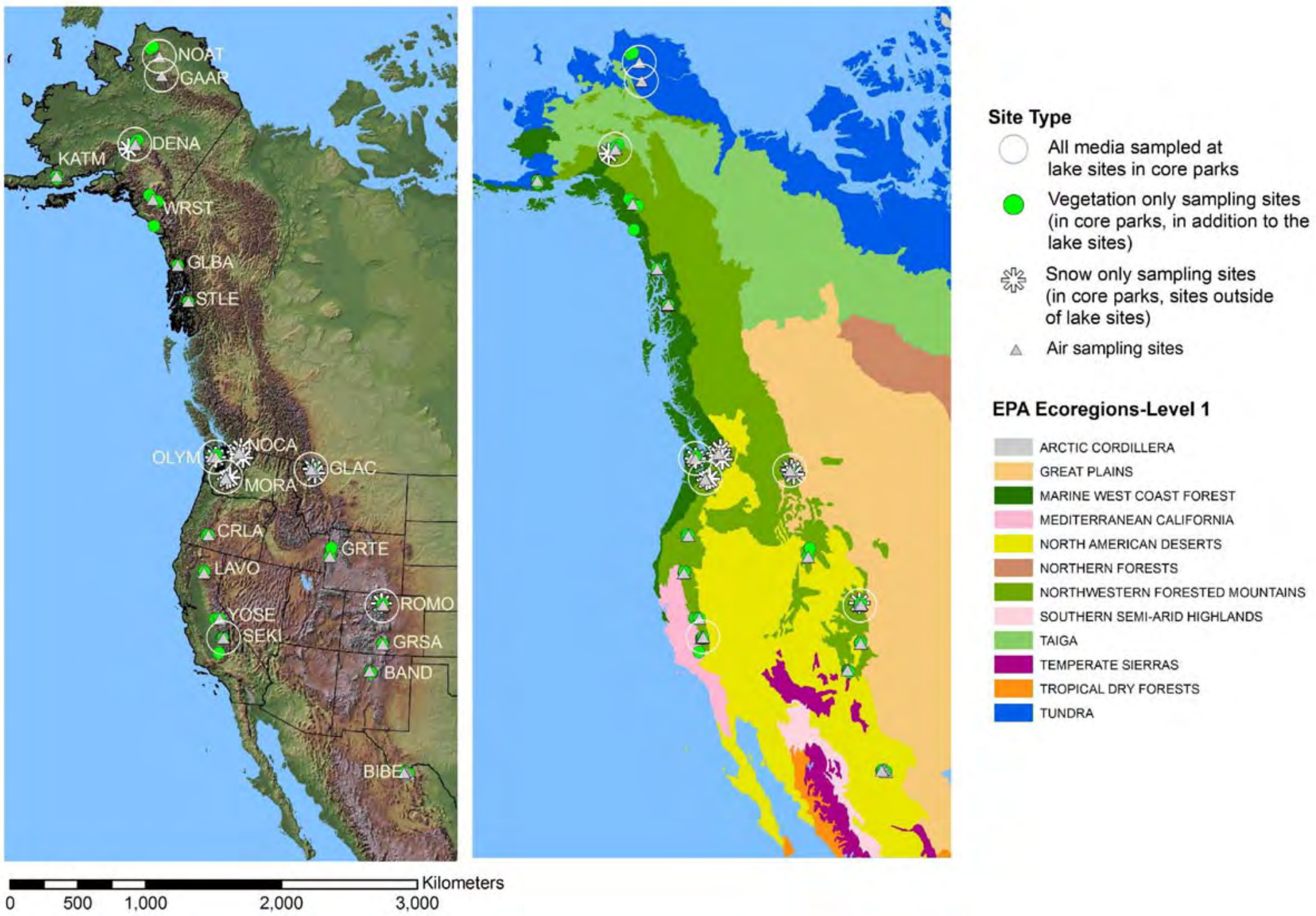


Figure 1-2. WACAP Sites Mapped on North American Shaded Relief Map and EPA Level 1 Ecoregions (Biomes). See Table 1-4 for key to national park abbreviations. Vegetation-only sampling sites in core parks designate sites used in elevational transect in addition to lake sites. Snow-only sampling sites in core parks designate alternate sampling locations when lake sites could not be reached safely.

- Safe access is possible by available means in late spring and summer.
- Gill netting of fish is acceptable.
- Catchments are located within the seasonally persistent, non-melting snowpack development for the park.
- Both catchments are located in the same general quadrant within the park.

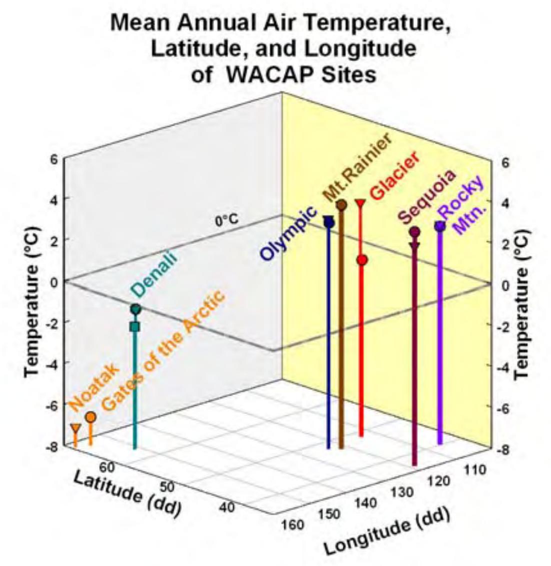


Figure 1-3. Relationships among Latitude, Longitude, and Mean Annual Temperature in the 8 National Parks and 14 Sites Sampled in WACAP.

Variability with respect to biogeophysical setting (e.g., lake and basin morphometry, vegetation, fish, etc.) was large among candidate catchments within and among parks as the WACAP research team set out to select appropriate sites. Given the large geographic scale of WACAP, several major ecological regions were included in the final selection (see Figure 1-2). We selected sites within parks that were located at similar elevations and generally in the same type of biogeophysical setting, where possible.

Candidate sites were evaluated by Dr. Dan Jaffe (WACAP atmospheric science lead) prior to final selection to maximize the possibility that atmospheric transport pathways between sites in the same park would be similar, based on available deposition and atmospheric data available only at a fairly coarse scale. The two exceptions to this strategy are in ROMO and GLAC, where the selected lakes are at almost the same elevation but on opposite sides of the Continental Divide.

Our final catchment selections in each core park represent "elevation duplicates," in the sense that they are located at approximately the same elevation. Table 1-5 summarizes the attributes of the selected catchments/lakes for each core park. Appendix 1A contains more detailed tables of site physical and chemical characteristics for both the lake catchments in the core parks and the vegetation sites in the secondary parks. Chapter 2 provides maps showing the locations of the selected sites within each park, along with bathymetric maps of the lakes. In addition, Chapter 2 summarizes much of this site information, as well as the analytical results graphically for each site within each park within the context of the overall range of conditions found in all core WACAP parks.

Figure 1-4 depicts the relationships among WACAP indicators and the broader contaminant pathways, sources, sinks, and ecosystem components. The diagram is not all inclusive; it shows key components addressed by WACAP and some of the components and contaminant pathways that were not evaluated. The diagram should assist the unfamiliar reader with some of the complexity that WACAP examined and the ecological position and interrelationships among key areas of investigation.

Table 1-5. WACAP Lake Sites: Selected Physical and Surface (1 m) Chemical Characteristics[1] Collected during WACAP Site Visits According to Methods Listed in Chapter 3. Parks are listed by latitude, from north to south.

Park Code	Lake Name (Site)	Lake Surface Area[2] (ha)	Watershed Area (ha)	Fish Species	pH	Specific Cond. (µS/cm)	ANC (µeq/L)	DOC (mg/L)	Total P (µg/L)	Chl-a (µg/L)
NOAT	Burial	65.5	264.9	Lake trout	7.57	35.08	272.98	3.32	9.1	0.81
GAAR	Matcharak	300.7	2388.3	Lake trout	8.31	248.10	1967.03	4.71	1.1	0.96
DENA	Wonder	265.6	3212.4	Lake trout	8.18	190.10	1693.60	2.10	0.5	0.49
DENA	McLeod	35.9	236.8	Burbot Round whitefish	7.24	8.41	51.02	2.25	1.0	0.61
GLAC	Snyder	2.6	303.7	Westslope Cutthroat trout	6.42	16.80	162.08	0.65	2.7	4.73
GLAC	Oldman	18.2	230.3	Yellowstone River Cutthroat trout	8.24	159.10	1573.73	0.70	0.6	0.77
OLYM	PJ	0.8	56.2	Brook trout	8.14	127.40	1092.95	1.05	2.8	1.77
OLYM	Hoh	7.7	43.9	Brook trout	7.52	63.69	512.45	0.74	1.2	0.83
MORA	Golden	6.6	106.1	Brook trout	6.47	10.08	69.05	1.88	0.6	0.35
MORA	LP19	1.8	44.9	Brook trout	6.63	10.72	80.14	1.37	0.9	0.60
ROMO	Mills	6.1	1208.9	Rainbow Cutthroat trout	6.61	12.04	50.81	1.55	3.3	3.02
ROMO	Lone Pine	4.9	1830.0	Brook trout	6.67	14.02	91.52	1.74	2.7	1.95
SEKI	Pear	7.3	142.0	Brook trout	6.10	4.02	23.99	0.82	0.6	0.64
SEKI	Emerald	2.5	121.3	Brook trout	6.22	5.42	26.34	0.94	1.5	0.62

[1] Specific Cond.= Specific Conductance; ANC = acid neutralizing capacity, DOC= dissolved organic carbon, Total P = total phosphorus, Chl a = chlorophyll a.

[2] ha = hectare.

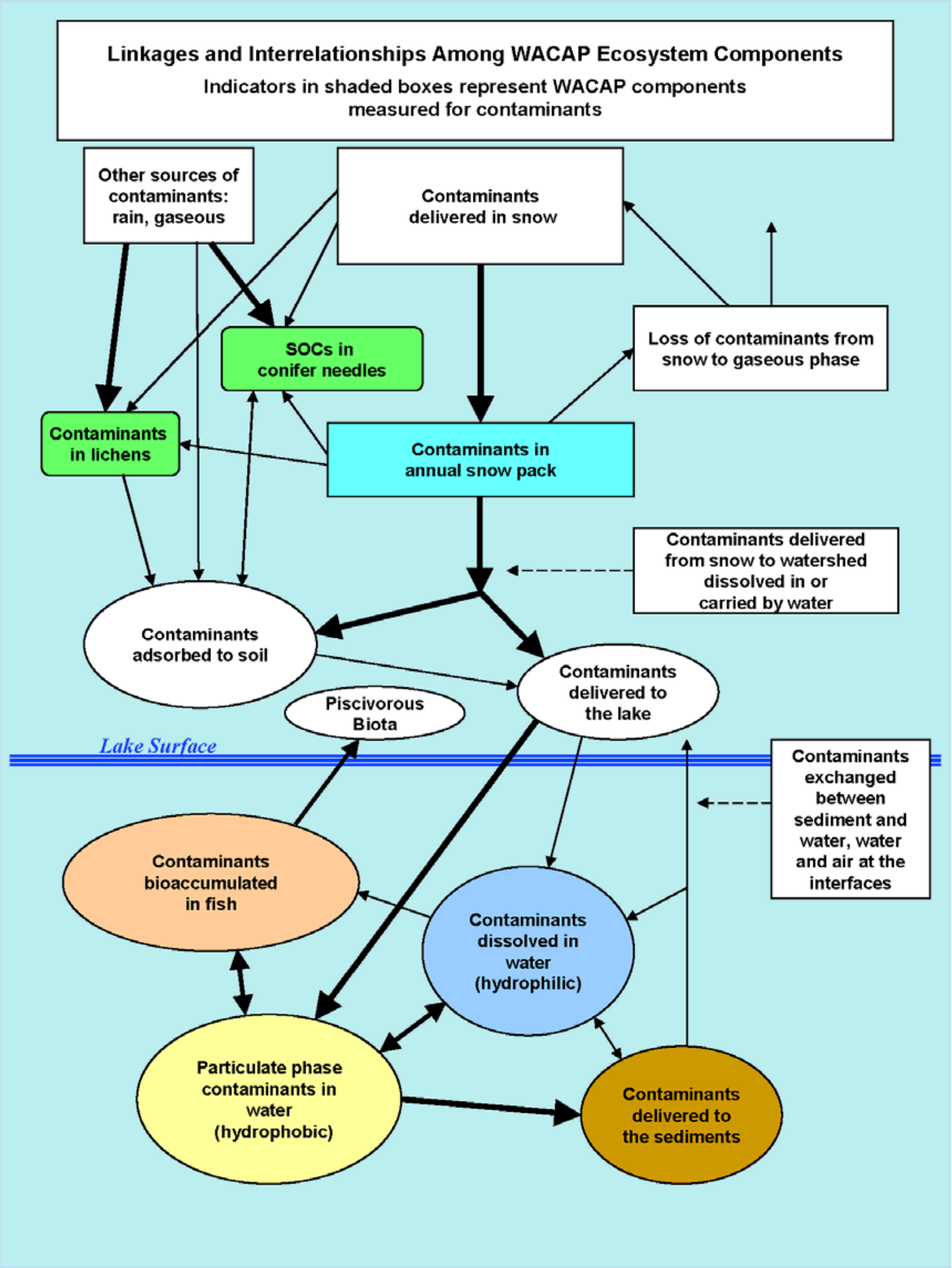


Figure 1-4. Linkages among Major WACAP and Ecosystem Components, Contaminant Pools, and Pathways. Colored components indicate those investigated for contaminants as part of WACAP.

1.5 Measurements and Contaminants

A wide variety of measurements could be used to provide information regarding the degree to which airborne contaminants have become entrained in national park ecosystems. Similarly, a large group of contaminants could be measured. One of the early WACAP design tasks was to winnow the expansive list of possible measurements, as well as contaminants, down to a manageable and affordable number. In doing this, we frequently referred back to the WACAP goal and objectives to ensure that selected indicators collectively fulfilled broad, and in some cases, multiple, purposes. Moreover, a secondary concern was to select indicators that would compare to other similar ongoing and historic studies (e.g., the European Union EMERGE program; Livingstone, 2005) regarding contaminant impacts in remote alpine and arctic locations. Chapter 3 in this report identifies the contaminants of interest and discusses the methods used in their analyses.

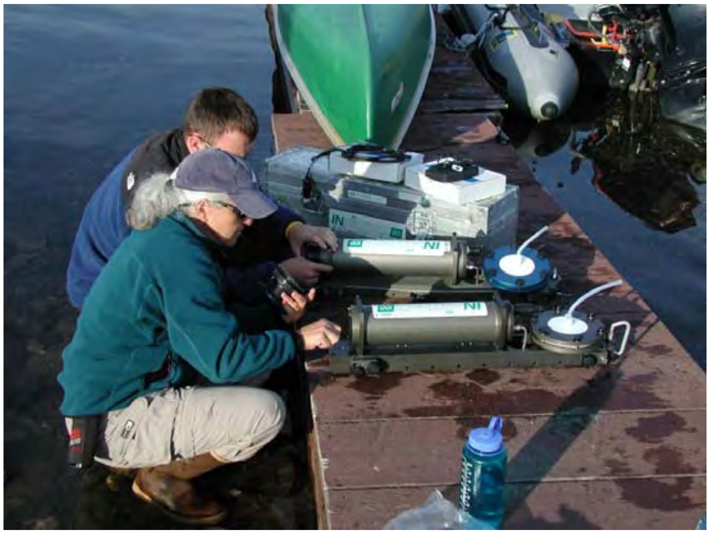
1.6 Timeline, Implementation, and Reporting

The 6-year WACAP began in fiscal year 2002 (October 2001 through September 2002) and continued through fiscal year 2007. Year 1 was a pilot year devoted to design, organization, funding for principal investigators, and methods development for the project. Some methods development continued into fiscal year 2003. Fieldwork and associated laboratory work were conducted during fiscal years 2003, 2004, and 2005. The final two years, 2006–2007, were devoted to finishing analytical work, analyzing data, writing the final report, preparing and publishing the final WACAP database, and publishing the results in the peer literature. Table 1-6 depicts the sequencing and timing of field collections acquired as part of WACAP.

Table 1-6. WACAP Timeline and Site Sampling Strategy.

Year	Activity			
Year 1 (2002)	Design, organization, methods development, written research plan, peer review, quality assurance plan			
	Annual snow sampling	***Intensive Study Year (fish, water, sediment)***	***Vegetation/Air Sampling***	***Moose Sampling***
Year 2 (2003)	All 8 parks (14 sites)	SEKI, ROMO (4 sites)	Pilot study to choose target vegetation & needle age	
Year 3 (2004)	All 8 parks (14 sites)	NOAT, DENA, and GAAR (4 sites)	Lichen and conifer needle sampling in 8 core parks (14 sites)	Moose from DENA
Year 4 (2005)	All 8 parks (14 sites)	OLYM, MORA, and GLAC (6 sites)	Lichen and conifer needle sampling in 12 secondary parks (61 sites); PASD installation in all parks	Moose from DENA
Year 5 (2006)	Data analyses, synthesis, publications, PASD retrieval in all parks			
Year 6 (2007)	Final NPS report, final database			

1.7 Data Management and Quality Assurance/Quality Control



Data management occurred at several levels throughout the project. Laboratory analyses were summarized, along with all QA/QC results at the batch level. This data management activity was guided by the QAPP (Quality Assurance Project Plan available on the WACAP web site: http://www2.nature.nps.gov/air/Studies/air_toxics/wacap.cfm. In this document, we use the term "media" to describe the major environmental compartments we analyzed (e.g., snow, water, fish). Batches of data were combined for each medium/indicator and forwarded to the appropriate principal investigators. Copies of these data were maintained by the analytical laboratories and a copy was sent to the WACAP coordination group at EPA (Corvallis). The coordination group confirmed laboratory QA/QC procedures and worked with each laboratory group to verify and validate the data on a batch-by-batch basis. The overall objective was to incorporate these data, along with metadata derived from a variety of sources (e.g., reconnaissance, field work, principal investigators, laboratories, park resources), into a working, integrated database. Modeled and GIS-derived data were also entered into this database. The database was combined into a final master database of the WACAP data in 2007. The final database is intended as a final repository for the data resulting from the work conducted during WACAP and will contain all data and associated QA/QC information. The final database will be published as a peer reviewed EPA report and made available to the public via several government website locations. It will also be stored permanently in NPS and USEPA searchable data archival systems. The general website address for the NPS Data Store is http://science.nature.nps.gov/nrdata/ and the general website address for the EPA location is http://www.epa.gov/nheerl/wacap/.

We participated in four levels of reporting for the WACAP data:

1. Professional papers (journal articles, dissertations, theses) generated by individual principal investigators
2. Synthesis journal articles prepared by various combinations of principal investigators
3. Annual information summaries prepared as NPS brochures
4. Final report

In addition, principal investigators and other key WACAP personnel have been active in their disciplinary societies by making oral presentations at annual national and international meetings.

1.8 WACAP Direction and Funding

WACAP was administered and funded primarily by the Air Resources Division (ARD) of the NPS, directed by Ms. Christine Shaver, in Lakewood, Colorado. Funding was derived from a variety of sources (base funding, competitive, and fee-demo) within ARD and NPS that varied among years and funding cycles. In this context, interagency agreements between the NPS and the US Geological Survey (USGS), the USEPA, and the US Forest Service (USFS) facilitated funding. Supplemental funding with in-kind services was provided by these federal agencies, the Oregon Cooperative Fish and Wildlife Research Unit and the Center for Fish Disease Research, OSU. NPS funding for university participants was accomplished through the NPS Cooperative Ecosystem Studies Unit (CESU) Cooperative Agreements process. In addition, several principal investigators have sought and received funding from a variety of sources external to the NPS to supplement funding they receive from ARD/NPS. These funds have been targeted to support graduate students, supply research equipment, and provide supplemental technical support. The USGS has contributed additional funding for the snow contaminants work. The success of WACAP depended upon continued funding from the NPS and its collaborators at annual levels sufficient to support the core WACAP efforts described in the research plan (USEPA, 2003). Funding was forthcoming and WACAP proceeded to completion as planned.

1.9 Organization of this Report

This final WACAP interpretive report is organized into six major chapters. An overview of each chapter and the name of the chapter organizer follow.

Chapter 1. Introduction (Dixon Landers)

Chapter 1 (this chapter) provides the background, goals, objectives, approach, and design considerations for WACAP.

Chapter 2. Park Summaries (Dixon Landers)

The park-by-park summaries provide a quick but in-depth graphical overview of the key results from the two sites within each core park and show how key variables associated with these sites compare with each other and among results from all other parks. The two-page graphical summary for each park is followed by a one-page written summary that identifies key findings for the sites and the specific park, along with major differences and similarities among the various measurements and the group of WACAP parks as a whole.

Chapter 3. Contaminants Studied and Methods Used (Staci Simonich)

In this chapter, all contaminants are identified and discussed regarding their occurrence in the environment and the methods used to sample, extract, and quantify them in the various media, or components, of the ecosystems sampled.

Chapter 4. Contaminant Distribution (Dan Jaffe)

This chapter interprets results of the WACAP effort for all components spatially, vertically, and temporally. Media-specific spatial results are evaluated across the geographic area encompassing the entire project. Vertical evaluations are limited to vegetation results among both core and secondary parks and among all contaminants. Snow and sediment analyses are used to evaluate inter-annual variation (snow) and decennial resolution and trends (sediment).

Chapter 5. Biological and Ecological Effects (Linda Geiser)

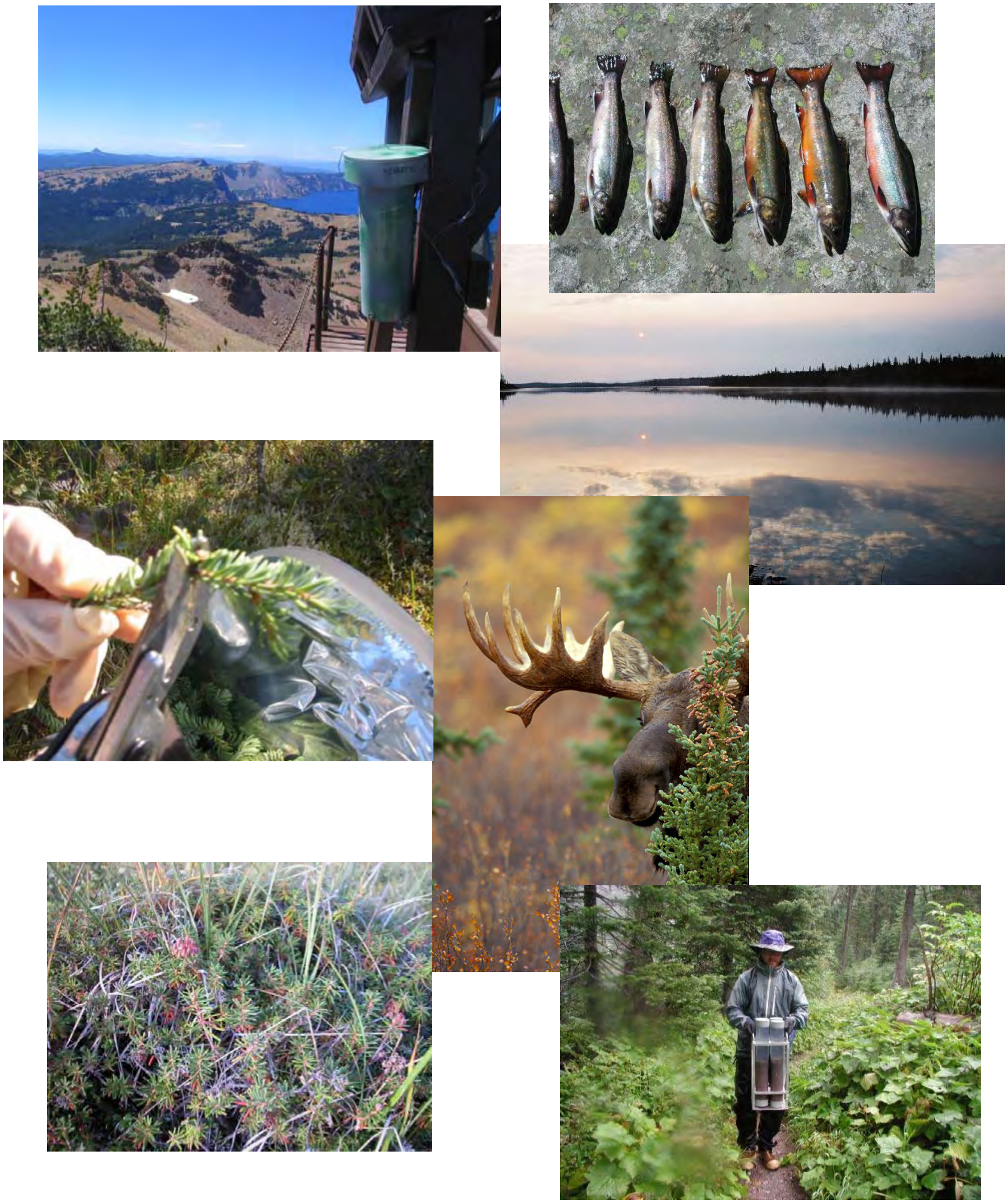
In this chapter, a variety of results that lend themselves to evaluation of the impacts and effects of contaminants in various media are examined. For fish, accepted pathological and physiological indicators of contaminant exposure are related to contaminant concentrations. Inferences on reproductive and overall health are made based on these relationships.

Chapter 6. Conclusions and Recommendations

Chapter 6 contains recommendations to the National Park Service that respond to the question, "What did you learn in this project that could help guide or focus future work within the NPS on contaminants in western U.S. parks?" These recommendations are specific to the original five project objectives. Also included is a list of additional research questions posed by WACAP scientists. These questions define fertile areas for future research into processes, mechanisms, and ecological interactions of contaminants in western ecosystems.

Volume II. Appendices

The appendices provide supplemental information about the WACAP findings.



CHAPTER 2

Park Summaries

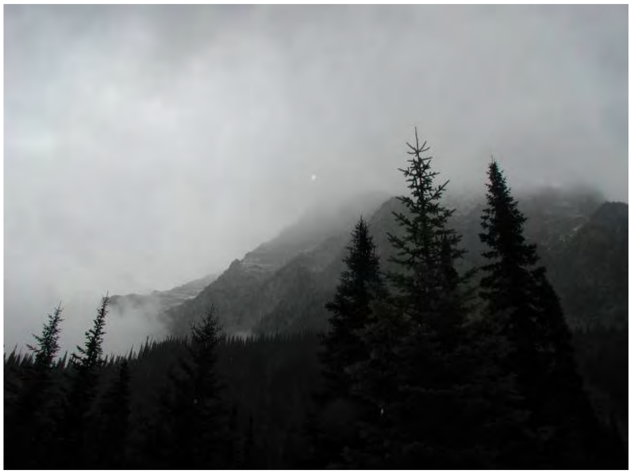
Introduction

This chapter contains summary information for the eight core parks (pages 2-4 to 2-31) and the twelve secondary parks (pages 2-34 to 2-45). Information for the core parks includes a one-page written summary organized by media (air, snow, vegetation, fish, and sediment), and a two-page graphical summary of the results. The key to these two-page graphical summaries is on pages 2-2 and 2-3. The air and vegetation summary results from the secondary parks begin on page 2-32, with the key to the one-page graphical summaries for these parks on page 2-33.

Core Parks

The park summaries that follow in this chapter have been prepared to provide the reader with an overview of selected contaminant results for each core WACAP national park. The descriptions for the Arctic parks, GAAR and NOAT, with one lake site each, have been combined into one summary.

These summaries contain a considerable amount of information, but do not represent all data and information available for the parks. The two-page key for the core parks provides explicit detail regarding each block of information the reader will encounter on the two-page graphic summaries and is intended to guide the reader through the summaries. Summaries for all core parks are presented in the same format. The summaries are designed so that the two lake sites within each park can easily be compared and the relative position of these sites within the context of all WACAP core parks can also be visualized. The reader is encouraged to consult the other chapters of this report for more detailed information on the full range of WACAP results and their interpretation.

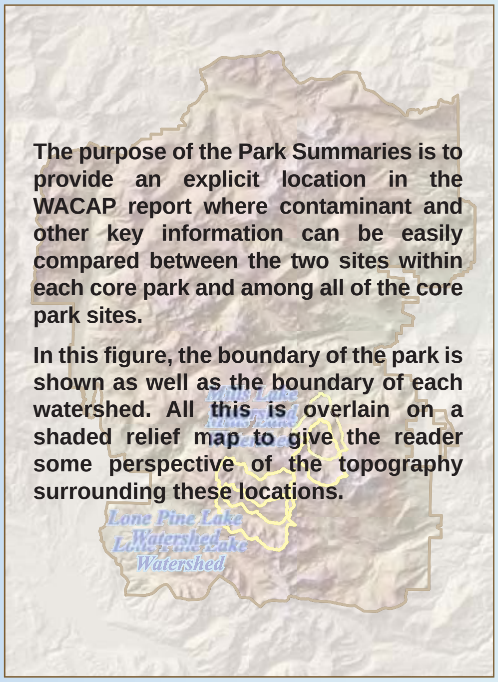


Key to Park Summaries: *Site Characteristics*

KEY

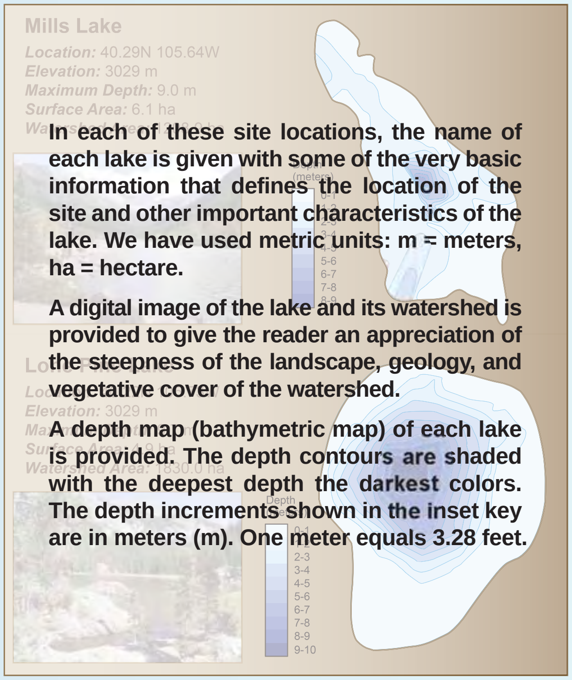
The Park Summaries that follow in this chapter have been prepared to provide the reader with a summary of selected contaminant results for each core WACAP national park. A set of reduced summaries for the secondary parks that contain only vegetation results follows the core park summaries, with a separate key. The Arctic parks GAAR and NOAT, with one lake site each, have been combined into one summary. These summaries contain a considerable amount of information, but do not represent all data and information available for the parks. This two-page Key provides explicit detail regarding each block of information the reader will encounter on the two-page graphical summaries and is intended to guide the reader through the summaries. Summaries for all parks are presented in the same format. The summaries are designed so the two lake sites within each park can easily be compared and the relative position of these sites within the context of all WACAP core parks can be visualized. The reader is encouraged to consult the other chapters of this report for more detailed information on the full range of WACAP results and their interpretation.

Park and Lake Setting



The purpose of the Park Summaries is to provide an explicit location in the WACAP report where contaminant and other key information can be easily compared between the two sites within each core park and among all of the core park sites.

In this figure, the boundary of the park is shown as well as the boundary of each watershed. All this is overlain on a shaded relief map to give the reader some perspective of the topography surrounding these locations.

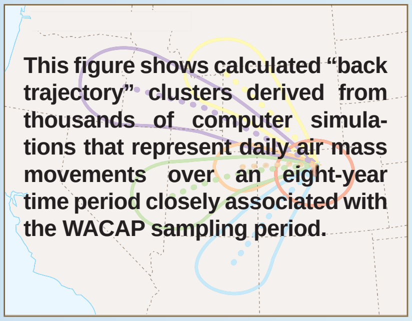


In each of these site locations, the name of each lake is given with some of the very basic information that defines the location of the site and other important characteristics of the lake. We have used metric units: m = meters, ha = hectare.

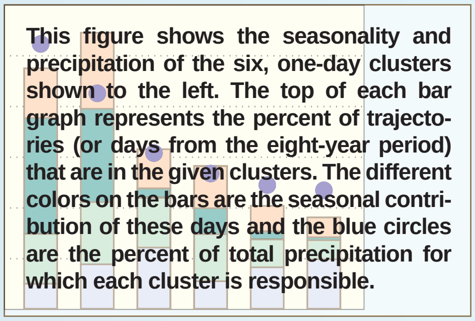
A digital image of the lake and its watershed is provided to give the reader an appreciation of the steepness of the landscape, geology, and vegetative cover of the watershed.

A depth map (bathymetric map) of each lake is provided. The depth contours are shaded with the deepest depth the darkest colors. The depth increments shown in the inset key are in meters (m). One meter equals 3.28 feet.

Atmospheric Transport

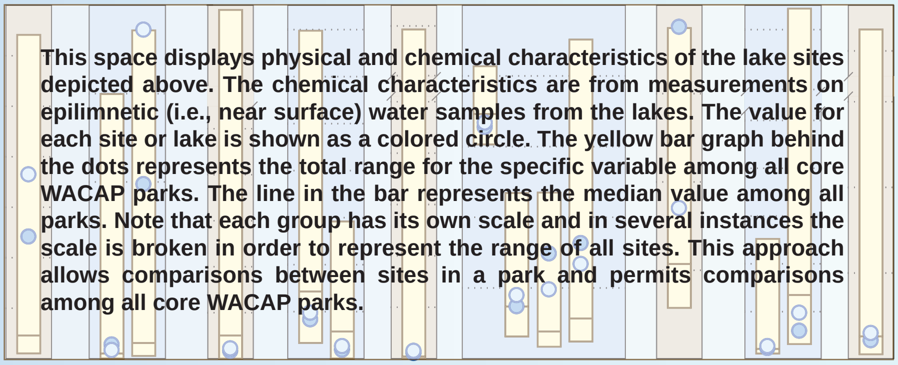


This figure shows calculated "back trajectory" clusters derived from thousands of computer simulations that represent daily air mass movements over an eight-year time period closely associated with the WACAP sampling period.



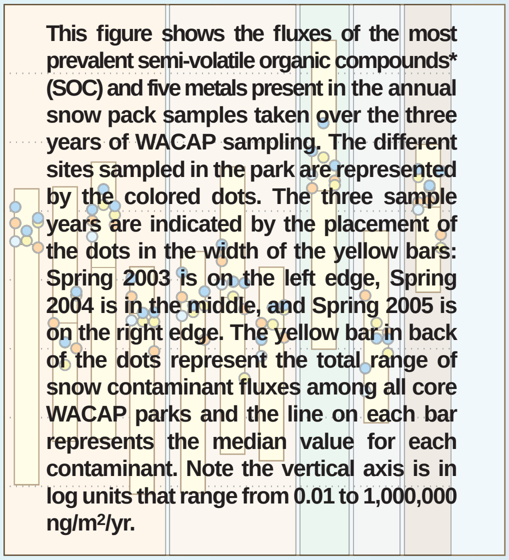
This figure shows the seasonality and precipitation of the six, one-day clusters shown to the left. The top of each bar graph represents the percent of trajectories (or days from the eight-year period) that are in the given clusters. The different colors on the bars are the seasonal contribution of these days and the blue circles are the percent of total precipitation for which each cluster is responsible.

Physical and Chemical Characteristics



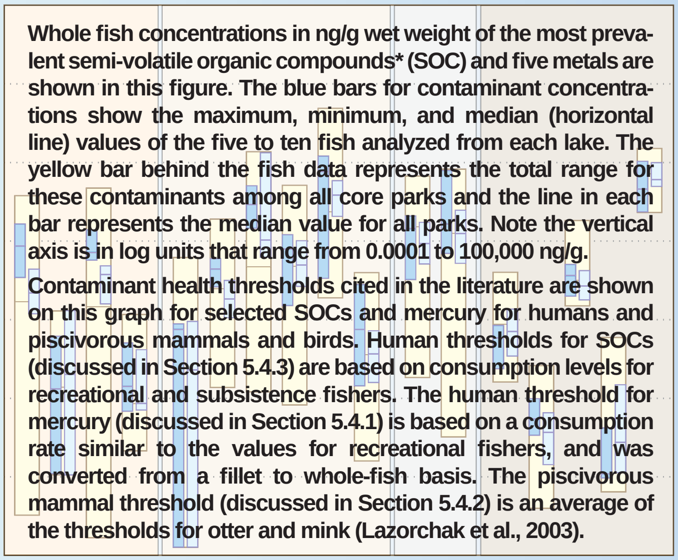
This space displays physical and chemical characteristics of the lake sites depicted above. The chemical characteristics are from measurements on epilimnetic (i.e., near surface) water samples from the lakes. The value for each site or lake is shown as a colored circle. The yellow bar graph behind the dots represents the total range for the specific variable among all core WACAP parks. The line in the bar represents the median value among all parks. Note that each group has its own scale and in several instances the scale is broken in order to represent the range of all sites. This approach allows comparisons between sites in a park and permits comparisons among all core WACAP parks.

Snow Contaminant Fluxes



This figure shows the fluxes of the most prevalent semi-volatile organic compounds* (SOC) and five metals present in the annual snow pack samples taken over the three years of WACAP sampling. The different sites sampled in the park are represented by the colored dots. The three sample years are indicated by the placement of the dots in the width of the yellow bars: Spring 2003 is on the left edge, Spring 2004 is in the middle, and Spring 2005 is on the right edge. The yellow bar in back of the dots represent the total range of snow contaminant fluxes among all core WACAP parks and the line on each bar represents the median value for each contaminant. Note the vertical axis is in log units that range from 0.01 to 1,000,000 ng/m^2/yr.

Whole Fish Contaminant Concentrations

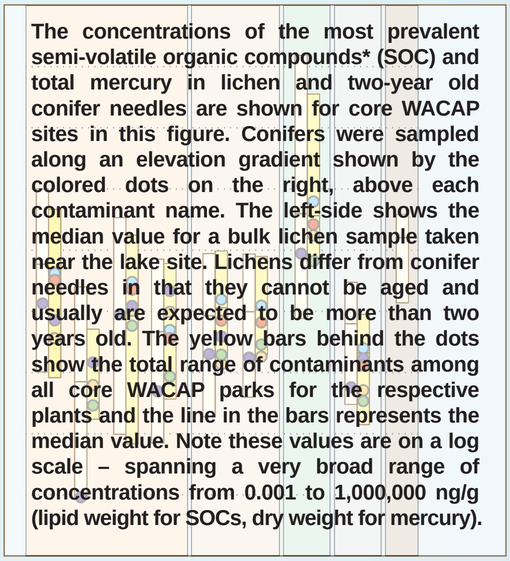


Whole fish concentrations in ng/g wet weight of the most prevalent semi-volatile organic compounds* (SOC) and five metals are shown in this figure. The blue bars for contaminant concentrations show the maximum, minimum, and median (horizontal line) values of the five to ten fish analyzed from each lake. The yellow bar behind the fish data represents the total range for these contaminants among all core parks and the line in each bar represents the median value for all parks. Note the vertical axis is in log units that range from 0.0001 to 100,000 ng/g.

Contaminant health thresholds cited in the literature are shown on this graph for selected SOCs and mercury for humans and piscivorous mammals and birds. Human thresholds for SOCs (discussed in Section 5.4.3) are based on consumption levels for recreational and subsistence fishers. The human threshold for mercury (discussed in Section 5.4.1) is based on a consumption rate similar to the values for recreational fishers, and was converted from a fillet to whole-fish basis. The piscivorous mammal threshold (discussed in Section 5.4.2) is an average of the thresholds for otter and mink (Lazorchak et al., 2003).

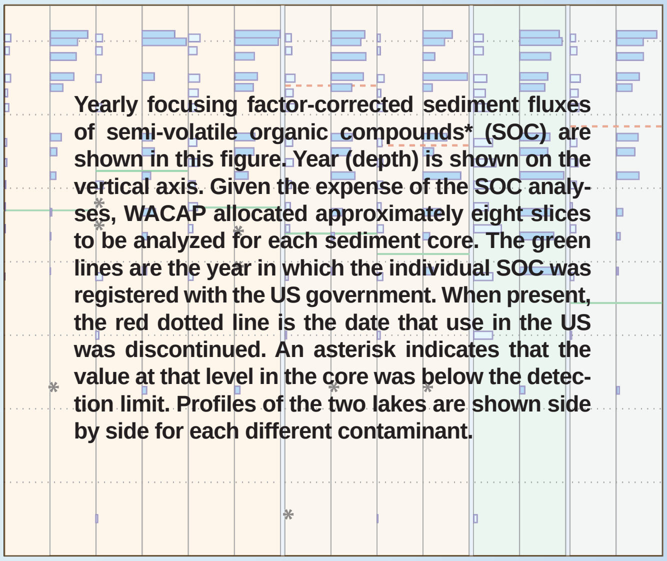
**SOC groupings by compound class are listed in Table 4-1.*

Vegetation Contaminant Concentrations



The concentrations of the most prevalent semi-volatile organic compounds* (SOC) and total mercury in lichen and two-year old conifer needles are shown for core WACAP sites in this figure. Conifers were sampled along an elevation gradient shown by the colored dots on the right, above each contaminant name. The left-side shows the median value for a bulk lichen sample taken near the lake site. Lichens differ from conifer needles in that they cannot be aged and usually are expected to be more than two years old. The yellow bars behind the dots show the total range of contaminants among all core WACAP parks for the respective plants and the line in the bars represents the median value. Note these values are on a log scale – spanning a very broad range of concentrations from 0.001 to 1,000,000 ng/g (lipid weight for SOCs, dry weight for mercury).

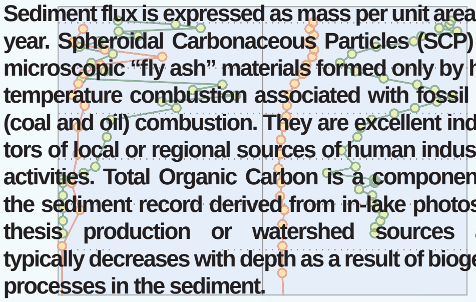
Sediment Organic Contaminant Fluxes



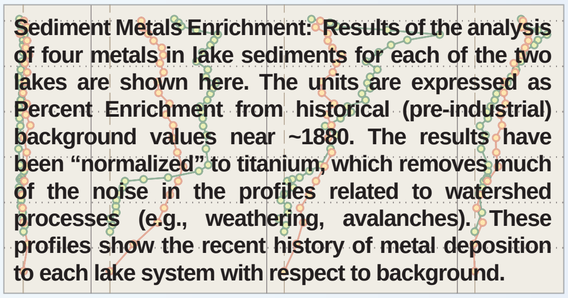
Yearly focusing factor-corrected sediment fluxes of semi-volatile organic compounds* (SOC) are shown in this figure. Year (depth) is shown on the vertical axis. Given the expense of the SOC analyses, WACAP allocated approximately eight slices to be analyzed for each sediment core. The green lines are the year in which the individual SOC was registered with the US government. When present, the red dotted line is the date that use in the US was discontinued. An asterisk indicates that the value at that level in the core was below the detection limit. Profiles of the two lakes are shown side by side for each different contaminant.

Sediment Contaminant Fluxes

These figures are sediment profiles for each site. The top of the graph represents the surface of the sediment core; the dates on the vertical axis are derived from ^{210}Pb dating. Each point on a graph represents results of an analysis of a sediment slice having an average date represented by the circle.



Sediment flux is expressed as mass per unit area per year. Spheroidal Carbonaceous Particles (SCP) are microscopic "fly ash" materials formed only by high temperature combustion associated with fossil fuel (coal and oil) combustion. They are excellent indicators of local or regional sources of human industrial activities. Total Organic Carbon is a component of the sediment record derived from in-lake photosynthesis production or watershed sources and typically decreases with depth as a result of biogenic processes in the sediment.



Sediment Metals Enrichment: Results of the analysis of four metals in lake sediments for each of the two lakes are shown here. The units are expressed as Percent Enrichment from historical (pre-industrial) background values near ~1880. The results have been "normalized" to titanium, which removes much of the noise in the profiles related to watershed processes (e.g., weathering, avalanches). These profiles show the recent history of metal deposition to each lake system with respect to background.

Noatak National Preserve and Gates of the Arctic National Park and Preserve

Summary: Noatak National Preserve and Gates of the Arctic National Park and Preserve

Burial and Matcharak lakes both have small watersheds, contributing to long hydraulic residence times. Burial Lake's surface area and volume are considerably smaller, but it had the highest total phosphorus of all WACAP lakes. Both lakes had fairly high dissolved organic carbon, an important factor in mercury methylation in lake systems. Acid neutralizing capacity of both lakes was high.

Air

The primary SOCs detected in air were HCB and a-HCH, both historic-use pesticides known to be distributed by cold fractionation. Low concentrations of endosulfans chlordanes, g-HCH, and PAHs were also detected.

Snow

Mercury flux to the snowpack at Burial and Matcharak lakes was low compared to that at the other parks. SOCs varied considerably among collection sites and inter-annually. Compared to values at the other parks, SOC flux was low for dacthal and chlorpyrifos and mid to high for endosulfans and a-HCH.

Vegetation

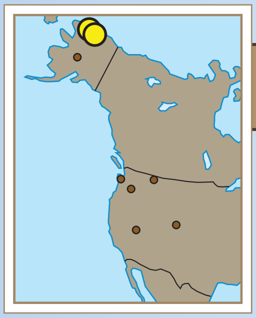
No conifers were present at these Arctic sites, so we collected only lichens. Here we observed the lowest concentrations of SOCs, nutrients, and toxic metals, including Hg, among the parks. Concentrations approached detection limits for many SOCs. However, we detected dacthal, endosulfans, HCB, a-HCH, PCB153, and the PAHs retene, CHR/TRI, and FLA. Compared to values at other parks, concentrations of many rare and trace elements were relatively high at Matcharak Lake. High mineral content in regional lithology is the likely source.

Fish

Numerous parasites (worms) were found in the overall normal lake trout from both lakes. Fish analyzed were the oldest in WACAP, with maximum ages of 33 and 41 years for fish analyzed for SOC and metals, respectively. Spleen macrophage aggregates were positively related to mercury in fish less than 15 years of age from Burial Lake. Concentrations of historic-use SOCs in fish were generally mid-range compared with those at all other sites, whereas current-use SOCs were some of the lowest measured in fish. The median dieldrin concentration in Burial Lake, as well as dieldrin concentrations in some individual Matcharak Lake fish, exceeded contaminant health thresholds for subsistence fishers. Mercury concentrations were high, indicating high mercury methylation and bioaccumulation in NOAT and GAAR. Mercury concentrations exceeded thresholds for wildlife health, and the median mercury concentration in Burial Lake and in some fish in Matcharak lake exceeded the human contaminant health threshold.

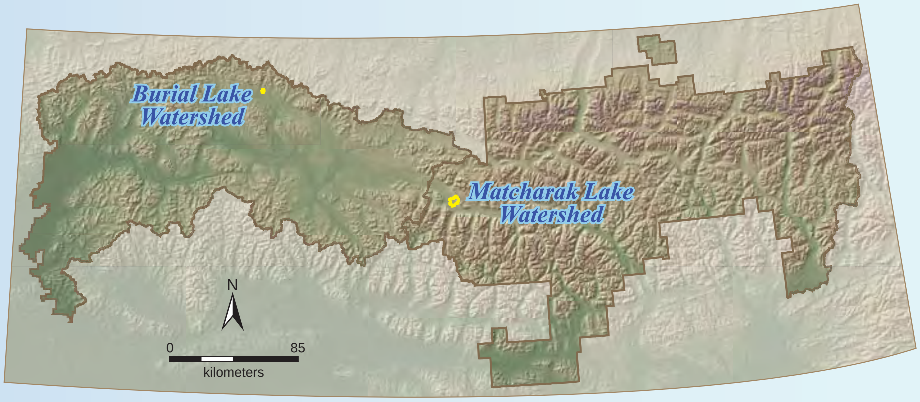
Sediment

Many of the SOCs were below detection limits in the sediment profiles for both lakes. In addition, SCPs were not present. Mercury percent enrichment profiles were generally very low, but showed similar increasing trends from about 1875 in each lake. This pattern reflects the general increase in the global background of Hg in the atmosphere caused by human activities, largely coal burning and smelting.



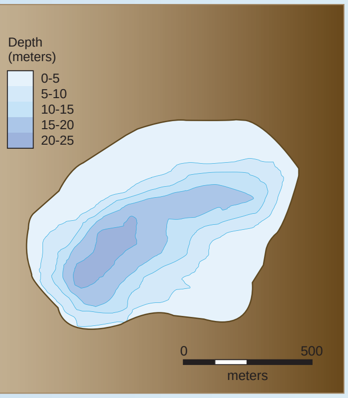
NOAT, GAAR

Noatak National Preserve and Gates of the Arctic National Park and Preserve: *Site Characteristics*



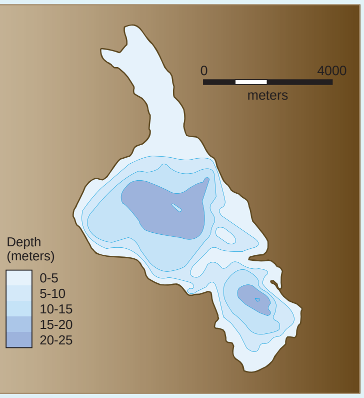
Burial Lake

Location: 68.43N 159.18W
Elevation: 429.8 m
Maximum Depth: 24.1 m
Surface Area: 65.5 ha
Watershed Area: 264.9 ha

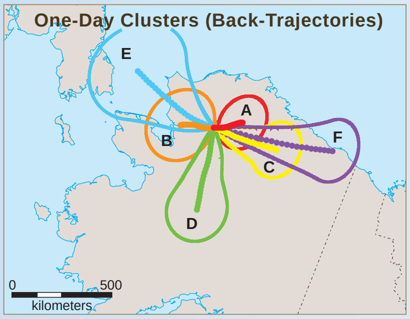


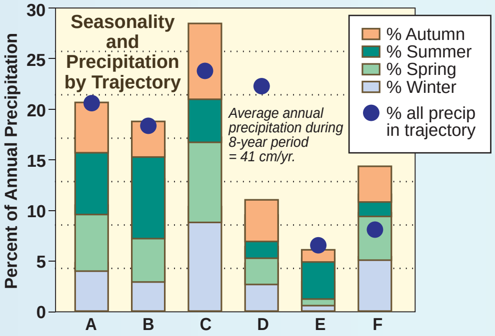
Matcharak Lake

Location: 67.75N 156.21W
Elevation: 502.3 m
Maximum Depth: 20.4 m
Surface Area: 300.7 ha
Watershed Area: 2388.3 ha

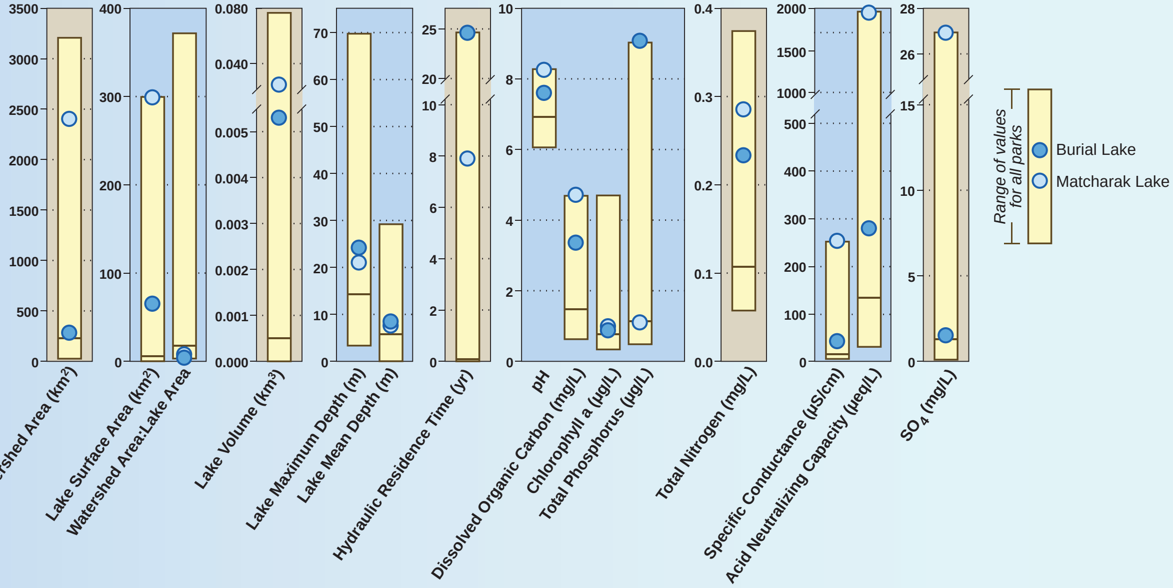


◆ Atmospheric Transport ◆

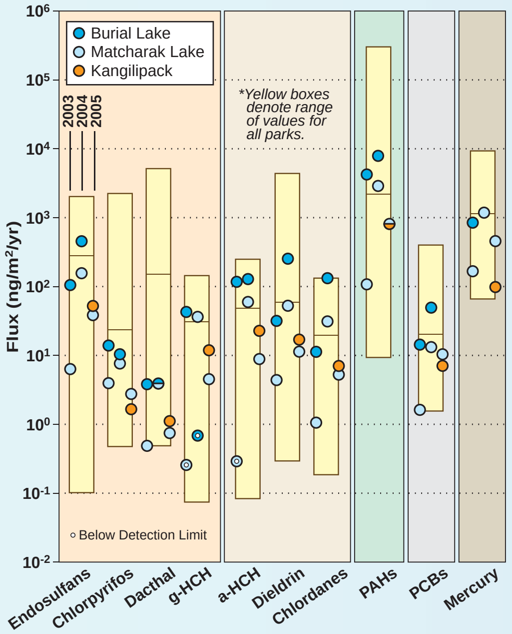




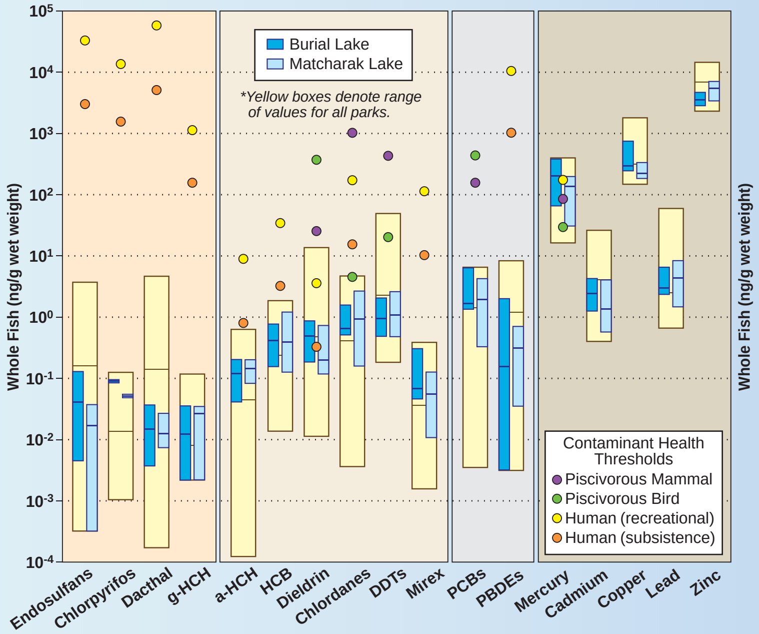
◆ Physical and Chemical Characteristics ◆



◆ Snow Contaminant Fluxes ◆

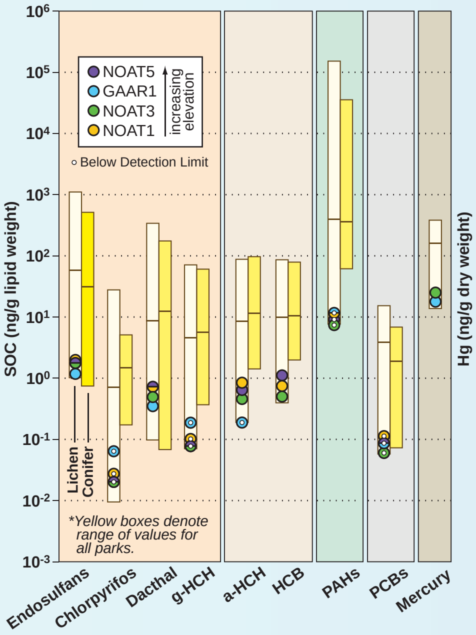


◆ Whole Fish Contaminant Concentrations ◆

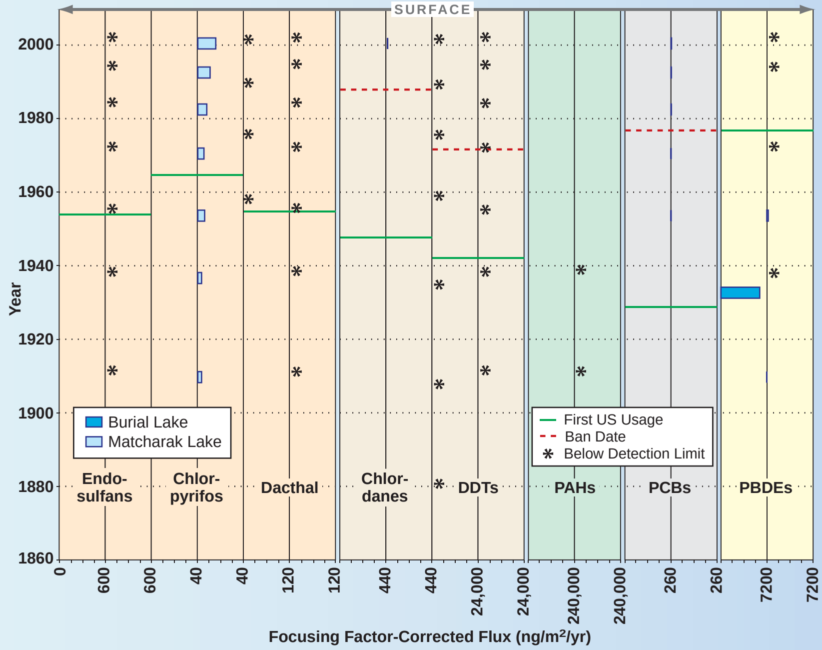


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

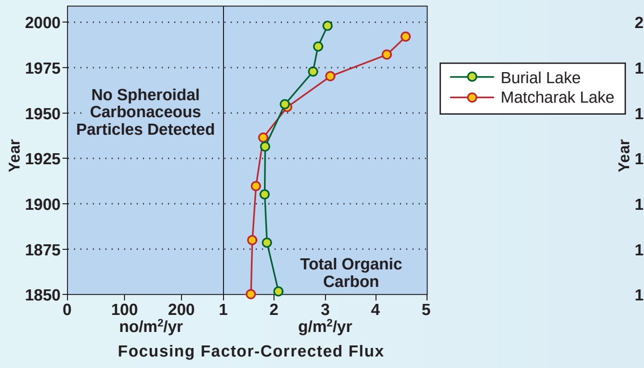
◆ Vegetation Contaminant Concentrations ◆



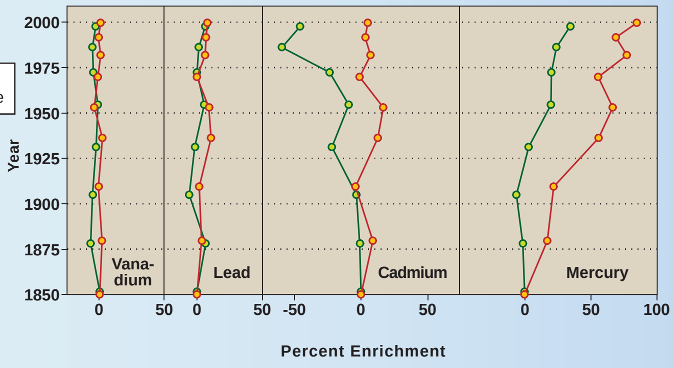
◆ Sediment Organic Contaminant Fluxes ◆



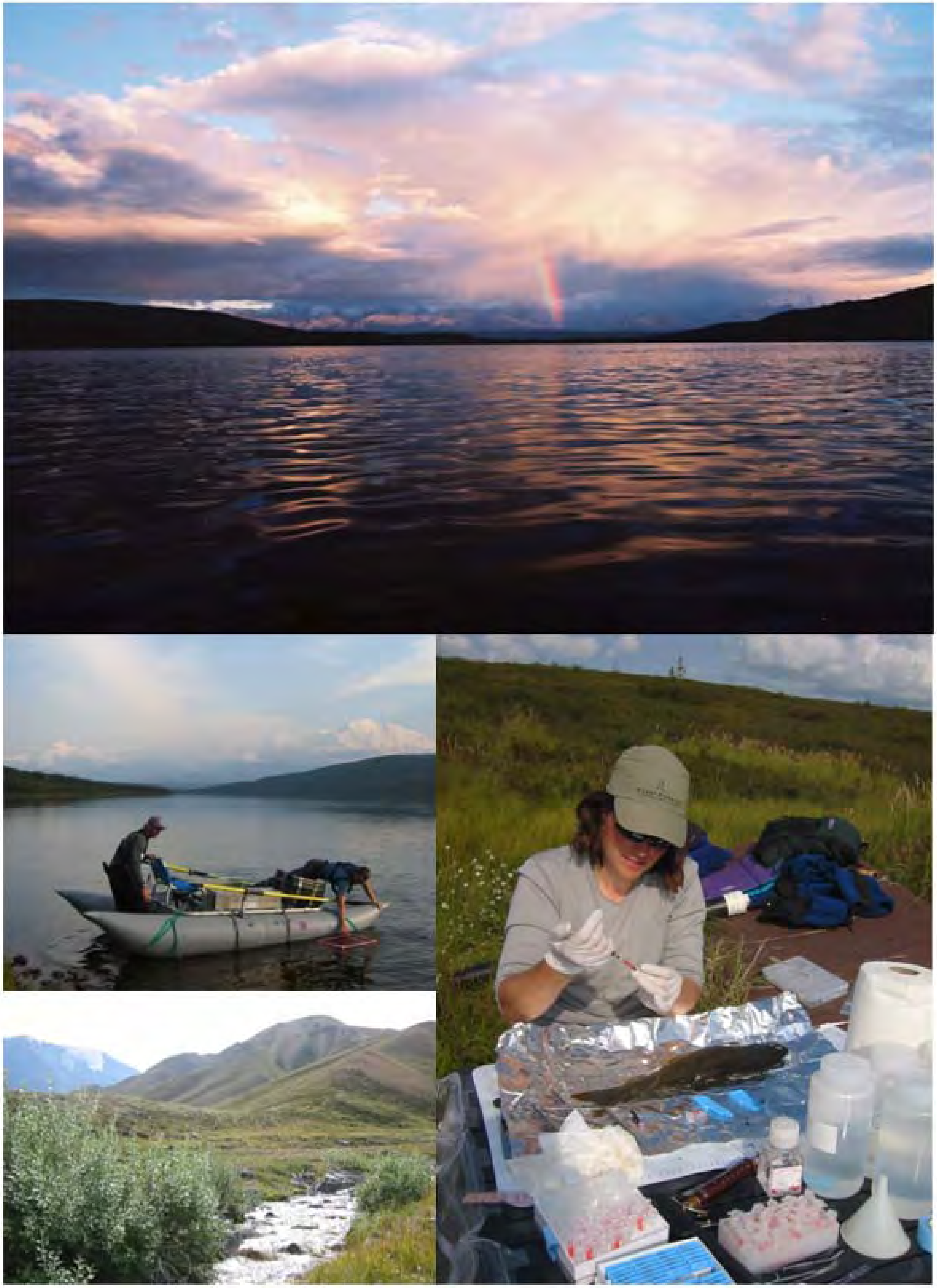
◆ Sediment Flux ◆



◆ Sediment Metals Enrichment ◆



Denali National Park and Preserve



Summary: Denali National Park and Preserve

Wonder Lake and McLeod Lake were very different from one another in most physical characteristics, as well as in many chemical parameters. Wonder Lake is a deep, large lake with high pH, specific conductance, acid neutralizing capacity, and sulfate concentration. McLeod Lake, by contrast, has very low specific conductance and acid neutralizing capacity. Both are characterized by fairly small watersheds.

Air

Similar to SOCs at sites in the Arctic, the primary SOCs detected in air were HCB and a-HCH, both historic-use pesticides. In addition, low concentrations of endosulfans, chlordanes, g-HCH, and PAHs were detected.

Snow

Contaminant deposition fluxes in snow for DENA were among the lowest in all the parks, with low concentrations and shallow snowpacks. Among the DENA snowpack samples, the Kahiltna site had the highest deposition fluxes of most contaminants. Concentrations were similar to those in the other samples in DENA, but greater snow water equivalent at this site caused contaminant fluxes to be higher than those measured at the lower elevation sites. This pattern is typical in mountains and other environments where large precipitation gradients are present. These results demonstrate that contaminant fluxes measured in snowpack at a single site might not be representative of an entire park.

Vegetation

After NOAT and GAAR, DENA had the lowest concentrations of SOCs, nutrients, metals, and mercury in vegetation among the parks. Concentrations were low for agricultural chemicals and PCBs, but higher for PAHs. The pesticides detected were HCB, endosulfans, a-HCH, and dacthal, and all increased with elevation. The dominant PAHs were retene and CHR/TRI, possibly attributable to wildfire, and decreased with increasing elevation.

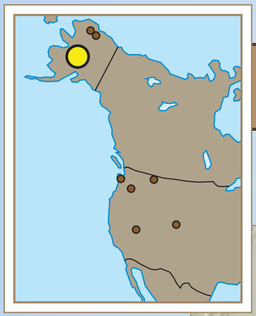
Fish

Fish historic-use SOC concentrations were in the mid to high range among parks for selected compounds and among the lowest measured for most current-use SOCs. Median dieldrin concentrations in Wonder Lake fish and in some individual fish in McLeod Lake exceeded contaminant health thresholds for subsistence fishers. Median mercury concentrations in both lakes exceeded contaminant health thresholds for piscivorous birds (kingfishers), and Wonder Lake also exceeded contaminant health thresholds for mammals (otter and mink). Spleen macrophage aggregates were significantly higher in Wonder Lake fish than those in lake trout from NOAT and GAAR. The reasons for this finding are unknown. Macrophage aggregates were positively related to mercury concentrations in Wonder Lake, a pattern that was observed for most of the lakes. Very few fish were available from McLeod Lake, despite two sampling efforts (2004 and 2005). All fish appeared reproductively normal.

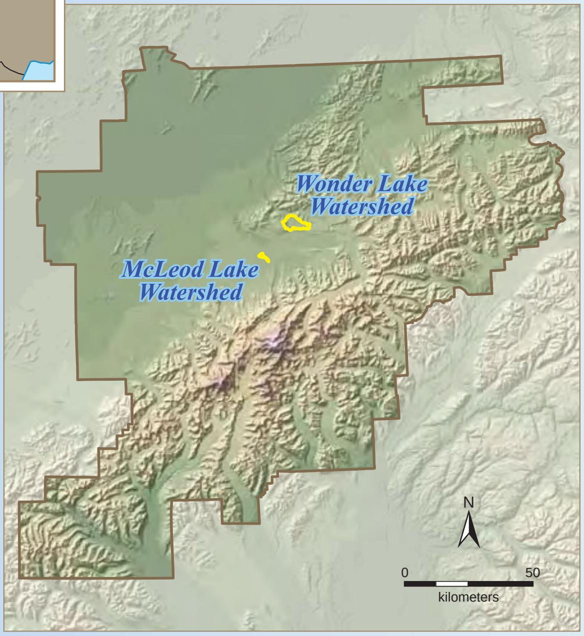
Sediment

Sediment fluxes of most of the SOCs found in other lakes were below detection in the DENA sediment profiles. PCBs were present, but at low concentrations—about the same order of magnitude as in the other Alaska lake sediments. Wonder Lake showed distinct and similar percent enrichment increases from at least 1920 to the surface for both mercury and lead, probably as a result of increasing global background concentrations. McLeod Lake sediments did not show a similar trend. No SCPs were found in either sediment profile.

Denali National Park: *Site Characteristics*

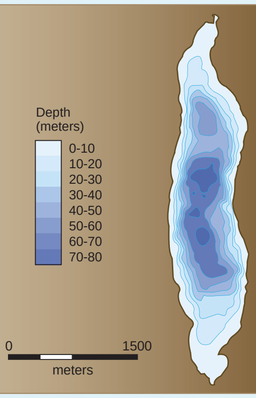


DENA



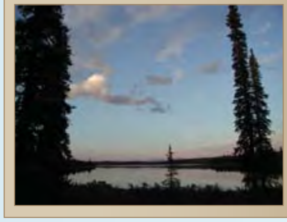
Wonder Lake

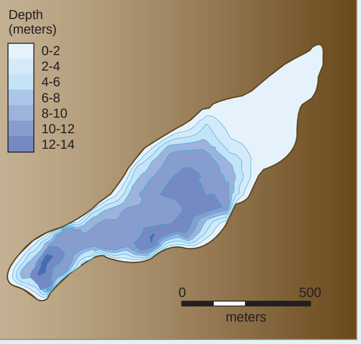
Location: 63.48N 150.88W
Elevation: 605.0 m
Maximum Depth: 70.0 m
Surface Area: 265.6 ha
Watershed Area: 3212.4 ha



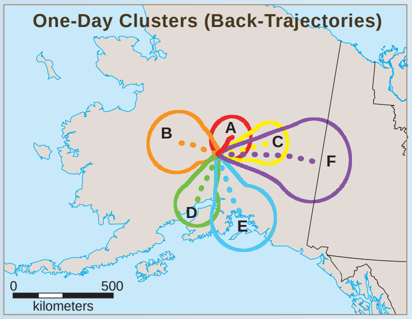
McLeod Lake

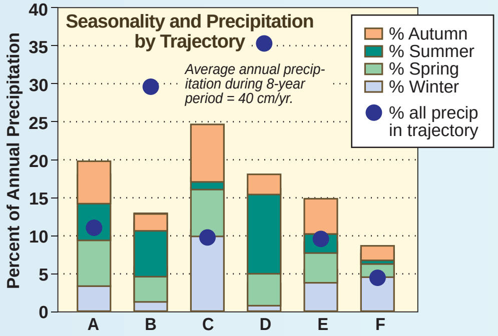
Location: 63.38N 151.07W
Elevation: 563.9 m
Maximum Depth: 13.5 m
Surface Area: 35.9 ha
Watershed Area: 236.8 ha



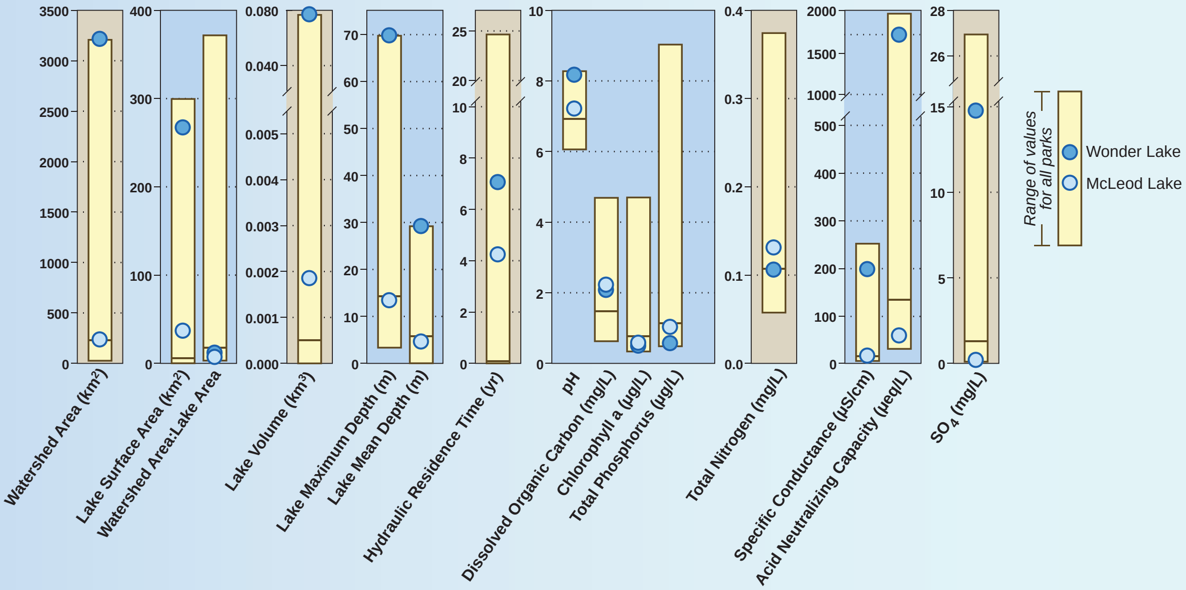


◆ Atmospheric Transport ◆



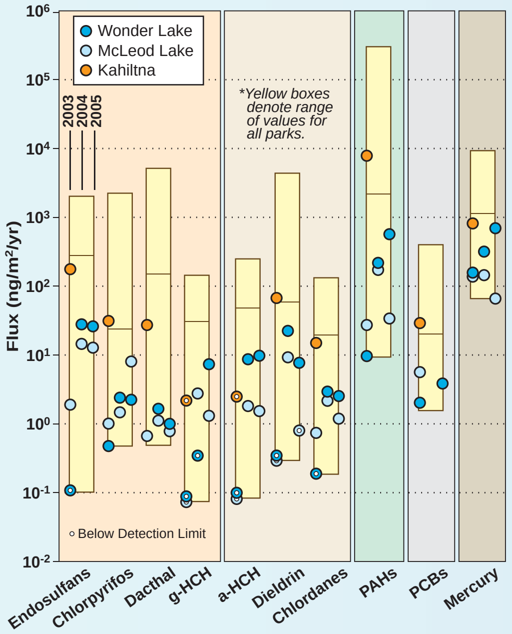


◆ Physical and Chemical Characteristics ◆

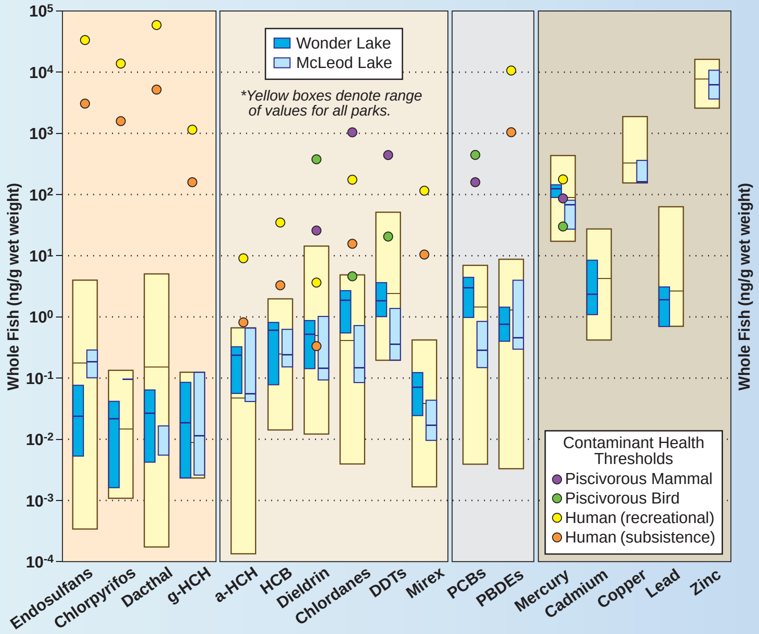


Denali National Park: *Contaminant Summaries*

◆ Snow Contaminant Fluxes ◆

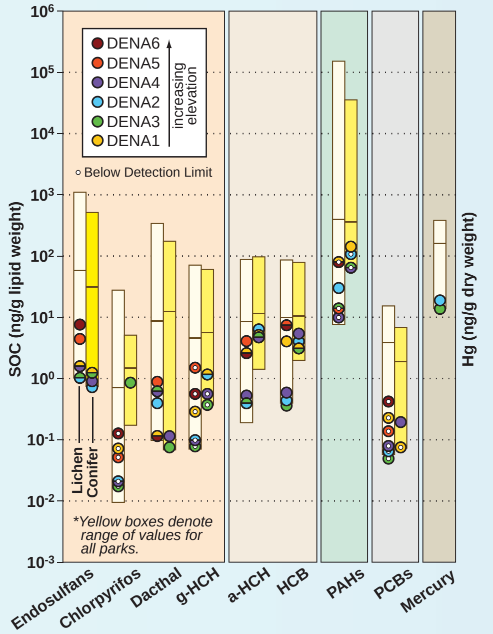


◆ Whole Fish Contaminant Concentrations ◆

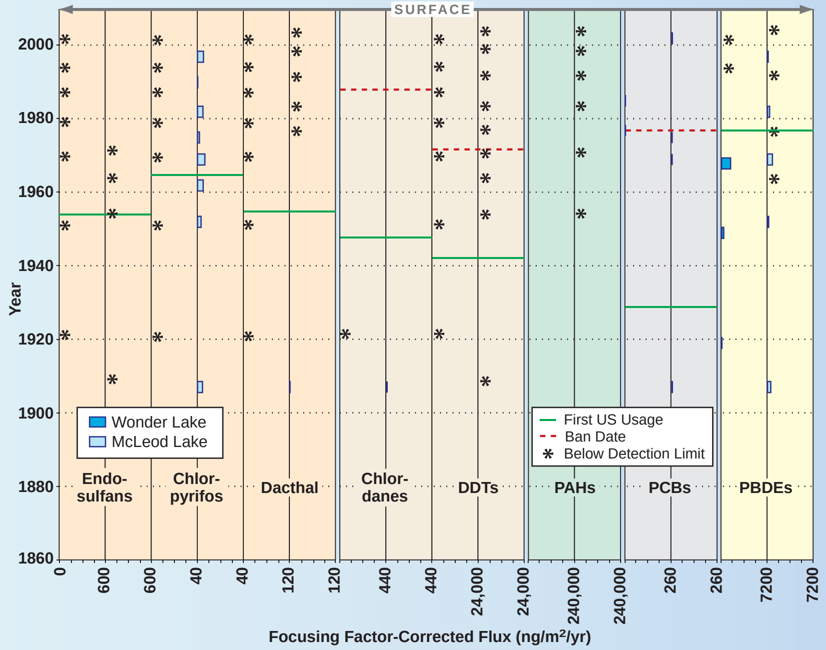


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

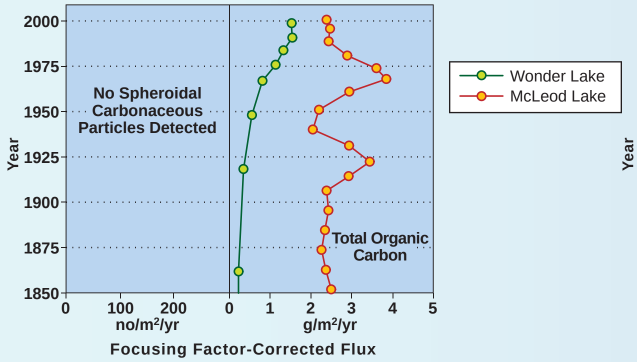
◆ Vegetation Contaminant Concentrations ◆



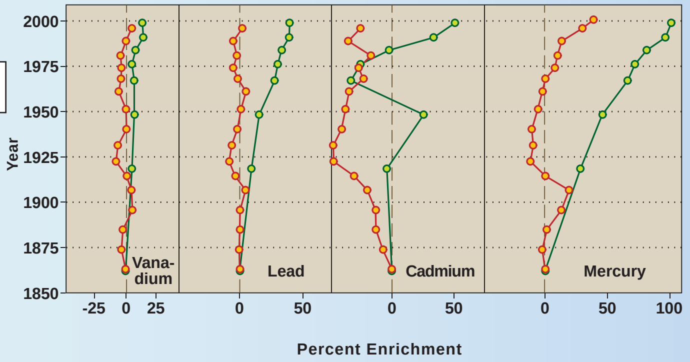
◆ Sediment Organic Contaminant Fluxes ◆



◆ Sediment Flux ◆



◆ Sediment Metals Enrichment ◆



Glacier National Park

Summary: Glacier National Park

Oldman and Snyder lakes share many physical characteristics. However, Oldman Lake has a much greater volume and greater maximum depth, as well as greater specific conductance, pH, and acid neutralizing capacity. Snyder Lake is more productive, with higher total phosphorus, nitrogen, and chlorophyll-*a*. At GLAC, air, vegetation, and snow had among the highest concentrations for current-use pesticides, compared with these media at the other parks. The source of these compounds probably was regional agriculture within a few hundred kilometers of the park.

Air

Compared to measurements at the other parks, high concentrations of SOCs detected in air include PAHs, dacthal, endosulfans, HCB, a-HCH, and g-HCH. Low concentrations of chlordanes and PCBs were also detected. Concentrations at Oldman Lake, east of the Continental Divide, were higher than those at Snyder Lake, west of the Continental Divide.

Snow

Snow water equivalents, contaminant concentrations (except PAHs), and contaminant flux to the snowpack in GLAC were similar to those at the other parks. For PAHs, the concentrations and fluxes at Snyder Lake were substantially higher than those at Oldman Lake. Mercury flux to the snowpack was near average among parks, but fish concentrations of mercury were below average, indicating low rates of mercury methylation and bioaccumulation, similar to rates at ROMO. SOC concentrations in snow varied considerably among the sites sampled. However, within the same year, the range for all contaminants in GLAC was typically within an order of magnitude. PAH concentrations in snow at Snyder Lake were always higher than at the other sites, and among the highest at all parks.

Vegetation

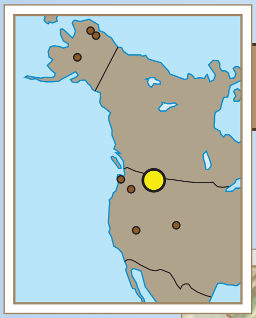
Numbers and concentrations of PAHs detected were highest at GLAC than at other parks. Proximity to an aluminum smelter suggests a local source of PAHs contributing to the high concentrations. Other SOCs (endosulfans, dacthal, DDTs, g-HCH, a-HCH, HCB, triallate, chlorpyrifos, and PCBs) were in the mid to upper ranges compared to those at other parks. Dacthal, endosulfans, HCB, a-HCH, chlorpyrifos, DDTs, PCBs, and PAHs were higher on the west side of the park, attributable to precipitation and temperature. Triallate, chlorpyrifos, and g-HCH were higher on the east side of the park, probably because of agricultural intensity. Enhanced nitrogen and sulfur deposition related to regional agricultural intensity is of concern. Many rare but not highly toxic elements were higher in lichen at GLAC than in lichen at other parks. Because forest productivity is high, pesticides scrubbed from the air by vegetation probably contribute significant contaminant loads to the ecosystem via canopy through-fall and needle litter-fall.

Fish

Pesticide concentrations (dacthal, g-HCH, HCB, dieldrin, and chlordanes) in fish in Oldman Lake were higher than those in Snyder Lake, possibly related to agricultural intensity. One fish from Oldman Lake exceeded contaminant health thresholds for piscivorous birds (kingfishers) for chlordanes, and the median concentration of DDTs from Oldman Lake exceeded the contaminant health thresholds for piscivorous birds. Fish in both lakes exceeded kingfisher thresholds for Hg. Lake average dieldrin and p,p′-DDE fish concentrations in Oldman Lake exceeded contaminant health thresholds for subsistence fishers. Dieldrin concentration in one fish from Oldman Lake exceeded the contaminant health threshold for recreational fishers. Mercury increased with increasing age of fish in Snyder Lake. Kidney and/or spleen macrophage aggregates were significantly related to mercury and age at both lakes. All fish appeared reproductively normal, but elevated concentrations of estrogen-responsive protein were found in males from both lakes. One intersex male was found at Oldman Lake. These data suggest endocrine disruption.

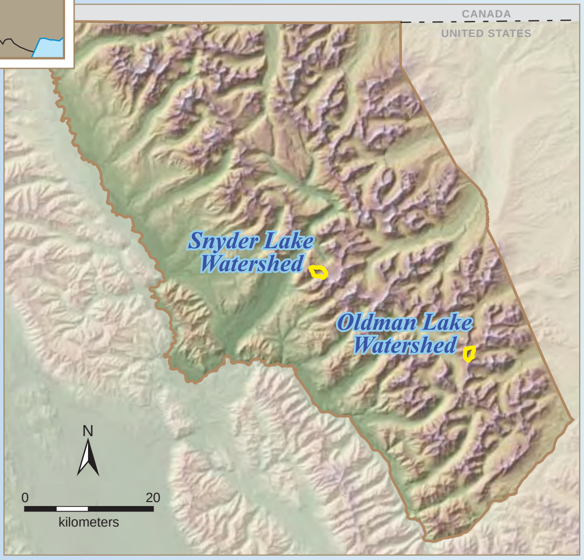
Sediment

SOC profiles are consistent with the first usage of these chemicals in the United States, but most have not decreased since use ceased. Snyder Lake profiles generally show greater contaminant flux than Oldman Lake profiles. PAHs in Snyder Lake indicate some decline in the recent sediments since approximately 1990. Lead, cadmium, and mercury profiles increase from approximately 1875 and decrease beginning in the 1960s. These profiles suggest a common historic source that might have been affected by reductions in emissions related to the Clean Air Act. This relationship is supported by the pattern observed in SCPs.



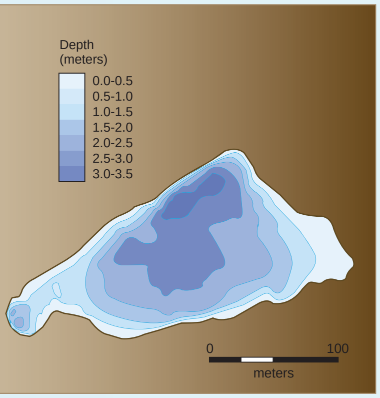
GLAC

Glacier National Park: *Site Characteristics*



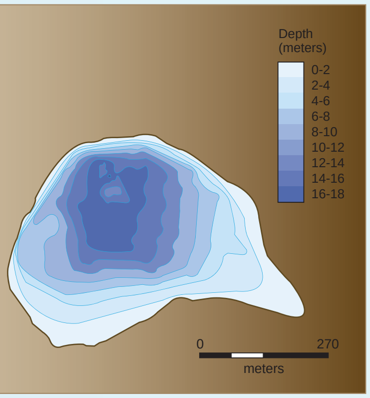
Snyder Lake

Location: 48.62N 113.79W
Elevation: 1597.2 m
Maximum Depth: 3.5 m
Surface Area: 2.6 ha
Watershed Area: 303.7 ha

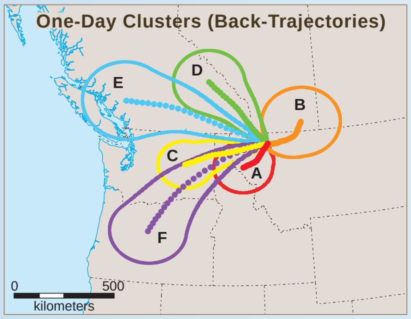


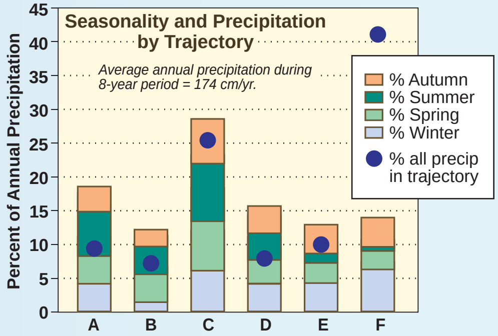
Oldman Lake

Location: 48.50N 113.46W
Elevation: 2025.7 m
Maximum Depth: 17.0 m
Surface Area: 18.2 ha
Watershed Area: 230.3 ha

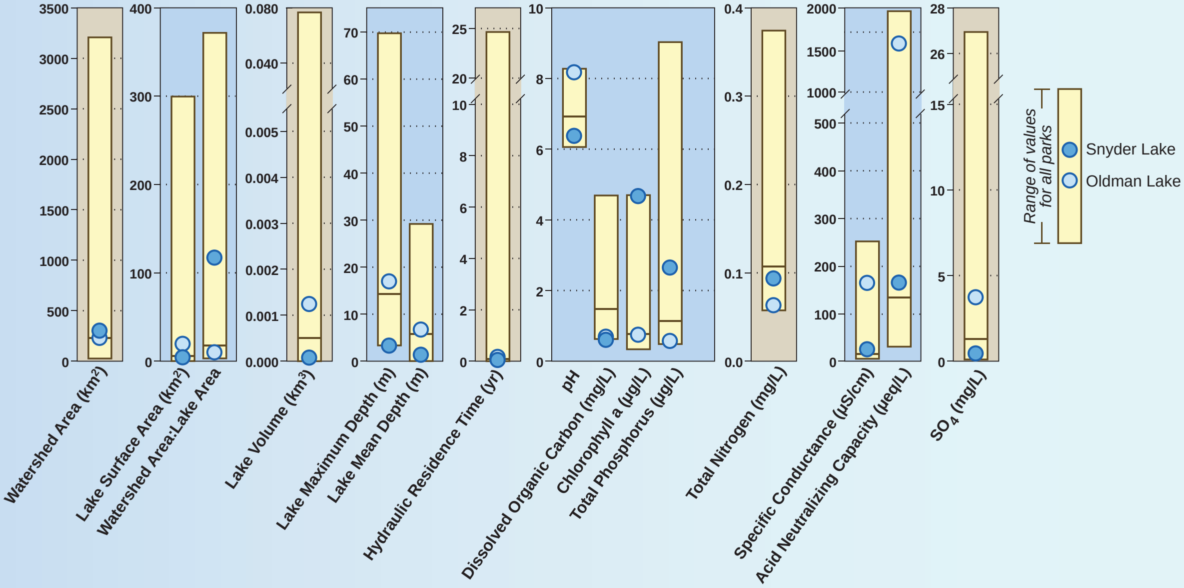


◆ Atmospheric Transport ◆

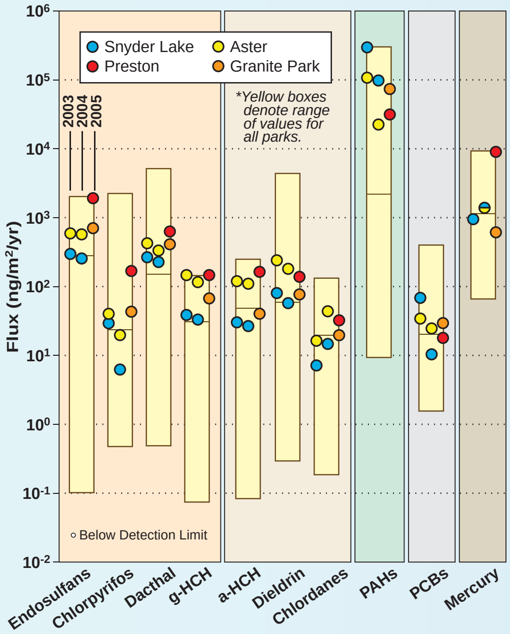




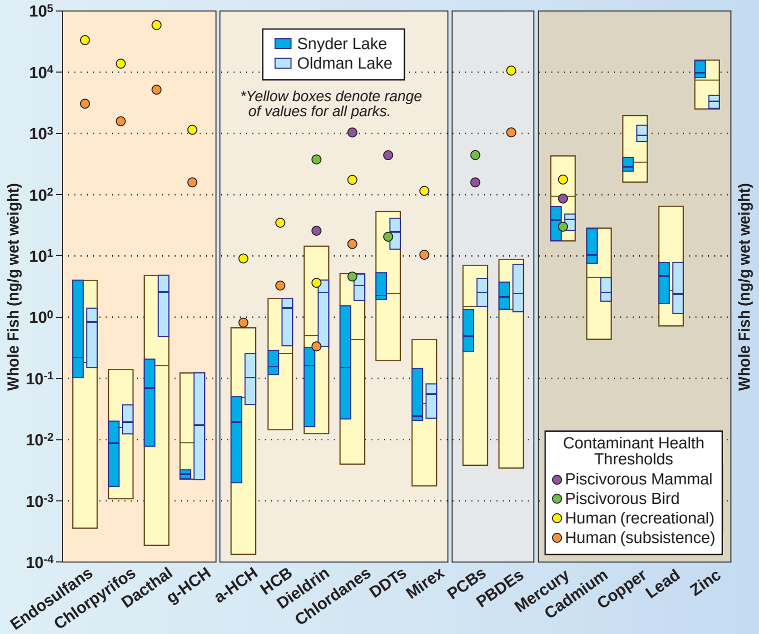
◆ Physical and Chemical Characteristics ◆



◆ Snow Contaminant Fluxes ◆

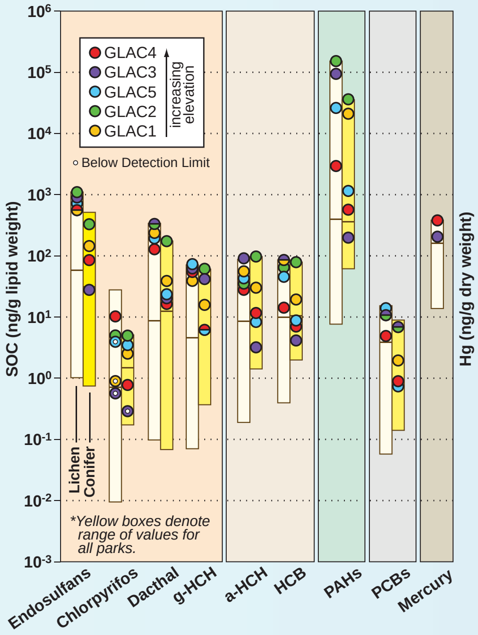


◆ Whole Fish Contaminant Concentrations ◆

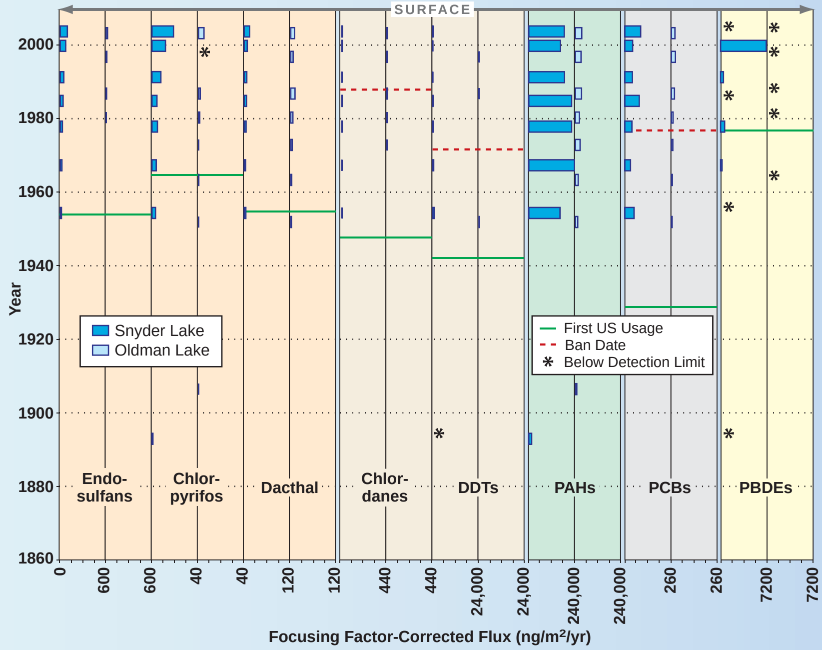


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

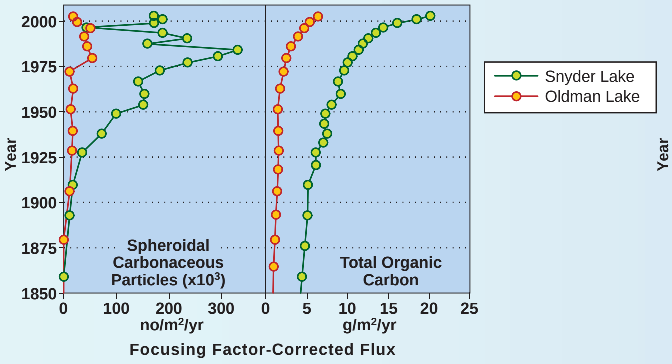
◆ Vegetation Contaminant Concentrations ◆



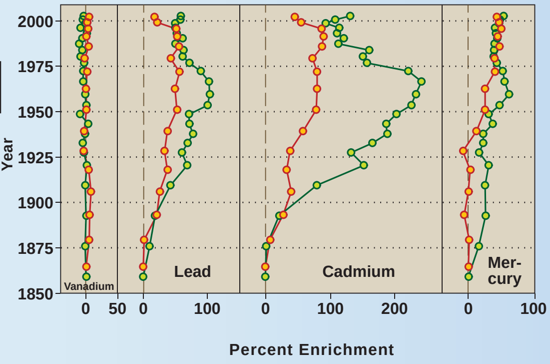
◆ Sediment Organic Contaminant Fluxes ◆



◆ Sediment Flux ◆



◆ Sediment Metals Enrichment ◆



Olympic National Park

Summary: Olympic National Park

The two OLYM lakes, Hoh and PJ, were similar in many ways, both physically and chemically. However, PJ Lake was clearly more productive, with higher total phosphorus, chlorophyll-*a*, pH, and specific conductance. PJ Lake had smaller mean and maximum depths and was frequently affected by avalanches that brought trees and other debris into the lake.

Air

The primary SOCs detected in air were endosulfans, HCB, and a-HCH. Low concentrations of PAHs, PCBs, g-HCH, trifluralin, dacthal, and chlordanes were also detected. SOC concentrations at Hoh Lake on the west side of the park and PJ Lake on the east side were nearly identical.

Snow

Unusually warm conditions with heavy mid-winter rains occurred during the study period (2002-2005). Because mid-winter rain or snowmelt can wash contaminants out of the snow, and ancillary data indicated substantial loss of water from the snowpack prior to spring sampling in 2003 and 2005, snowpack samples were collected in 2004 only. Two sites near PJ Lake had fairly high mercury fluxes in the 2004 snowpack, whereas mercury deposition flux in the Hoh Lake snowpack was somewhat less. These results were surprising, given that there are few known local or regional upwind sources. One possible explanation is that deposition from regional sources to the east can reach OLYM on easterly airflows.

Vegetation

Like those for MORA, SOC and Hg concentrations in vegetation were at mid to upper ranges compared to concentrations at other parks. PAHs were the dominant SOCs detected. Other SOCs were endosulfans, a-HCH, HCBs, and dacthal, and concentrations of these SOCs varied substantially. We observed low concentrations of chlorpyrifos, trifluralin, and PCBs. Nutrients and other metals in vegetation were within expected ranges. Because forest productivity is high, pesticides scrubbed from the air by the vegetation probably contribute significant contaminant loads to the ecosystem via canopy through-fall and needle litter-fall.

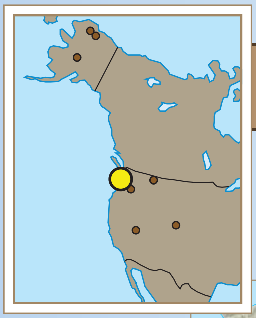
Fish

Concentrations of SOCs in OLYM were generally among the lowest for dieldrin, mirex, and chlordanes, and average for other pesticides. Fish mercury concentrations were among the highest of all parks, exceeding contaminant health thresholds for piscivorous mammals (otter, mink) and birds (kingfishers), and some fish from both lakes exceeded the human contaminant health threshold. Mercury and macrophage aggregates increased with increasing age of fish in both lakes. Spleen and kidney macrophage aggregates were also positively related to mercury in both lakes. All fish appeared reproductively normal.

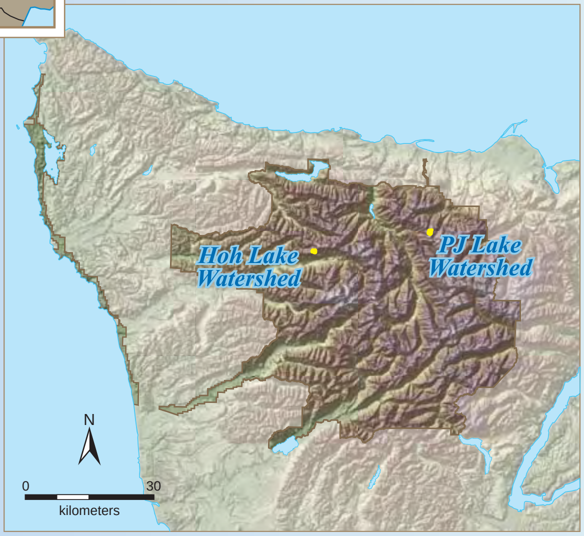
Sediment

Sediment profiles for SOCs in both lakes were generally below detection limits (except for PAH and PCB). Mercury, cadmium, and lead show increasing percent enrichment toward the surface (present time) beginning in the late 1800s, and stabilize at the surface at fairly high percent enrichment values. This relationship suggests a possible common source. SCPs showed a historic peak in both lakes around 1950 and generally decreased toward the surface.

Olympic National Park: *Site Characteristics*

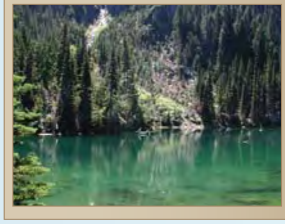


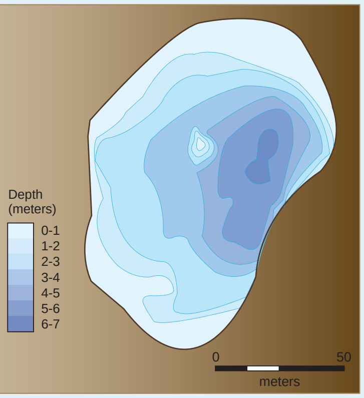
OLYM



PJ Lake

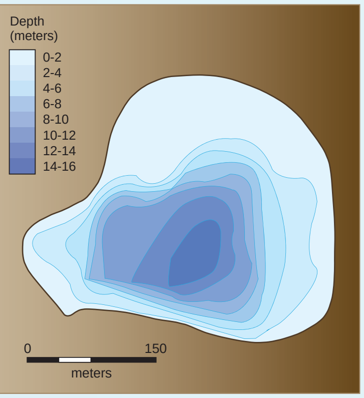
Location: 47.95N 123.42W
Elevation: 1383.8 m
Maximum Depth: 6.4 m
Surface Area: 0.8 ha
Watershed Area: 56.2 ha





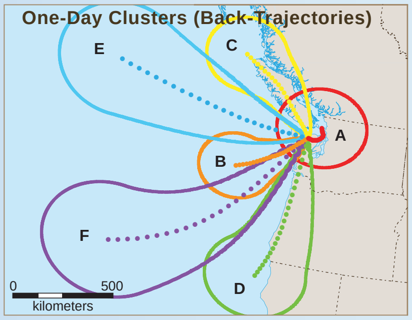
Hoh Lake

Location: 47.90N 123.79W
Elevation: 1379.2 m
Maximum Depth: 14.9 m
Surface Area: 7.7 ha
Watershed Area: 43.9 ha

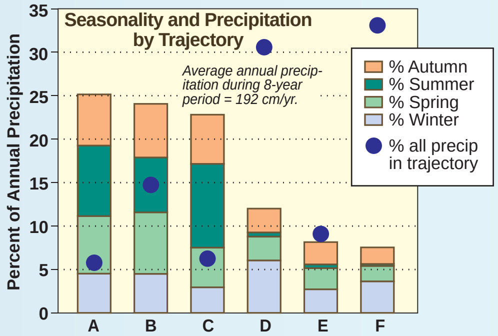


Atmospheric Transport

One-Day Clusters (Back-Trajectories)

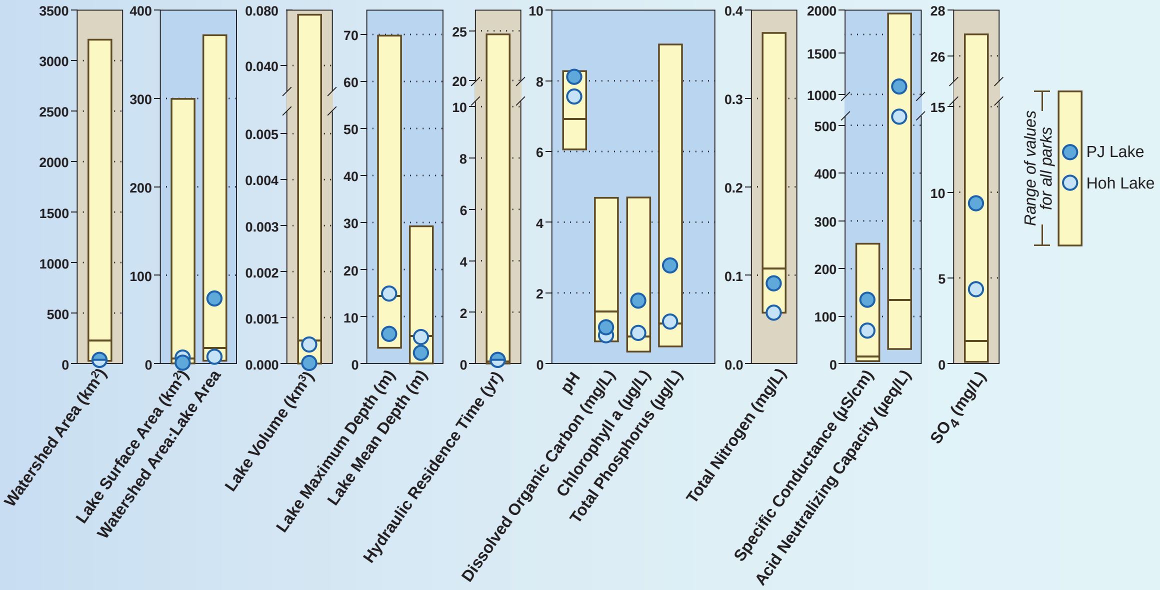


Seasonality and Precipitation by Trajectory

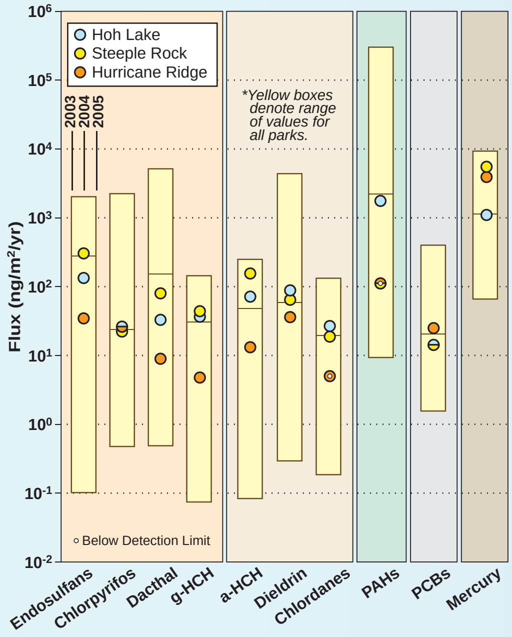


Average annual precipitation during 8-year period = 192 cm/yr.

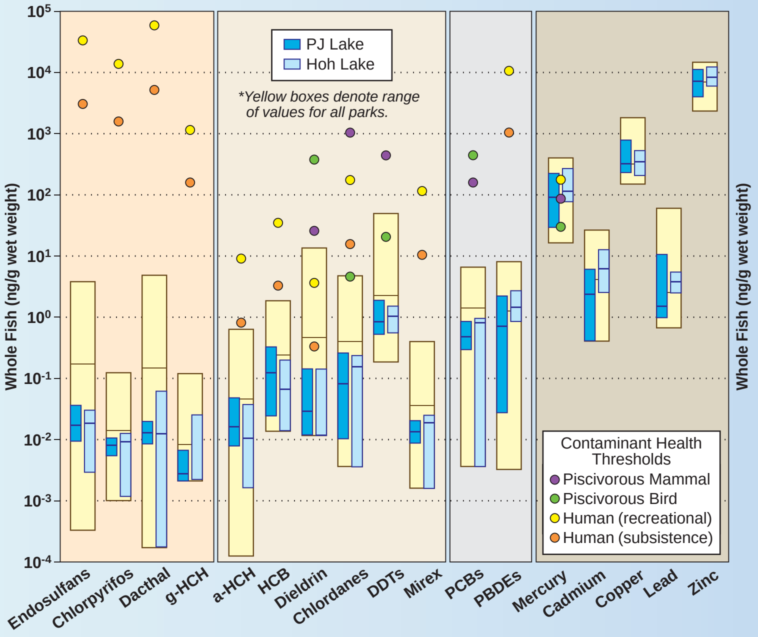
Physical and Chemical Characteristics



◆ Snow Contaminant Fluxes ◆

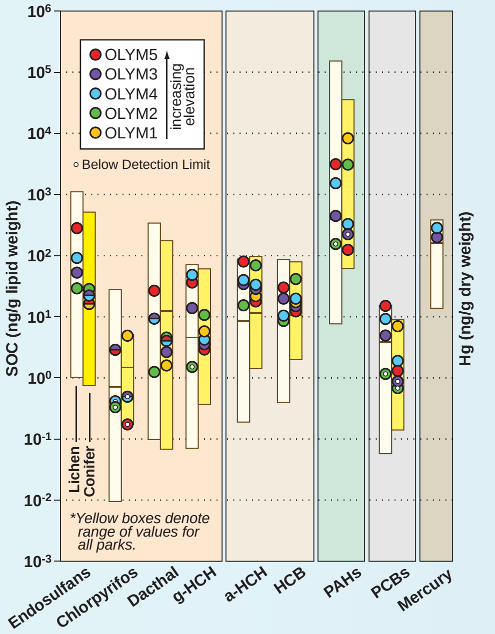


◆ Whole Fish Contaminant Concentrations ◆

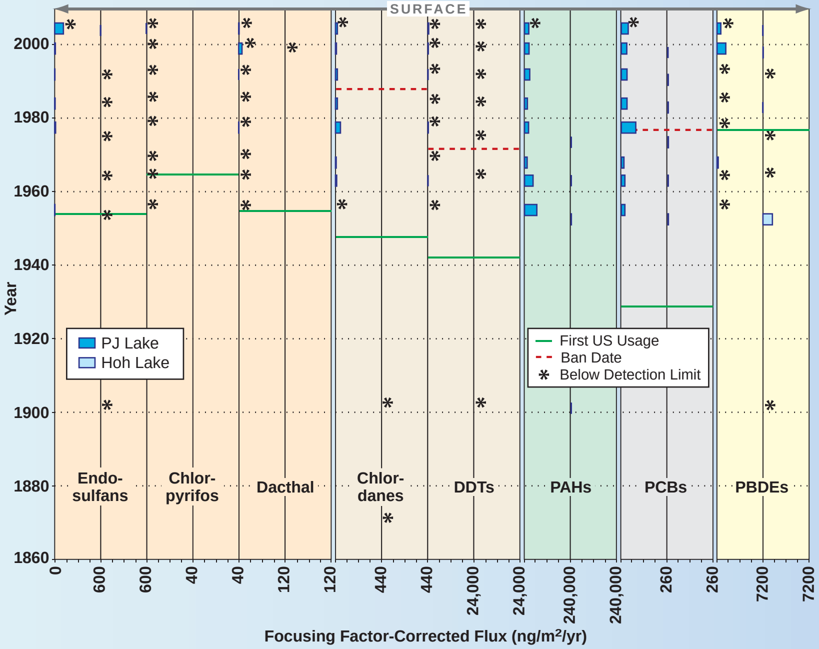


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

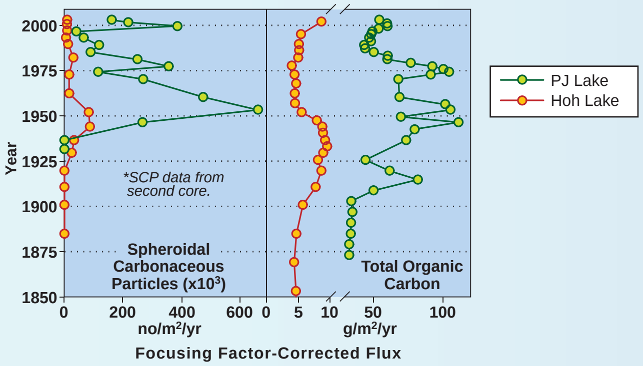
◆ Vegetation Contaminant Concentrations ◆



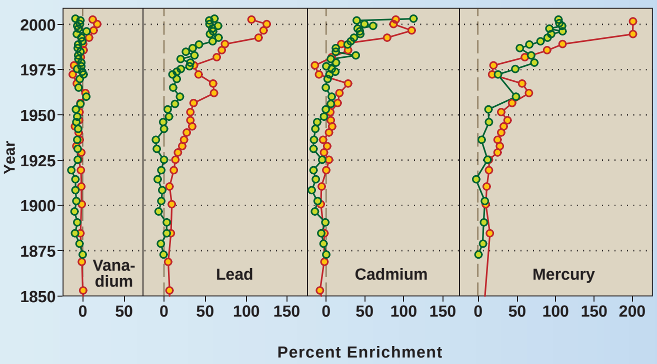
◆ Sediment Organic Contaminant Fluxes ◆



◆ Sediment Flux ◆



◆ Sediment Metals Enrichment ◆



Mount Rainier National Park

Summary: Mount Rainier National Park

Lake sites in MORA are very closely matched in both physical and chemical aspects. Golden Lake and LP19 are typical small sub-alpine lakes with low productivity, low conductivity, low nutrients, and small watersheds.

Air

The primary SOCs detected in air were the endosulfans, HCB, and a-HCH. Low concentrations of g-HCH, trifluralin, dacthal, and chlordanes were also observed.

Snow

Average winter precipitation rates at MORA are the highest among the parks, so contamination fluxes are moderate to high, even though snow concentrations are mid-range for the parks. Contaminant fluxes were fairly low in 2005, reflecting shallow snow accumulation and low snow water equivalent that year.

Vegetation

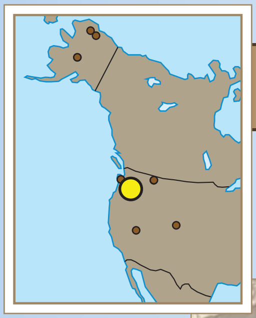
SOC and Hg concentrations in vegetation were at or well above the concentrations observed at the other parks. Dominant SOCs were PAHs, endosulfans, a-HCH, HCB, and dacthal. Detectable but low concentrations of chlorpyrifos, dieldrin, DDTs, and PCBs were also observed. Chlorpyrifos, dacthal, endosulfans, HCBs, HCHs, chlordanes, DDTs, and PCBs increased with elevation. PAHs, dominated by CHR/TRI, PHE, and retene, decreased with increasing elevation. Nutrients and metals were within expected ranges. Because forest productivity is high, pesticides scrubbed from the air by vegetation probably contribute significant contaminant loads to the ecosystem via canopy through-fall and needle litter-fall.

Fish

Contaminant concentrations in fish were generally mid-range, except for PBDEs in Golden Lake fish, which were the highest among all fish at all lakes. The median dieldrin concentration of fish in Golden Lake and some individual fish in LP19 exceeded contaminant health thresholds for subsistence fishers. Mercury concentrations in all fish from both lakes exceeded contaminant health thresholds for birds (kingfishers), and some fish exceeded thresholds for piscivorous mammals (otter, mink). Mercury concentrations in some fish from LP19 exceeded contaminant health thresholds for humans. These mercury values indicate favorable conditions for methylation and subsequent bioaccumulation of mercury. Mercury and macrophage aggregates increased with increasing age of fish in LP19, but not in Golden Lake. Spleen and kidney macrophage aggregates were positively related to mercury at LP19, but only kidney macrophage aggregates were related to mercury at Golden Lake. All fish appeared normal reproductively, although one male from Golden Lake had elevated concentrations of estrogen-responsive protein in the blood.

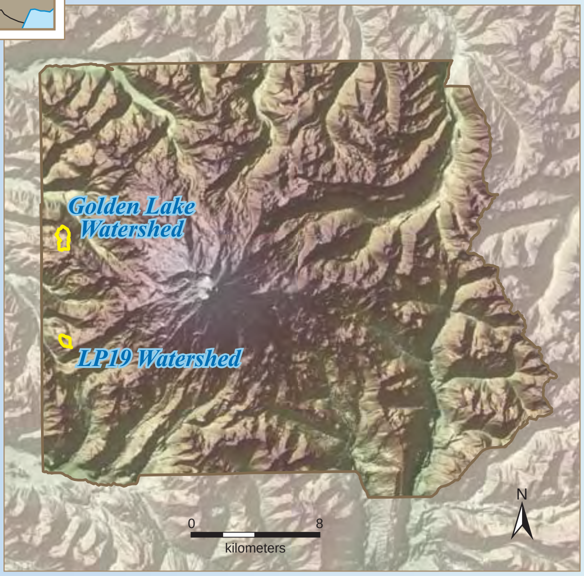
Sediment

Many of the sediment SOCs were below detection limits. When they were present, the two lake profiles showed some similarities. PAHs and PCBs showed the highest sediment fluxes. Mercury and lead had both increased since about 1900, suggesting a common source. Mercury showed a rapid percent enrichment near the surface (present time) of both lakes. The source of this increase is unknown, but global warming, increased global background, and/or trans-Pacific sources could be responsible. SCP profiles declined towards the surface, and did not correspond to changes in metal profiles.



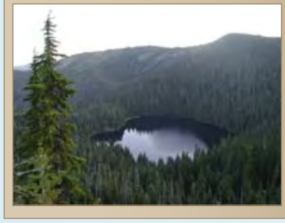
MORA

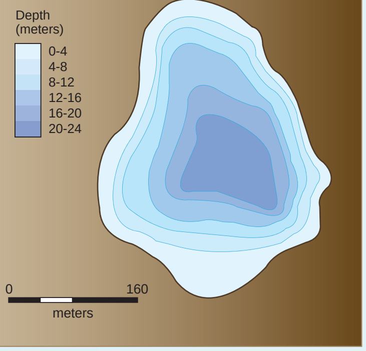
Mount Rainier National Park: *Site Characteristics*



Golden Lake

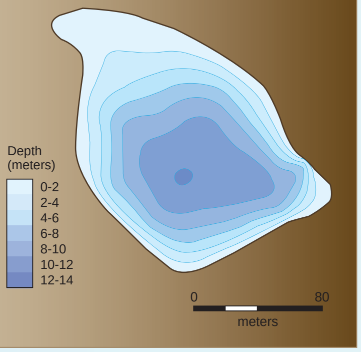
Location: 46.89N 121.90W
Elevation: 1368.6 m
Maximum Depth: 23.9 m
Surface Area: 6.6 ha
Watershed Area: 106.1 ha



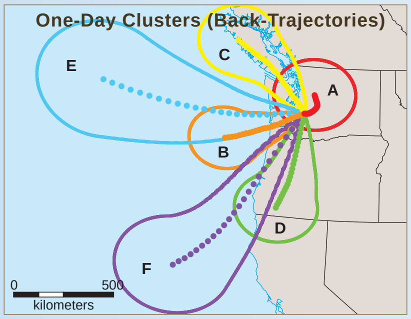


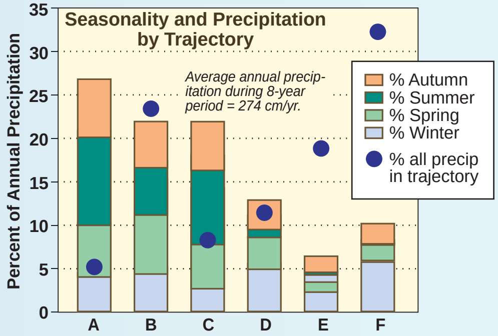
LP19

Location: 46.82N 121.89W
Elevation: 1371.6 m
Maximum Depth: 12.1 m
Surface Area: 1.8 ha
Watershed Area: 44.9 ha

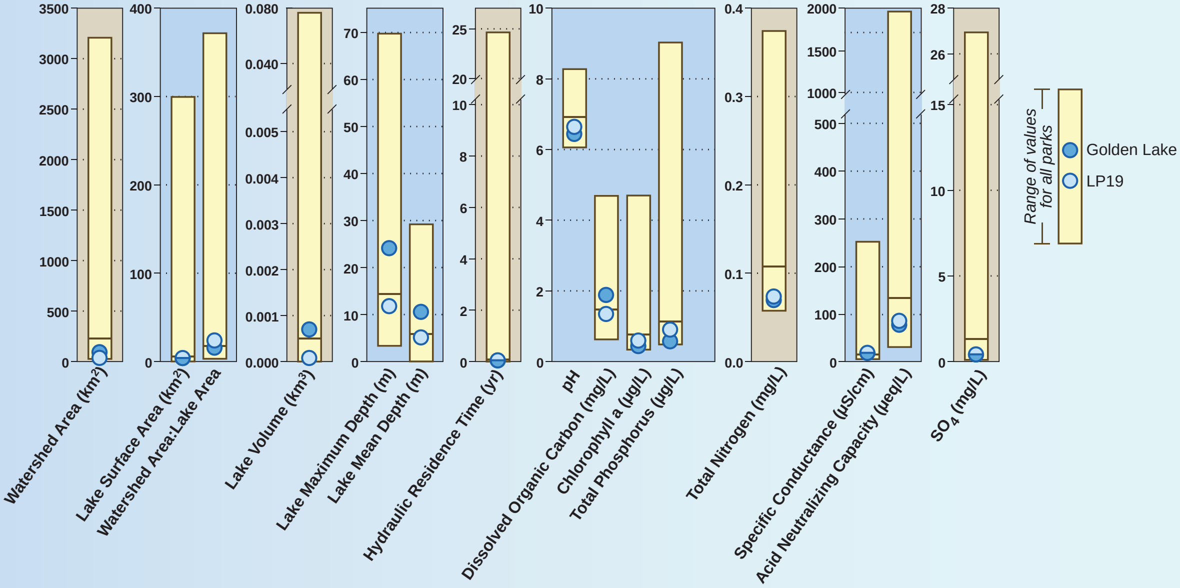


◆ Atmospheric Transport ◆

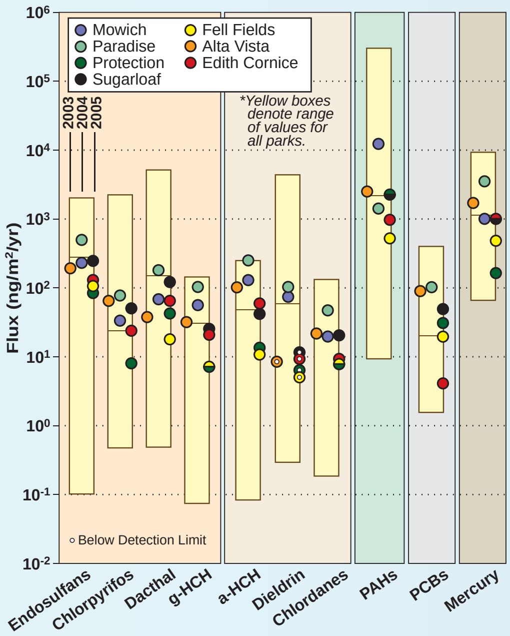




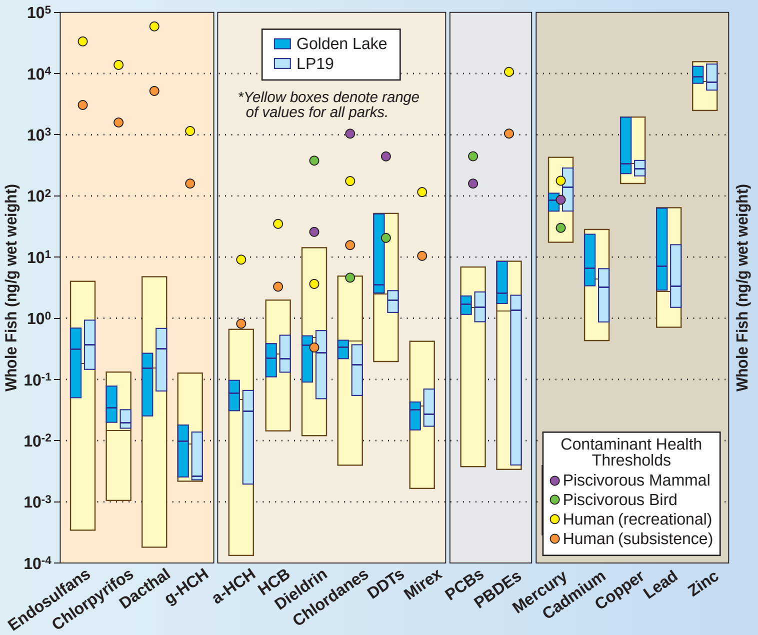
◆ Physical and Chemical Characteristics ◆



◆ Snow Contaminant Fluxes ◆

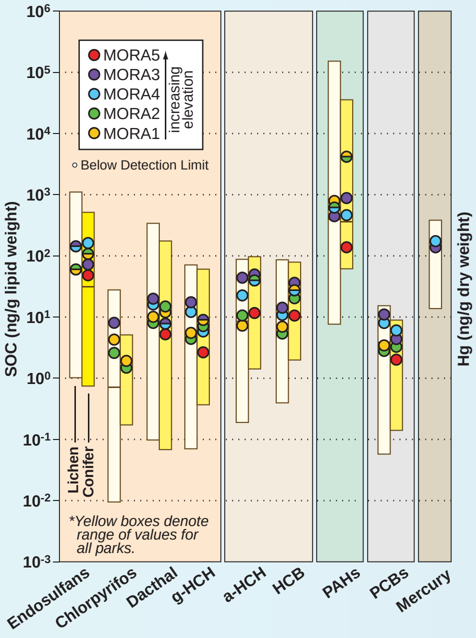


◆ Whole Fish Contaminant Concentrations ◆

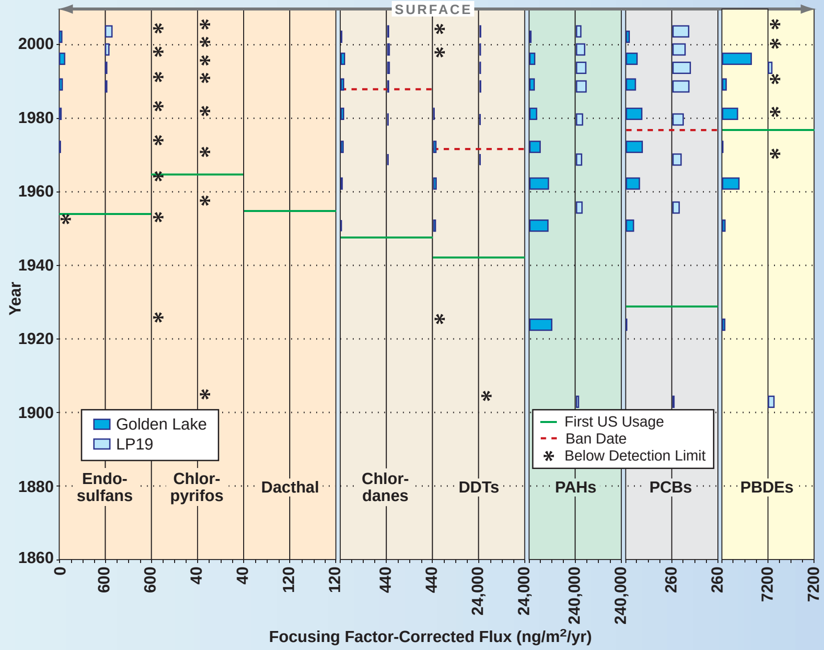


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

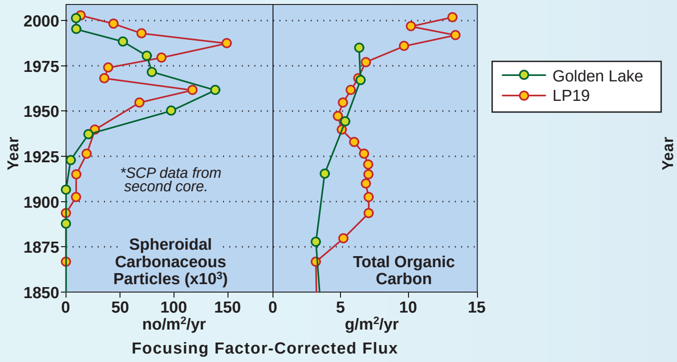
◆ Vegetation Contaminant Concentrations ◆



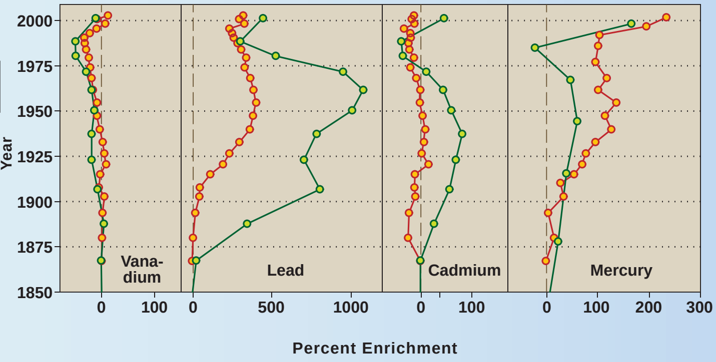
◆ Sediment Organic Contaminant Fluxes ◆



◆ Sediment Flux ◆



◆ Sediment Metals Enrichment ◆



Rocky Mountain National Park

Summary: Rocky Mountain National Park

Mills and Lone Pine lakes are characterized by low specific conductance and acid neutralizing capacity, typical of many sub-alpine lakes. Compared to lake surface area, their watershed areas are among the largest of all the lakes. Total nitrogen is fairly high at Mills Lake. For many SOCs, snow and sediment fluxes were higher at Mills Lake, on the eastern slope of the Continental Divide, where there is greater potential for transport from local and regional agricultural sources than for Lone Pine Lake on the western slope.

Air

There were four air monitors on the west side and one monitor on the east side of the Continental Divide. East-side concentrations for those SOCs detected by this method were similar to west-side concentrations, indicating no obvious east-west differences. The primary SOCs detected in air were PAHs, dacthal, endosulfans, HCB, a-HCH, and g-HCH. Low concentrations of the PCBs, chlordanes, and trifluralin were also detected.

Snow

Snowpack deposition fluxes of endosulfans and dacthal were high in ROMO compared to fluxes at most other parks, and fish concentrations of these compounds were high as well. Mercury deposition fluxes in the snowpack were high relative to those at other parks; however, fish mercury was low, indicating low rates of mercury methylation and bioaccumulation. Contaminant fluxes measured in the snowpack do not account for atmospheric deposition during summer rains. However, summer precipitation is higher in ROMO than in most other parks, and rainfall concentrations of many contaminants are also high, indicating that a larger significant source of contaminant deposition was unmeasured. Deposition fluxes of dieldrin in the snowpack were also consistently higher at Mills Lake than at sites to the west, suggesting re-emission from contaminated soils to the east (dieldrin was manufactured in Denver) and subsequent transport on upslope airflow.

Vegetation

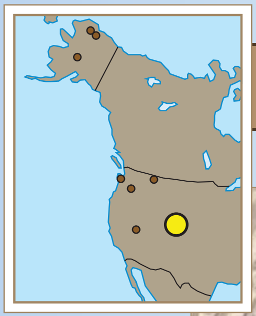
Unlike concentrations in sediments and snow, SOC concentrations in vegetation were in the low to median ranges compared to those at other parks and not different on east and west sides of the Continental Divide. SOCs detected in vegetation were PAHs (mostly CHR/TRI, retene, PHE, and ANT), endosulfans, g-HCH, a-HCH, dacthal, HCB, chlorpyrifos, DDTs, and PCBs. Lichen concentrations indicate enhanced nitrogen and sulfur deposition; metals were within expected ranges for remote sites.

Fish

Mercury and macrophage aggregates increased with increasing age of fish in both lakes, although mercury was fairly low. Spleen and kidney macrophage aggregates were also positively related to mercury in both lakes. Endosulfans and dacthal were fairly high. Additional lakes (9 total) were sampled as part of a related NPS study and elevated estrogen-responsive protein was found in males from four of the nine lakes. Poorly developed testes and/or intersex male trout were also found in five of the nine lakes sampled. These data suggest that endocrine and reproductive disruption is occurring in several park lakes. Dieldrin concentrations in all fish exceeded contaminant health thresholds for subsistence fishers and some fish from both lakes exceeded thresholds for recreational fishers. Mercury concentrations in some fish exceeded contaminant health thresholds for piscivorous mammals (otter or mink) and/or birds (kingfishers) at both lakes.

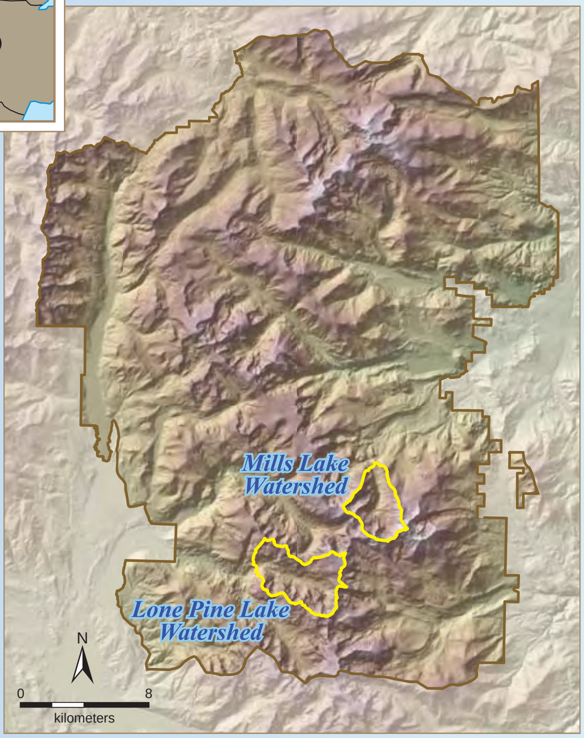
Sediment

Lake sediment profiles indicate that fluxes of most current-use pesticides, historic-use pesticides, and urban chemicals have steadily increased since their use in the USA began and no widespread decrease in flux or enrichment has occurred. In Lone Pine Lake, lead, cadmium, and mercury show a similar historic increase in the lake sediments beginning around 1875 that could be related to a common source, such as metal mining and smelting. Mills Lake shows similarity in the profiles for these metals beginning later, around 1915, but the two systems show similar mercury enrichment. All three metals have decreased in recent times.



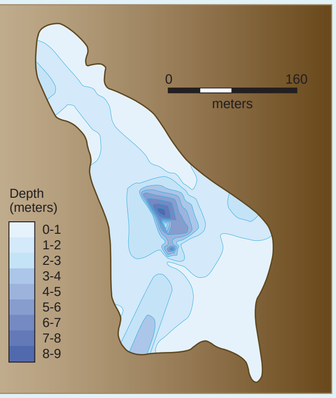
ROMO

Rocky Mountain National Park: *Site Characteristics*



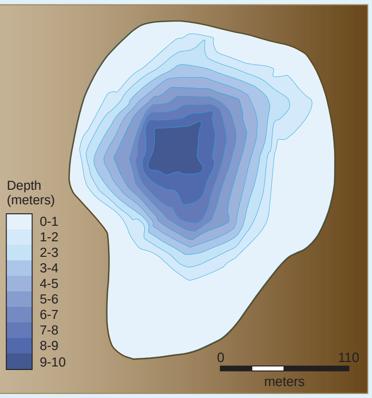
Mills Lake

Location: 40.29N 105.64W
Elevation: 3029.7 m
Maximum Depth: 9.0 m
Surface Area: 6.1 ha
Watershed Area: 1208.9 ha

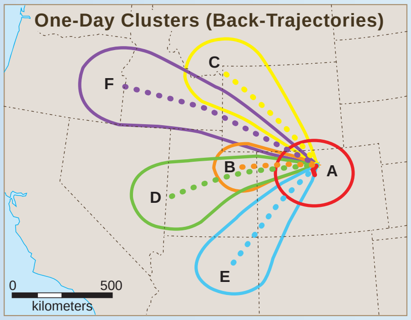


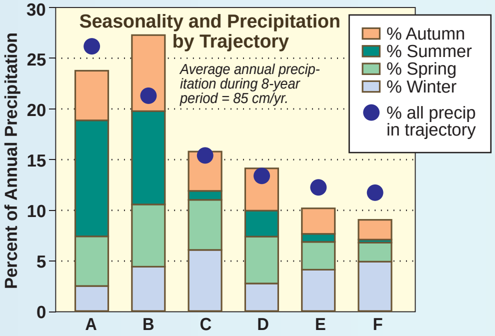
Lone Pine Lake

Location: 40.22N 105.73W
Elevation: 3017.5 m
Maximum Depth: 9.7 m
Surface Area: 4.9 ha
Watershed Area: 1830.0 ha

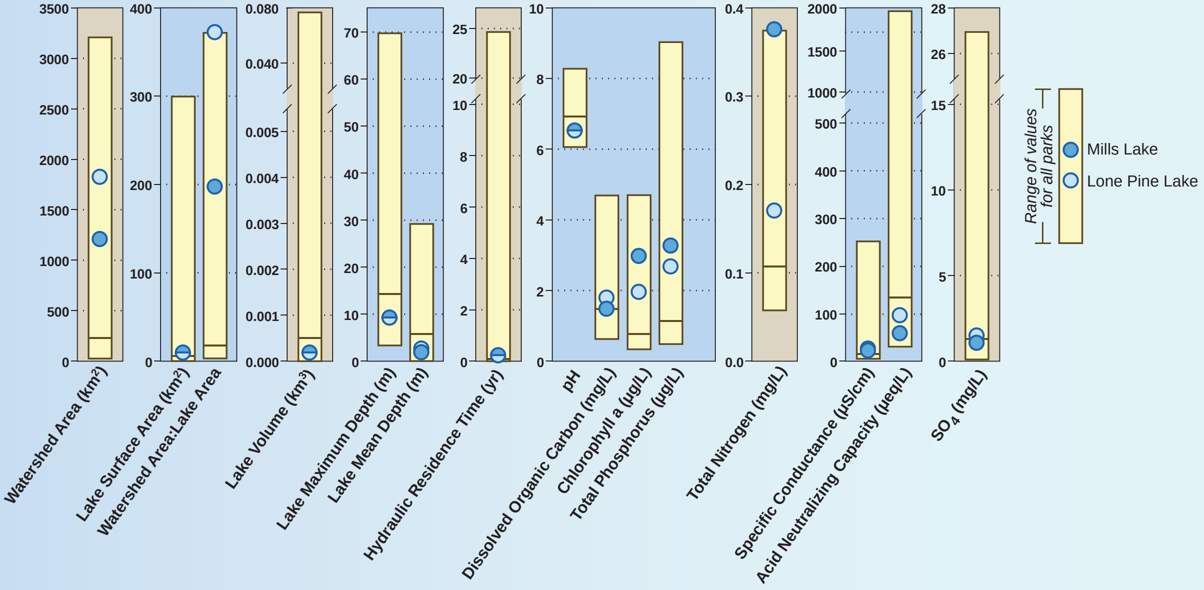


◆ Atmospheric Transport ◆

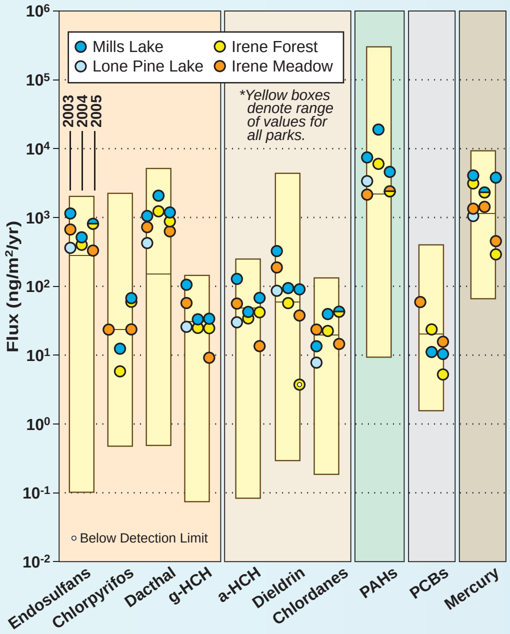




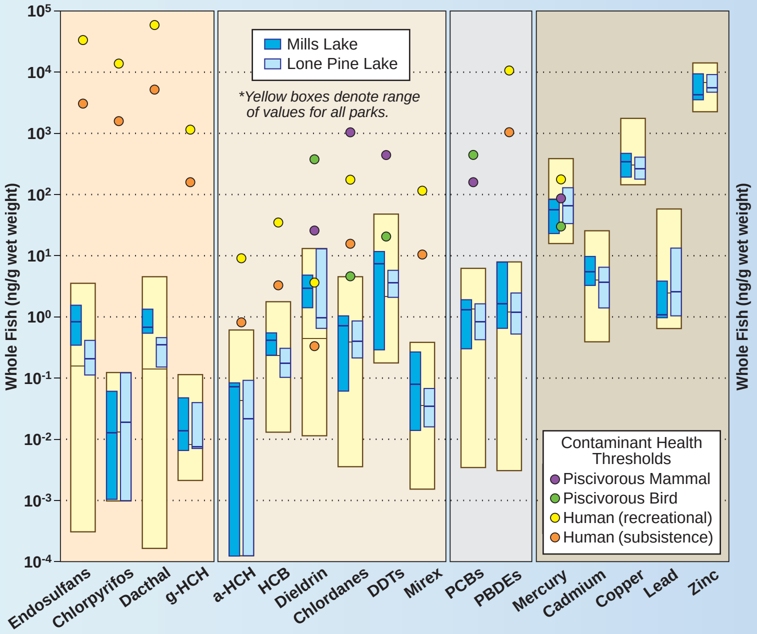
◆ Physical and Chemical Characteristics ◆



◆ Snow Contaminant Fluxes ◆

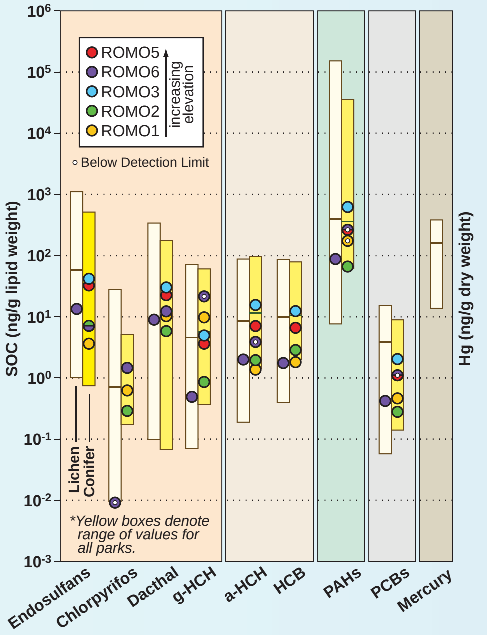


◆ Whole Fish Contaminant Concentrations ◆

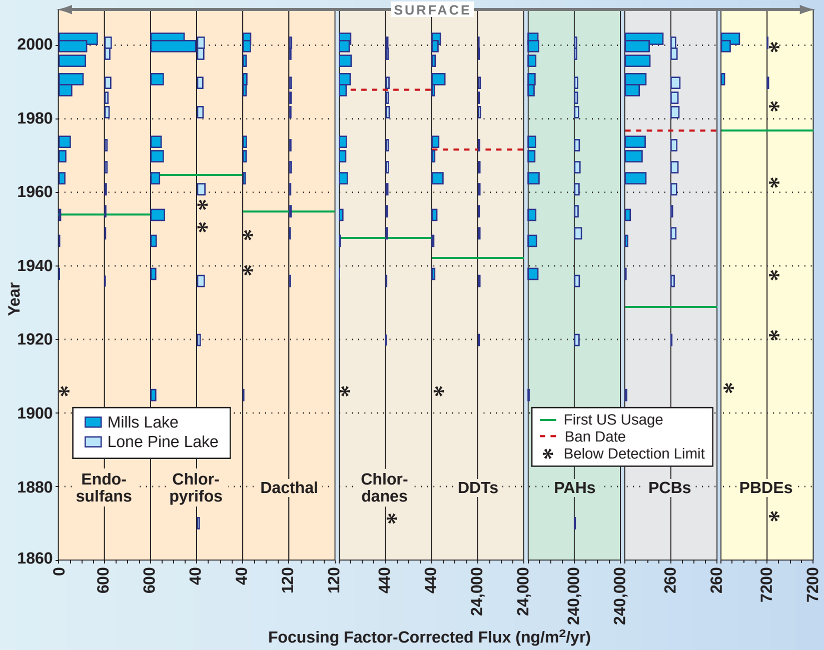


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

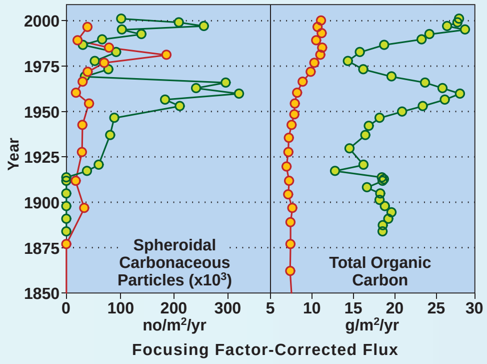
◆ Vegetation Contaminant Concentrations ◆



◆ Sediment Organic Contaminant Fluxes ◆

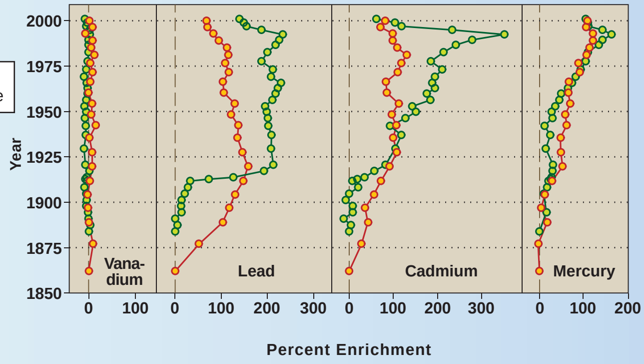


◆ Sediment Flux ◆



Mills Lake
Lone Pine Lake

◆ Sediment Metals Enrichment ◆



Sequoia and Kings Canyon National Parks

Summary: Sequoia and Kings Canyon National Parks

Emerald and Pear lakes are similar physically and chemically, although Emerald Lake is a bit shallower and has slightly higher total phosphorus and nitrogen. Compared to the other sites, they are among the most dilute, poorly buffered (i.e., have low acid neutralizing capacity), and oligotrophic (low productivity) systems. At SEKI, air, vegetation, and snow had among the highest concentrations for current-use pesticides, compared with these media in the other parks. The source of these compounds could be regional agriculture within a few hundred kilometers of the park.

Air

SOCs detected in air were trifluralin, dacthal, endosulfans, chlorpyrifos, and g-HCH, all of which are current-use pesticides. In addition, HCB, a-HCH, dieldrin, PCBs, and PAHs were detected. Most SOC concentrations in air ranked high relative to those in other parks and more SOCs were detected in SEKI than in other parks.

Snow

Atmospheric deposition in SEKI is dominated by deep snowpacks with high snow water equivalent. Concentrations of many current-use pesticides and historic-use pesticides were high, producing high deposition fluxes in the snow. In contrast, with few local or regional sources of mercury emissions upwind, mercury concentrations in the snow were generally low, producing only moderate fluxes of mercury deposition. Summers are generally quite dry in SEKI, providing less opportunity for wet deposition of contaminants in rainfall than wetter summers at parks in the Rocky Mountains.

Vegetation

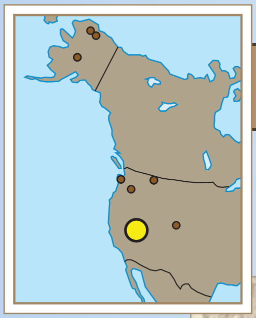
SOCs, Hg, and nutrient concentrations in SEKI vegetation were in the median to highest ranges among the parks, attributable partly to intensive regional agriculture. SOCs detected in vegetation were PAHs (mostly retene, CHR/TRI, PHE, FLO, FLA, and PYR), endosulfans, dacthal, DDTs, chlorpyrifos, HCB, g-HCH, dieldrin, a-HCH, and PCBs. Lichen concentrations indicate enhanced nitrogen and sulfur deposition. Concentrations of endosulfan, dacthal, HCH, HCB, and chlorpyrifos in lichens increased with elevation. Because forest productivity is high, pesticides scrubbed from the air by vegetation probably contribute significant contaminant loads to the ecosystem via canopy through-fall and needle litter-fall.

Fish

Mercury and macrophage aggregates increased with increasing fish age in both lakes. Spleen and kidney macrophage aggregates were positively related to mercury at Pear Lake, but only kidney macrophage aggregates were so related at Emerald Lake. All fish appeared normal reproductively. Current-use SOC concentrations in fish were among the highest measured. Lake average dieldrin and individual fish p,p′-DDE concentrations in both lakes exceeded contaminant health thresholds for subsistence fishers; the dieldrin concentration in one fish in Pear Lake exceeded the threshold for recreational fishers. In at least one fish from each lake, contaminant health thresholds for mercury and DDTs were exceeded for one or more piscivores (otter, mink, kingfishers). Two fish from Pear Lake exceeded the human contaminant health threshold for mercury.

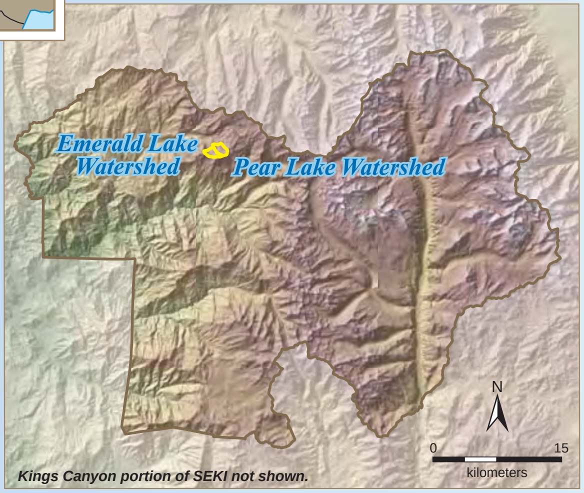
Sediment

SOC flux profiles are very similar in both lakes, and SOCs appear after being registered for use in the USA. DDTs and chlordanes decrease after being banned in the USA, but PCBs are still accumulating. Mercury began to increase in both lakes in the late 1800s, and lead began to increase around 1900. Mercury profiles are similar in both lakes, in that they tend to stabilize, noisily, at about 100% enrichment. Lead and cadmium profiles are similar in Pear Lake, both peaking in the 1970s and decreasing toward the surface (present time). SCPs were first detected in the late 1800s, but the patterns in both lakes are not closely associated with metal flux profiles, suggesting that major high temperature combustion sources were not the primary historic source of metals to the sediments.



SEKI

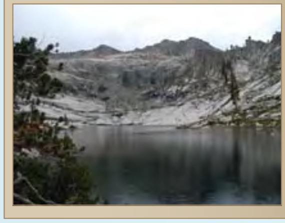
Sequoia and Kings Canyon National Parks: *Site Characteristics*

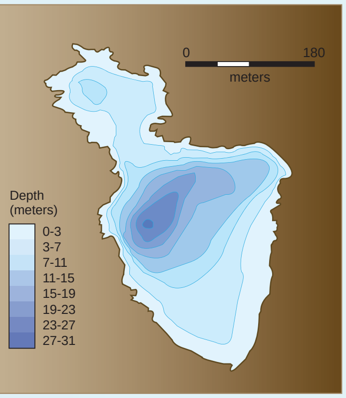


Kings Canyon portion of SEKI not shown.

Pear Lake

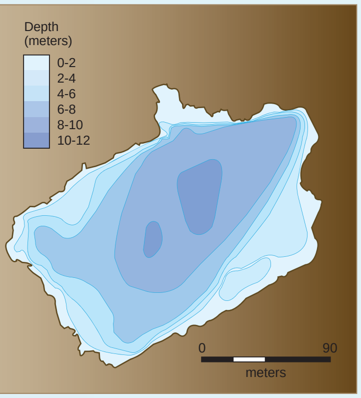
Location: 36.60N 118.67W
Elevation: 2907.8 m
Maximum Depth: 27.0 m
Surface Area: 7.3 ha
Watershed Area: 142.0 ha



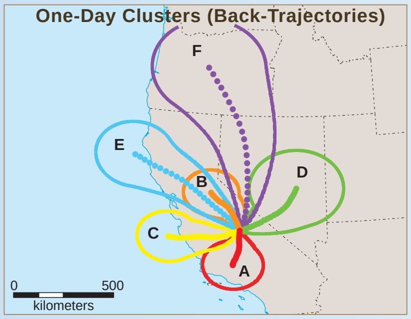


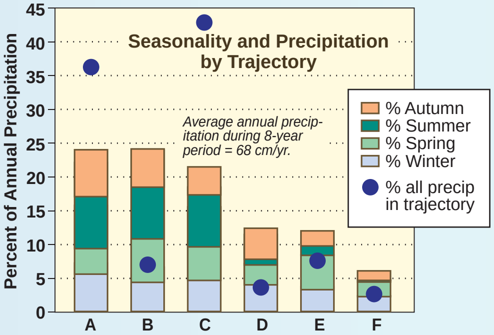
Emerald Lake

Location: 36.58N 118.67W
Elevation: 2810.3 m
Maximum Depth: 10.0 m
Surface Area: 2.5 ha
Watershed Area: 121.3 ha

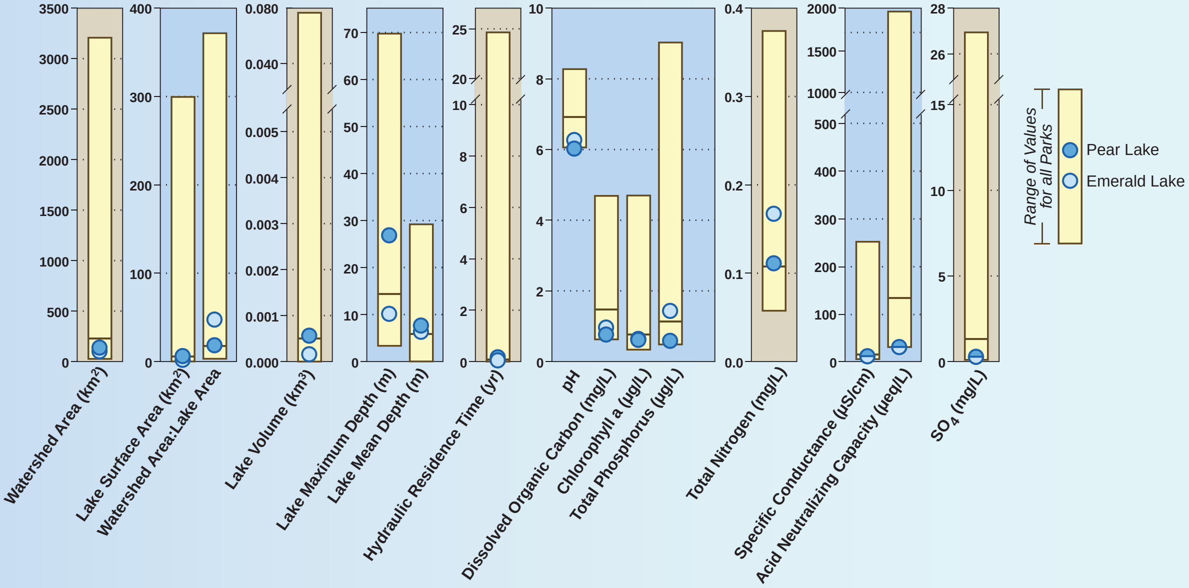


◆ Atmospheric Transport ◆

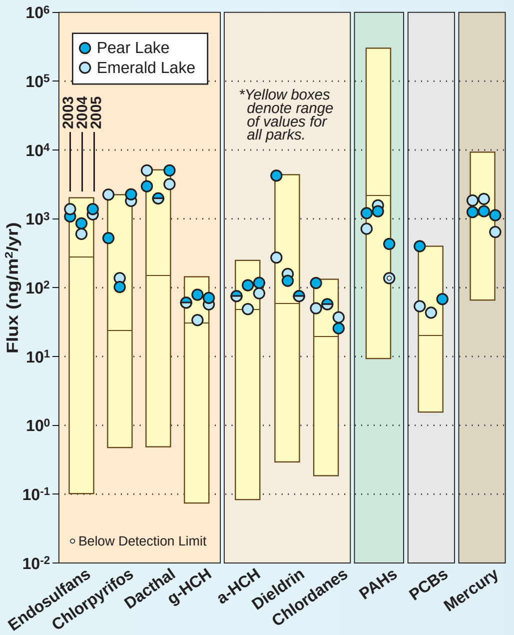




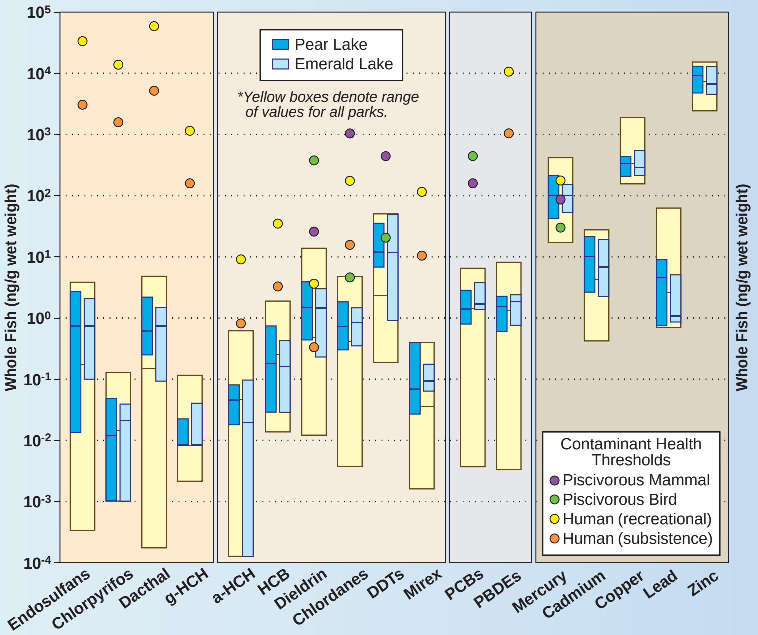
◆ Physical and Chemical Characteristics ◆



◆ Snow Contaminant Fluxes ◆

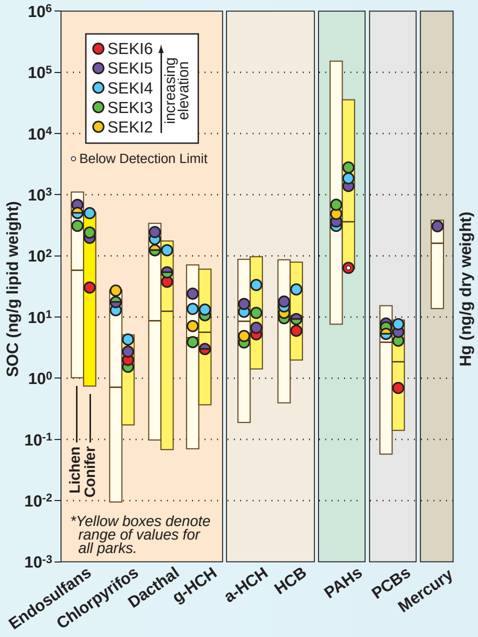


◆ Whole Fish Contaminant Concentrations ◆

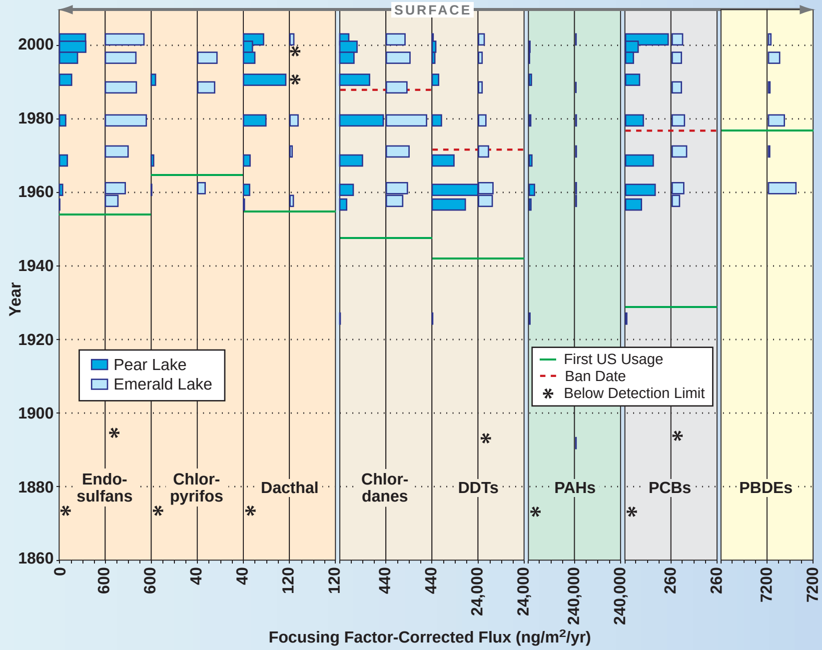


☐ Current-Use Pesticides ☐ Historic-Use Pesticides ☐ Combustion By-products ☐ Industrial Compounds ☐ Metals ☐ Current-Use Chemical

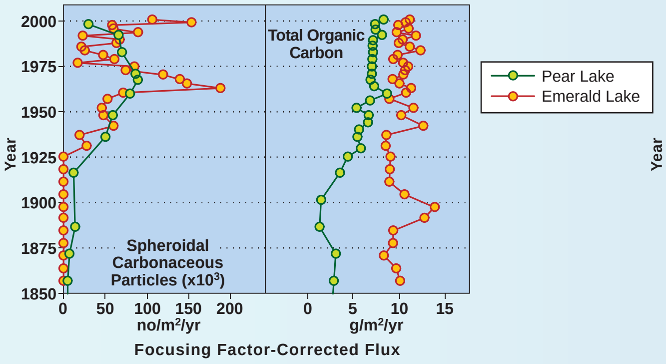
◆ Vegetation Contaminant Concentrations ◆



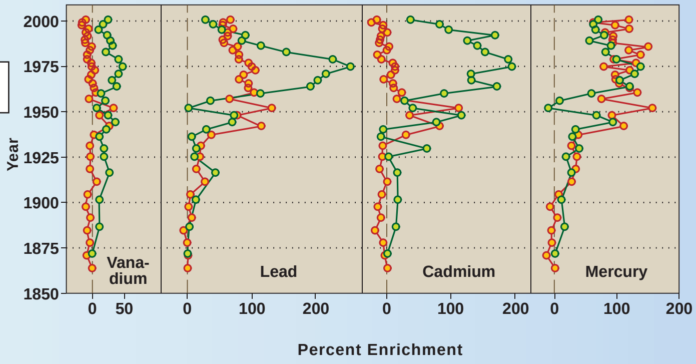
◆ Sediment Organic Contaminant Fluxes ◆



◆ Sediment Flux ◆



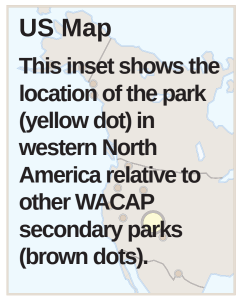
◆ Sediment Metals Enrichment ◆



Secondary Parks

The pages that follow have been prepared to provide the reader with a summary of contaminant results for air and vegetation sampling in each secondary WACAP park. The word *park*, as used here, encompasses federally managed lands, including national parks, monuments, preserves, and wilderness. The objectives and design for sampling in the secondary parks are described this report in Section 1.3, Park Selection, Section 3.4.3, Air, and Section 3.4.4, Vegetation.

The one-page key on page 2-33 provides explicit detail regarding each block of information the reader will encounter. Summaries for all secondary parks are presented in the same format. The summaries are designed so that the location and contaminant concentrations at the four to six sampling sites within each park and across all parks can easily be visualized and compared. The reader is encouraged to consult the other chapters of this report and the primary park summaries for more information on the full range of WACAP results and their interpretation.



US Map

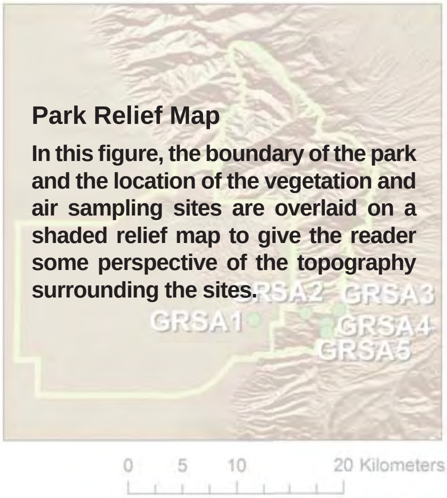
This inset shows the location of the park (yellow dot) in western North America relative to other WACAP secondary parks (brown dots).

KEY

The pages that follow have been prepared to provide the reader with a summary of contaminant results for air and vegetation sampling in each secondary WACAP park. The word *park,* as used here, encompasses federally managed lands, including national parks, monuments, preserves, and wilderness. This one-page key provides explicit detail regarding each block of information the reader will encounter. Summaries for all secondary parks are presented in the same format. The summaries are designed so that the location and contaminant concentrations at the four to six sampling sites within each park and across all parks can be easily visualized and compared. The reader is encouraged to consult the other chapters of this report and the primary park summaries for more information on the full range of WACAP results and their interpretation.

Site Photos

A photograph of the environs at each site is provided to give the reader an appreciation of the vegetative cover, steepness of the landscape, climate, and geology. The name of the sampling site is given with some very basic information: a short verbal description of the site location, latitude and longitude in decimal degrees, average annual temperature and precipitation estimated by the PRISM model, whether or not air was sampled at the site, and the scientific names of the conifer and lichen vegetation sampled at the site. Units follow the metric system: m = meters, cm = centimeters, °C = degrees Centigrade. N, W = north, and west.



Park Relief Map

In this figure, the boundary of the park and the location of the vegetation and air sampling sites are overlaid on a shaded relief map to give the reader some perspective of the topography surrounding the sites.

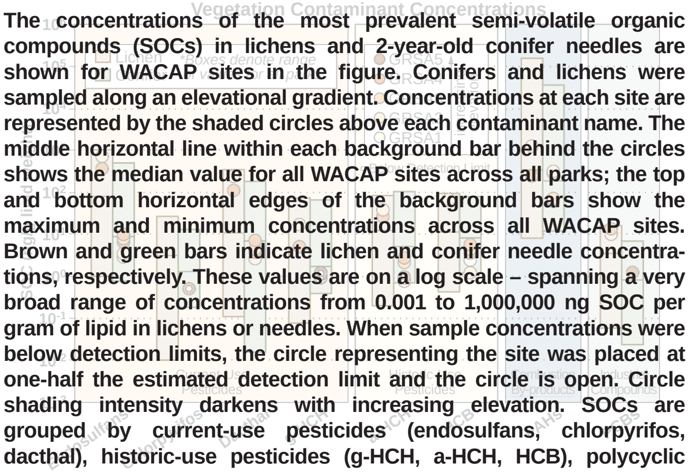
Air Summary Statements

This text block summarizes the results of the laboratory analysis of the passive air sampling devices (PASDs) and highlights the most important findings. These include the location of the monitors in the parks, the SOCs detected and their concentrations in picograms per gram XAD resin (dry weight), within-park differences in SOC concentrations if multiple samplers were deployed, and how park SOC concentrations ranked relative to other WACAP parks.

Vegetation Summary Statements

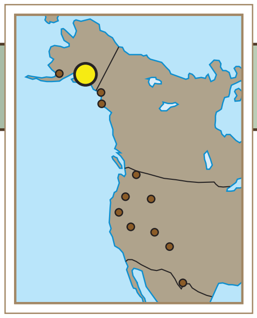
This text block summarizes the results of the laboratory analysis of vegetation samples and highlights the most important findings. These include: the SOCs detected and their concentrations in nanograms per gram conifer needle lipid or lichen lipid; differences between concentrations in needles versus lichens, if important; effects of elevation on concentrations of SOCs in lichens; ranking of SOC concentrations in vegetation relative to vegetation in other WACAP parks; concentrations of nitrogen and sulfur (nutrients), mercury and other toxic metals in lichens relative to known or expected background ranges; and ecological implications of, or concerns indicated by, the results.

Vegetation Contaminant Concentrations



The concentrations of the most prevalent semi-volatile organic compounds (SOCs) in lichens and 2-year-old conifer needles are shown for WACAP sites in the figure. Conifers and lichens were sampled along an elevational gradient. Concentrations at each site are represented by the shaded circles above each contaminant name. The middle horizontal line within each background bar behind the circles shows the median value for all WACAP sites across all parks; the top and bottom horizontal edges of the background bars show the maximum and minimum concentrations across all WACAP sites. Brown and green bars indicate lichen and conifer needle concentrations, respectively. These values are on a log scale – spanning a very broad range of concentrations from 0.001 to 1,000,000 ng SOC per gram of lipid in lichens or needles. When sample concentrations were below detection limits, the circle representing the site was placed at one-half the estimated detection limit and the circle is open. Circle shading intensity darkens with increasing elevation. SOCs are grouped by current-use pesticides (endosulfans, chlorpyrifos, dacthal), historic-use pesticides (g-HCH, a-HCH, HCB), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). Metals were not analyzed in vegetation samples at secondary parks.

Wrangell - St. Elias National Park and Preserve: *Summary*

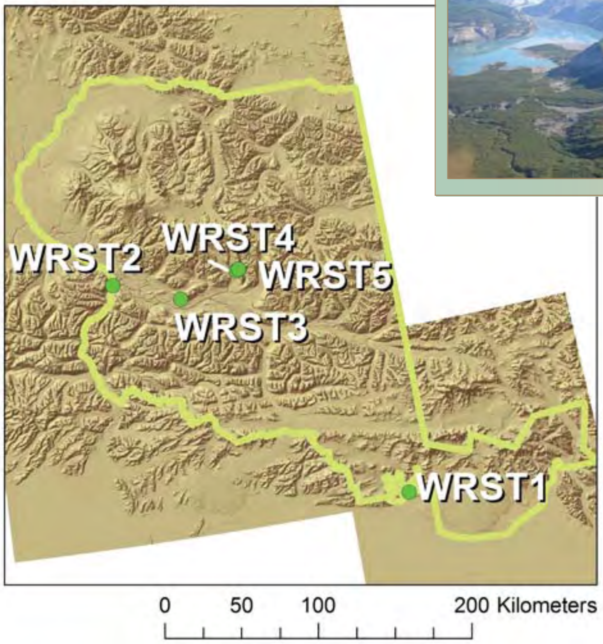


WRST

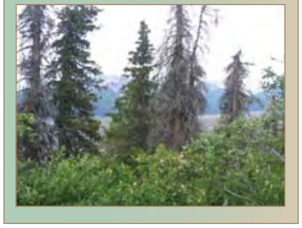
WRST1
Kageets Pt at Icy Bay
Location: 60.05N 141.31W
Elevation: 7 m
Ave. Ann. Temp: 3.1°C
Ave. Ann. Precip: 312 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca, Hypogymnia apinnata*

WRST2
Chintina and Copper R confluence
Location: 61.52N 144.40W
Elevation: 219 m
Ave. Ann. Temp: -1.9°C
Ave. Ann. Precip: 31 cm
Air Sampler: No
Conifer: *Picea glauca*
Lichen: None

WRST3
Crystalline Hills Trail
Location: 61.39N 143.60W
Elevation: 648 m
Ave. Ann. Temp: -1.7°C
Ave. Ann. Precip: 62 cm
Air Sampler: Yes
Conifer: *Picea glauca*
Lichen: *Hypogymnia physodes*



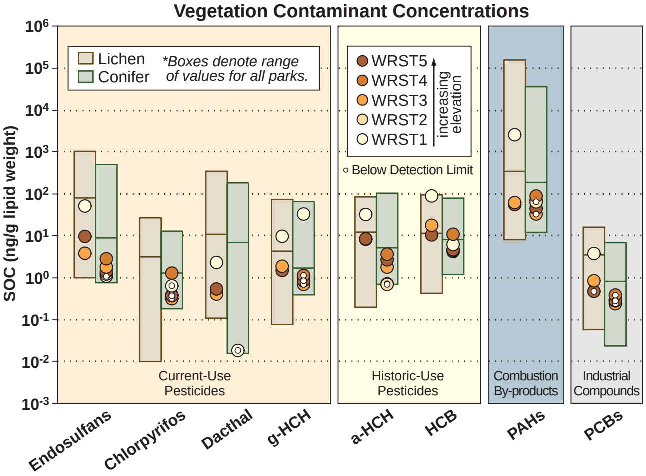
WRST4
Bonanza Mine Trail 1020m
Location: 61.50N 142.87W
Elevation: 1020 m
Ave. Ann. Temp: -2.2°C
Ave. Ann. Precip: 85 cm
Air Sampler: No
Conifer: *Picea glauca*
Lichen: None



WRST5
Bonanza Mine Trail 1421m
Location: 61.50N 142.84W
Elevation: 1421 m
Ave. Ann. Temp: -2.7°C
Ave. Ann. Precip: 127 cm
Air Sampler: No
Conifer: *Picea glauca*
Lichen: *Flavocetraria cucullata, Cladina arbuscula*

Air Summary

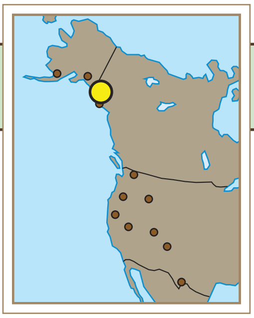
- The air sampler, at WRST3 in the Crystalline Hills, near McCarthy, Alaska, had the lowest number of detected SOCs among the 20 WACAP parks.
- Only PAHs (285 pg/g dry XAD, a mid-range level compared with concentrations in other WACAP parks) and low concentrations of g-HCH (18 pg/g dry XAD) were detected.



Vegetation Summary

- Among the 20 WACAP parks, SOCs in vegetation from interior WRST (sites 2-5) were at or below the median, or were not detected.
- Dominant SOCs were PAHs (17-74 ng/g lipid in conifers, 43-4346 in lichens), HCB (3-11 in conifers, 9-150 in lichens), a-HCH (4-54), and g-HCH (1-36).
- Small amounts of PCBs (<5 ng/g lipid), chlorpyrifos (<1), dacthal, and chlordanes (<4) were also detected.
- Highest concentrations of g-HCH and chlordanes in lichens and conifer needles, and highest concentrations of endosulfans, HCB, a-HCH, dacthal, PCBs, and PAHs in lichens were observed at the high precipitation, marine site at Icy Bay (WRST1).
- Nitrogen concentrations in lichens were within background ranges, indicating that nitrogen deposition is not elevated.

Glacier Bay National Park: *Summary*



GLBA

GLBA1
Beartrack Cove
Location: 58.60N 135.88W
Elevation: 8 m
Ave. Ann. Temp: 4°C
Ave. Ann. Precip: 261 cm
Air Sampler: Yes
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca*

GLBA2
Beartrack Mtn footslopes
Location: 58.61N 135.88W
Elevation: 168 m
Ave. Ann. Temp: 4°C
Ave. Ann. Precip: 261 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Sphaerophorus globosus*

GLBA3
Beartrack Mtn glacial trim line
Location: 58.61N 135.87W
Elevation: 457 m
Ave. Ann. Temp: 4°C
Ave. Ann. Precip: 261 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Sphaerophorus globosus*

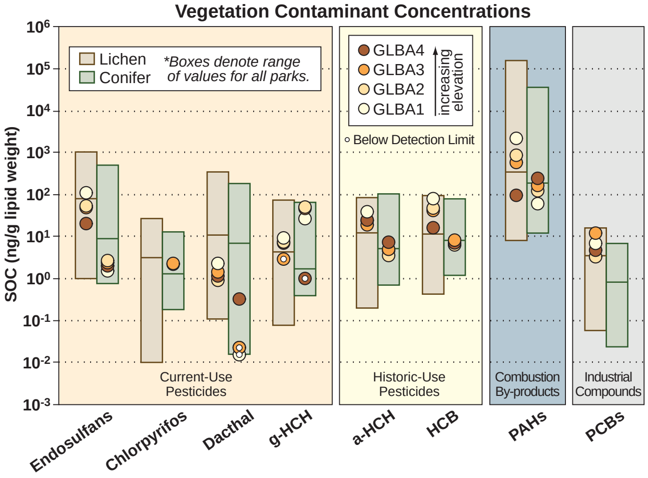
GLBA4
Beartrack Mtn treeline
Location: 58.61N 1035.87W
Elevation: 625 m
Ave. Ann. Temp: 4°C
Ave. Ann. Precip: 261 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Alectoria sarmentosa*

Vegetation Summary

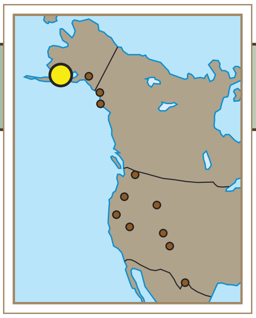
- The dominant SOCs detected in lichens were PAHs (100-3000 ng/g lipid), endosulfans (21-115), HCB (17-80) and a-HCH (20-41); the dominant SOCs detected in conifer needles were PAHs (45-23), g-HCH (1-53), HCB (7-9), and a-HCH (4-8).
- Concentrations of HCBs and a-HCH in lichens and g-HCH (all HUPs) in conifers ranked very high compared to concentrations at other WACAP parks.
- Other SOCs detected in vegetation were low concentrations of dacthal (<2.5), chlordanes (0.2-8), and PCBs (3-10).
- Although pesticide concentrations and compounds detected essentially replicate STLE in both lichens and conifer needles, with respect to PAHs, GLBA had a higher proportion of 4-5 ring PAHs and more retene than STLE to the south and WRST to the north, pointing to a local source.
- As at other parks, PAH concentrations decreased with increasing elevation. Pesticides and PCBs that were observed to increase with elevation in other parks did not increase at GLBA. A possible explanation is that a very good accumulator, *Platismatia glauca*, was collected at sea level and the poorest accumulator, *Alectoria sarmentosa*, was collected at the highest elevation.
- Lichen nitrogen concentrations were elevated at sea level, but concentrations at higher elevations were within species-specific background ranges expected for southeastern Alaska and remote sites in the Pacific Northwest.

Air Summary

- The air sampler was near sea level at GLBA1, Beartrack Cove.
- Moderate concentrations of HUPs HCB (15 pg/g dry XAD) and a-HCH (17) and low concentrations of CUPs trifluralin (1.4), endosulfans (24), and HUP g-HCH (17) were detected.
- Overall, SOC concentrations in air at GLBA ranked very low compared to those at other WACAP parks.



Katmai National Park and Preserve: *Summary*



KATM

KATM1
3 Forks Overlook Road 2 km

Location: 58.55N 155.78W
Elevation: 36 m
Ave. Ann. Temp: 2.2°C
Ave. Ann. Precip: 50 cm
Air Sampler: No
Conifer: *Pinus glauca*
Lichen: *Hypogymnia physodes*

KATM2
Dumpling Mtn Trail at 183 m

Location: 58.57N 155.79W
Elevation: 213 m
Ave. Ann. Temp: 1.9°C
Ave. Ann. Precip: 54 cm
Air Sampler: No
Conifer: *Pinus glauca*
Lichen: *Hypogymnia physodes*

KATM3
Dumpling Mtn Trail at 366 m

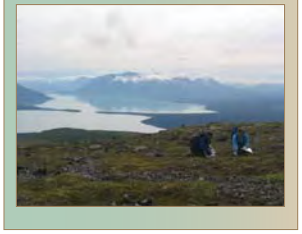
Location: 58.57N 155.80W
Elevation: 370 m
Ave. Ann. Temp: 1.9°C
Ave. Ann. Precip: 54 cm
Air Sampler: Yes
Conifer: *Pinus glauca*
Lichen: *Hypogymnia physodes*

KATM4
Dumpling Mtn Trail at 563 m

Location: 58.57N 155.84W
Elevation: 563 m
Ave. Ann. Temp: 1.4°C
Ave. Ann. Precip: 68 cm
Air Sampler: No
Conifer: *Pinus glauca*
Lichen: *Flavocetraria cucullata*

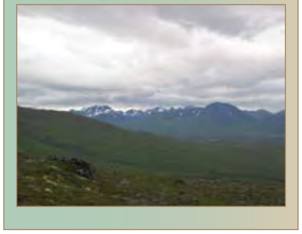
KATM5
Dumpling Mtn summit

Location: 58.58N 155.86W
Elevation: 724 m
Ave. Ann. Temp: 1.4°C
Ave. Ann. Precip: 68 cm
Air Sampler: No
Conifer: *Pinus glauca*
Lichen: *Flavocetraria cucullata*



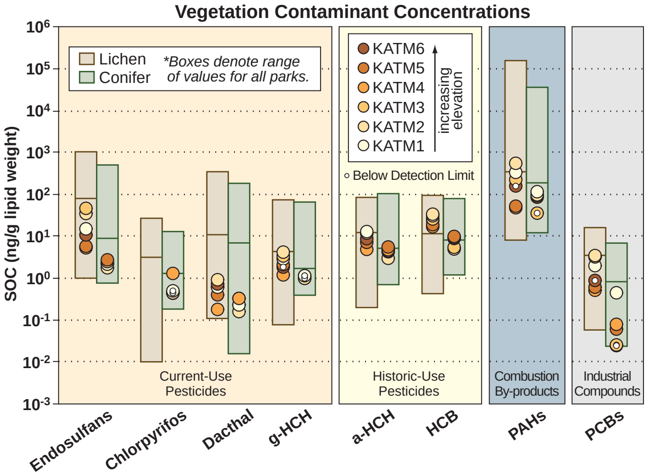
KATM6
Mt. Katolinat

Location: 58.47N 155.49W
Elevation: 1112 m
Ave. Ann. Temp: 0.1°C
Ave. Ann. Precip: 83 cm
Air Sampler: No
Conifer: None
Lichen: *Flavocetraria cucullata*



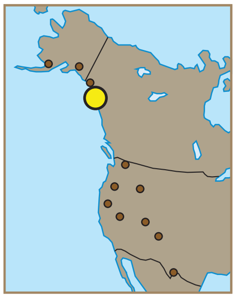
Air Summary

- The air sampler was at KATM3.
- Concentrations of HUPs HCB (1260 pg/g dry XAD), a-HCH (340), and g-HCH (57) were among the highest values recorded from WACAP parks.
- Endosulfans (61 pg/g dry XAD), trifluralin (1), and chlordanes (14) were also detected, but concentrations were low compared to those at other WACAP parks.



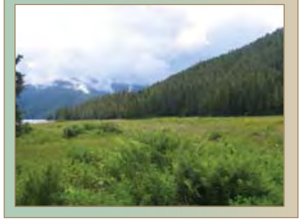
Vegetation Summary

- Concentrations in vegetation of all SOCs except HCB were at or below the median for WACAP parks; in general, KATM was one of the least contaminated WACAP parks.
- Dominant SOCs in KATM vegetation were PAHs (10-600 ng/g lipid), endosulfans (<2 in conifers, 5-47 in lichens), HCB (5-35), and a-HCH (10-24).
- Low concentrations of chlorpyrifos and dacthal (<1 ng/g lipid), g-HCH, chlordanes (<5), and PCBs (<3) were also detected.
- Small increases in spruce needle concentrations of endosulfans, dacthal, a-HCH, and HCB were observed with increasing elevation from 36 to 724 m; lichens also showed this trend when the tundra lichen, *Flavocetraria cucullata*, collected at the top three elevations, and the epiphyte, *Hypogymnia physodes*, a better accumulator, collected at the lowest three elevations, were considered separately.
- Lichen nitrogen concentrations were within background ranges, indicating that nitrogen deposition is not elevated.



STLE

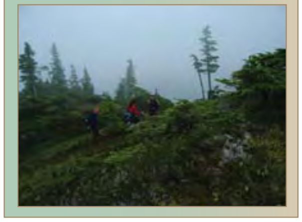
STLE1
Bussey Creek outlet in Icy Bay
Location: 56.79N 132.51W
Elevation: 1 m
Ave. Ann. Temp: 4.5°C
Ave. Ann. Precip: 318 cm
Air Sampler: Yes
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca, Alectoria sarmentosa*



STLE2
Bussey Creek ridge line
Location: 56.80N 132.53W
Elevation: 254 m
Ave. Ann. Temp: 3.6°C
Ave. Ann. Precip: 378 cm
Air Sampler: Yes
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca, Lobaria oregana*

STLE3
Muskeg bench over Bussey Creek
Location: 56.81N 132.54W
Elevation: 567 m
Ave. Ann. Temp: 3.6°C
Ave. Ann. Precip: 378 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Alectoria sarmentosa*

STLE4
0.4 km NW of Bussey Lake
Location: 56.83N 132.57W
Elevation: 815 m
Ave. Ann. Temp: 2.7°C
Ave. Ann. Precip: 488 cm
Air Sampler: Yes
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca, Alectoria sarmentosa*



STLE5
Thunder Mtn summit
Location: 56.82N 132.61W
Elevation: 1064 m
Ave. Ann. Temp: 3.6°C
Ave. Ann. Precip: 431 cm
Air Sampler: No
Conifer: *Picea sitchensis*
Lichen: *Platismatia glauca, Cladina arbuscula*

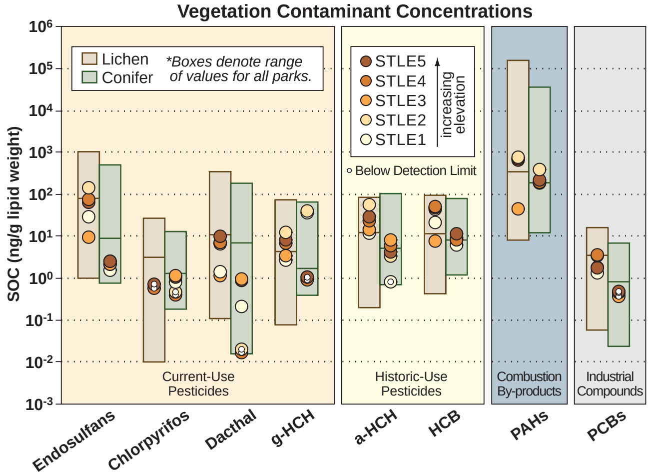
Vegetation Summary

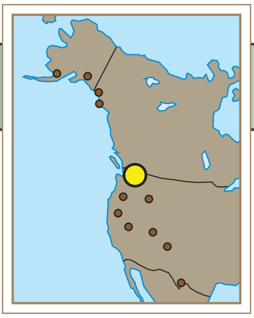
- Among the 20 parks, vegetation samples from STLE were at or below the median for CUPs, PCBs, and PAHs, and at or above the median for HUPs; this pattern was also observed at other high precipitation sites along coastal southeastern Alaska (i.e., WRST1, GLBA all).
- Dominant SOCs were PAHs (27-2251 ng/g lipid), endosulfans (<2 in conifers, 5-272 in lichens), a-HCH (3-110), HCB (5-100), and g-HCH (1-42); low concentrations of chlorpyrifos (<1), dacthal (0.2-20), and chlordanes (0.2-10) were also detected.
- Significant increases in pesticide concentrations and decreases in PAH concentrations in lichens with increasing elevation were discernible when the poorest (*Alectoria sarmentosa*) and best (*Platismatia glauca*) accumulators, sampled at alternating sites, were considered separately.
- Because needle productivity (kg/ha/yr) is high, the ecological effects of cumulative SOCs contributed by needle litter-fall are a potential concern.
- Nitrogen concentrations in lichens were within background ranges, indicating that nitrogen deposition is not elevated.

Air Summary

- Air was sampled at STLE1, 2, and 4.
- SOCs that increased with elevation in vegetation also increased in air. These were current-use endosulfans (17-96 pg/g dry XAD) and the HUPs HCB (490-1150), a-HCH (100-390), g-HCH (4-38), and chlordanes (10-21).
- Other SOCs were not detected or were near instrument detection limits (trifluralin and dacthal, <2 pg/g dry XAD).
- All SOC concentrations ranked low at the lowest elevation; concentrations at the highest elevation ranked moderate (g-HCH, chlordanes) to high (HCB, a-HCH) relative to concentrations at other WACAP parks.

Vegetation Contaminant Concentrations



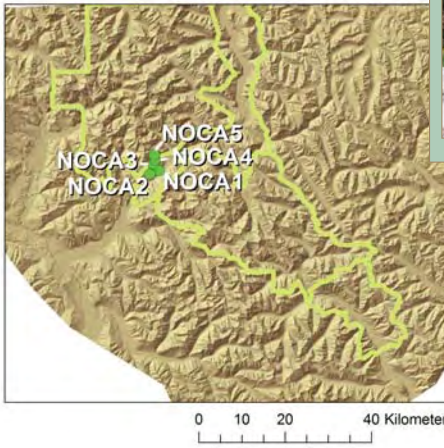


NOCA

NOCA1
Thorton Creek
Location: 48.65N 121.31W
Elevation: 198 m
Ave. Ann. Temp: 8.6°C
Ave. Ann. Precip: 198 cm
Air Sampler: No
Conifer: *Pseudotsuga menziesii*
Lichen: *Alectoria sarmentosa*

NOCA2
Lower S slope Mt Triumph
Location: 48.64N 121.34W
Elevation: 614 m
Ave. Ann. Temp: 8.6°C
Ave. Ann. Precip: 196 cm
Air Sampler: No
Conifer: *Tsuga heterophylla*
Lichen: *Platismatia glauca*

NOCA3
SE slope Mt Triumph
Location: 48.66N 121.33W
Elevation: 945 m
Ave. Ann. Temp: 8.3°C
Ave. Ann. Precip: 222 cm
Air Sampler: No
Conifer: *Abies amabilis*
Lichen: *Alectoria sarmentosa*

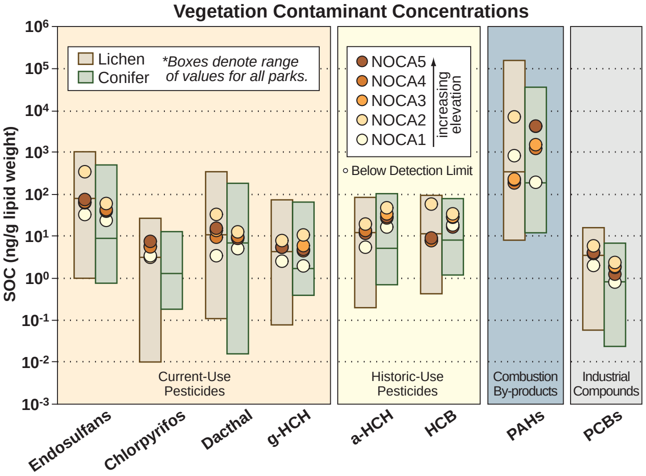


NOCA4
Upper SE slope Mt Triumph
Location: 48.67N 121.32W
Elevation: 1228 m
Ave. Ann. Temp: 8.7°C
Ave. Ann. Precip: 198 cm
Air Sampler: No
Conifer: *Abies amabilis*
Lichen: *Alectoria sarmentosa*

NOCA5
S ridge Trappers Peak near treeline
Location: 48.68N 121.32W
Elevation: 1600 m
Ave. Ann. Temp: 8.2°C
Ave. Ann. Precip: 194 cm
Air Sampler: Yes
Conifer: *Abies amabilis*
Lichen: *Alectoria sarmentosa*

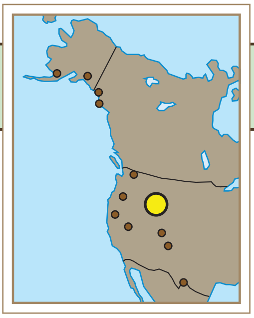
Air Summary

- Air was sampled at NOCA5.
- SOCs detected, in order by decreasing concentration, were HCB (910 pg/g dry XAD), endosulfans (492), chlorpyrifos (220), a-HCH (200), PAHs (192), heptachlor (150), dacthal (91), chlordanes (63), g-HCH (32), and trifluralin (13); PCBs, dieldrin and DDTs were not detected.
- NOCA was the only park in which heptachlor was detected; concentrations of PAHs, CUPs chlorpyrifos, trifluralin, and endosulfans, and HUPs HCB, a-HCH, and chlordanes ranked well above the medians for the 20 WACAP parks.



Vegetation Summary

- Among samples from the 20 WACAP parks, vegetation samples from NOCA were at or above medians for all SOCs. Dominant SOCs were PAHs (216-7768 ng/g lipid), endosulfans (24-355), dacthal (3-34), HCB (8-60), a-HCH 12-49), and g-HCH (3-11).
- Low concentrations of trifluralin (<0.2), chlorpyrifos (3-8), chlordanes (1-5), DDTs (2-7), and PCBs (<4) were also detected.
- Total SOC concentrations were similar to those in other Pacific Northwest parks (CRLA, MORA, OLYM). Pesticide and PCB concentrations in the lichen, *Alectoria sarmentosa*, increased with elevation.
- Because needle productivity (kg/ha/yr) is high, the ecological effects of cumulative SOCs contributed by needle litter-fall are a potential concern.
- Nitrogen concentrations in lichens were within background ranges, indicating that nitrogen deposition is not elevated.



GRTE

GRTE1
Lupine Meadows

Location: 43.73N 110.74W
Elevation: 2073 m
Ave. Ann. Temp: 2.2°C
Ave. Ann. Precip: 69 cm
Air Sampler: No
Conifer: *Pinus contorta*
Lichen: *Usnea*

GRTE2
Bradley Lake

Location: 43.73N 110.76W
Elevation: 2362 m
Ave. Ann. Temp: 2.2°C
Ave. Ann. Precip: 79 cm
Air Sampler: No
Conifer: *Abies lasiocarpa*
Lichen: *Letharia vulpina*

GRTE4
0.5 km E of Sunrise Lake

Location: 43.73N 110.77W
Elevation: 2804 m
Ave. Ann. Temp: 1.1°C
Ave. Ann. Precip: 103 cm
Air Sampler: No
Conifer: *Pinus flexilis*
Lichen: None

GRTE5
S rim above Amphitheater Lake

Location: 43.13N 110.78W
Elevation: 3048 m
Ave. Ann. Temp: 2.2°C
Ave. Ann. Precip: 68 cm
Air Sampler: Yes
Conifer: *Pinus albicaulis*
Lichen: None

GRTE3
Midslope Amphitheater Lake and valley floor

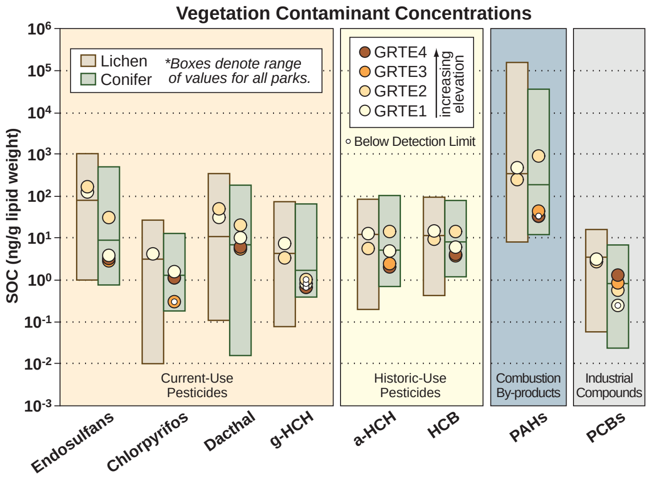
Location: 43.73N 110.77W
Elevation: 2591 m
Ave. Ann. Temp: 1.1°C
Ave. Ann. Precip: 102 cm
Air Sampler: No
Conifer: *Pinus flexilis*
Lichen: None

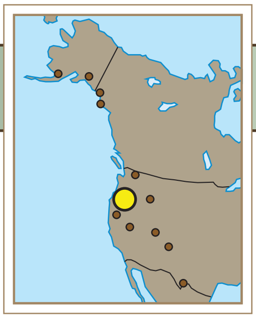
Vegetation Summary

- As in other parks of the conterminous 48 states, the dominant SOCs in vegetation were PAHs (90-3300 ng/g lipid) and CUPs endosulfans (3-165) and dacthal (5-50).
- Compared with other WACAP parks, lichen SOC concentrations were at or above the median; conifer needle concentrations were at or below medians, except at GRTE2, where fir was collected, with concentrations at or above the median. (Pine, collected at other GRTE sites, tends to accumulate 2-10x lower SOC concentrations than to other WACAP conifers.)
- All other SOCs detected in WACAP vegetation were also detected at GRTE: trifluralin (<1 ng/g lipid), triallate (<6), chlorpyrifos (1-5), HCB (4-17), a-HCH (2-15), g-HCH (1-9), chlordanes (0.1-6), dieldrin (<2), DDTs (12-20), and PCBs (2-4).
- Elevation effects were not observed in lichens; there were only two sites, with different species. The two highest conifer sites often had lowest SOC concentrations, possibly related to extended snow burial in winter.
- Lichen nitrogen concentrations were within background ranges, indicating that nitrogen deposition is not elevated.

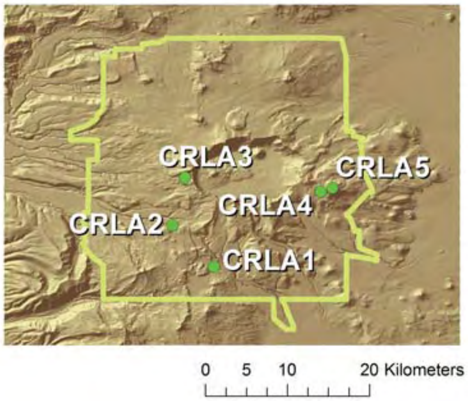
Air Summary

- The air sampler was at GRTE5.
- Concentrations of detected SOCs were above medians for the 20 parks [PAHs (232); CUPs dacthal (390 pg/g dry XAD) and endosulfans (359); HUPs HCB (840), a-HCH (140), g-HCH (44), and chlordanes (19)].





CRLA



CRLA1
Lodgepole picnic area

Location: 42.84N 122.15W
Elevation: 1798 m
Ave. Ann. Temp: 4.2°C
Ave. Ann. Precip: 152 cm
Air Sampler: No
Conifer: *Abies magnifica*
Lichen: *Letharia vulpina*

CRLA4
Mt. Scott Trail 1.6 km

Location: 42.92N 122.03W
Elevation: 2423 m
Ave. Ann. Temp: 3.5°C
Ave. Ann. Precip: 108 cm
Air Sampler: No
Conifer: *Pinus albicaulis*
Lichen: *Letharia vulpina*

CRLA5
Mt. Scott Summit

Location: 42.92N 122.02W
Elevation: 2713 m
Ave. Ann. Temp: 3.5°C
Ave. Ann. Precip: 108 cm
Air Sampler: Yes
Conifer: *Pinus albicaulis*
Lichen: None

CRLA2
Whitehorse Pond

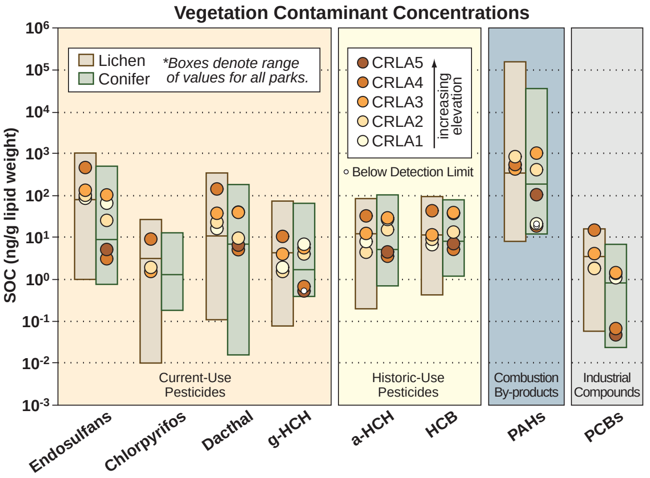
Location: 42.88N 122.19W
Elevation: 1859 m
Ave. Ann. Temp: 3.5°C
Ave. Ann. Precip: 155 cm
Air Sampler: No
Conifer: *Abies concolor*
Lichen: *Letharia vulpina*

CRLA3
Lightning Sprgs Trail near Rim Drive

Location: 42.93N 122.18W
Elevation: 2043 m
Ave. Ann. Temp: 3.4°C
Ave. Ann. Precip: 158 cm
Air Sampler: No
Conifer: *Abies magnifica*
Lichen: *Letharia vulpina*

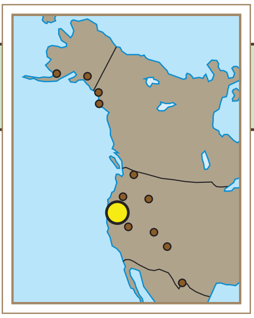
Air Summary

- The air sampler was deployed at CRLA5.
- Compared with other WACAP parks, concentrations of all SOCs detected were moderate [CUPs dacthal (160 ng/g dry XAD), endosulfans (467), and HUPs a-HCH (120), g-HCH (36), chlordanes (17), and PAHs (191)] to high [HCB (920)].
- No elevational or east-west patterns were observed.



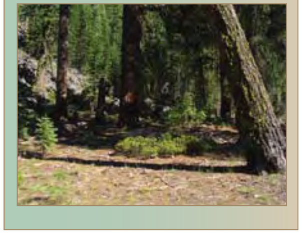
Vegetation Summary

- The CUPs endosulfans (3-486 ng/g lipid) and dacthal (10-150) comprised most of the pesticide burden in vegetation; other dominant SOCs were PAHs (1-3850) and the HUPs HCB (5-45), a-HCH (4-34), chlordanes (3-33), and DDT (5-17). Low concentrations of g-HCH (1-11), trifluralin (<0.4), chlorpyrifos (2-10), and PCBs (1-12) were also detected.
- Pesticide concentrations were at or above the median relative to other WACAP parks, except for consistently low values in conifers at the two highest sites, possibly related to deep snow burial in winter.
- Concentrations of endosulfans, dacthal, HCB, HCHs, and PCBs increased in lichens with elevation, most by an order of magnitude or more.
- Lichen nitrogen concentrations were within background ranges for remote sites in the Pacific Northwest, indicating that nitrogen deposition is not elevated.



LAVO

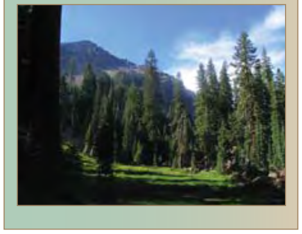
LAVO1
Sunflower Flat
Location: 40.56N 121.53W
Elevation: 1829 m
Ave. Ann. Temp: 7.4°C
Ave. Ann. Precip: 123 cm
Air Sampler: No
Conifer: *Abies concolor*
Lichen: *Letharia vulpina*



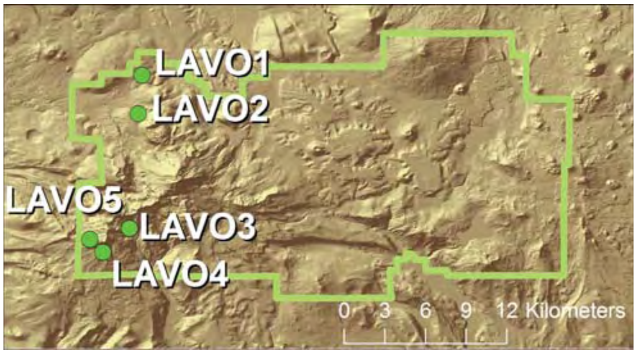
LAVO2
Chaos Crags Trail 2.4 km
Location: 40.53N 121.53W
Elevation: 2012 m
Ave. Ann. Temp: 6.6°C
Ave. Ann. Precip: 168 cm
Air Sampler: No
Conifer: *Abies concolor*
Lichen: *Letharia vulpina*

LAVO3
Ridge Lake Basin
Location: 40.46N 121.54W
Elevation: 2271 m
Ave. Ann. Temp: 4.1°C
Ave. Ann. Precip: 267 cm
Air Sampler: No
Conifer: *Abies magnifica*
Lichen: *Letharia columbiana*

LAVO4
Broke-off Top Mtn Trail 3.2 km
Location: 40.44N 121.56W
Elevation: 2499 m
Ave. Ann. Temp: 4.8°C
Ave. Ann. Precip: 235 cm
Air Sampler: No
Conifer: *Abies magnifica*
Lichen: *Letharia vulpina*



LAVO5
Broke-off Top Mtn summit
Location: 40.45N 121.57W
Elevation: 2713 m
Ave. Ann. Temp: 4.8°C
Ave. Ann. Precip: 235 cm
Air Sampler: Yes
Conifer: *Abies magnifica*
Lichen: *Letharia vulpina*

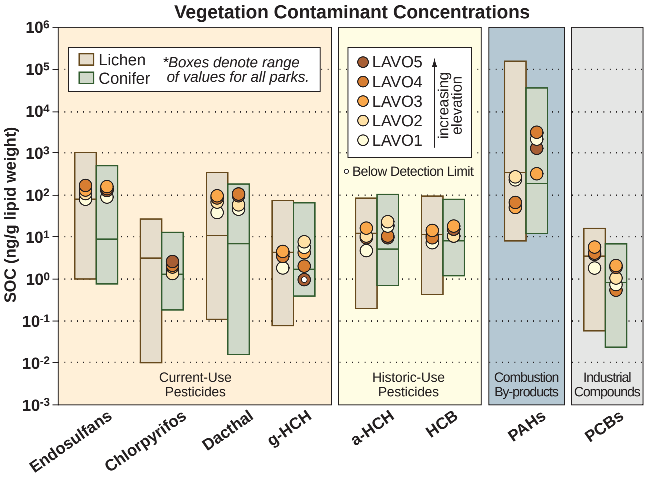


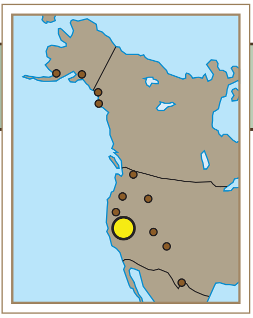
Vegetation Summary

- The same genera (wolf-lichen and true fir) were collected at all sites.
- SOC concentrations in LAVO vegetation were close to, above, or well above the median for the WACAP parks.
- The dominant SOCs were PAHs (90-3300 ng/g lipid), endosulfans (90-180), dacthal (40-110), DDTs (2-65), and HCB (10-24). Proportions of PAHs were similar to those in southern Oregon and other California parks.
- Low concentrations of chlorpyrifos (<3 ng/g lipid), a-HCH (2-15), g-HCH (2-8), chlordanes (5-14), dieldrin (1-6), and PCBs (1-5) were also detected.
- Increases in endosulfans, chlorpyrifos, and dacthal, and decreases in PAH concentrations in lichens were observed with increasing elevation.
- Lichen nitrogen concentrations were within background ranges, indicating that nitrogen deposition is not elevated.

Air Summary

- Air was sampled at LAVO5.
- Compared with other WACAP parks, concentrations of all SOCs detected were above the median [CUPs trifluralin (5 ng/g dry XAD), dacthal (380), and endosulfans (363), and HUPs HCB (840), a-HCH (150), g-HCH (30), and chlordanes (34), and PAHs (77)].





Yosemite National Park: *Summary*

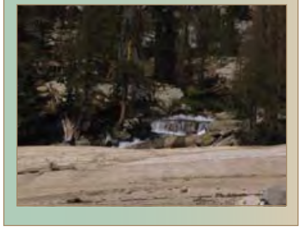
YOSE

YOSE1
Hwy 140 park boundary
Location: 37.68N 119.75W
Elevation: 661 m
Ave. Ann. Temp: 12.1°C
Ave. Ann. Precip: 87 cm
Air Sampler: No
Conifer: *Pinus sabiniana*
Lichen: *Xanthoparmelia*

YOSE2
Turtleback Dome
Location: 37.72N 119.68W
Elevation: 1433 m
Ave. Ann. Temp: 10.7°C
Ave. Ann. Precip: 92 cm
Air Sampler: No
Conifer: *Pinus ponderosa*
Lichen: *Letharia vulpina*

YOSE3
Nevada Falls
Location: 37.72N 119.53W
Elevation: 1829 m
Ave. Ann. Temp: 10.3°C
Ave. Ann. Precip: 104 cm
Air Sampler: No
Conifer: *Pinus lambertiana*
Lichen: *Letharia vulpina*

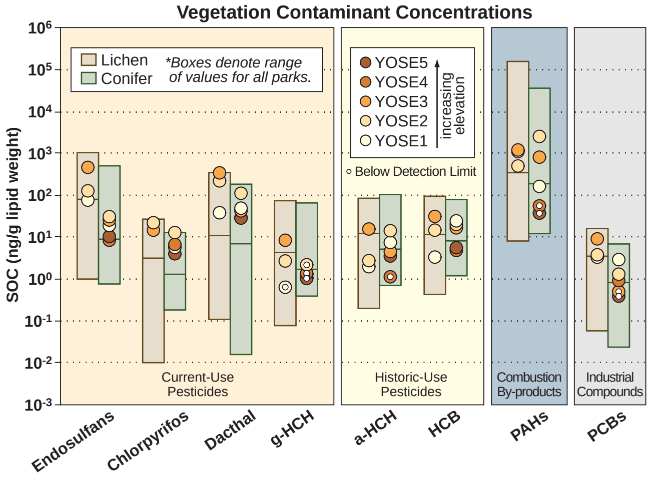
YOSE4
Lewis Creek at Cony Crags
Location: 37.75N 119.36W
Elevation: 2713 m
Ave. Ann. Temp: 4.2°C
Ave. Ann. Precip: 112 cm
Air Sampler: No
Conifer: *Pinus contorta*
Lichen: None



YOSE5
Lewis-Gallison Creek confluence
Location: 37.77N 119.34W
Elevation: 3048 m
Ave. Ann. Temp: 3.1°C
Ave. Ann. Precip: 109 cm
Air Sampler: Yes
Conifer: *Pinus contorta*
Lichen: None

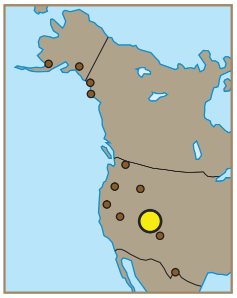
Air Summary

- Air was sampled at YOSE5.
- Concentrations of all SOCs detected, except PAHs (97 pg/g dry XAD), ranked above medians for the 20 parks. CUPs detected were dacthal (36), endosulfans (413); HUPs detected were a-HCH (120), g-HCH (33), and chlordanes (30).



Vegetation Summary

- The dominant SOCs were PAHs (517-19,326 ng/g lipid), the CUPs endosulfans (10-474), dacthal (30-350), and chlorpyrifos (4-31), and the HUPs DDTs (10-72) and HCB (3-32), all of which were at or well above medians for the 20 WACAP parks. Low concentrations of trifluralins (<1), g-HCH (1-9), and PCBs (0.1-7) were also detected.
- SOC concentrations were about 10x higher in lichens than conifers.
- A strong elevational effect was observed in lichens: concentrations of endosulfans, dacthal, HCHs, and PCBs increased by one-half to one order of magnitude, from 660 to 1830 m.
- Pine, the only conifer genus sampled in YOSE, appears to be a poor accumulator of SOCs compared with spruce, fir, and hemlock sampled in other west coast parks; had these species been collected, total pesticides would probably have ranked intermediate compared with concentrations in LAVO and SEKI, as did the lichen data.
- Lichen nitrogen concentrations were at or slightly above uppermost Pacific Northwest background ranges, indicating potential enhancement of depositional nitrogen.



GRSA

GRSA1

Park headquarters

Location: 37.73N 105.53W
Elevation: 2469 m
Ave. Ann. Temp: 5.3°C
Ave. Ann. Precip: 25 cm
Air Sampler: No
Conifer: *Pinus edulis*
Lichen: None

GRSA2

Mosca Pass Trail midpoint

Location: 37.73N 105.49W
Elevation: 2774 m
Ave. Ann. Temp: 4.3°C
Ave. Ann. Precip: 48 cm
Air Sampler: No
Conifer: *Pinus edulis*
Lichen: *Xanthoparmelia*

GRSA3

Mosca Pass

Location: 37.73N 105.46W
Elevation: 2941 m
Ave. Ann. Temp: 3.9°C
Ave. Ann. Precip: 60 cm
Air Sampler: No
Conifer: *Pinus flexilis*
Lichen: None

GRSA4

Carbonate Mtn sideslope

Location: 37.72N 105.47W
Elevation: 3109 m
Ave. Ann. Temp: 4.3°C
Ave. Ann. Precip: 48 cm
Air Sampler: No
Conifer: *Pinus flexilis*
Lichen: *Xanthoparmelia*

GRSA5

Carbonate Mtn peak

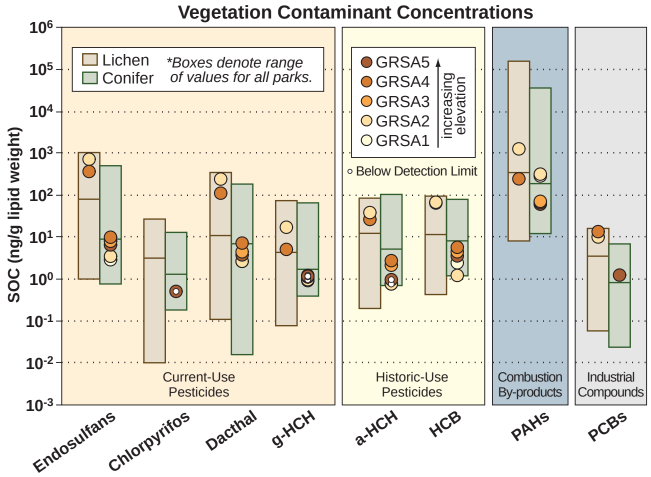
Location: 37.71N 105.47W
Elevation: 3338 m
Ave. Ann. Temp: 4.3°C
Ave. Ann. Precip: 52 cm
Air Sampler: Yes
Conifer: *Pinus flexilis*
Lichen: None

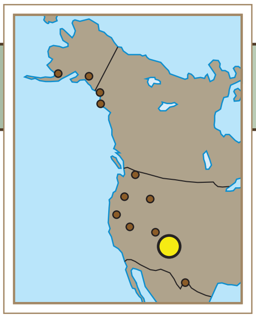
Vegetation Summary

- The dominant SOCs detected in vegetation were PAHs, especially 4-5 ring compounds (30-1000 ng/g lipid), endosulfans (3-710, 10x higher in lichens than conifers), and dacthal (2-110, 10x higher in lichens), DDTs (10-100), HCB (1-67), a-HCH (0.1-40), chlordanes (24-32), and g-HCH (5-17); low concentrations of PCBs (1-11) were detected.
- Lichen concentrations were generally higher than conifer needle concentrations by at least an order of magnitude.
- Although SOC concentrations in conifer needles from GRSA were comparable to those at BAND and BIBE, where the same target genus (pine) was collected, SOC concentrations in lichens were disproportionately high at GRSA compared to ROMO, BAND, and BIBE even though the same rock-dwelling lichen, *Xanthoparmelia,* was collected there.
- Field notes and the park website indicate that the two sites where lichens were collected were very windy. It is possible that a disproportionately high absorption of SOCs from soil particulates contributed to high lichen SOC concentrations.
- Lichen nitrogen concentrations were within background ranges, indicating that nitrogen deposition is not elevated.

Air Summary

- The air sampler was at GRSA5.
- Compared with concentrations at other WACAP parks, concentrations of all SOCs detected were moderate [(CUPs dacthal (300), endosulfans (353), and HUPs HCB (580), a-HCH (120), and chlordanes (15)] to high [g-HCH (73),PAHs (1342 ng/g dry XAD)].





BAND

BAND1

Burro Tr above Lummis Canyon

Location: 35.73N 106.27W
Elevation: 1854 m
Ave. Ann. Temp: 10.5°C
Ave. Ann. Precip: 35 cm
Air Sampler: No
Conifer: *Pinus edulis*
Lichen: *Xanthoparmelia*

BAND2

NW of Juniper Campground

Location: 35.80N 106.28W
Elevation: 2076 m
Ave. Ann. Temp: 9.9°C
Ave. Ann. Precip: 41 cm
Air Sampler: No
Conifer: *Pinus edulis*
Lichen: *Usnea*

BAND3

Lower E slopes of Frijoles Park

Location: 35.82N 106.36W
Elevation: 2348 m
Ave. Ann. Temp: 8.1°C
Ave. Ann. Precip: 51 cm
Air Sampler: No
Conifer: *Pinus ponderosa*
Lichen: *Xanthoparmelia*

BAND4

Lower SW slope of Cerro Grande

Location: 35.83N 106.39W
Elevation: 2576 m
Ave. Ann. Temp: 6.4°C
Ave. Ann. Precip: 58 cm
Air Sampler: No
Conifer: *Pinus ponderosa*
Lichen: *Usnea*

BAND5

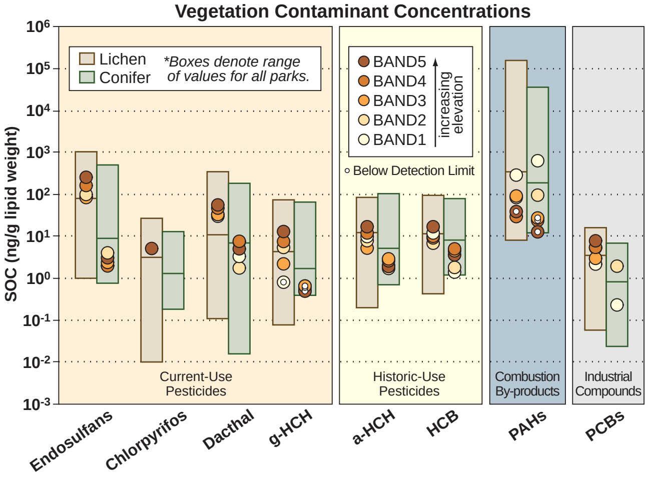
Saddle SW of Cerro Grande Peak

Location: 35.86N 106.42W
Elevation: 2926 m
Ave. Ann. Temp: 5.4°C
Ave. Ann. Precip: 67 cm
Air Sampler: Yes
Conifer: *Pinus ponderosa*
Lichen: *Usnea*

Air Summary

- Compared with concentrations at the 20 WACAP parks, concentrations of all pesticides detected in the air sampler at BAND5 were near the median.
- Pesticides detected were the CUPs [endosulfans (494 ng/g dry XAD), dacthal (150), trifluralin (9)], and HUPs [HCH (11), g-HCH (37), chlordanes (19)]; PAHS were low (21).

Vegetation Contaminant Concentrations



Vegetation Summary

- Concentrations of CUPs [endosulfans (2-256 ng/g lipid), dacthal (1-56), chlorpyrifos (<5)] were at or above medians and concentrations of HUPs [HCB and HCHs (1-17)] were at or below medians for the 20 WACAP parks.
- Other pesticides detected were trifluralin (<0.5) and DDTs (4-53).
- Pine is a poor accumulator of SOCs compared to other conifers and lichens, explaining the large range in concentrations observed within individual SOCs.
- Pesticides and PCBs increased and PAHs decreased in lichens with elevation.
- Abundance of nitrophytic lichens and elevated nitrogen concentrations in *Xanthoparmelia* and *Usnea*, relative to clean sites in the Pacific Northwest and northern Rockies, indicate enhanced nitrogen deposition.

Big Bend National Park: *Summary*

BIBE1
Rio Grande Village

Location: 29.19N 102.97W
Elevation: 560 m
Ave. Ann. Temp: 21°C
Ave. Ann. Precip: 26 cm
Air Sampler: Yes
Conifer: None
Lichen: None

BIBE2
Water Tank near Panther Jct

Location: 29.31N 103.18W
Elevation: 1067 m
Ave. Ann. Temp: 18.6°C
Ave. Ann. Precip: 37 cm
Air Sampler: Yes
Conifer: None
Lichen: None

BIBE3
Panther Pass

Location: 29.29N 103.28W
Elevation: 1608 m
Ave. Ann. Temp: 17.5°C
Ave. Ann. Precip: 46 cm
Air Sampler: No
Conifer: *Pinus cembroides*
Lichen: None

BIBE4
Pinnacles Campground

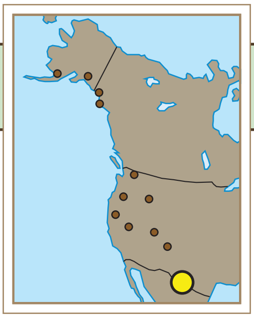
Location: 29.25N 103.30W
Elevation: 1920 m
Ave. Ann. Temp: 16.7°C
Ave. Ann. Precip: 51 cm
Air Sampler: Yes
Conifer: *Pinus cembroides*
Lichen: *Usnea*

BIBE5
Emory Peak

Location: 29.25N 103.30W
Elevation: 2316 m
Ave. Ann. Temp: 16.7°C
Ave. Ann. Precip: 50 cm
Air Sampler: Yes
Conifer: *Pinus cembroides*
Lichen: *Usnea*

Vegetation Summary

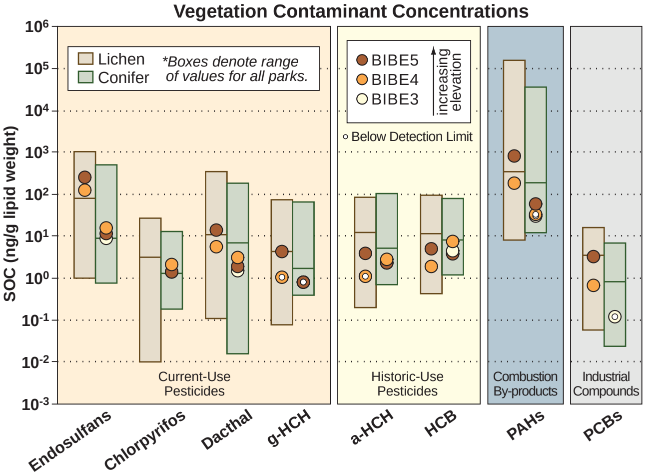
- Compared with other parks, concentrations in lichens and conifer needles were at or slightly above medians for CUPs, and at or below medians for HUPs, PAHs, and PCBs.
- Pine, the only conifer available at BIBE, is a poorer accumulator of SOCs than the spruce, fir, and hemlock collected in the northern Rockies, Pacific Coast, and Alaska parks.
- SOCs detected were CUPs [chlorpyrifos (<2 ng/g lipid), dacthal (1-14), endosulfans (9-255, up to 25x higher in lichens than pine)], HUPs [HCB, a-HCH, g-HCH, and chlordanes (<5), DDE (8-17)], PCBs (<3), and PAHs (10-828, up to 80x higher in lichens than pine).
- Lichen nitrogen concentrations and abundance of nitrophytic lichens at sites indicate enhanced nitrogen deposition; IMPROVE data indicate ammonium sulfate could be the main culprit.



BIBE

Air Summary

- Air was sampled at four sites from the Rio Grande to Emory Peak (BIBE1, BIBE2, BIBE4, and BIBE5).
- Dramatic differences among sites in annual precipitation, humidity, vegetation cover, and airborne soil particulates might have masked elevation effects on pesticide concentrations in air, although PAHs decreased markedly with increasing elevation from moderate to low concentrations (1491, 200, 276, 1 ng/g dry XAD).
- Pesticides that ranked high compared with other WACAP parks were endosulfans (472-1096) and DDE (n.d.-43).
- Dacthal (67-390), HCB (6-21), HCHs (2-21), and chlordanes (16-37) ranked below or near the median; very low concentrations (7-11) of trifluralin were detected.



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CHAPTER 3

Contaminants Studied and Methods Used

3.1 Introduction

This chapter introduces the organic and inorganic contaminants measured in the WACAP environmental media and describes the methods used to collect and analyze these media. Table 3-1 lists the analytes measured in each environmental medium, along with the abbreviation for the responsible laboratory for each medium and analyte. Table 3-2 provides the full identification and contact information for each laboratory. Appendix 3A summarizes the sampling and analysis plan for each environmental medium and lists the years in which each medium was sampled in each park. Details of the methods and data quality control are provided in Appendix 3B and in the peer-reviewed literature cited throughout this chapter.

Table 3-1. Analytical Laboratories by Media and Analyte. Abbreviations for laboratories, along with contact information, are provided in Table 3-2.

Analyses	Snow	Sediment	Fish	Vegetation	Air*	Water	Moose
SOC	SEC	SEC	SEC	SEC	SEC	SEC	SEC
Hg	USGS-WWSC	WRS	WRS	WRS	NA*	NA	WRS
Metals	USGS-NRP Boulder	USGS-NRP Boulder	USGS-NRP Boulder	USGS-NRP Boulder	NA	NA	USGS-NRP Boulder
Major ions/ Nutrients/ Physical	USGS-CWSC	WRS	NA	UMNRAL	NA	WRS	NA
SCP*	ECRC	ECRC	NA	NA	NA	NA	NA
Particulate C and N	CBL	NA	NA	NA	NA	NA	NA
Sediment Dating	NA	ERRC	NA	NA	NA	NA	NA
Fish Physio/ Path*	NA	NA	OSU-Fish	NA	NA	NA	NA

*Air = measured by SOC concentrations in Amberlite XAD-2 resin-filled passive air sampling devices (PASDs). NA = not applicable; SCP = spheroidal carbonaceous particle; Fish Physio/Path = Fish physiology and pathology assessments.

3.2 Contaminants Studied

3.2.1 Semi-Volatile Organic Compounds (SOCs)

Over 100 different semi-volatile organic compounds (SOCs) were measured in WACAP. Table 3-3 lists the SOCs measured in WACAP in four separate categories: North American current-use pesticides (CUPs), North American historic-use pesticides (HUPs), combustion byproducts, and industrial/urban use compounds (IUCs). Table 3-3 also provides the common names of the SOCs, the abbreviations for the SOCs used throughout this report, the compound chemical class, and the use or source of the SOC. When available, the year of the first product registration in the United States, as well as the 2006 regulatory status of these compounds in the United States, Canada, China, Korea, and Japan, are also given in Table 3-3. Regulatory status is at the federal level only. State regulations can be more strict. It is also important to know that many of the banned or restricted SOCs went though prolonged phase-out periods that took several years to complete.

Table 3-2. WACAP Analytical Laboratories.

Laboratory Abbreviation	Laboratory	Address	Contact Information
SEC	Simonich Environmental Chemistry Laboratory	1161 Agricultural and Life Sciences Dept. of Environmental and Molecular Toxicology Oregon State University Corvallis, OR 97331	Prof. Staci Simonich 541-737-9194 staci.simonich@orst.edu
WRS	Willamette Research Station Analytical Laboratory	U.S. EPA 200 SW 35th Street Corvallis, OR 97333	Dr. Dixon Landers 541-754-4427 Landers.Dixon@epa.gov
USGS-NRP Boulder	Trace Element Environmental Analytical Chemistry Project	U.S Geological Survey, WRD National Research Program 3215 Marine St., Suite E-127 Boulder, CO 80303	Dr. Howard Taylor 303-541-3007 hetaylor@usgs.gov
OSU-Fish	OSU Kent Laboratory	Dept. of Microbiology 220 Nash Hall Oregon State University Corvallis, OR 97331	Prof. Michael Kent 541-737-8652 michael.kent@orst.edu
USGS-WWSC	USGS Wisconsin Water Science Center Mercury Research Laboratory	USGS Water Resources Division 8505 Research Way Middleton, WI 53562	Dr. David Krabbenhoft 608-821-3843 dpkrabbe@usgs.gov
USGS-CWSC	USGS Colorado Water Science Center Alpine Hydrological Research Team	USGS – WRD, Colorado Denver Federal Center MS-415, Bldg. 53 Lakewood, CO 80225	M. Alisa Mast 303-236-4882 mamast@usgs.gov
CBL	Chesapeake Biological Laboratory, University of Maryland	Chesapeake Biological Laboratory Center for Environmental and Estuarine Studies 1 Williams St.; PO Box 38 Solomons, MD 20688	Carl. F. Zimmermann 410-326-7252 carlz@cbl.umces.edu
UMNRAL	University of Minnesota Research Analytical Laboratory	University of Minnesota Rm. 135 Crops Research Bldg. 1902 Dudley Ave. St Paul, MN 55108-6089	Dr. Roger Eliason 612- 625-3101 ral@soils.umn.edu
ERRC	Environmental Radioactivity Research Centre	The University of Liverpool Liverpool, UK L69 3BX	Prof. Peter Appleby +44 (0)151 794 4020 Appleby@liv.ac.uk
ECRC	Environmental Change Research Centre	University College London Pearson Building, Gower Street London UK WC1E 6BT	Prof. Neil Rose +44 (0) 20 7679 0543 nrose@geog.ucl.ac.uk

Table 3-3. Semi-Volatile Organic Compounds (SOCs) Measured in WACAP.

					Federal Regulatory Status 2007*				
Compound Name	**Abbreviation**	**Chemical Class**	**Use/Source**	**First U.S. Usage**	**U.S.**	**Canada**	**China**	**Korea**	**Japan**
Current-Use Pesticides (CUPs)									
Acetochlor	ACLR	Chloroamide	Herbicide	1994	A				
Alachlor	ALCLR	Chloroamide	Herbicide	1969	A				
Metolachlor	MCLR	Chloroamide	Herbicide	1976	R	A			
Propachlor	PCLR	Chloroamide	Herbicide	1964	A				
Endosulfan I	ENDO I	Organochlorine Sulfide	Insecticide	1954	A	A			
Endosulfan II	ENDO II	Organochlorine Sulfide	Insecticide	1954	A	A			
Endosulfan sulfate	ENDO S	Organochlorine Sulfide	Degradation Product	NA	NA	NA	NA	NA	NA
Ethion	ETHN	Phosphorothioate	Insecticide	1958	B 2004	B 2000			
Malathion	MTHN	Phosphorothioate	Insecticide		A	A			
Methyl parathion	M-PTHN	Phosphorothioate	Insecticide	1954	A	A	R		
Parathion	PTHN	Phosphorothioate	Insecticide		B	B 2003	R		
Diazinon	DIAZ	Phosphorothioate	Insecticide	1956	A	A			
Chlorpyrifos	CLPYR	Phosphorothioate	Insecticide	1965	R	A			
Chlorpyrifos oxon	CLPYR O	Phosphorothioate	Degradation Product	NA	NA	NA	NA	NA	NA
EPTC	EPTC	Thiocarbamate	Herbicide	1968	A	A			
Pebulate	PBLT	Thiocarbamate	Herbicide	1961	R	B 2003			
Triallate	TRLTE	Thiocarbamate	Herbicide	1961	A	A			
Atrazine	ATRZ	Triazine	Herbicide	1958	R	A			
Prometon	PMTN	Triazine	Herbicide		A				
Simazine	SIMZ	Triazine	Herbicide		A	A			
Cyanazine	CYAZ	Triazine	Herbicide		B	B 2004			
Dacthal	DCPA	ChloroPhthalate	Herbicide	1955	A	A			
Trifluralin	TFLN	Dinitroaniline	Herbicide	1963	A	A			

Table 3-3. Semi-Volatile Organic Compounds (SOCs) Measured in WACAP (continued).

					Federal Regulatory Status 2007*				
Compound Name	**Abbreviation**	**Chemical Class**	**Use/Source**	**First U.S. Usage**	**U.S.**	**Canada**	**China**	**Korea**	**Japan**
Etridiazole	ETDZL	Terrazole	Fungicide	1963	A	A			
Metribuzin	MBZN	Triazinone	Herbicide	1973	A	A			
γ-HCH (Lindane)	g-HCH or gHCH	Organochlorine	Insecticide	1948	R	B 2004	R	B 1979	
Historic-Use Pesticides (HUPs)									
α-HCH	a-HCH or aHCH	Organochlorine	Insecticide	1948	B 1978	B 1971	B 1983	B 1979	
β-HCH	b-HCH or bHCH	Organochlorine	Insecticide	1948	B 1978	B 1971	B 1983	B 1979	
δ-HCH	d-HCH or dHCH	Organochlorine	Insecticide	1948	B 1978	B 1971	B 1983	B 1979	
Hexachlorobenzene	HCB	Chlorobenzene	Fungicide	1945	B 1984	B 1972			
Aldrin	Aldrin	Organochlorine	Insecticide	1949	B 1987	B 1990	N	B 1971	B 1975
Dieldrin	Dieldrin	Organochlorine	Insecticide	1949	B 1987	B 1990	N	B 1971	B 1975
Endrin	Endrin	Organochlorine	Insecticide	1949	B 1991	B 1990	N	B 1971	B 1975
Endrin aldehyde	Endrin A	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
Chlordane, trans	t-CLDN	Organochlorine	Insecticide	1948	B 1988	B 1995	R	B	R
Chlordane, cis	c-CLDN	Organochlorine	Insecticide	1948	B 1988	B 1995	R	B	R
Nonachlor, trans	t-NCLR	Organochlorine	Impurity/Insecticide	1948	B 1988	B 1995	R	B	R
Nonachlor, cis	c-NCLR	Organochlorine	Impurity/Insecticide	1948	B 1988	B 1995	R	B	R
Chlordane, oxy	o-CLDN	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
Heptachlor	HCLR	Organochlorine	Insecticide	1952	B 1988	B 1985	B	B 1979	R
Heptachlor epoxide	HCLR E	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
Methoxychlor	MXCLR	Organochlorine	Insecticide	1948	R	B 2005			
p,p'-DDT	pp-DDT	Organochlorine	Insecticide	1942	B 1972	B 1989	B	B 1973	B 1981

Table 3-3. Semi-Volatile Organic Compounds (SOCs) Measured in WACAP (continued).

					Federal Regulatory Status 2007*				
Compound Name	**Abbreviation**	**Chemical Class**	**Use/Source**	**First U.S. Usage**	**U.S.**	**Canada**	**China**	**Korea**	**Japan**
							1983		
o,p'-DDT	op-DDT	Organochlorine	Insecticide	1942	B 1972	B 1989	B 1983	B 1973	B 1981
p,p'-DDD	pp-DDD	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
o,p'-DDD	op-DDD	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
p,p'-DDE	pp-DDE	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
o,p'-DDE	op-DDE	Organochlorine	Degradation Product	NA	NA	NA	NA	NA	NA
Mirex	Mirex	Organochlorine	Insecticide	1959	B 1978	B 1978	R		
Combustion Byproducts									
Acenaphthylene	ACY	PAH	Combustion	NA	NA	NA	NA	NA	NA
Acenaphthene	ACE	PAH	Combustion	NA	NA	NA	NA	NA	NA
Fluorene	FLO	PAH	Combustion	NA	NA	NA	NA	NA	NA
Phenanthrene	PHE	PAH	Combustion	NA	NA	NA	NA	NA	NA
Anthracene	ANT	PAH	Combustion	NA	NA	NA	NA	NA	NA
Fluoranthene	FLA	PAH	Combustion	NA	NA	NA	NA	NA	NA
Pyrene	PYR	PAH	Combustion	NA	NA	NA	NA	NA	NA
Benzo(a)anthracene	B[a]A	PAH	Combustion	NA	NA	NA	NA	NA	NA
Chrysene+Triphenylene	CHR/TRI	PAH	Combustion	NA	NA	NA	NA	NA	NA
Benzo(b)fluoranthene	B[b]F	PAH	Combustion	NA	NA	NA	NA	NA	NA
Benzo(k)fluoranthene	B[k]F	PAH	Combustion	NA	NA	NA	NA	NA	NA
Benzo(e)pyrene	B[e]P	PAH	Combustion	NA	NA	NA	NA	NA	NA
Benzo(a)pyrene	B[a]P	PAH	Combustion	NA	NA	NA	NA	NA	NA
Indeno(1,2,3-cd)pyrene	I[123-cd]p	PAH	Combustion	NA	NA	NA	NA	NA	NA
Dibenz(a,h)anthracene	D[ah]A	PAH	Combustion	NA	NA	NA	NA	NA	NA

Table 3-3. Semi-Volatile Organic Compounds (SOCs) Measured in WACAP (continued).

					Federal Regulatory Status 2007*				
Compound Name	**Abbreviation**	**Chemical Class**	**Use/Source**	**First U.S. Usage**	**U.S.**	**Canada**	**China**	**Korea**	**Japan**
Benzo(ghi)perylene	B[ghi]P	PAH	Combustion	NA	NA	NA	NA	NA	NA
Retene	Retene	PAH	Combustion	NA	NA	NA	NA	NA	NA
Industrial/Urban Use Compounds (IBCs)									
PCB 74	PCB74	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 101	PCB101	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 118	PCB118	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 138	PCB138	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 153	PCB153	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 183	PCB183	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
PCB 187	PCB187	PCB	Industrial	1929	B 1977	B 1977	N		B 1972
mono-PBDEs (1, 2, 3)		PBDE	Flame Retardant	1977					
di-PBDEs (7, 8, 10, 11, 12, 13, 15)		PBDE	Flame Retardant	1977					
tri-PBDEs (17, 25, 28, 30, 32, 33, 35, 37)		PBDE	Flame Retardant	1977					
tetra-PBDEs (47, 49, 66, 71, 75, 77)		PBDE	Flame Retardant	1977					
penta-PBDEs (89, 99, 100, 116, 118, 126)		PBDE	Flame Retardant	1977	R				
hexa-PBDEs (138, 153, 154, 155, 166)		PBDE	Flame Retardant	1977					
hepta-PBDEs (181, 183, 190)		PBDE	Flame Retardant	1977					

*Regulatory status legend: A = current active use, B = banned for use, R = some restricted uses, N = not likely used in the given country, and NA = not applicable (Primbs et al., 2007; UNEP, 2002; Breivik et al., 2002; USEPA, 2007c; Pesticide Action Network; Purdue University, National Pesticide Information Retrieval System; Environment Canada, EDDENet). The SOC ban year is included if this information is available.

We selected the list of SOCs in Table 3-3 by evaluating the existing scientific literature to determine which SOCs have been shown to undergo atmospheric transport and deposition to remote ecosystems, including high latitude and high elevation ecosystems. In addition, the SOCs measured in WACAP span a wide range of volatility, water solubility, and hydrophobicity, as well as persistence in the environment. The SOC physico-chemical properties have been used to interpret the atmospheric transport, deposition, and accumulation of these compounds to the ecosystems assessed in WACAP. Finally, some of the SOCs measured in WACAP are classified as persistent, bioaccumulative, and toxic (PBT) chemicals by the USEPA. These PBT chemicals include aldrin, benzo(a)pyrene, chlordane, DDT, DDD, DDE, hexachlorobenzene, mirex, and PCBs.

Not all of the SOCs measured in WACAP were consistently detected in all WACAP media and national parks. Figure 3-1 summarizes the current status of SOC contamination in all WACAP parks and media. The figure shows the SOCs that were detected in at least one WACAP environmental medium. The horizontal bars represent the percentage of all WACAP samples that had an SOC concentration above the estimated detection limit.

Figure 3-1 also highlights some of the key SOCs that are the focus of this report. Total endosulfans (sum of ENDO I, ENDO II, and ENDO S), g-HCH, chlorpyrifos (CLPYR), and dacthal (DCPA) were among the most commonly detected CUPs and are markers for recent agricultural sources. a-HCH, hexachlorobenzene (HCB), dieldrin, total DDTs (sum of p,p′-DDT, o,p′-DDT, p,p′-DDD, o,p′-DDD, p,p′-DDE, and o,p′-DDE), and total chlordanes (sum of t-CLDN, c-CLDN, t-NCLR, c-NCLR, and o-CLDN) were among the most commonly detected HUPs and are markers for historic agricultural sources. The polycyclic aromatic hydrocarbons (PAHs) are markers for combustion sources. Finally, the polybrominated diphenyl ether (PBDE) flame retardants and the polychlorinated biphenyls (PCBs) are markers for industrial/urban sources.

3.2.2 Mercury

Mercury, an element found in the earth’s crust, is a common component of coal and ore rich in minerals. In nature, the mineral cinnabar (HgS, mercury sulfide) occurs in concentrated deposits and has been used as the primary source of commercially mined mercury since Roman times. When coal is burned or ores are smelted, mercury enters the atmosphere. In 2000, as much as two-thirds of the total anthropogenic emissions world-wide (ca. 2,190 tons of Hg) was from the combustion of fossil fuels (Pacyna et al., 2006), mostly coal. On a global scale, Hg emissions increased from 1,881 tons in 1990 to 2,235 tons in 1995, then decreased only slightly in 2000 to approximately 2,190 tons. It is estimated that over the last 100 years, anthropogenic Hg has accounted for approximately 70% of the total atmospheric deposition of mercury at the location of the Upper Freemont Glacier (4,100 m, Wyoming) in the western United States, with the remainder coming from geologic (e.g., weathering of the lithosphere, volcanoes) and biogenic sources (Schuster et al., 2002). This estimate is consistent with the analysis of Wiener et al. (2006), who determined that anthropogenic Hg inputs from atmospheric deposition to Voyageurs National Park (Minnesota, USA) accounted for 63% ± 13% of the mercury accumulated in the park’s lake sediments during the twentieth century.

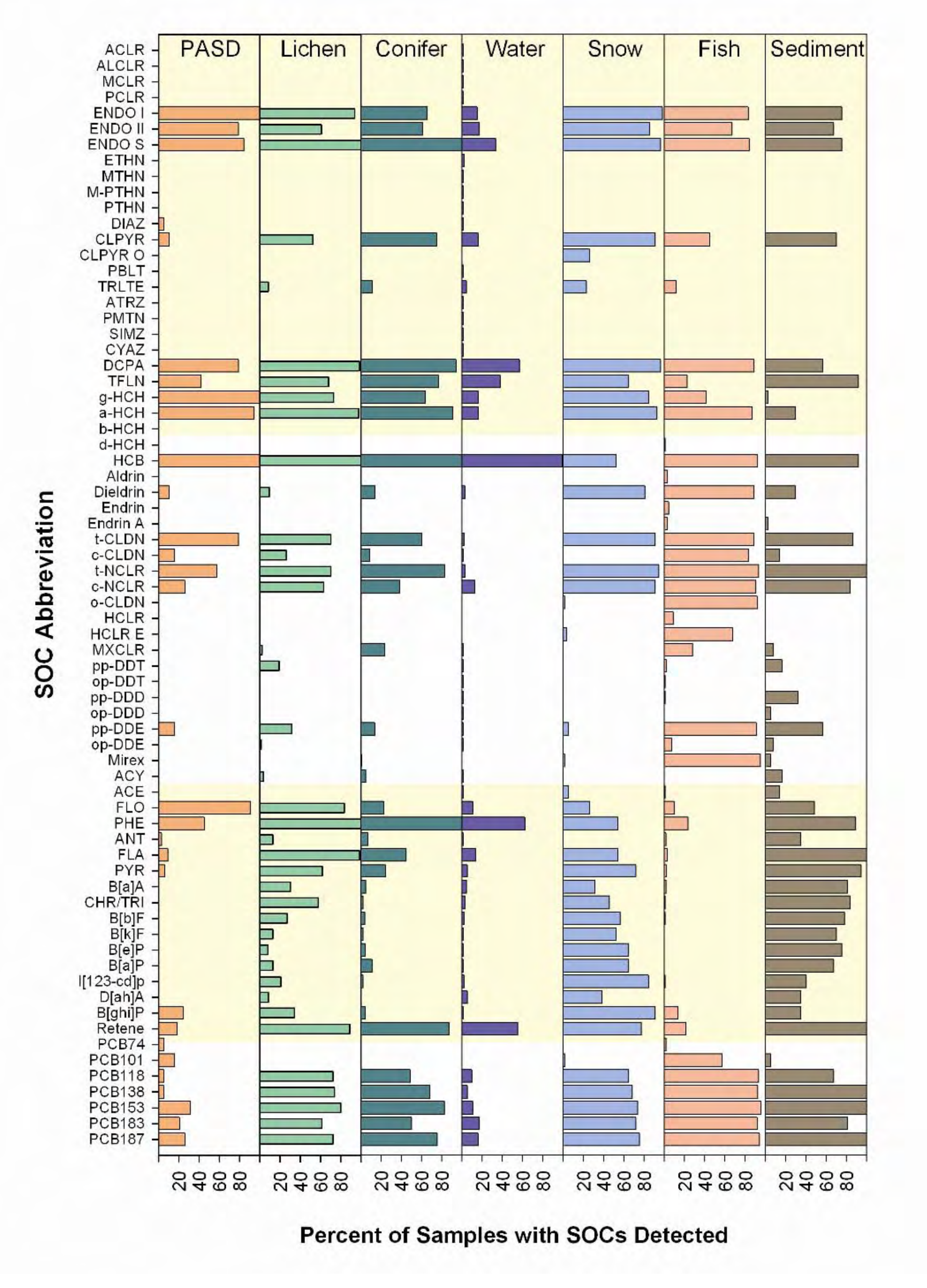

Figure 3-1. Current Status of SOC Contamination in WACAP Parks. The percent of all WACAP samples with SOC concentrations above the estimated detection limit is given for each medium. Only recent sediment samples from 1990 to present are included in the sediment column. PBDEs are not included because they were measured only in fish and sediment samples. PASD = passive air sampling device; SOC concentrations in PASDs are a measure of concentrations in ambient air.

Among the world's nations, the United States was the sixth greatest emitter of Hg to the atmosphere in 2000, with 109.2 tons (5% of the total annual world emissions). China topped the global 2000 list of Hg emitters with 604.7 tons (28% of world total; Pacyna et al., 2006). USEPA estimates that about one-fourth of the mercury emitted in the United States is deposited in the United States, while the remaining 75% enters the atmospheric component of the global mercury cycle where it can reside for up to 2 years, circling the earth approximately every 3 weeks.

Mercury is a contaminant of concern because of its detrimental neurological effects, as well as other effects, on humans, fish, and other organisms; it is classified by USEPA as a PBT chemical (Wiener et al., 2003). Mercury concentrations in the atmosphere have greatly increased because of the greater use of fossil fuels (particularly coal) since industrialization, and because of the ease with which mercury is distributed globally through the atmospheric mercury cycle. Moreover, once mercury has been deposited to a watershed and finds its way into aquatic systems, it can be methylated by reducing bacteria and, only while in this form, incorporated into aquatic food webs where it can be biomagnified, accumulating in the top predators of the aquatic food web at concentrations 10 to 1,000 times greater than in the water itself. These top aquatic predators often are targeted food sources of terrestrial wildlife and humans, particularly subsistence fishers and terrestrial wildlife, adding another final step to the biomagnification pattern of Hg.

3.2.3 Metals

As with SOCs, the metals chosen for measurement in WACAP media were selected because they serve as markers for a variety of different sources (Table 3-4). These include anthropogenic sources such as coal combustion, petroleum combustion, industrial emissions, agricultural, medical waste, incineration, and automotive sources, as well as biogenic sources such as sea aerosols, volcanic deposits, and minerals.

Table 3-4. Environmentally Significant Metals.

Coal Combustion	
Aluminum	Al
Antimony	Sb
Arsenic	As
Barium	Ba
Beryllium	Be
Boron	B
Cadmium	Cd
Chromium	Cr
Cobalt	Co
Copper	Cu
Gallium	Ga
Iron	Fe
Lead	Pb
Manganese	Mn
Mercury	Hg
Molybdenum	Mo
Nickel	Ni
Selenium	Se
Thallium	Tl
Vanadium	V
Zinc	Zn
Zirconium	Zr
Sea Aerosols	
Boron	B
Calcium	Ca
Magnesium	Mg
Sodium	Na
Strontium	Sr
Volcanic	
Aluminum	Al
Arsenic	As
Bismuth	Bi
Cadmium	Cd
Iron	Fe
Manganese	Mn

Table 3-4. Environmentally Significant Metals (continued).

Volcanic (continued)		**Automotive**	
Nickel	Ni	Barium	Ba
Vanadium	V	Cadmium	Cd
Petroleum Combustion		Lead	Pb
Arsenic	As	Nickel	Ni
Barium	Ba	**Mineral (Earth's crust)**	
Beryllium	Be	Aluminum	Al
Cadmium	Cd	Barium	Ba
Chromium	Cr	Calcium	Ca
Copper	Cu	Cerium	Ce
Lead	Pb	Cesium	Cs
Manganese	Mn	Holmium	Ho
Molybdenum	Mo	Iron	Fe
Nickel	Ni	Lanthanum	La
Selenium	Se	Lithium	Li
Vanadium	V	Magnesium	Mg
Zinc	Zn	Manganese	Mn
Industrial (nonferrous metal production)		Mercury	Hg
Cadmium	Cd	Neodymium	Nd
Chromium	Cr	Praseodymium	Pr
Copper	Cu	Rhenium	Re
Lead	Pb	Rubidium	Rb
Manganese	Mn	Samarium	Sm
Vanadium	V	Sodium	Na
Zinc	Zn	Strontium	Sr
Agricultural		Tellurium	Te
Arsenic	As	Terbium	Tb
Mercury	Hg	Thulium	Tm
Selenium	Se	Thulium	Tm
Zinc	Zn	Tungsten	W
Waste Incineration		Uranium	U
Cadmium	Cd	Vanadium	V
Copper	Cu	Yttrium	Y
Lead	Pb	Ytterbium	Yb
Mercury	Hg	Zirconium	Zr
Zinc	Zn	**Medical**	
		Neodymium	Nd

3.3 Data Quality Summary

The WACAP Quality Assurance (QA) Project Plan (Western Airborne Contaminants Assessment Project, 2004), completed in May 2004, outlines the quality assurance and quality control objectives and procedures for WACAP. It establishes methods for assessing data quality for each analyte and media type, and includes analysis of replicate samples, surrogate spikes, field and laboratory blanks, and SRMs when available. WACAP data quality is described primarily by precision of replicate analyses, accuracy as indicated by difference from SRM or recoveries of surrogate spikes, and detection limits. Appendix 3B provides detailed results of these indicators of data quality. The following subsections summarize the data quality of the major WACAP contaminants studied.

3.3.1 SOC Data Quality

All SOC analyses were conducted at the Simonich Environmental Chemistry Laboratory at Oregon State University. Table 3-5 summarizes SOC data quality, with means of estimated detection limits (EDLs), surrogate recoveries, replicate sample analyses, and percent difference of the SRMs for sediment and fish. EDLs were calculated for each compound by the approach described in Method 8280A (USEPA, 1996), and are listed by media in the tables in Appendix 3B. For statistical comparisons, concentrations less than the EDL were replaced by concentrations representing one-half of the EDL (Antweiler, R.C., and H.E. Taylor, written communications), following the guidelines listed in Section 3.5.1.

Target analyte loss was corrected via target analyte-to-surrogate response ratios in calibration curves. Laboratory blanks were generated by the use of designated extraction disks spiked with surrogate solution, after which all elution and clean-up steps were followed. Method blanks consisted of sodium sulfate and were taken through the entire analytical method. Reported SOC concentrations were blank-subtracted, according to the laboratory blank, and then recovery corrected. Concentrations are not reported for cases in which the mass in the laboratory blank exceeded 33% of that in the sample.

SRMS were available for sediment and fish analyses. Baltimore Harbor sediment certified reference material (NIST SRM #1941b) was analyzed for 27 certified compounds, with percent difference from the certified values ranging from 0 to 55.4% difference and a mean of 16.8%. Fish certified reference material (NIST SRM #1946) was analyzed for 31 certified compounds, with percent difference from the certified values ranging from 0 to 30% difference and a mean of 7%.

3.3.2 Mercury Data Quality

Total mercury on unfiltered snow samples was measured at the USGS Wisconsin Water Science Center Mercury Research Laboratory (USGS-WWSC) by cold vapor atomic fluorescence spectrometry (Olson and DeWild, 1999). The detection limit was 0.04 ng/L. In addition, methyl mercury was measured on the 2005 unfiltered snow samples. Field replicate samples were analyzed at the USGS-WWSC laboratory for total mercury. Percent relative standard deviation of field replicates was higher for total mercury than for most constituents, because much of the snowpack mercury is associated with particulates. Particulates vary substantially at scales of a meter or less, which is typical of the spacing between replicate samples. Additional replicate samples were analyzed in the in the USGS Trace Element Environmental Analytical Chemistry Research (USGS-NRP Boulder) Laboratory in Boulder, Colorado, by cold vapor atomic fluorescence spectrophotometry, with a detection limit of 0.4 ng/L (Roth, 1994). The relation of the values between the two laboratories is described by the equation:

$$\text{(USGS-WWSC lab values)} = 1.2\text{(USGS-NRP Boulder lab values)} + 0.64\ (n = 28,\ R^2 = 0.71) \qquad [3\text{-}1]$$

Table 3-5. Summary of Data Quality Indicators for SOCs by Media.[1]

Media	Units[2]	Estimated Detection Limit[3]		Method Recoveries		Replicate Sample Injections Mean %RSD	Mean %Difference of NIST SRM	NIST SRM
		Range	Mean	Range	Mean			
Snow	pg/L	0.20 to 125	22	28.1 to 206.2%	68.3%	3.5	na	Na
Air	ng/g dw XAD	0.00 to 0.2	0.03	20.9 to 210.0 %	93.7%	49.5	na	Na
Lichen	ng/g lipid	0.01 to 54.3	4.6	31.3 to 139.5%	73.9%	18.9	na	Na
Conifer needles	ng/g dw	0.01 to 72.3	5.7	24.6 to 97.3%	73.2%	19.4	na	Na
Lake water	pg/L	0.5 to 385	13	24.7 to 158.8%	99.0%	26.5	na	Na
Sediment	ng/g dw	0.1 to 204.7	23.8	20.9 to 136%	60.3%	6.2	16.8	1941b
Fish	pg/g ww	0.2 to 920	78.7	31.4 to 98.3%	61.4%	23.4	7	1946

[1] Detailed recovery and EDLs for moose were not conducted because there were so few moose samples. However, the SOC recoveries and EDLs were similar to those for fish.

[2] dw = dry weight, ww = wet weight, lipid = lipid weight; XAD = Amberlite XAD-2 styrene divinylbenze resin beads 460 µm in diameter.

[3] Estimated detection limits determined by U.S. EPA Method 8280A.

The slightly higher values from the Wisconsin laboratory might have resulted from more complete oxidation of the mercury in the method used by the Wisconsin laboratory compared to the Colorado laboratory's methods.

Total mercury in lichen, sediment, fish, and moose was measured at the WRS Analytical Laboratory by combustion atomic absorption spectrophotometry (CAAS) with a LECO AMA254 Mercury Analyzer (LECO, St. Joseph, Michigan, USA) according to EPA method 7473 (USEPA, 1998). This method uses thermal decomposition, catalytic removal of interference, collection onto a gold alloy amalgamate, and thermal release of Hg from the amalgamate. Hg released from the amalgamate is measured by atomic absorption spectrophotometry (254 nm) with a high voltage (2 kV) mercury lamp. Each sample was analyzed in duplicate, with the average of the duplicates reported as the sample concentration. Samples were rerun if the percent relative standard deviation (%RSD) of the duplicates was greater than 15%.

Table 3-6 summarizes the data quality of the mercury analyses, with method detection limits, mean precision of replicate samples, and mean percent differences of standard reference materials (SRMs). Method detection limits were determined according to Taylor (1987), with repeated analyses of a low concentration sample. SRMS were available for snow, lichens, sediment, and fish from the National Research Council of Canada (NRCC), the National Institute of Standards and Technology (NIST), and the Standards, Measurements, and Testing Program of the European Commission (ECSMTP). Moose samples were analyzed with the fish SRMs.

Table 3-6. Summary of Data Quality Indicators for Mercury by Media.[1]

Media	Units[2]	Method Detection Limit[3]	%RSD from Replicate Samples	SRM[4]	Mean %Difference of SRM
Snow	ng/L	0.04	29.4[5]	NIST 3133 (Diluted to theoretical value of 5 ng/L)	0.51
Lichen	ng/g ww	8.8	4.5	ECSMTP Lichen CRM 482 (480 ± 20 ng/g)	-3.5
Sediment	ng/g dw	3.3	5.3	NRCC Marine Sediment: PACS-2 (3040 ± 200 ng/g)	3.8
				NRCC Marine Sediment: MESS-3 (91 ± 9 ng/g)	2.9
Fish	ng/g ww	6.0	6.6	NRCC DORM-2 dogfish (4640 ± 260 ng/g)	3.3
				NIST 2976 Mussel Tissue (61.0 ± 3.6 ng/g)	-7.9

[1] Method detection limits and precision from replicate samples were not determined for moose because there were so few moose samples (6 over 2 years). Moose samples were analyzed with the same SRMs used for fish analyses.

[2] ww = wet weight, dw = dry weight

[3] Method detection limits determined as described in Taylor (1987)

[4] NRCC= National Research Council of Canada; NIST= National Institute of Standards and Technology; ECSMTP = Standards, Measurements, and Testing Program of the European Commission.

[5] %RSD values for snow are from the analysis of replicate samples collected at the field sites, while the %RSD values for the other media are from analysis of samples split into replicates in the laboratory.

3.3.3 Metals Data Quality

All trace metals analyses were conducted at the USGS-NRP Boulder (Trace Element Environmental Analytical Chemistry Project, National Research Program) Laboratory. Quality control at this laboratory involves the systematic analysis of blanks, replicates, SRMs, and spike addition samples. All sample measurements were made at least in triplicate, with the mean value reported as the sample concentration. Table 3-7 summarizes the data quality of metal analyses, with mean method detection limits, median precision of replicate samples, and mean percent differences from analyses of SRMs for Cd, Cu, Ni, Pb, V, and Zn.

Table 3-7. Summary of Data Quality Indicators for Metals by Media.[1]

Mean Method Detection Limits[2]

Media	Units	Cd	Cu	Ni	Pb	V	Zn
Snow	µg/L	0.003	0.01	0.008	0.008	0.02	0.1
Lichen	µg/g	0.01	0.2	0.1	0.04	0.1	0.9
Sediment	µg/g	0.01	0.1	0.06	0.03	0.4	0.7
Fish Fillet	µg/g	0.005	0.03	0.06	0.01	0.05	0.4
Fish Liver	µg/g	0.01	0.1	0.06	0.009	0.05	0.4

Median Precision of Replicate Samples

Media	Units	Cd	Cu	Ni	Pb	V	Zn
Snow	%RSD	13.1	9.2	11.4	19	59.8	22.7
Lichen	%RSD	2.7	2.4	9.7	1.9	3.2	4.6
Sediment	%RSD	2.6	1.6	1.7	1.2	2.1	1.7
Fish Fillet	%RSD	14.5	1.7	15.2	11.9	18.9	1.5
Fish Liver	%RSD	2.3	2.1	39.4	12.2	10.3	2.8

Mean %Difference of SRMs[3]

Media	Units	Cd	Cu	Ni	Pb	V	Zn
Snow	% Difference	0.3	-1.8	0.6	-2.2	-0.2	1.6
Lichen	% Difference	8.6	7.9	-1.2	14.2	33.3	9.5
Sediment	% Difference	-2.1	0.8	2.7	4.2	1.0	0.4
Fish Fillet	% Difference	-4.0	7.1	16.8	10.4	na	5.5
Fish Liver	% Difference	2.23	11.4	-7.2	15.9	-0.7	10.2

[1] Results for moose meat and moose liver are not included here, but are provided in the Quality Assurance/Quality Control Report for Trace and Major Elements with the database;

na = not available; %RSD = percent relative standard deviation.

[2] Median value of detection limits are provided for sediment. Method detection limits calculated as described in Taylor (2001).

[3] One to five SRMs were analyzed for each metal for each media. The mean value of the percent differences for all SRMs is presented here.

Detection limits for each metal vary slightly, depending on specific analysis conditions for each analytical run (Taylor, 2001). Appendix 3B provides the mean detection limits, by media, for all the metals analyzed. Actual calculated detection limits are listed in the database. For statistical comparisons, concentrations less than the detection limits were replaced by concentrations representing one-half of the detection limit (Antweiler and Taylor, written communications), following the guidelines listed in Section 3.5.1. Details, results, and figures describing the data quality of all metals analyses are provided in the Quality Assurance/Quality Control Report for Trace and Major Elements, included with the documentation for the WACAP database.

3.4 Methods Used

3.4.1 Air Modeling

Because of the remote locations of the WACAP sites, atmospheric transport modeling was an integral part of understanding how the contaminants were transported to the sites. Atmospheric transport was modeled via back-trajectory cluster analysis on three different time scales for each of the WACAP core parks. A back-trajectory represents a meteorological calculation of the path that an individual air particle has traveled over a specific time period. By grouping similar trajectories into clusters, we obtained information about the routes of contaminant transport, as well as the climatology for each park.

Using the National Oceanic and Atmospheric Administration's (NOAA) HYSPLIT model and the National Centers for Environmental Prediction (NCEP) meteorological grids (Draxler and Hess, 2004), we calculated back trajectories for each WACAP core park daily, from 1998 through 2005, for 1-, 5-, and 10-day durations, making a total of 2,922 trajectories for each WACAP park and duration, and a total of 21 sets of trajectories. Figure 3-2 shows all the 2,922 1-day back-trajectories for MORA. The individual points are the hourly locations of each trajectory.

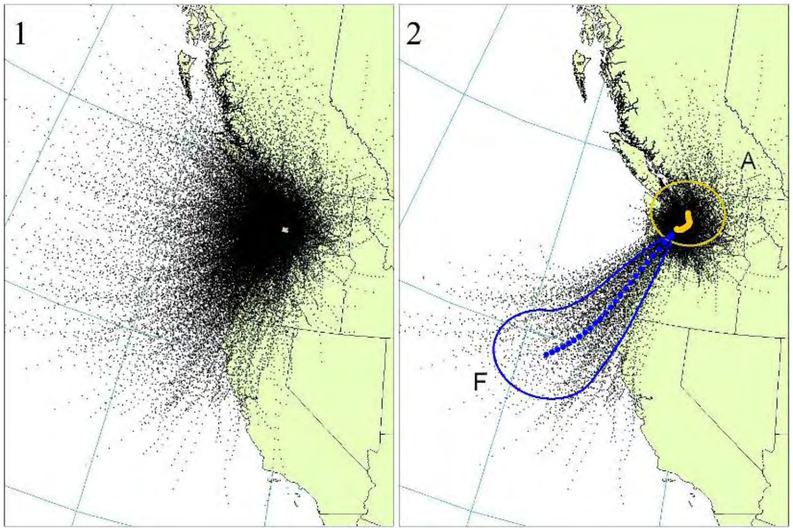

Figure 3-2. All 2,922 One-Day Back-Trajectories for MORA. The figure on the left (1) shows 2,922 individual one-day trajectories for MORA. The figure on the right (2) shows cluster means (dots), standard deviations (ellipsoid shapes), and member trajectories for clusters A and F.

The goals of cluster analysis were to group the trajectories so as to minimize the variability of trajectories within a cluster, and maximize the variability among clusters (Owen, 2003; Hafner et al., 2007). Using a non-hierarchical clustering algorithm (meaning the number of clusters are pre-determined), we separated each set of 2,922 trajectories into 6 clusters consisting of 55 to 1,125 member trajectories. Clusters are graphically represented by the cluster mean and standard deviation, which are the average position of all trajectories in that cluster, and the standard deviation of the trajectories about the cluster mean, respectively. In each set, the clusters were labeled alphabetically, with the shortest being A and the longest F. The graph on the right in Figure 3-2 shows an example of the mean and standard deviation for clusters A and F from the 1-day cluster results at MORA (member trajectories of these clusters are included).

Daily precipitation totals from nearby metrological stations were applied to the member trajectories from each cluster. Using these data, we were able to calculate the sum of precipitation for which each cluster was responsible, and normalize this amount to total precipitation. This relative amount of precipitation per cluster is a useful metric for determining the pathways of wet deposition. Table 3-8 lists the starting locations and altitudes of the trajectories, as well as the locations and names of the precipitation stations.

Table 3-8. Starting Locations for Back Trajectories and Precipitation Data Used for Cluster Analysis. Latitude and longitude are in decimal degrees, altitude is in meters above ground level.

	Trajectory Starting Locations				
WACAP Site	Latitude	Longitude	Altitude	**Precipitation Data**	**Distance from WACAP Site**
NOAT and GAAR	68.0	-158.5	0	Bettles WBAN	320 km SE
DENA	63.3	-151.3	0	Den417 CASTNET	125 KM NE
GLAC	48.5	-113.5	580	Flattop Mountain Snotel	43 km NW
OLYM	47.9	-123.5	1100	Mount Crag Snotel	38 km SE
MORA	46.9	-121.9	1100	Paradise Snotel	18 km SE
ROMO	40.3	-105.6	600	Lake Irene Snotel	23 km NW
SEKI	36.6	-118.7	700	Virginia Lakes Ridge Snotel	171 km NW

3.4.2 Snow

3.4.2.1 Snowpack Sample Collection

The objective was to sample the seasonal snowpack from at least one site in or near the WACAP sampling watersheds during each of the 3 years of the study, in order to assess inter-annual variability of contaminant loading. This objective was generally met, with a few exceptions caused by either poor snow conditions or consideration for safety of field crews.

All snow sampling tools were pre-cleaned in the laboratory with high-purity deionized water, and stored in sealed polyethylene bags. Teflon^{TM} bags for organics aliquots were pre-rinsed with ethyl acetate, followed by a 1:1 mixture of hexane and acetone; Teflon^{TM} bags for inorganics aliquots were pre-rinsed with high-purity deionized water. Each sample bag was sealed in 2 ziploc bags, and groups of these were stored in large polyethelene bags.

Snowpack samples were collected in small forest clearings or open areas, near the time of annual maximum snow accumulation but before the onset of spring snowmelt (Ingersoll et al., 2001). A snowpit was dug from snow surface to ground surface, and physical properties of the snowpack were measured, including snow grain type and size, hardness, temperature, and density. Snow density was measured with a volumetric cutter (250 or 1,000 cc) inserted into the snowpit wall, tared, and weighed on a portable electronic balance. Density was measured at 10-cm intervals in shallow snowpacks, or at an interval that provided at least 10 measurements in deeper snowpacks. We calculated snow water equivalent (SWE) by multiplying the average density by total snow depth. Later, we calculated fluxes of contaminants in the snowpack by multiplying concentrations by SWE.

Snowpits were dug with steel and ordinary polycarbonate shovels used for avalanche safety, then the pre-cleaned polycarbonate shovels and scoops were used to create a fresh face in the snowpit. A vertical column of snow was cut from the pit face and placed in pre-cleaned Teflon^{TM} bags. The vertical column integrated snow that accumulated throughout the snowfall period. Snow samples were collected carefully to prevent contamination. The top 5 cm and bottom 10 cm of snow from the pit face were excluded from the sample to reduce the possibility of contamination. The sealed Teflon^{TM} sample bags were placed in thin black polyethylene bags to exclude light, then in clean heavy-duty polyethylene bags for protection. Samples were frozen within 12 hours on dry ice to minimize chemical and biological reactivity during transport and shipping. Frozen samples were sent by overnight express shipping service to laboratories at USGS-CWSC (inorganic fraction) and Oregon State University (organic fraction).

Two sub-samples were collected from each snowpit: one sample for analysis of inorganic constituents, including major ions, nutrients, dissolved organic carbon, trace metals, mercury, and particulate matter; and one sample for analysis of organic contaminants (see Appendix 3A). Each sample for inorganic analysis was collected in a single Teflon^{TM} bag containing approximately 6 liters of snow, yielding about 2 liters of meltwater. Each sample for organic analyses consisted of six large, solvent-rinsed Teflon^{TM} bags containing a total of approximately 150 liters of snow, yielding about 50 liters of meltwater.

3.4.2.2 Analytical Methods for Major Ions and Nutrients in Snow

Snow samples for inorganic analyses, including analyses for major ions, nutrients, and trace metals, were processed in the USGS Colorado Water Science Center (CWSC) Laboratory according to protocols established for related projects (Ingersoll, 2001). To melt the samples, Teflon^{TM} collection bags were placed in clean polyethylene buckets at room temperature for approximately 12 hours. Buckets were placed on a shaker table to homogenize the distribution of fine particulate matter. Sample aliquots were drawn through a small hole in the top of the sealed bag. The sample was drawn through a tube connected to a peristaltic pump. Sample aliquots were then distributed to various laboratories for analysis.

Calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and silicon (dissolved SiO_2) were determined on an acidified (0.4% by volume ultra-high-purity nitric acid) filtered (0.45 µm) aliquot by direct calibration inductively coupled plasma-atomic emission spectrophotometry (ICP-AES), with a Perkin Elmer model 3300DV multi-channel emission spectrometer (Garbarino and Taylor, 1979; Boss and Fredeen, 1999; Mitko and Bebek, 1999, 2000). Samples were introduced into the spectrometer via a Teflon™ parallel path nebulizer.

Ammonium (NH_4^+), potassium (K), sodium (Na), nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}) concentrations were determined, within 2 weeks of melting, on a filtered (0.45 µm) refrigerated aliquot by ion chromatography (Fishman, 1993). Detection limits were less than 0.5 µeq/L for all major ions.

Specific conductance, pH, and alkalinity were determined on an unfiltered, chilled aliquot. Specific conductance was measured with a platinum electrode; pH was measured with a combination glass electrode designed for low-ionic strength waters; and alkalinity was determined by automatic titration and Gran calculation. Dissolved organic carbon (DOC) concentration was determined on a filtered, chilled aliquot stored in a pre-combusted glass bottle. DOC determinations were by infrared detection with a detection limit of 0.5 mg/L.

An aliquot for particulate carbon and nitrogen analysis was filtered through a glass-fiber filter, which was shipped to the University of Maryland Chesapeake Biological Laboratory in Solomons, Maryland. The filter was combusted and the products of combustion were analyzed by thermal conductivity detector (http://www.cbl.umces.edu/nasl/index.htm; USEPA, 1997).

3.4.2.3 Analytical Methods for SOCs in Snow

Snowpack samples were stored at –20ºC. At the time of analysis, samples were removed from the freezer and allowed to melt in the dark, without heat, for ~36 hrs in sealed Teflon™ bags. Once a sample was melted, a methanol solution containing isotopically labeled SOCs, for use as recovery surrogates, was spiked into the sample (Usenko et al., 2005; Hageman et al., 2006). The SOCs were extracted from melted snow with solid-phase extraction disks (combination of hydrophobic and hydrophilic 1-g divinylbenzene Speedisks™ from Mallinckrodt Baker, Phillipsburg, New Jersey) (Usenko et al., 2005; Hageman et al., 2006). No effort was made to analyze dissolved-phase SOCs and SOCs sorbed on particulate matter separately because their phase distribution in the snowpack is not maintained when the snow melts. Thus, the snow concentrations reported in this report are for total SOC concentrations in snow (i.e., the sum of SOCs in the dissolved and sorbed phases).

Gel permeation and silica gel adsorption chromatography were performed to remove media interferants (Usenko et al., 2005; Hageman et al., 2006). The final extract was spiked with an ethyl acetate solution containing four isotopically labeled internal standards. Analyte separation, detection, and identification were performed on Agilent (Palo Alto, California) 6890N gas chromatographs equipped with Agilent DB-5MS 30 m × 0.25 mm × 0.25 µm columns and 5943N mass selective detectors (Usenko et al., 2005; Hageman et al., 2006). Approximately one-half of the target analytes were quantified by means of electron impact (EI) ionization, whereas the other half were quantified by means of electron capture negative ionization. EDLs and method recoveries for specific SOCs are provided in Table 3B-1 in Appendix 3B.

3.4.2.4 Analytical Methods for Metals in Snow

Total mercury was analyzed on whole-water samples (unfiltered) by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry in the USGS Wisconsin Water Science Center Mercury Laboratory (Olson and DeWild, 1999). For the 2003 and 2004 field seasons, subsamples for other trace-metals were processed for both total (whole-water) and dissolved (filtered) determinations. For 2005 and 2006 field seasons, only filtered samples were analyzed.

The aliquot for analysis of dissolved constituents was filtered through a 0.4-µm, pore-size polycarbonate membrane filter. After filtration, the sample was preserved by acidification to 1% by volume with concentrated ultra-high-purity nitric acid. The nitric acid was purified in the laboratory by double distillation (Kuehner et al., 1972).

The aliquot for analysis of whole-water constituents was preserved by the addition of 2 mL of concentrated ultra-high-purity nitric acid to 250 mL of sample, and then subjected to a modified in-bottle digestion with 5 mL of concentrated ultra-high-purity hydrochloric acid per 200 mL of sample in a water bath at “near boiling” conditions (Garbarino and Hoffman, 1999). Following digestion, the samples were filtered as described in subsection 3.4.2.2 to remove undissolved particulate.

Metals present at trace concentration levels, including aluminum (Al), antimony (Sb), arsenic (As), boron (B), beryllium (Be), barium (Ba), bismuth (Bi), cadmium (Cd), cerium (Ce), cesium (Cs), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lithium (Li), manganese (Mn), molybdenum (Mo), neodymium (Nd), nickel (Ni), lead (Pb), praseodymium (Pr), rhenium (Re), rubidium (Rb), samarium (Sm), selenium (Se), strontium (Sr), tellurium (Te), terbium (Tb), thallium (Tl), thulium (Tm), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), yttrium (Y), zinc (Zn) and zirconium (Zr), were determined by a multi-element inductively coupled plasma-mass spectrometric (ICP-MS) method (Garbarino and Taylor, 1995; Taylor, 2001).

These determinations were performed with a Perkin Elmer model Elan 6000 mass spectrometer. Aerosols of nitric acid preserved sample solutions were introduced into the spectrometer with a Teflon^{TM} parallel path nebulizer. Multiple internal standards (indium, iridium, and rhodium) were used to normalize the system for drift. Detection limits for metals in snow samples are listed in Table 3B-2 in Appendix 3B.

3.4.3 Air

3.4.3.1 Passive Air Sampling Device (PASD) Deployment

Passive air sampling devices (PASDs) were used to (1) obtain a measure of SOCs in ambient air by means of a simple, standardized technology to compare loadings between parks and across geographic and elevational gradients, (2) compare PASD and vegetation concentrations, and (3) compare ambient air SOC concentrations in WACAP parks to ambient air concentrations at other national and international locations measured with the same PASD design.

In total, 37 PASDs were strategically deployed in all core and secondary WACAP parks. Multiple PASDs were deployed in the eight core WACAP parks and in two secondary parks to sample target watersheds and to obtain data along elevational gradients (see Table 3-9). All but four of the PASDs (two in SEKI and two in ROMO) were co-located with WACAP vegetation sampling sites.

The PASD design followed Wania et al. (2003). Each PASD consisted of a stainless steel wire mesh cylinder (1.6 cm in diameter, 20 cm long) filled with 460-μm-diameter styrene divinylbenze resin beads (Amberlite XAD-2), suspended in an aluminum stove pipe housing with an aluminum cap to prevent wetting of the cylinder from precipitation (see Figure 3-3a). The PASD housing was open at the bottom to allow air circulation, but covered with chicken wire to prevent incursion by small mammals or birds. The housing had been previously spray-painted green to camouflage the device and baked at 66°C for 2 hours to off-gas SOCs.

Freshly loaded resin cartridges were mailed to field offices in air-tight stainless steel containers by overnight mail a few days before field deployment. Cartridges were exposed and assembled in their housing at field sites and hung from exposed tree branches with stainless steel wire or nylon rope (Figure 3-3b). In WACAP park sites with few or no trees (GAAR, NOAT, CRLA), the PASDs were attached to structures (e.g., Figure 3-3c). All 37 PASD samplers were installed in summer 2005 and retrieved 1 year later (±2 weeks). A small temperature data logger was hung inside the PASD housing to record mean temperature at hourly intervals. To retrieve a PASD, field personnel disassembled it at the field site, placed the resin cartridge into the air-tight cylinder, and mailed it back to the Simonich laboratory, where it was stored at –40°C until analysis.

Table 3-9. Summary of Passive Air Sampling Device Distribution among WACAP Parks.

No. of Monitors	Park	Lake Watersheds	Elevation(s) (m)
1	GAAR	Matcharak	505
	NOAT	Burial	388
	BAND, CRLA, GLBA,GRSA, GRTE, KATM, LAVO, NOCA, WRST, YOSE		2926, 2713, 8, 3338, 3048 370, 2713, 1600 648, 3048
2	GLAC	Snyder & Oldman	1609, 2036
	MORA	LP19 & Golden	1372, 1369
	OLYM	PJ & Hoh	1392, 1433
	DENA	Wonder	564, 686
4	BIBE		560, 1067, 2316, 2713
	SEKI	Emerald	658, 670, 2300, 2816
	STLE		0, 254, 567, 815
5	ROMO	Mills & Lone Pine	2560, 2720, 3018, 3042, 3536

Figure 3-3. Passive Sampler: (a) Hooking resin cartridge to underside of housing cap, (b) Deployment from an exposed tree branch in the Stikine-LeConte Wilderness, and (c) Deployment from a fire tower in Crater Lake National Park.

3.4.3.2 Analytical Methods for SOCs in PASDs

Before deployment, the sampling resin (Amberlite XAD-2) was cleaned by means of a high temperature and high pressure extraction method (pressurized liquid extraction). The XAD-2 was spiked with d-hexachlorocyclohexane (d-HCH) and polychlorinated biphenyl PCB 166 before shipping, to track SOC volatilization from the PASDs during shipping and deployment (Wania et al., 2003). Once collected, the XAD-2 was removed from its sampling tube and spiked with 14 isotopically labeled surrogates and extracted by means of pressurized liquid extraction (see Tables 3B-3 and 3B-4 in Appendix 3B). The extract was concentrated and spiked with isotopically labeled internal standards. The extract was analyzed for the SOCs listed in Table 3-3 by means of gas chromatographic mass spectrometry. The PASD concentrations were surrogate recovery corrected and travel blank subtracted. EDLs and method recoveries for specific SOCs are provided in Table 3B-4 in Appendix 3B.

3.4.4 Vegetation

3.4.4.1 Vegetation Sample Collection

The vegetation sampling objectives were to (1) determine which SOCs accumulate in vegetation in each WACAP park and their respective concentrations, (2) compare individual SOC concentrations within and across parks, especially along latitudinal and elevational gradients, to test for a cold fractionation effect (higher concentrations in colder sites, i.e., higher latitudes and elevations), (3) evaluate metal and nutrient burdens in lichens in relation to known ranges for clean sites and accumulation of SOCs, (4) determine the relationship between environmental factors such as geographical location, proximity to urban-industrial and agricultural areas, nitrogen concentrations in ambient particulates, and lichen nitrogen content with SOC concentrations in vegetation, and (5) make rough estimates of total burdens of SOCs in conifer needles at WACAP sites in g/ha as a way of evaluating SOC inputs to watersheds via litterfall.

3.4.4.1.1 Vegetation Selection

Conifer needles were chosen as the primary form of vegetation for SOC analysis because samples representing a defined exposure period (second-year needles) could be collected. In addition, coniferous trees were a dominant component of the vegetation at all WACAP parks, excluding the arctic (NOAT, GAAR). Conifer needles have been previously used to study SOCs in North American high elevation and high latitude ecosystems (Howe et al., 2004; Davidson et al., 2003).

Lichens were collected from the core parks for SOC, mercury, metals, nitrogen (N), and sulfur (S) analyses, and from the secondary parks for N and SOC analyses. Lichens have been used extensively for N, S, and metals analysis, plus their use allowed sampling of treeless sites (tundra and alpine ecosystems). In addition, they generally had higher concentrations of SOCs than conifer needles collected from the same sites, facilitating detection of site-to-site differences.

3.4.4.1.2 General Sampling Strategy

The general sampling strategy was to collect two forms of vegetation, when available, at each site: second year needles from one species of conifer and multiple thalli representing the on-site population of one species of lichen. A sample consisted of ≥ 150 g dry weight (dw) of conifer needles or ≥ 40 g dw of lichens. Collection sites were ~ 1 ha in size. Five collection sites were selected within each park, evenly spaced between the lowest and highest vegetated elevations, and included the target watersheds. Conifer needle and epiphytic lichen samples were sampled from a minimum of 8 trees, but usually ≥ 20 trees from the 1-ha collection site. Rock lichens (*Xanthoparmelia*) and tundra lichens (*Flavocetraria cucullata* and *Masonhalea richardsonii*) were sampled from a minimum of eight rocks or ground patches, respectively. To obtain field replicates, the 1 ha area was resampled, with collection from different trees, rocks, or ground patches.

3.4.4.1.3 Site Selection

Prior to the field season, resource specialists at each park were consulted to pre-select collection sites in order to minimize the number of species needed to sample across all elevations (sites) within each vegetation type (needles and lichens). Collection sites emphasized the west side of each park to increase the probability of detecting trans-Pacific contaminants. Although sites were not located along linear transects, an effort was made to keep all sites in the same quadrant of the park. A total of 20 species of conifer needles and 16 species of lichens were collected across the WACAP parks (Table 3-10). Of the 354 samples collected, 302 were analyzed for SOCs, 157 lichen samples were analyzed for total N, and 52 lichen samples were analyzed for S and metals, including mercury.

Table 3-10. Vegetation Sample Summary. See Appendix 1A-3 for scientific names of the species sampled at each site.

Sample Type	Genera	Genus Count	Species Count	Samples for SOC Analysis	Samples for N but not S or Metals Analysis	Samples for N, S and Metals Analysis
Conifer needles	Fir, spruce, pine, Douglas-fir, hemlock	5	19	157	0	0
Lichens	*Alectoria, Bryoria, Cladina, Flavocetraria, Hypogymnia, Letharia, Lobaria, Masonhalea, Platismatia, Sphaerophorus, Thamnolia, Usnea, Xanthoparmelia*	13	16	143	105	52
Total Count		**18**	**35**	**296**	**105**	**52**

3.4.4.1.4 Differences in Sampling Strategy between Core and Secondary Parks

The sampling strategy differed slightly between core and secondary WACAP parks. At the core parks (NOAT, GAAR, DENA, OLYM, MORA, SEKI, ROMO, GLAC), the study design called for collection of three replicate samples of conifer needles and whole lichen thalli from one species of conifer and two species of lichens at each of five elevations in each park (3 repetitions × 3 species × 5 elevations = maximum of 45 samples/park). Every effort was made to use the same species across elevations. However, in parks with large elevational gradients, this was not possible. Also, in treeless areas, only lichens could be collected, and in very dry locations, only conifers could be collected. Conifer needles were analyzed for SOCs, one species of lichen was analyzed for SOCs, and both species of lichen were analyzed for mercury, metals, N, and S. Core park vegetation samples were collected during summer 2004.

At the secondary parks (BAND, BIBE, CRLA, GLBA, GRSA, GRTE, KATM, LAVO, NOCA, STLE, WRST, YOSE), the study design called for the collection of one sample each of needles and lichen thalli from one species of conifer and one species of lichen at each of five elevations (2 species × 5 elevations = maximum of 10 samples/park). Ten percent of the samples were replicated. Secondary park vegetation samples were collected during summer 2005.

3.4.4.1.5 Field Protocols for Vegetation Sampling

The WACAP Research Plan (USEPA, 2003) provides details of the field protocol for vegetation sampling. Briefly, field personnel established collection site centers, staying within the 1-ha area, and collected samples into 2-liter, Silverpac metalized polyester bags (Ampac Flexibles, Product # 602B-IM, 5305 Parkdale Dr., St. Louis Park, MN 55416). The bags were pre-tested in the laboratory to ensure they would not contribute to sample SOC or metal concentrations. Conifer branches were clipped at the first- and second-year terminal bud scars with solvent-washed hand-pruners; lichens were collected by hand, by personnel wearing disposable latex or nitrile gloves. Filled bags were weighed, sealed with laboratory tape, and placed inside two zipper-locking plastic bags (see Figure 3B-1 in Appendix 3B for field photographs). Samples were kept cold in freezers or packed with crushed ice in plastic coolers, depending on the remoteness of the field site, in order to prevent decay. At the conclusion of sampling within each park, a 2-5 day process, samples were shipped in coolers filled with crushed ice in overnight or second-day mail to the Simonich laboratory. At the laboratory, samples were stored at –40° C until analysis.

On-site observations made by field personnel included location coordinates of the sampling site center; elevation; slope; aspect; cover of dominant trees, shrubs, and herbs; size of the sampling area; landform; exposure; and canopy cover. Notes were made on vegetation condition and potential local sources of SOC, nutrient, or metals contamination. See Appendix 3B for complete site data, sample records, and a sample field data record sheet.

3.4.4.2 Analytical Methods for SOCs in Vegetation

Frozen 2-year-old conifer needles and lichen were ground with a Buchi mixer with ceramic knives. A ground sub-sample of ~10-20 g [wet weight (ww)] was mixed with sodium sulfate, spiked with isotopically labeled surrogates, and extracted at a high temperature and pressure with dichloromethane. The extract was purified with water extractions and solid phase extraction with silica. Conifer needles required gel-permeation chromatography (GPC) as an extra clean-up step. The extract was concentrated to 300 µL, spiked with isotopically labeled internal standards, and measured for the SOCs listed in Table 3-3 by means of gas chromatography mass spectrometry (GC/MS). EDLs and method recoveries for specific SOCs are provided in Tables 3B-7 and 3B-8 in Appendix 3B.

3.4.4.3 Analytical Methods for Metals in Lichen

Lichen samples for metals, total nitrogen and sulfur, and mercury were collected from 11 sites in 7 core parks in 2004. No lichens were available for collection from Pear Lake in SEKI, and the lichen collected from the two sites in ROMO were on rock substrate with potential for interference from soil contamination.

These lichen samples were prepared for analyses at the USGS-Boulder laboratory. The samples were rinsed with deionized water to remove potential surface contamination from soils. Each sample was finely chopped with a ceramic knife, subsampled, and freeze-dried to remove residual moisture. After drying, samples were pulverized to a fine powder. Subsamples of the dried, ground lichens were then collected for metals, total nitrogen and sulfur, and mercury analyses.

The subsamples for metals analyses were digested with ultra-high-purity nitric acid in a closed Teflon^{TM} container in a microwave oven (Barber et al., 2003). Following dissolution, the samples were analyzed in triplicate for metals present at high concentrations, including calcium (Ca), iron (Fe), magnesium (Mg), potassium (K), and sodium (Na) by inductively coupled plasma-atomic emission spectrophotometry ICP-AES.

Trace metals present at low concentrations were determined by a multi-element inductively coupled plasma-mass spectrometric method (Garbarino and Taylor, 1995; Taylor, 2001) with a Perkin Elmer model Elan 6000 mass spectrometer. Typical detection limits for metals analyzed in lichen are listed in Table 3B-9 in Appendix 3B.

3.4.4.4 Analytical Methods for Total Nitrogen and Sulfur in Lichen

The subsamples of the dried, ground lichen samples for total N and S analyses were shipped to the University of Minnesota Research Analytical Laboratory. Nitrogen was measured by the Dumas total combustion method (Simone et al., 1994; Matejovic, 1995), with a LECO Model FP-528 nitrogen analyzer. Samples of 150 to 200 mg were combusted in an O_2-rich atmosphere at 859^{o}C. A 3-mL aliquot of the cooled combustion material was integrated into a He carrier stream and passed through a hot copper column to remove O_2 and convert NO_x to N_2. N_2 was measured with a thermal conductivity cell, which displayed the result as % N. The batch size was 30 samples.

For sulfur analysis, a 0.100-0.150-g sample was weighed into a ceramic boat, covered with tungsten oxide Com-Cat Accelerator and dry combusted in an O_2-rich atmosphere at 1,350^{o}C. Total % S was determined by infrared absorption of evolved sulfur dioxide on a LECO Model No. S144-DR Sulfur Determinator. The batch size was 45 samples.

Total percent dry weight nitrogen and sulfur concentrations in all samples were above method detection limits, which was 0.01% for both elements. See Appendix 3B for information on the quality control checks used and analysis of sources of variability.

3.4.4.5 Analytical Methods for Mercury in Lichen

The subsamples of the dried, ground lichen samples for mercury analyses were shipped to the WRS Analytical Laboratory. Total mercury was measured with a LECO® AMA254 Mercury Analyzer in accordance with EPA method 7473 (USEPA, 1998).

3.4.5 Lake Water

3.4.5.1 Lake Water Sample Collection

Lake water samples were collected from each catchment during the ice-free summer season to characterize the condition of the WACAP lakes by assessing the chemical and physical characteristics of water quality, including trophic state, chemical contamination, and acidification status. Analytes included pH, alkalinity, specific conductance, dissolved organic carbon, dissolved inorganic carbon, chlorophyll-*a*, total nitrogen, total phosphorus, and major cations and anions. Samples were collected at a depth of 1 m, from the deepest area of the lake, with a 2-L Kemmerer sampler, and stored in a 4-L cubitainer. Syringe samples were collected from a port in the Kemmerer for closed-system analyses of pH and dissolved inorganic carbon.

Twenty-five to 50 liters of lake water were sampled, filtered, and extracted for SOCs in situ with an Infiltrex 100 submersible pump (Axys, B.C., Canada) (Usenko et al., 2005). The Infiltrex 100 contained a 1-μm glass fiber filter (GFF) (14.2 cm diameter) to remove SOCs sorbed to particulate matter followed by a modified Speedisk to extract SOCs dissolved in the aqueous phase. Field blanks consisting of a GFF and modified Speedisk were taken during sample collection and placed in the Infiltrex 100, but not submerged in or exposed to lake water (Usenko et al., 2005). The blank GFF and modified Speedisk were removed from the Infiltrex 100 and treated identically to the GFF and modified Speedisk used for sampling. After the in situ extraction, the GFF was removed from the Infiltrex 100 and stored in a 40-mL clean glass vial. The modified Speedisk was also removed from the Infiltrex 100 and resealed with a Teflon^{TM} cap and a polypropylene syringe needle cap and stored in a clean polypropylene jar. The GFF and modified Speedisk were placed on dry ice and stored in coolers in the field and during overnight transport to the Simonich laboratory. Once in the laboratory, the GFF and modified Speedisk were stored at -12 °C.

3.4.5.2 Analytical Methods for SOCs in Lake Water

For lake water SOC analysis, analytes were eluted from the modified Speedisk with ethyl acetate (EA), dichloromethane (DCM), and DCM:EA, and the GFF was extracted with a pressurized liquid extraction (Usenko et al., 2005). A modified Speedisk and GFF were spiked directly before elution/extraction with 15 μL of 10 ng/μL isotope labeled surrogate-EA solution (Usenko et al., 2005). Eluants from both the Speedisk and the GFF were dried separately with sodium sulfate. Extracts were concentrated and then purified on a 20-g silica solid phase extraction cartridge. The lake water extracts were analyzed for the SOCs listed in Table 3-3 by GC/MS, by means of both EI ionization and electron capture negative ionization (ECNI) (Usenko et al., 2005). The analytical method was validated for efficiency with triplicate spike and recovery experiments over modified Speedisks with 50-L samples of reverse osmosis water (Usenko et al., 2005). Method recoveries for specific SOCs are provided in Table 3B-11 in Appendix 3B.

3.4.5.3 Analytical Methods for Inorganic Compounds in Lake Water

Water samples were collected and analyzed following the water chemistry protocols from the Environmental Monitoring and Assessment Program’s Surface Water (EMAP-SW) group (Chaloud and Peck, 1994). A portion of the sample from the cubitainer was filtered with a hand pump through a glass fiber filter for chlorophyll analyses. The cubitainer, syringes, and chlorophyll filters were stored on ice in a cooler, and shipped via overnight FedEx as soon as possible after collection to the WRS Analytical Laboratory. These water samples were collected on the last day at each lake site to minimize the holding times.

3.4.6 Sediment

3.4.6.1 Sediment Sampling

Lake sediment cores were collected to provide information about the accumulation and sources of contaminants in the WACAP catchments during the last ~150 years. Cores were collected from the profundal areas of each lake with a UWITEC gravity corer fitted with a Plexiglas tube with an 86-mm internal diameter. Cores were sectioned in the field the same day samples were collected, and were stored in 250-mL, solvent-rinsed glass jars. The core was extruded and sliced in 0.5-cm intervals (12-18 g ww) from 0 to 10 cm, then 1.0-cm intervals (30-40 g ww) from 10 cm to the bottom of the core. Sediment samples were shipped overnight in 50-L coolers with ice-packs to the WRS Analytical Laboratory where they were stored at 4ºC until physical and elemental analyses were conducted.

Each wet sediment interval was split in the laboratory, with approximately 12 cm^3 removed for inorganic analyses [dating, percent moisture, spheroidal carbonaceous particles (SCPs), mercury, carbon, and metals) and the remaining wet sediment, approximately 17 cm^3, was stored at –20°C for analysis of SOCs by the Simonich Laboratory. Each core was processed beginning with the bottom intervals and proceeding to the top intervals to ensure that the cleanest samples were processed first. Each interval was homogenized to a uniform color and texture with a Teflon^{TM} spatula before the inorganic subsample was removed.

The inorganic subsample was freeze-dried and percent moisture determined. A 0.15-g subsample was removed for SCP analyses, and the remaining dried sediment was lightly ground with a mortar and pestle. Dried, ground sediment from 10 to 12 intervals from each core was used to determine the dating chronology to ensure that the stratigraphy of the core was intact, i.e., the layers of sediment were deposited in chronological order and had not been disturbed. The main dating technique used was the ^{210}Pb method, but the artificial radionuclides ^{137}Cs and ^{241}Am were also used, with the peak in fallout of these radionuclides reached in 1963 (Appleby et al., 1986; Appleby et al., 1991). The radionuclide analysis was performed at the Environmental Radioactivity Research Centre at the University of Liverpool by direct gamma assay, with an Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detector. Two models were used to determine the sediment core chronologies: the CRS (constant rate of ^{210}Pb supply) and the CIC (constant initial concentration) (Appleby, 2001).

Two cores were collected and sectioned from each lake, and if the dating results from the primary core indicated the stratigraphy was not intact, the second core was dated. The core with the most acceptable chronology was used for the other analyses, including SOCs, mercury, metals, SCPs, total carbon (TC), total organic carbon (TOC), and, by difference, total inorganic carbon (TIC). At five sites, the amount of sediment material in the primary core was limited, so SCP analyses were conducted on the secondary core. Metal analyses were conducted on both cores from five sites (LP19, Golden, Hoh, PJ, and Snyder) to provide additional information about the secondary cores.

3.4.6.2 Lake Sediment Focusing Factors

Correcting for the redistribution of particulate matter in lake sediment is important because lipophilic SOCs and metals sorb to particulate matter. The erosion and accumulation of particulate matter can also result in the erosion and accumulation of SOCs and metals from one area of the lake to another. For examination of the spatial and temporal trends of SOCs and metals in multiple cores, all SOC and metal sediment concentrations (ng/g dry wt) were multiplied by the mass sedimentation rate ($g/cm^2/y$) and normalized to the unitless focusing factors to arrive at the focus-corrected flux ($ng/m^2/yr$ or $\mu g/m^2/yr$).

Focusing factors (FF) were calculated for each sediment core in order to correct for differences in sediment focusing among the WACAP lake sites. Sediment focusing describes the redistribution of particulate matter throughout the lake (Likens and Davis, 1975).

$$\mathrm{FF} = \frac{{}^{210}\mathrm{Pb\ Inventory}}{{}^{210}\mathrm{Pb\ Fallout}} \qquad [3\text{-}2]$$

In equation [3-2], ^{210}Pb inventory is derived by plotting unsupported ^{210}Pb against the mass sedimentation accumulation rate (Zhu and Hites, 2005). The ^{210}Pb atmospheric fallout was modeled from ice cores, soil samples, and atmospheric collectors near sampling sites. ^{210}Pb fallout values from Alaska and the Yukon were used for DENA, GAAR, and NOAT; values from Seattle, Washington, were used for OLYM and MORA; values from mid-California were used for SEKI; and values for Colorado were used for ROMO and GLAC (Granstein and Turekian, 1986; Carpenter et al., 1984; Monaghan, 1989; Monaghan and Holdworth, 1990; Nevissi, 1985). ^{210}Pb atmospheric fallout can vary over short time periods; however, over the time frame of these sediment cores (<150 years), the ^{210}Pb atmospheric fallout is considered to be fairly constant (Appleby et al., 1986; Appleby, 2001). In areas of a lake where the particulate matter is accumulating, the FF is greater than one. In areas of a lake where the particulate matter is eroding, the FF is less than one. The FFs of the WACAP lake sediment cores ranged from 0.78 to 4.55.

3.4.6.3 Measurement of Spheroidal Carbonaceous Particles (SCPs) in Lake Sediments

Fossil fuels are burned at high temperatures to produce heat and power for electricity generation and other industries. At temperatures of up to 1,750°C (Commission on Energy and the Environment, 1981) and at a rate of heating approaching 10^4°C/s (Lightman and Street, 1983), the droplets, or pulverized grains of fuel, are efficiently burned, even though they remain in the furnace only for a matter of seconds. The products of this combustion are porous spheroids of mainly elemental carbon (Goldberg, 1985) and fused inorganic spheres formed from the mineral component of the original fuel (Raask, 1984). These SCPs (Figure 3-4) and inorganic ash spheres (IASs) are collectively known as fly-ash, the term used to describe the particulate matter within emitted flue-gases.

Figure 3-4. Scanning Electron Micrograph of a Spheroidal Carbonaceous Particle (SCP). Photo: Neil Rose.

SCPs are not produced from wood, biomass, or charcoal combustion, and hence have no natural sources. Therefore, they are unambiguous indicators of deposition from industrial combustion of fossil fuels. Their use as markers in sediments and other depositional sinks is enhanced by their easily identifiable morphology and, because of their elemental carbon composition, by their relatively simple extraction from the sediment matrix. In addition, the elemental composition of SCPs can give clues as to their source fuel type (Rose et al., 1996).

Composed of elemental carbon, and thus physically fragile, SCPs are resistant to chemical attack. Strong reagents were therefore used to remove unwanted fractions of sediment without doing physical damage to the SCPs. The method used for the WACAP sediment samples has been previously described (Rose, 1994). Briefly, the dried, unground sediment subsample was digested in polytetrafluoroethylene (PTFE) tubes in a water bath. Unwanted sediment fractions were removed by sequential chemical attack, with nitric acid (HNO_3), hydrofluoric acid (HF), and hydrochloric acid (HCl) used to remove organic, siliceous, and carbonate material, respectively. A starting sediment mass of 0.15 g was reduced to less than 0.001 g by this technique, thus removing more than 99.3% of the sediment (Rose, 1994).

The sediment digestion procedure results in a suspension of mainly carbonaceous material in water. A known fraction of this suspension is evaporated onto a microscope coverslip and mounted onto a slide using Naphrax (a low refractive index mountant). SCPs on the entire coverslip are then counted at 400× magnification under a light microscope. SCPs are positively identified with reference to the criteria of morphology, color, and porosity. The number of SCPs counted is then converted to a concentration in units of “number of SCPs per gram dry mass of sediment,” or gDM^{-1}. Reference sediment material of known SCP concentration and sediment blanks were analyzed in all sediment sample digestions for quality assurance/quality control.

3.4.6.4 Analytical Methods for SOCs in Lake Sediments

Sediment samples for SOC analysis were allowed to thaw in sealed glass jars, ground with sodium sulfate, and extracted with a pressurized liquid extraction. Sediment samples were spiked directly before extraction with 15 µL of 10-ng/µL isotope labeled surrogate-EA solution. Interferences were removed from the sediment extract with a 20-g silica solid phase extraction cartridge and GPC. The sediment extracts were analyzed for the SOCs listed in Table 3-3 by GC/MS, with both EI ionization and ECNI. EDLs, recoveries, and percent difference of the sediment SRM for specific SOCs are listed in Table 3B-13 in Appendix 3B.

3.4.6.5 Analytical Methods for Mercury in Lake Sediments

Total mercury was measured on freeze-dried, ground sediment samples at the WRS Analytical Laboratory with a LECO® AMA254 Mercury Analyzer in accordance with EPA method 7473 (USEPA, 1998).

3.4.6.6 Analytical Methods for Carbon in Lake Sediments

Total carbon was measured on untreated, freeze-dried, ground sediment samples with a Carlo Erba 1108A CN analyzer. TOC was determined by measuring TC on samples after acid treatment to remove carbonates (i.e., inorganic carbon). The TC remaining after treatment is attributed to organic carbon. Total inorganic carbon (TIC) was determined by the difference between TC and TOC. The mean precision of analytical duplicate samples was 2.2 percent relative standard deviation, and the mean percent difference from certified reference materials was 2.6%.

3.4.6.7 Analytical Methods for Metals in Lake Sediments

Subsamples of freeze-dried sediment intervals were dissolved by ultra-high-purity HNO_3, HCl, (Kuehner et al., 1972), and HF acid digestion in a closed Teflon™ container in a microwave oven (Roth et al., 1997; Hart et al., 2005). Excess fluoride and chloride were removed by successive evaporation to dryness followed by reconstitution with 1% (volume) ultra-high-purity HNO_3 acid. Following dissolution, the samples were analyzed in triplicate for metals present at higher concentrations, including calcium (Ca,) iron (Fe), magnesium (Mg), potassium (K), and sodium (Na) by ICP-AES. Trace metals present at lower concentrations (listed in Section 3.4.2.4) were determined by multi-element inductively coupled plasma-mass spectrometric method (Garbarino and Taylor, 1995; Taylor, 2001) with a Perkin Elmer model Elan 6000 mass spectrometer. Typical detection limits for the metals analyzed are listed in Table 3B-14 in Appendix 3B.

3.4.7 Fish

3.4.7.1 Fish Sampling

Fish were used as the vertebrate indicators of SOC, Hg, and metal exposure because they are continually immersed in the lake and provide an indication of impacts to the food web. Contaminant and fish health analyses were performed on the same fish, allowing a direct correlation of SOC, Hg, and metal body burdens to fish health parameters. Where possible, lakes were chosen based on the known presence of salmonid fishes. We sampled 15 fish for SOCs, Hg, and physiological analyses and 5-10 different fish for trace metals analysis. The objective was to provide a wide age distribution and an even sex ratio. Fish were captured primarily by single-line angling, but gillnets and set-lines were also used in DENA. Some fish remained in gillnets for up to 4 hours because of the large distance between the nets. The species captured are listed in Table 3-11.

In terms of the trophic levels of the fish, we presume that lake trout (*Salvelinus namaycush*) eat other fish when possible. However, at the time of sampling, gastropods dominated the stomach contents. It is also presumed that the burbot (*Lota lota*) are piscivorous. The remaining fish we assumed to be insect- or planktivorous.

Table 3-11. Species of Fish Captured.

Park	Lake	Common Name	Scientific Name
NOAT	Burial	Lake trout	*Salvelinus namaycush*
GAAR	Matcharak	Lake trout	*Salvelinus namaycush*
DENA	Wonder	Lake trout	*Salvelinus namaycuch*
DENA	McLeod	Round Whitefish, Burbot	*Prosopium cylindraceum, Lota lota*
GLAC	Snyder	Westslope cutthroat	*Oncorhynchus clarki lewisi*
GLAC	Oldman	Yellowstone cutthroat	*Oncorhynchus clarki bouvieri*
OLYM	PJ	Brook trout	*Salvelinus fontinalis*
OLYM	Hoh	Brook trout	*Salvelinus fontinalis*
MORA	Golden	Brook trout	*Salvelinus fontinalis*
MORA	LP19	Brook trout	*Salvelinus fontinalis*
ROMO	Mills	Rainbow trout	*Oncorhynchus mykiss*
ROMO	Lone Pine	Brook trout	*Salvelinus fontinalis*
SEKI	Pear	Brook trout	*Salvelinus fontinalis*
SEKI	Emerald	Brook trout	*Salvelinus fontinalis*

In general, each lake was sampled once during the months of July, August, and September, from 2003 to 2005. After the fish had been captured, they were placed in mesh bags in the lake near the shoreline and held for up to 1 hour prior to sampling. Fish were killed with a blow to the head and placed on acetone rinsed and combusted aluminum foil for the necropsy. The necropsy took 15 minutes and included an assessment of any gross internal or external abnormalities. Sex was determined by visual inspection of the gonads and confirmed by histology. Fork length and mass were recorded. Blood was collected by heparinized syringe and transferred to tubes placed in ice-cold water. Plasma was separated within 15 minutes with a hand-driven centrifuge mounted on a custom machined tri-pod anchored to the ground by guy-lines. Plasma was stored immediately on dry ice and then at –80°C at the laboratory. Small pieces of posterior kidney, liver, spleen, gill, and gonad samples were removed and fixed in 10% buffered formalin for histological examination. Sagittal otoliths were removed and stored in 70% ethyl-alcohol for age determination. Stomach and gut contents were removed and preserved with 70% ethyl-alcohol.

After the necropsy, the fish were wrapped in the same foil on which the organ sampling occurred or were transferred to metalized bags, then double bagged in Ziplocs and frozen on dry ice. The samples were received frozen solid, with approximately 5 kg of dry ice remaining, and transferred to –20°C. Because of a power outage, some of the fish captured in 2005 thawed, but remained cool, and were refrozen within 12 hours. For fish collected only for elemental analysis, the fish sex was determined visually and otoliths were removed in order to age the fish.

3.4.7.2 Fish Health Analytical Methods

In the field, length was used as a surrogate for age; however, fish from these environments are often stunted. Therefore, very old fish could be as large as some younger fish. Overall we could not definitively assemble the age distribution until the fish were aged in the laboratory. The fish were aged in the fish pathology laboratory at Oregon State University, Department of Microbiology. We counted a dark and a light ring as 1 year on hand-ground otoliths using transmitted light microscopy. Otoliths were read from two to five times. If agreement in years was reached after two readings, then the age was recorded. However, several required three to five readings before agreement was reached. Brook, rainbow, and cutthroat trout were aged following Hall (1991) and the lake trout were aged following Simoneau et al. (2000).

Posterior kidney, liver, spleen, gill, and gonad were processed for routine histological examination according to standard procedures, sectioned, and stained with hematoxylin and eosin. Using compound light microscopy, we examined all sections for histopathological changes (e.g., lesions, intersex) and quantification of macrophage aggregates (Schwindt et al., 2006). Blood plasma vitellogenin was determined following Schwindt et al. (2007), except that the male fish plasma was diluted 100×, and for all analytes, the secondary antibody concentration was 1:5,000. The detection limit (DL) was 3.9 ng/mL and was determined by visual inspection of the linear portion of the standard curve. The intra- and inter-assay RSDs were 6% and 16%, respectively, and recovery was 95-100%.

For the sex steroids, steroids were extracted from the plasma following the method of Fitzpatrick et al. (1986). Plasma testosterone, 11-ketotestosterone, and 17ß-estradiol concentrations were measured by radioimmunoassay (RIA), as described by Sower and Schreck (1982) and modified by Feist et al. (1990). All steroid assay results were corrected for recovery. The DL ranged from 1.25 to 3.12 pg/tube, depending on the assay. Intra-assay RSD was < 7%, inter-assay RSD was 11-12%, and extraction efficiency ranged from 64% to 97%, depending on the assay. For all blood analytes, concentrations were determined in the fish physiology laboratory at Oregon State University, Department of Fisheries and Wildlife. Samples were assayed in duplicate, and concentrations were validated by determining that serial dilutions were parallel to standard curves. Values that were below the DL were reported and analyzed as one-half the DL.

3.4.7.3 Analytical Methods for SOCs in Whole Fish

Whole fish carcasses were homogenized while frozen in a stainless steel food processor with liquid nitrogen at the WRS Analytical Laboratory. A subsample of the fish homogenate was collected for Hg analyses, and the remaining homogenate was used for SOC analyses. Twenty gram subsamples were spiked with isotopically labeled recovery surrogates and the analytes were extracted with organic solvent and pressurized liquid extraction. Lipid in each fish was measured by evaporating the solvent from a portion of the extract and weighing the remaining lipid. The extracts were cleaned with silica solid phase extraction, gel-permeation chromatography (GPC), and concentrated to 0.3 mL. Fish extracts were spiked with isotopically labeled internal standards and the SOCs listed in Table 3-3 were quantified by GC/MS analysis.

3.4.7.4 Analytical Methods for Mercury in Fish Tissue

Total mercury was analyzed on a subsample of the whole body homogenate at the WRS Analytical Laboratory with a LECO® AMA254 Mercury Analyzer in accordance with EPA method 7473 (USEPA, 1998). The fish tissue homogenate samples were stored at –6° C, and were allowed to thaw before analysis. The freezing process causes homogenate to separate into phases, so the homogenate was mixed before removing subsamples to be placed in the instrument sampling containers.

3.4.7.5 Analytical Methods for Metals in Fish Tissue

Five to ten fish were collected for trace metal analysis, and were shipped frozen, on dry ice, to the USGS-NRP Boulder laboratory for processing at the end of each year's sampling. Fish tissue was sampled from two parts of each fish specimen, the fillet tissue and the liver tissue. The skin and bony material were removed from the fillet tissue, and the fillet tissue was finely chopped with a ceramic knife, subsampled, and freeze-dried to remove residual moisture. After drying, the fillet samples were pulverized to a fine powder. Liver samples were carefully dissected from the fish entrails, manually homogenized, and freeze-dried. Subsamples of both the fillet and the liver samples were digested with ultra-high-purity nitric acid in a closed Teflon™ container in a microwave oven (Barber et. al., 2003). Following dissolution, the samples were analyzed in triplicate for metals present at higher concentrations, including Ca, Fe, Mg, K, and Na, using the ICP-AES methods described in Section 3.4.2.2. Trace metals present at lower concentrations (listed in Section 3.4.2.4) were determined by an ICP-MS method (Garbarino and Taylor, 1995; Taylor, 2001).

Typical detection limits for the metals analyzed in fillet samples are listed in Table 3B-16 in Appendix 3B, with detection limits for metals in liver samples in Table 3B-17 in Appendix 3B. Because the sample size for livers was generally small, detection limits were often dramatically poorer than those observed for fillet samples. Although detection limits listed in Appendix 3B are based upon 0.1-g sample size, as a result of variability in the size of the fish specimens, liver sample sizes actually varied between 0.04 and 0.11 g.

3.4.8 Moose

3.4.8.1 Moose Tissue Sampling


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Samples from moose were collected in order to understand the potential for the bioaccumulation of contaminants through the terrestrial food web. Samples from three moose donated by hunters in DENA were analyzed for mercury, metals, and SOCs. Sampling kits were provided to hunters in the park, with instructions to collect a three-pound sample of meat from the shoulder or rump area, a three-pound sample of the liver, and one incisor tooth to determine the animal's age. Meat and liver samples were provided from two moose collected in 2004, and from one moose in 2005. The exterior layers of each sample were removed, and a portion was sent to the Taylor laboratory for metals analyses. The remaining portions of both the meat and liver (approximately half of the original sample) were ground with liquid nitrogen in a stainless steel food processor for mercury and SOC analyses.

3.4.8.2 Analytical Methods for SOCs in Moose Tissue

A portion of the moose homogenate was ground with sodium sulfate and spiked with isotopically labeled recovery surrogates before extraction with dichloromethane (DCM) and pressurized liquid extraction. Sodium sulfate was added to the extract and it was cooled overnight at –18 °C. The extract was brought to 500-mL volume with DCM and a 10-mL fraction was taken for gravimetric lipid determination. The remaining extract was reduced in volume and purified with silica gel columns and gel permeation chromatography. The extract was measured for the SOCs listed in Table 3-3 by GC/MS analysis.

3.4.8.3 Analytical Methods for Mercury in Moose Tissue

Total mercury was measured on the ground samples with a LECO® AMA254 Mercury Analyzer at the WRS Analytical Laboratory in accordance with EPA method 7473 (USEPA, 1998).

3.4.8.4 Analytical Methods for Metals in Moose Tissue

Moose tissue from the meat and liver samples was finely chopped with a ceramic knife, subsampled, and freeze-dried to remove residual moisture. After drying, samples were pulverized to a fine powder. Subsamples were digested with ultra-high-purity nitric acid in a closed Teflon™ container in a microwave oven similar to that used for fish tissue (Barber et al., 2003). Following dissolution, the samples were analyzed in triplicate for metals present at higher concentrations, including Ca, Fe, Mg, K, and Na, by methods described in Section 3.4.2.2. Trace metals present at lower concentrations (listed in Section 3.4.2.4) were determined by an ICP-MS technique previously described (Section 3.4.2.4). Typical detection limits for the metals analyzed are listed in Table 3B-18 in Appendix 3B.

3.4.9 Other Data Sources

The following additional data were assembled for use with back trajectory calculations, fish physiological marker data, and other environmental and physical variables measured at the sample collection sites (e.g., geographic coordinates, elevation, and habitat characteristics) to interpret and predict SOC, nutrient and metal accumulation in the WACAP media.

3.4.9.1 Climate Data

PRISM (Parameter-Elevation Regressions on Independent Slopes Model), developed at Oregon State University (http://www.ocs.orst.edu), uses point measurements of climate data and a digital elevation model to generate estimates of annual and monthly climatic variables. Climate estimates are converted to a horizontal grid and are compatible for use with Geographic Information Systems (GIS).

3.4.9.1.1 Individual Years

Annual and monthly means for total precipitation (cm), maximum daily temperature (°C), and minimum daily temperature (°C) were obtained for the individual years 2002 through 2005 from the Climate Data Source (http://www.climatesource.com) for all WACAP target lake, snow, and vegetation sampling sites, excluding Alaska (no data available). Grid cell size was 2 km.

3.4.9.1.2 Long-Term Averages

Thirty-year (1971-2000) annual and monthly means for total precipitation (cm), daily maximum temperature (°C), and daily minimum temperature (°C) were obtained for all WACAP target lake, snow, and vegetation sampling sites. Grid cell size was 800 m for the lower 48 states and 2 km for Alaska. Twenty-year (1971-1990) means for annual, January, and August daily temperature (°C), relative humidity (%), dew point temperature (°C), and number of days with measurable precipitation were obtained for target lake and vegetation sampling sites. Resolution was 2 km for the conterminous 48 states; only mean temperatures and mean precipitation were available for Alaska; grid cell size was 4 km. We calculated values by overlaying site coordinates (in decimal degrees, accurate to 4 decimal places) on climate grids obtained from http://www.ocs.orst.edu/prism via GIS.

3.4.9.2 Radial Population Estimates

We calculated population estimates for the core and secondary parks using radial distances of 25, 75, 150, and 300 km. To compare human population with SOC concentrations, we needed both a consistent method and a consistent population data set.

LandScan, created by the Oak Ridge National Laboratory's (ORNL) Global Population Project, is a worldwide human population database on a 30- by 30-second (30″ × 30″, or approximately 0.84 km × 0.84 km) latitude/longitude grid. Census counts form the basis of the LandScan population estimates, with the population being further distributed based on nighttime lights, proximity to roads, land cover and slope, and other data sets. The LandScan database compiled in 2002 was used for this project; see http://www.ornl.gov/landscan; Hafner et al. (2005).

The LandScan data for North America were downloaded in the form of a raster dataset, and ArcGIS 9.0 (ESRI, Redlands, California) was used to calculate populations for each site. The raster dataset was projected via the North America Albers Equal Area projection, with an output grid size of 841.002833 meters. Using the same projection, separate point feature classes were created for each of the WACAP sites. Within each feature class was a field with an assigned value of 1. Each point was buffered with radii of 25, 75, 150, and 300 km. The respective radial buffers were converted to raster datasets with an output grid size matching the size of the population grid. With reference to the times function in raster math, the radial raster datasets were multiplied by the population grid, resulting in radial raster data containing the appropriate population values. To get the total radial population, data were exported and summed.

3.4.9.3 Radial Agriculture Estimates

Agricultural estimates for the core and secondary parks were calculated at a radial distance of 150 km using a dataset compiled from the 2002 United States Census of Agriculture and the 2001 Canadian Census of Agriculture:

http://www.nass.usda.gov/Census_of_Agriculture/index.asp

http://www.statcan.ca/english/agcensus2001/index.htm

For the United States, the total area of cropland per county was used, and for Canada, the amount of land in crops (excluding Christmas trees) per census division was used. All units of area were converted to square meters, and the census data were added to the attribute table for all US counties and the provinces of Alberta and British Columbia.

Operating under the assumption that no crops are grown on national forest and national park lands, park areas were erased from the county/province map. With the parks removed, county areas were recalculated. Dividing cropland area by the recalculated county area gave the percent of agriculture in each county, or agricultural intensity, minus parks (Hageman et al., 2006).

The agricultural intensity map was projected with reference to the North America Albers Equal Area projection. As was done for the population calculation, a separate point feature class was created for each of the WACAP sites. Each point was buffered at 150 km. The clip function was used to remove the buffer area from the agricultural intensity map. In doing so, some counties were cut in half. The area of each county within the clipped buffer area was recalculated and multiplied by the agricultural intensity, resulting in cropland area for each county or part of a county within the buffer. The total cropland within the buffer was summed, and divided by the total area of the county.

3.4.9.4 Ambient Ammonium Nitrate and Ammonium Sulfate in Fine Particulates

The Interagency Monitoring of Protected Visual Environments (IMPROVE) program (http://vista.cira.colostate.edu/improve) is a cooperative effort to aid the protection of visibility in 156 national parks and wilderness areas. An IMPROVE site is operating at each WACAP park in the conterminous 48 states and at DENA and STLE in Alaska. Each IMPROVE site deploys an aerosol sampler to measure speciated fine aerosols for a 24-hour period every third day. Mean annual ammonium nitrate ($\mu g/m^3$) and ammonium sulfate ($\mu g/m^3$) in ambient particulates < 2.5 µm diameter for the years 1998-2004 were downloaded from the website:

http://vista.cira.colostate.edu/views/Web/IMPROVE/SummaryData.aspx

Annual data from 1998-2004 that met QA/QC standards (Guidance for Tracking Progress under the Regional Haze Rule (http://www.battelle.org/projects/epa-environment/default.htm) were averaged to produce a single value per park. There were at least 5 years of data for all monitors except SEKI (1999-2001 and 2004 only), OLYM (2002-2004 only), NOCA (2001-2002 only), and STLE (no data yet). Sulfate and nitrate IMPROVE data were used as a measure of nitrogen and sulfur availability in the parks.

3.4.9.5 Ammonia Emissions Density

Projected 2001 county ammonia emissions density data (tons/square mile), based on the USEPA 1999 National Emissions Inventory database (USEPA, 2007b), was obtained for the county in which each site was located, and all adjacent counties (http://www.epa.gov/air/data/geosel.html). Most emissions estimates are supplied to USEPA by state environmental agencies. Some estimates are for individual sources, such as factories, and some estimates are county totals for classes of sources, such as vehicles. Emissions estimates for individual sources are based on their normal operating schedules, and take into account the effects of installed pollution control equipment and of regulatory restrictions on operating conditions. Because most ammonia emissions are related to agriculture, ammonia emissions data were tested in correlations with other agricultural indicators, such as agricultural intensity, as a measure of local agricultural activity.

3.5 Data Handling and Statistical Analysis Methods Used

3.5.1 Data Handling of Contaminant Concentrations Below the Detection Limit

Throughout this report, the following rules were applied to contaminant concentrations below the method or estimated detection limits used in data analyses:

1. If more than 70% of the measured concentrations were above the detection limit, a value of one-half of the detection limit was substituted for below detection limit values (Antweiler and Taylor, written communications).
2. If 50-70% of measured concentrations were above the detection limit, a value of one-half of the detection limit was substituted for below detection limit values, and the resulting averages were noted with superscript “1”.
3. If less then 50% of the measured concentrations were above the detection limit, a value of one-half of the detection limit was substituted for below detection limit values, and the resulting averages were noted with superscript “2”.
4. In calculating a compound class sum concentration (e.g., Σendosulfans), if a compound concentration in the sum was below the detection limit, a value of one-half of the detection limit was substituted. If more than 50% of the total value of the compound class sum was made up of values below the detection limit, the entire sum was flagged as below the detection limit for consideration in steps 1 through 3.

3.5.2 Evidence and Magnitude of the Cold Fractionation Effect

One of the objectives of WACAP was to attain a better understanding of latitudinal and elevational influences on SOC concentrations in WACAP ecosystems, i.e., to look for evidence of increased SOC concentrations at the colder temperatures associated with increased latitudes and elevations. Specifically, we wanted to (1) identify which SOCs showed the cold fractionation effect and (2) quantify the magnitude of the concentration enhancement by SOC and by park in vegetation, within the vegetated zone of each park. Because accurate estimates of temperature at WACAP sites were not available, we used elevation as a within-park surrogate for temperature. Vegetation was chosen over other WACAP media for this analysis because it is a biotic media in direct contact with the atmosphere. In addition, SOC concentration data were available from 3-5 different site elevations within most of the core and secondary parks.

Exploration of the vegetation and snow SOC concentration data indicated that park proximity to regional sources influences SOC concentrations much more than latitude. For example, current-use pesticides were not detected or were much lower in concentration in the Alaska parks than in the other parks, even though the Alaska parks are at higher latitudes and experience colder temperatures year-round. The vegetation species sampled and the amount of precipitation also contributed to the SOC concentration variability observed between and within parks. Because of these complexities, we did not attempt to demonstrate a latitudinal effect with vegetation SOC concentrations.

Early in our data interpretation, we observed that conifer needle SOC concentrations in many of the parks increased across the lowest 2-3 elevations but then leveled off or decreased in the top 2-3 highest elevations. Re-examination of field notes and discussions with field observers revealed that the conifer needles at some sites (sampled according to protocol with handclippers by field personnel standing on the ground) were probably buried under snow for variable periods of time during the winter months, especially at the higher elevation sites. The duration of snow burial was unknown and is likely to have resulted in decreased conifer needle exposure to SOCs in the atmosphere and, ultimately, decreased conifer needle SOC concentrations at these sites. In contrast, epiphytic lichens do not survive snow burial and, therefore, were collected only above the lichen snow-line visible on tree trunks or from litterfall. This factor made epiphytic lichens a more suitable media for analysis of potential elevation trends.

In summary, elevation analyses were restricted to lichen SOC data that met the following criteria:

1. The same lichen species was collected from at least three different elevations within the park.
2. Samples of the same species came from the same geographic quadrant in the park, i.e., they were exposed to similar pollution sources and weather patterns.
3. Only SOCs for which data were above detection limits in at least 50% of samples were tested.
4. Only epiphytic lichens, exposed to the air all year round, were used. Two exceptions to this criterion were (1) KATM, where adequate data from both tundra and epiphytic lichens were available, and could be compared, and (2) DENA, for which no other vegetation type was available.

Samples from arctic parks (NOAT, GAAR) were not included in analyses of elevational trends because most of the SOCs were below detection limits, the elevation gradient was small (450 m from lowest to highest site), and arctic parks experience frequent temperature inversions, which contradicts the assumption that higher elevations would be associated with colder temperatures.

Multiple regression analysis was used to identify statistically significant trends in lichen SOC concentration with elevation. The statistical software package used was S-Plus 2000 (Mathsoft. 1999. Data Analysis Products Division, Seattle Washington). Models for each SOC were first constructed using *Park* and *Elevation* as explanatory variables. The regression model was:

$$Y = \beta_0 + \beta_{1i}\,\text{Park} + \beta_2\,\text{Elevation} \qquad [3\text{-}3]$$

Where:

Y = the mean of the response variable (SOC concentration)
β_0 = the coefficient for the intercept
β_{1i} = the coefficient for the *i*th Park
β_2 = the coefficient for site Elevation

This model assumes equal slopes for all parks and tests for an overall trend of SOC concentration over elevation. This analysis answers the question: “After accounting for differences between parks, is there a trend in SOC concentration over elevation?" Differences between parks must be accounted for because SOC concentrations differ between parks because of proximity to sources and varying application rates of SOCs near the parks. This analysis takes these differences into account by assuming they are additive (i.e., the average SOC concentration difference between parks is the same at all elevations) and estimates an average relationship between compound concentration and elevation. Summary results of the regression analyses are reported in Chapter 4 (Table 4-3); model details are reported in Appendix 4A.1.

Within each park, a simple regression analysis was used to investigate the trend in SOC concentration over elevation. The regression model was:

$$Y = \beta_0 + \beta_1 \text{ Elevation} \qquad [3\text{-}4]$$

Where:

Y = the mean of the response variable (SOC concentration)
β_0 = the coefficient for the intercept
β_1 = the coefficient for site Elevation (the slope of the compound concentration trend in the Park)

This model estimates the trend of SOC concentration over elevation within each park. This analysis answers the question "What are the trends of SOC concentration over elevation within each park?" The results of the regression interaction analyses are reported in Chapter 4 (Table 4-4). Only those parks that met the data criteria for analysis were analyzed.

Residual plots, plots of the residuals of the regression versus the fitted values, were used to assess the need for transformations of the response variable (SOC concentration) to stabilize the variance (Ramsey and Schafer, 1997). Two transformations were used, the natural logarithm and the square root, depending on the patterns of the residual plots. The results of log-transformed data are reported as the percent change in SOC concentration over 500 m elevation. The results of square root-transformed data were back-transformed and are reported as the increment of SOC concentration change over 500 m elevation.

Outliers were identified using Cook's Distance to determine the overall influence of a data point on the regression (Neter et al., 1990). Regressions were run with and without the outliers to assess their influence on the overall statistical significance of the model and on the model coefficients. Influential data points were identified for further investigation (see Appendix 4A.11, elevation regressions); however, no outliers were removed from the final models.

3.5.3 Comparison of Park and Site Means for SOC and Element Concentrations in Vegetation and Air

The Tukey-Kramer multiple means comparison test (Ramsey and Schafer, 1997) was used to provide statistical evidence of significantly different mean concentrations of SOCs and elements in vegetation or air samples, between parks. This multiple comparison procedure controls for family-wise error rate. For example, suppose that we want to compare the mean concentration of a target SOC in each of four parks, i.e., park 1 vs. park 2, 1 vs. 3, 1 vs. 4, 2 vs. 3, 2 vs. 4, and 3 vs. 4. Such a set of comparisons is called a family. If we use a T-test to compare each pair of parks at a certain significance level (α), then the probability of Type I error (incorrect rejection of the null hypothesis of equality of means) is guaranteed equal to α for any single pair-wise comparison, but not for the whole family. The Tukey-Kramer test, based on the studentized range distribution (standardized maximum difference between the means) is adjusted for unbalanced designs (i.e., unequal number of samples from each site) and controls for family-wise error rate. The statistical software package JMP (JMP, Version 5. SAS Institute Inc., Cary, North Carolina, 1989-2002) was used to perform these analyses. Although the SOC data were not normally distributed, T-tests are robust to non-normality of data when sample sizes are similar (see Ramsey and Schafer, 1997, Chapter 3.2).

Concentrations of elements (N, S, Hg, Pb, and Cd) and some SOCs (dacthal, endosulfan 1, endosulfan sulfate, a-HCH, and HCB) exceeded EDLs in all samples. The concentrations of the remaining SOCs were below EDLs in some samples. When SOC concentrations were not above the EDLs within a park, the park was not compared to other parks. When at least one vegetation or air sample from a park was above the EDL, half of the EDL was substituted for any sample below the EDL and the park was included in comparison tests.

3.5.4 Correlations

Correlations summarize the strength of relationships between variables and provide a measure of the predictive potential of any variable for another. Correlations between contaminants in vegetation and environmental variables such as regional agricultural intensity, ambient particulate nitrogen, and population density were calculated with the statistical software package JMP (JMP, Version 5. SAS Institute Inc., Cary, North Carolina, 1989-2002). Because some of the data were half EDLs and concentrations of some compounds encompassed several orders of magnitude across parks, many of the data did not meet the normality assumptions for a parametric analysis. Therefore, a non-parametric measure of association, Spearman’s Rho, was used. Spearman’s Rho is a correlation coefficient computed on the ranks of the data values instead of on the values themselves, by the formula for Pearson’s (parametric) correlation (Sokal and Rohlf, 1981).

Concentrations of some elements (N, S, Hg, Pb, and Cd) and some SOCs (dacthal, endosulfan 1, endosulfan sulfate, a-HCH, and HCB) exceeded EDLs in all samples. The concentrations of the remaining SOCs were below EDLs in some samples. When no samples were above detection limits within a park, the park was not included in the correlation. When at least one sample from a park was above the EDL, then half of the EDL was substituted for park values below the EDL, and the park was included in comparison tests. Significance probabilities were also calculated and reported.

3.5.5 Paired T-tests

Paired T-tests were used to test for significant differences in mean SOC concentrations between lichens and conifers. Individual SOC data for up to 69 matched pairs of lichens and conifer needles collected at the same sites were used. The matched pairs platform in the statistical software package, JMP (JMP, Version 5. SAS Institute Inc., Cary, North Carolina, 1989-2002) was used to compare means between the two response columns (lichen SOC concentrations vs. conifer SOC concentration) by means of a paired Student’s T-test.

Starting from the master WACAP vegetation database, all sites without both lichen and conifer samples were deleted. If all samples within a vegetation type (i.e., lichens or conifer needles) at a site had SOC concentrations below the EDLs , then no data were used for that vegetation type at that site. Otherwise, half of the EDLs were used for all samples where SOC concentrations were less than the EDL within a site and vegetation type. Within-site field replicate SOC concentrations were averaged before comparisons were made between sites. At the nine sites where more than one species was collected within a vegetation type, the species SOC concentrations were averaged after the field replicate SOC concentrations were averaged. After these steps, 69 sites remained from which both lichens and conifer needles had been collected and SOCs measured above the EDLs. After averaging as described, there was one concentration value for conifer needles and one concentration value for lichens for each SOC, at each site. A matched pairs test was carried out to test for significant differences in concentrations between lichens and conifer needles for each SOC, across the 69 sites. The SOCs tested were: trifluralin, triallate, chlorpyrifos, methoxychlor, dacthal, endosulfans, HCB, a-HCH, g-HCH, dieldrin, DDTs, chlordanes, PCBs, and PAHs. The standard error used was a pooled estimate of variance. For any given SOC, the number of sites for each vegetation type is not always equal, because at some sites, all samples of a vegetation type had SOC concentrations less than the EDLs.

CHAPTER 4

Contaminant Distribution

4.1 Introduction

This chapter is organized by contaminant category, beginning with semi-volatile organic compounds (SOCs), and followed by mercury, trace metals, spheroidal carbonaceous particles (SCPs), and finally nutrients. Atmospheric transport is also addressed. The SOCs include current- and historic-use pesticides (CUPs and HUPs), and industrial compounds such as polychlorinated biphenyls (PCBs) and combustion tracers (polycyclic aromatic hydrocarbons; PAHs). Within each section, data are discussed by medium— snow, air, vegetation, fish, and lake sediments. Lake water concentrations were generally very low and often below detection limits (see Figure 3-1 in Chapter 3). As such, lake water data are not reported in this chapter.

The contaminants found in greatest general abundance within each category are discussed with respect to both their spatial and their temporal distributions. Spatial distributions include the horizontal differences in contaminants among parks, as well as the elevational gradients. Whenever possible, study-wide data are displayed in order of decreasing latitude. Throughout each section, source attribution of individual contaminants is discussed. A separate section details the principal airsheds of each park.

4.2 Semi-Volatile Organic Compounds (SOCs)

For all results reported in this chapter, SOC compounds are grouped by compound classes, as listed in Table 4-1.

Table 4-1. Compound Groupings Used in Chapter 4.

Term Used	Definition
PCBs[1] or "sum PCBs"	Sum of 5 PCB congeners (118, 138, 153, 183, 187)
PBDEs[1] or "sum PBDEs"	Sum of 5 PBDE congeners (47, 99, 100, 153, 154)
PAHs[1] or "sum PAHs"	Sum of 16 PAHs (fluorene, anthracene, phenanthrene, fluoranthene, pyrene, retene, benzo(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, and benzo(ghi)perylene)
Endosulfans or "sum Endosulfans"	Sum of 3 endosulfans (I, II and sulfate)
Chlordanes or "sum Chlordanes"	Sum of 4 chlordanes (cis- and trans-chlordane, cis- and trans-nonachlor, excludes oxy-chlordane)
DDTs or “sum DDTs”	Sum of p,p′-DDT, o,p′-DDT, p,p′-DDE, o,p′-DDE, p,p′DDD, and o,p′-DDD
Total Pesticide	Sum of endosulfans, chlorpyrifos, dacthal, HCB, g-HCH, a-HCH, dieldrin, DDTs, and chlordanes

[1] PCBs = polychlorinated biphenyls; PBDEs = polybrominated diphenyl ethers; PAHs = polycyclic aromatic hydrocarbons

Figures 4-1 to 4-6 show key SOC compounds across all WACAP parks and in each medium—snow, air, lichen, conifer, fish, and surficial sediment (top-most sediment layer). The plots present average (arithmetic mean) concentrations or fluxes and their standard deviations. Polybrominated diphenyl ethers (PBDEs) were measured only in sediment and fish samples. Sections 4.2.1 to 4.2.5 discuss each medium separately. To minimize species differences, SOC concentrations in fish and lichens are reported per gram of lipid, rather than weight. Data are often presented on a log scale.

4.2.1 SOCs in Snow

Figures 4-1 to 4-5 show both concentrations and fluxes of SOCs in snow. Fluxes, in ng/m^2/yr, represent the total SOC input to the watershed from the accumulated springtime snowpack. The fluxes are calculated by multiplying the SOC concentration in the melted snow water (ng/L) by the accumulated amount of snow at the time of sampling, in liters water per m^2 per year (this is simply related to the height of the snowpack and its density or water equivalence). In general, CUPs, including endosulfans, chlorpyrifos, and dacthal, were detected in more than 90% of the snow samples (see Figure 4-1). Both a- and g-HCH (hexachlorocyclohexane) show similar spatial trends for snow (see Figure 4-2). NOAT and GAAR have higher a- and g-HCH fluxes than DENA, and the fluxes in the sites in the conterminous 48 states fall into a close range between 40 and 90 ng/m^2/yr. Within this range, g-HCH at GLAC has the highest flux and concentration. Hexachlorobenzene (HCB), dieldrin, and sum chlordanes are frequently detected in snow, even in the Alaska parks (see Figure 4-3). NOAT and GAAR have the highest measured snow concentrations for HCB and sum chlordane, at 0.023 and 0.057 ng/L, respectively.

Within each WACAP watershed, snow samples were collected at the same site for 3 consecutive years, providing important insight into the variability associated with contaminant deposition via snow. Samples collected at the same site at the same time (site replicates) show less than 20% relative standard deviation (RSD) in concentrations. Within one park, for the same year, the inter-site variability was 40-60%. Combined, inter-site and inter-annual variability within a park was much larger, at 80-120% RSD, for parks in the conterminous 48 states. For the Alaska parks, variability was even higher, approaching 140% RSD for the 3 years of sampling. The higher variability in snow concentrations and deposition in Alaska probably reflects the lower concentrations and lower snow amounts. The high variability among sampling years within a park highlights the importance of using same-year data to make inter-park comparisons and the importance of multi-year sampling to understand contaminant inputs to the park ecosystems.

Figure 4-7 shows the distribution of pesticides in snow observed at SEKI and MORA in the 3 years of sampling. For these parks, the concentration of pesticides in snow showed substantial year-to-year variability. For example, total pesticide concentrations at SEKI ranged from a low of 3.5 ng/g to a high of 10 ng/g. At MORA, total pesticides ranged from 0.38 ng/g to 0.63 ng/g. Despite this result, the pattern of SOCs at each park is clearly different from the other and is consistent for each park from year to year. At MORA, endosulfans have the highest concentration in all 3 years, whereas at SEKI, dacthal is highest in all 3 years. So, despite significant year-to-year variations in total concentrations, the pattern of pesticides deposited to each park is consistent for all 3 years of the WACAP study. This finding implies that the sources of pesticides to each park do not change significantly from year to year. It also implies that the sources influencing MORA and SEKI are different, given the different patterns of pesticides deposited. The year-to-year variation in snowpack concentration and flux implies that the SOC inputs to the ecosystem, via annual snowpack, vary substantially from year to year.

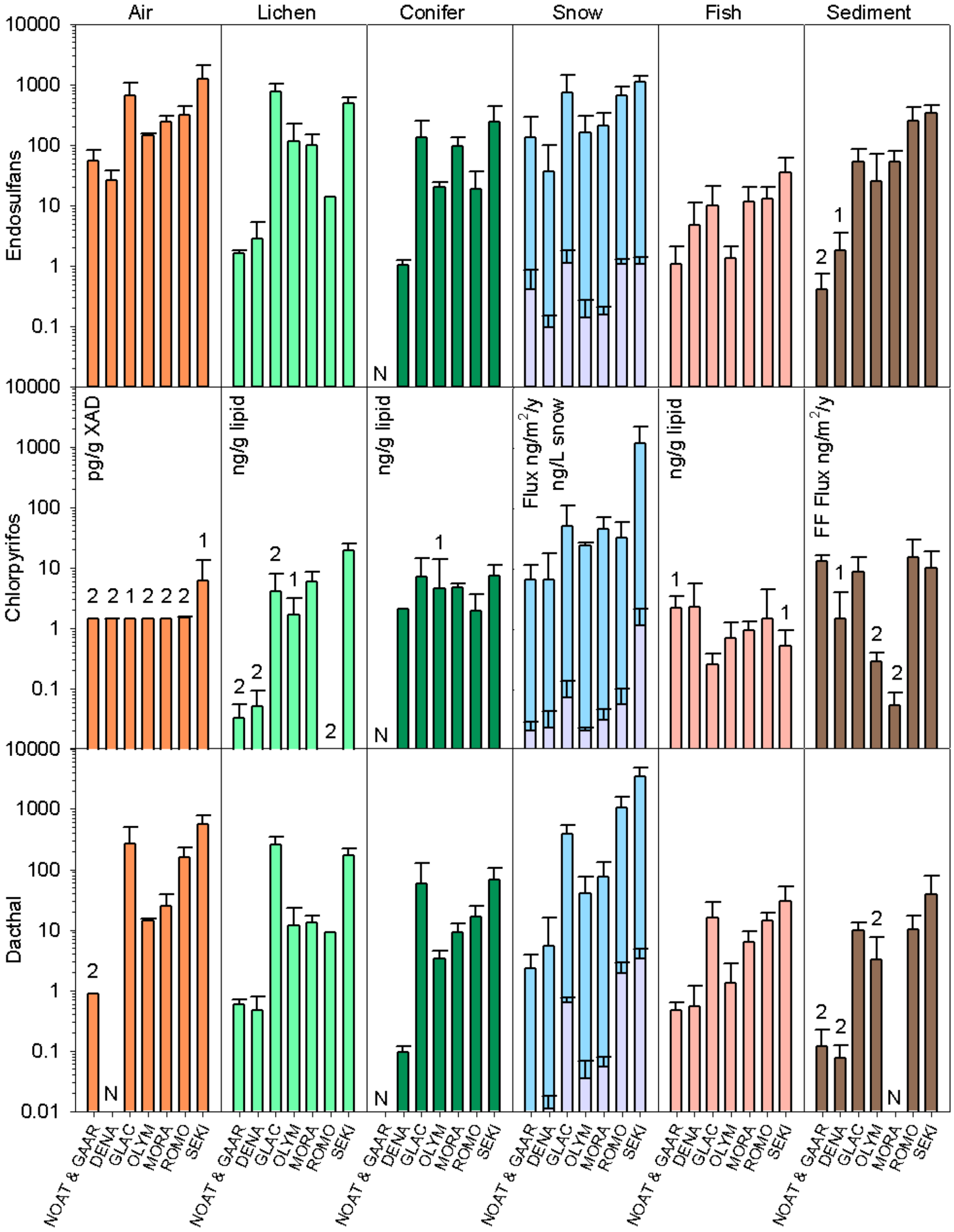


Figure 4-1. Current-Use Pesticides (CUPs): Average Concentrations and Fluxes of Sum Endosulfans, Chlorpyrifos, and Dacthal across Parks and Media. Snow data include fluxes in blue and concentrations in gray. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment (top-most sediment layer) only. Conifer samples were not collected at NOAT and GAAR. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. Below detection limit (BDL) values were replaced with half the estimated detection limit (EDL). 1 indicates that the analyte was detected in 50-70% of the samples and BDL values were replaced with half the EDL. 2 indicates that the analyte was detected in <50% of the samples and the value on the graph is half the EDL. N = no data.

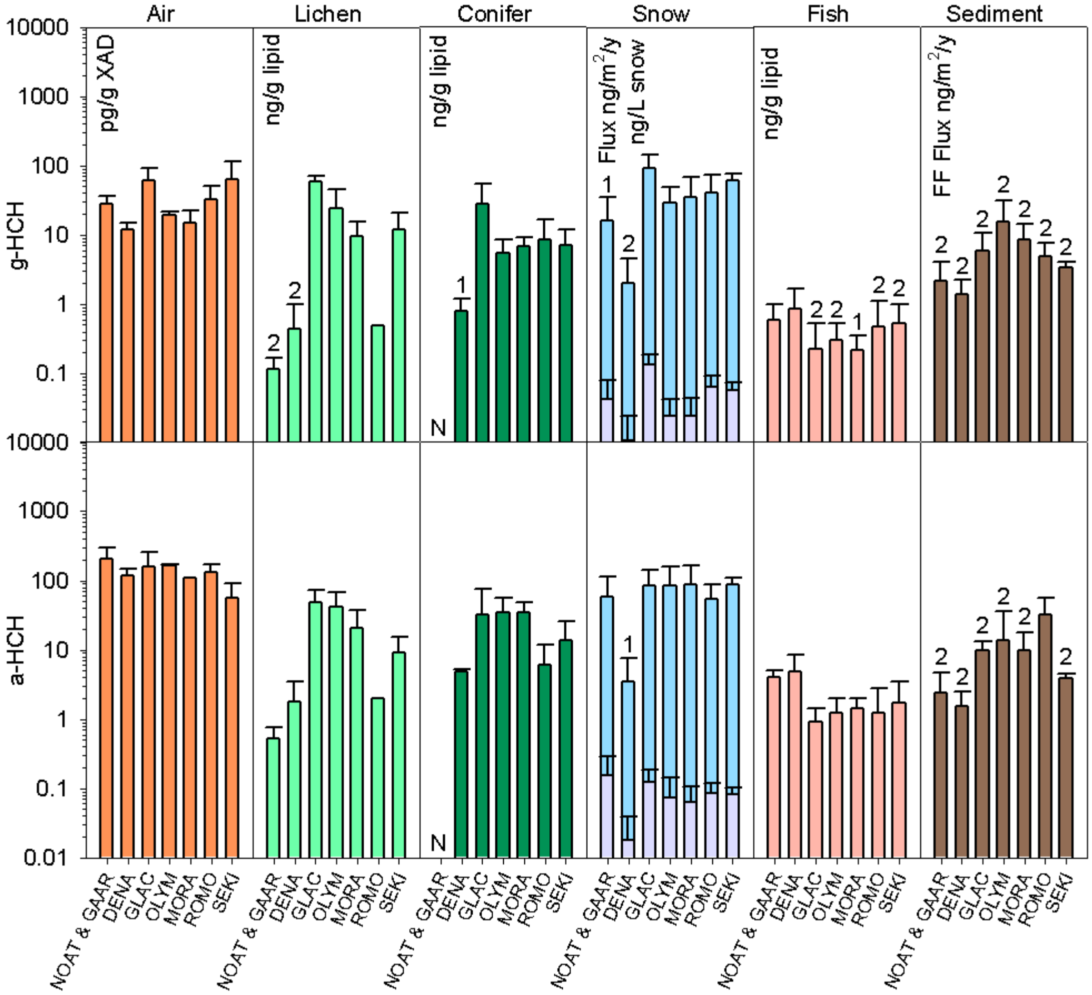


Figure 4-2. HCHs: Average Concentrations and Fluxes of a-HCH and g-HCH across Parks and Media. Snow data include fluxes in blue and concentrations in gray. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. Conifer samples were not collected at NOAT and GAAR. 1, 2, and N codes are the same as for Figure 4-1.

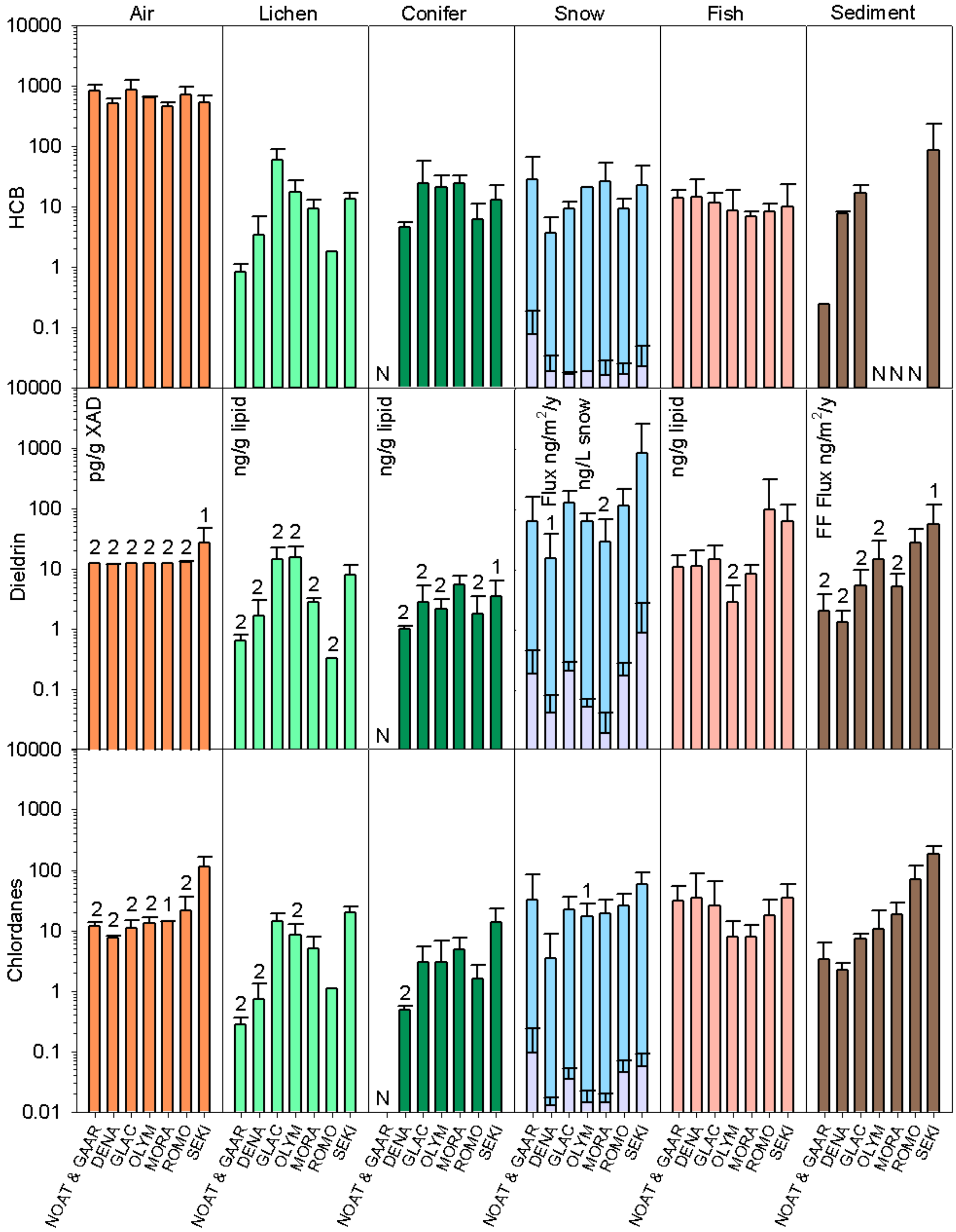


Figure 4-3. Historic-Use Pesticides (HUPs): Average Concentrations and Fluxes of HCB, Dieldrin, and Sum Chlordanes across Parks and Media. Snow data include fluxes in blue and concentrations in gray. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. Conifer samples were not collected at NOAT and GAAR. 1, 2, and N codes are the same as for Figure 4-1.

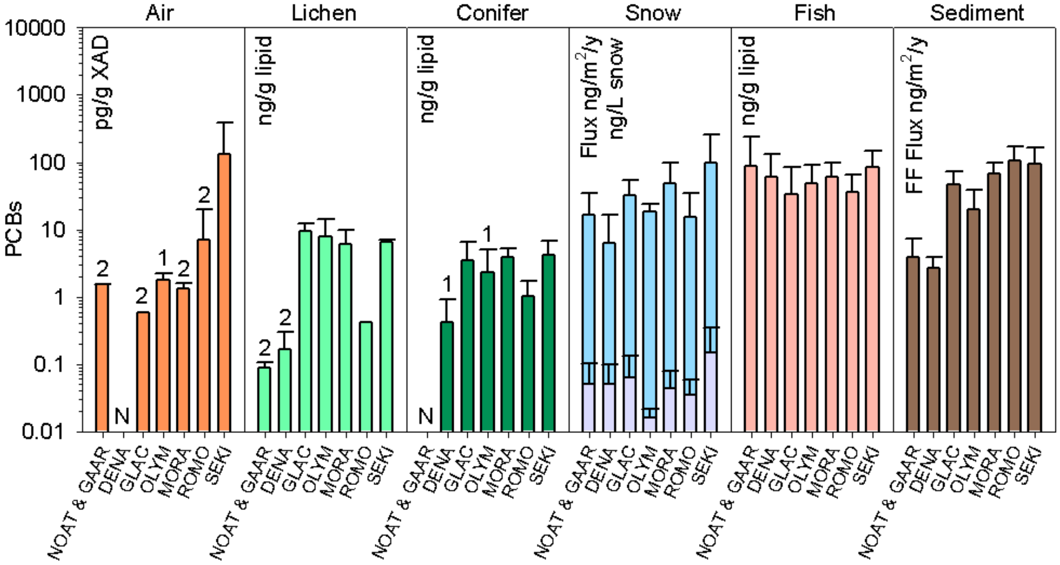


Figure 4-4. PCBs: Average Concentrations and Fluxes of Sum PCBs across Parks and Media. Snow data include fluxes in blue and concentrations in gray. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. Conifer samples were not collected at NOAT and GAAR. 1, 2, and N codes are the same as for Figure 4-1.

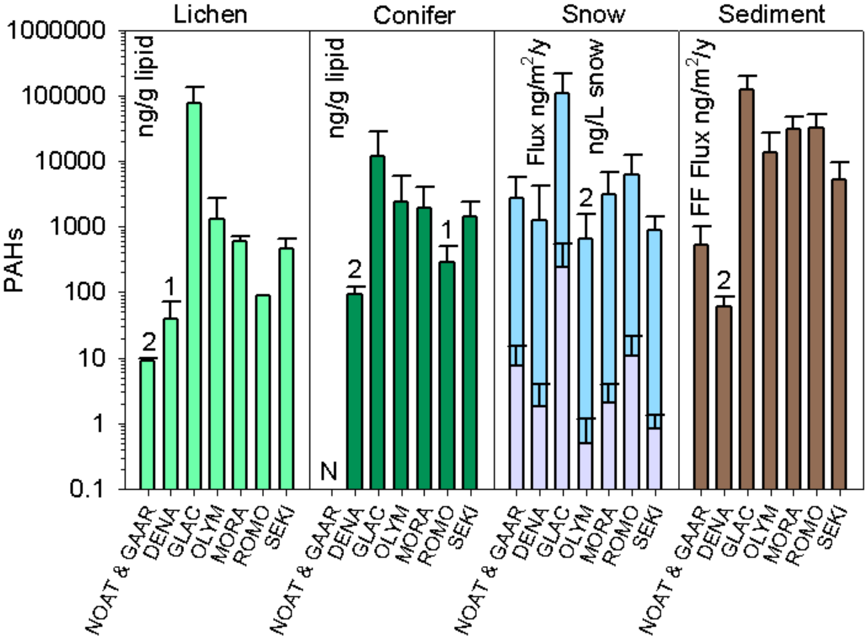


Figure 4-5. PAHs: Average Concentrations and Fluxes of Sum PAHs across Parks and Media. Snow data include fluxes in blue and concentrations in gray. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. Conifer samples were not collected at NOAT and GAAR. 1, 2, and N codes are the same as for Figure 4-1.

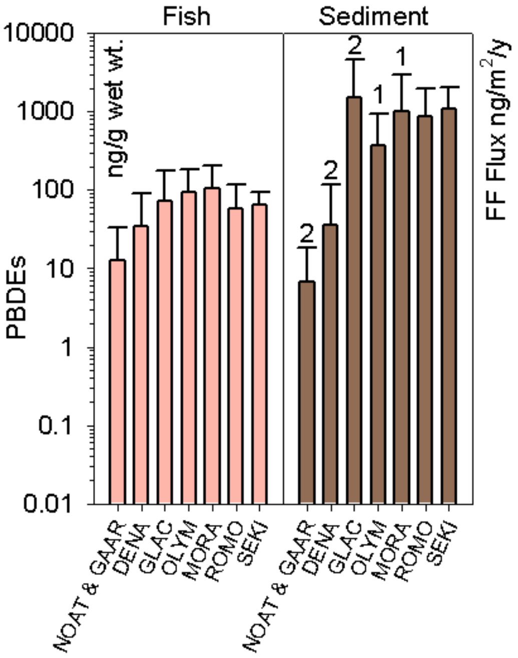


Figure 4-6. PBDEs: Average Concentrations and Fluxes of Sum PBDEs in Fish and Sediments across Parks. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. 1, 2, and N codes are the same as for Figure 4-1.

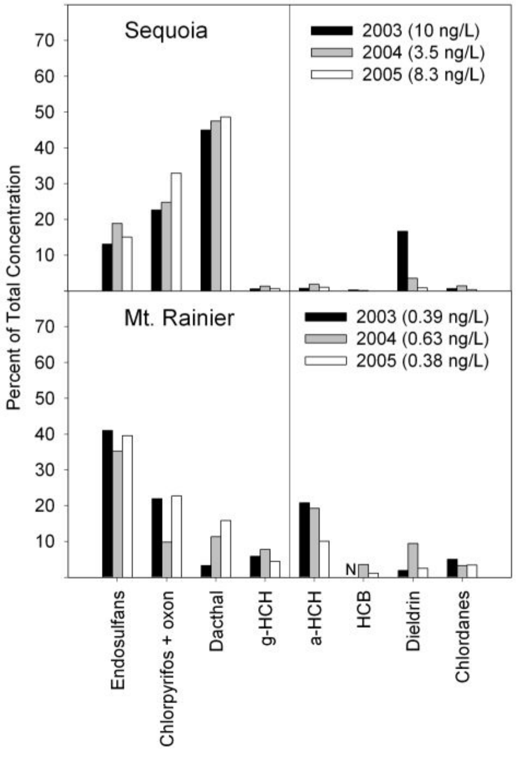


Figure 4-7. Annual Percent of Total Concentration in Snow for Current- and Historic-Use Pesticides at SEKI and MORA (after Hageman et al., 2006).

4.2.2 SOCs in Air

As described in Chapter 3, PASDs (passive air sampling devices) were deployed at both core and secondary parks for one year (± 2 weeks) to give a qualitative picture of atmospheric contamination. Following collection, the PASDs were analyzed to indicate regional patterns of SOC concentrations in ambient air.

The SOCs detected in air were similar to those detected in other media for each park, e.g., snow and vegetation (Figure 3-1 in Chapter 3); however, the concentrations of SOCs were generally much lower in the PASD sampling material, XAD (pg/g dry XAD), compared with concentrations in vegetation (ng/g lipid lichens or conifer needles; see Figures 4-1 to 4-4). Current-use pesticides, especially dacthal and endosulfans, were highest in parks in the conterminous 48 states (Figure 4-8), notably at SEKI. Of the historic-use pesticides, HCB and chlordanes appeared similar across all parks, whereas HCHs were as high in some Alaska parks as they were in parks in the conterminous 48 states (Figure 4-8). A few SOCs were detected primarily in the air of only one or two parks: heptachlor at NOCA; chlorpyrifos (almost entirely as the degradation product Chlorpyrifos-oxon) at NOCA and SEKI; dieldrin and PCBs at SEKI; and p,p′-DDE at SEKI, CRLA, and BIBE (Figure 4-8). The fact that these contaminants occur at only one park suggests a regional source.

Simple linear regression of individual SOCs by latitude (Figure 4-9) yielded convincing evidence ($p < 0.003$) that concentrations of a-HCH *increase* and that concentrations of dacthal, endosulfans, and chlordanes *decrease* in the air with increasing latitude. There was suggestive evidence ($p < 0.1$) that PAHs and g-HCH also *decrease* with increasing latitude; p,p′-DDE was detected only at a few sites, all in the conterminous 48 states. The latitudinal increase of a-HCH in air in North America has been reported previously (Shen et al., 2005; Simonich and Hites, 1995) and is generally attributable to greater fractionation and lower revolatilization of this compound at colder temperatures. In Europe, HCB has been shown to increase with latitude (Meijer et al., 2003); however, this result was not observed in the WACAP data.

4.2.3 SOCs in Vegetation

4.2.3.1 Spatial Patterns of SOCs in Vegetation

4.2.3.1.1 Regional Patterns of Pesticide Accumulation in Lichens

Average total pesticide concentrations (Figure 4-10) in lichens were lowest (~5-10 ng/g lichen lipid) in parks in the Arctic and interior Alaska (GAAR, NOAT, and DENA), and increased southward with decreasing latitude. Mean park total pesticide concentrations were ~100 ng/g lipid in southern coastal Alaska (KATM, WRST, GLBA, and STLE) and were up to two orders of magnitude higher than concentrations in parks in the Arctic and interior Alaska (500-1,000 ng/g lipid) in some parks in the conterminous 48 states, notably YOSE, SEKI, GLAC, and GRSA. Pesticide concentrations in much of the central and southern Rockies (GRTE, ROMO, BAND, and BIBE) were comparable to the concentrations in the Pacific Northwest (200-300 ng /g lichen lipid). Means concentration comparisons are provided in Table 4-2.

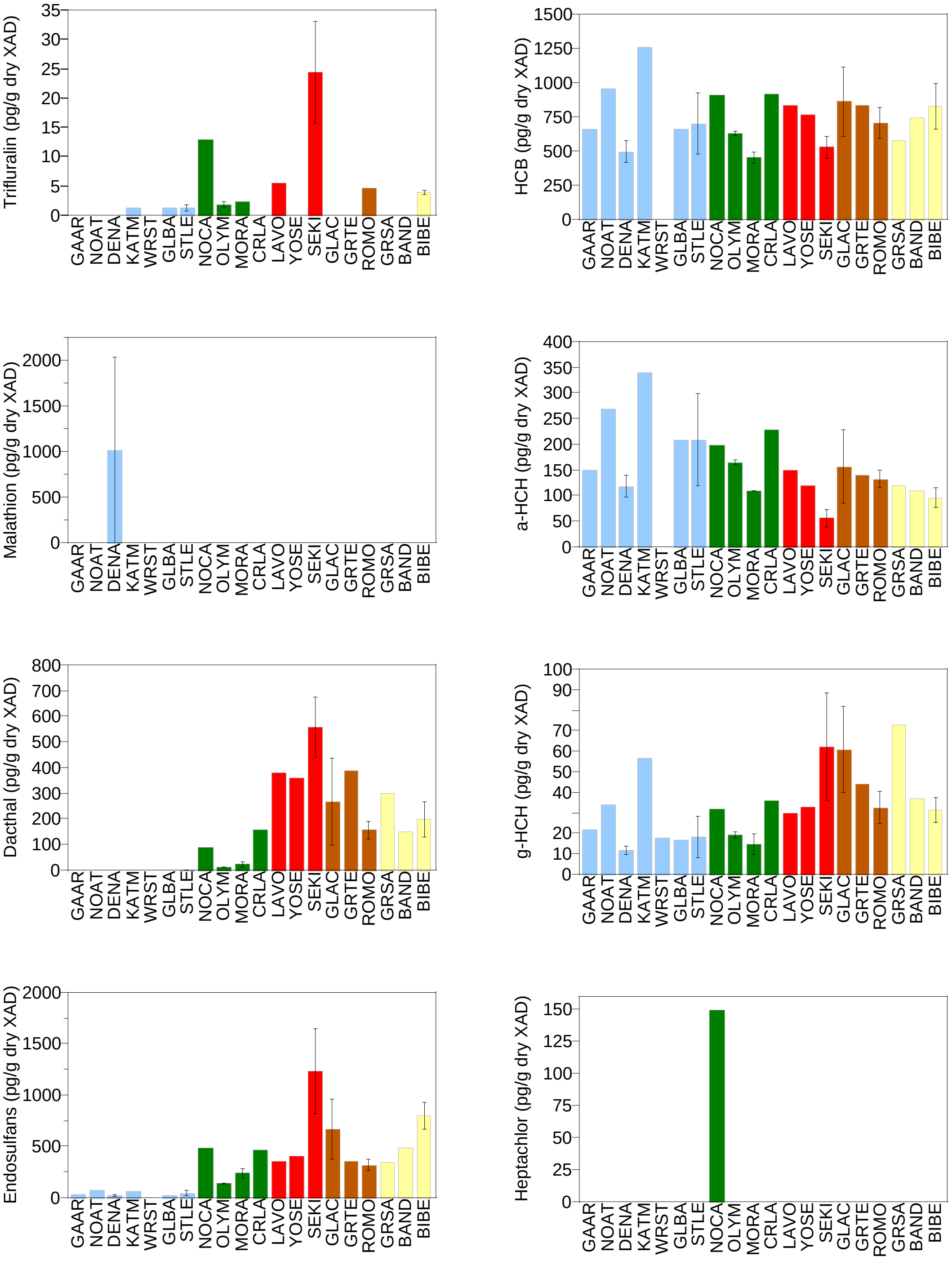


Figure 4-8. Regional Patterns of SOCs in Ambient Air as Indicated by Concentrations Accumulated in XAD Resin in Suspended Passive Air Sampling Devices (PASDs). From one to four PASDs were deployed in each WACAP park for one year beginning July 2005. Parks are listed from north to south from Alaska (light blue) through the Pacific Northwest (green) to California (red) and from the northern (brown) to southern (pale yellow) Rocky Mountains. Error bars indicate one standard error. (Figure continued on page 4-10.)

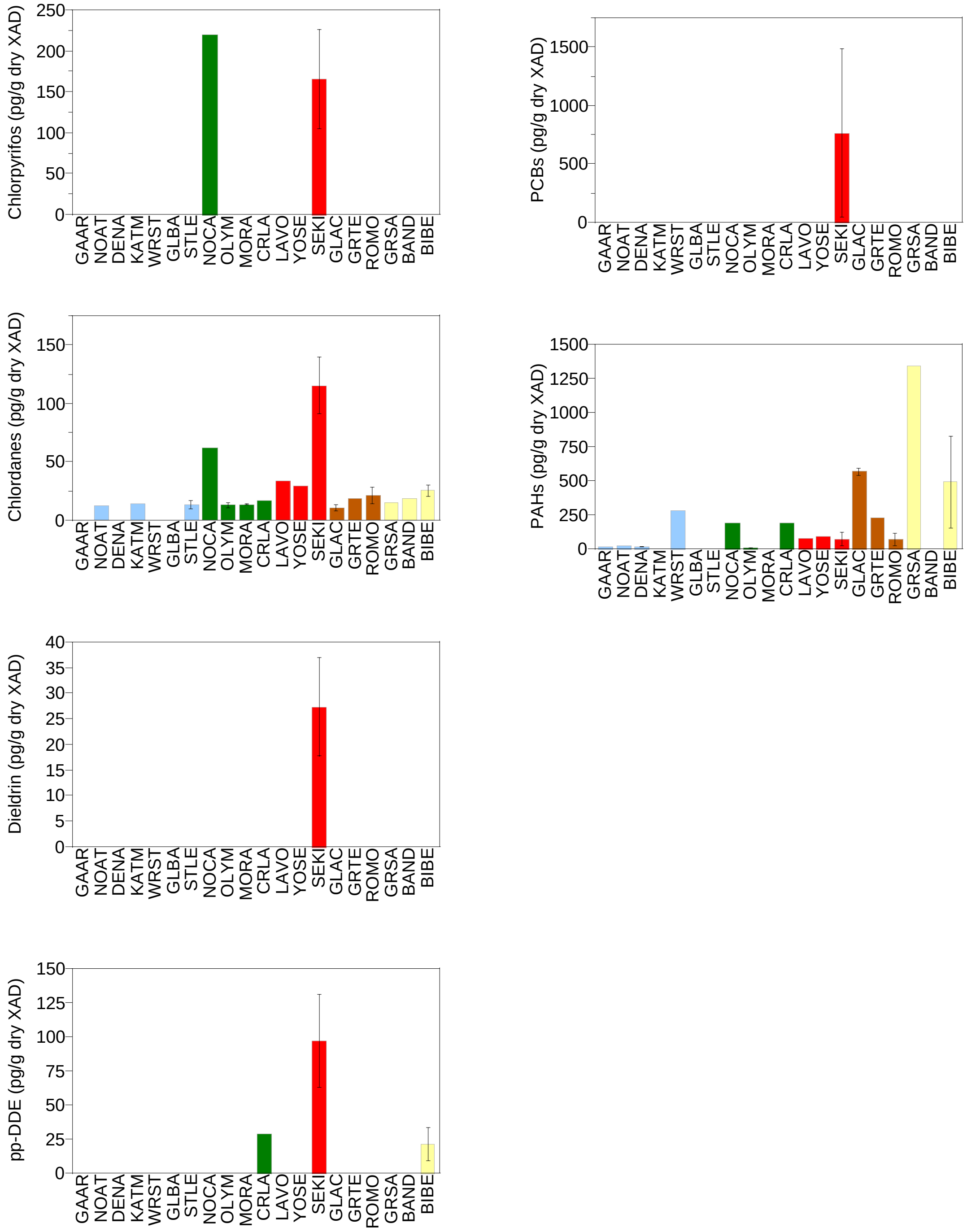


Figure 4-8 (continued).

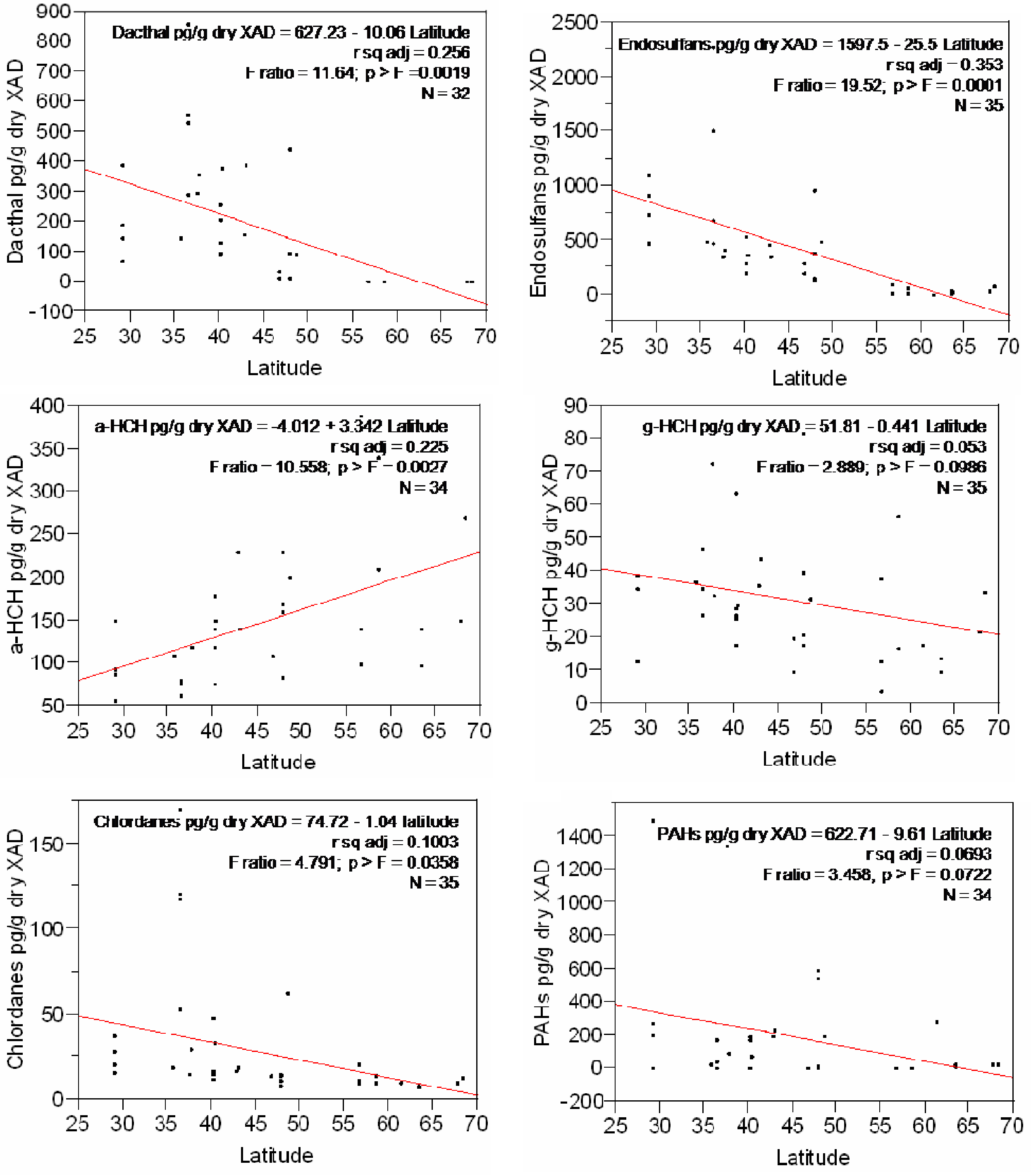


Figure 4-9. Simple Linear Regression of Individual SOCs Determined in the XAD Resin by Latitude.

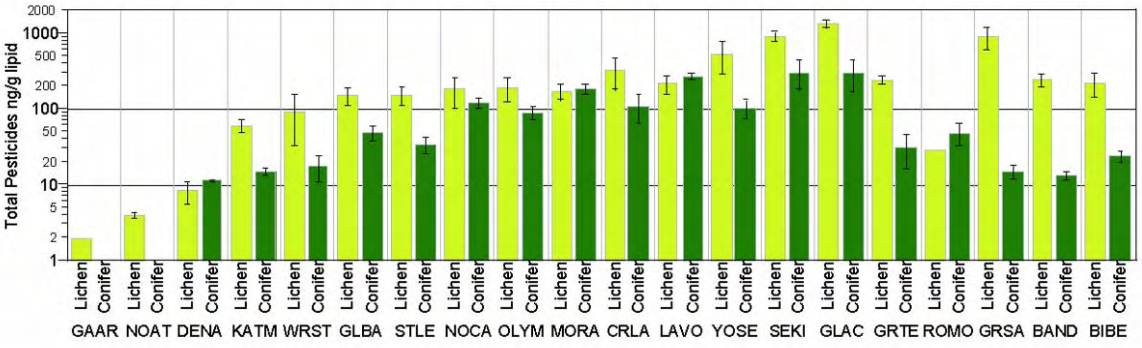


Figure 4-10. Comparison of Total Pesticide Concentrations in Lichen and Conifer Needle Vegetation from WACAP Parks in the Arctic (NOAT, GAAR), Interior Alaska (DENA), Coastal Alaska (KATM, WRST, GLBA, STLE), the Pacific Northwest (NOCA, OLYM, MORA, CRLA), California (LAVO, YOSE, SEKI), the Northern Rocky Mountains (GLAC, GRTE), and the Southern Rocky Mountains (ROMO, GRSA, BAND, BIBE). Note log scale; error bars indicate one standard error. No conifer samples were collected in the Arctic. Lichen concentrations increased more than 2 orders of magnitude from Arctic Alaska to the conterminous 48 states. Conifer concentrations increased about 1 order of magnitude from interior Alaska to the conterminous 48 states (excluding the central and southern Rocky Mountains, which were similar to coastal Alaska.

One might ask whether the very low SOC concentrations in the Arctic and interior Alaska lichen samples (NOAT, GAAR, DENA) occurred because these parks are most remote from source regions, or whether the low concentrations are an artifact of species differences, or, in the case of tundra lichens, snow burial. The answer appears to be mixed: lichen species can differ as accumulators of organic contaminants, and snow burial can enhance these differences. Specifically:

1. In DENA, where the tundra lichens (*Flavocetraria cucullata* and *Masonhalea richardsonii*) were both collected at multiple elevations, total pesticide concentrations in *F. cucullata* were 12 times higher than those in *M. richardsonii* (see DENA5 in Appendix 4A.1; paired t-tests, equal variances, $p < 0.05$), but did not differ from total pesticide concentrations in *F. cucullata* from WRST or KATM (Appendix 4A.2; Tukey-Kramer multiple means comparison, $\alpha = 0.05$). Similarly, total pesticide concentrations in *M. richardsonii* samples from DENA did not differ from those from NOAT and GAAR (where no *F. cucullata* was collected) (Appendix 4A.2; Tukey-Kramer multiple means comparison, $\alpha = 0.05$). Inductive reasoning indicates that total pesticide concentrations would have been comparable in all Alaska parks, had the same species been collected. Figure 4-11 depicts these patterns.

2. In KATM (Appendix 4A.3), where both tundra and epiphytic lichens were sampled, the epiphyte, *Hypogymnia physodes*, had higher concentrations of all SOCs except chlordanes and dacthal (not different) than the tundra lichen, *Flavocetraria cucullata* (t-test, equal variances, $p < 0.05$), as one would expect, assuming the tundra lichens are buried under snow in winter. SOC concentrations in the epiphyte were 1.5- to 4.6-fold higher, depending on the SOC, which is not large enough to account for concentration differences between tundra lichens in Alaska and epiphytic lichens from some parks of the conterminous 48 states, notably GLAC, SEKI, and GRSA, but is large enough to account for differences between tundra lichens in Alaska and epiphytic lichens from southern coastal Alaska parks and parks of the Pacific Northwest.

Table 4-2. Mean SOC Concentrations in Lichens and Conifer Needles (ng SOC/g lipid in vegetation) from Each WACAP Park. For each contaminant (i.e., within columns), concentrations that do not share a T-K letter are significantly different. The T-K letter indicates grouping derived from the Tukey-Kramer multiple means comparison test, α = 0.05). Blank cells indicate that all samples were below laboratory detection limits.

Lichens	**Current-Use Pesticides**					**Historic-Use Pesticides**						**Total Pesticides**				
Park	Trifluralin	Triallate	Chlorpyrifos	Dacthal	Endosulfans	HCB	a-HCH	g-HCH	Chlordanes	Dieldrin	DDTs	CUPs	HUPs	%CUPs	PCBs	PAHs
NOAT, GAAR				0.60 d	1.61 c	0.84 ab	0.53 bc		0.03 e			2.2 e	1.4 c	61 abcd	0.03 c	3 b
DENA				0.54 d	2.83 c	3.56 b	1.85 c	0.45 c				3.4 e	5.9 c	37 cd		87 b
KATM				0.58 d	19.72 c	25.17 ab	9.65 abc	2.61 bc	2.42 cde			20.3 e	39.9 c	34 e	1.79 c	262 b
WRST				1.34 d	25.21 c	50.06 ab	20.28 abc	5.32 bc	1.77 de			26.6 de	77.4 bc	26 e	1.97 bc	1258 b
GLBA	1.51 a				60.70 c	48.75 ab	28.00 abc	6.96 bc	4.91 cde			62.2 de	88.6 bc	41 de	7.08 abc	1264 b
STLE		0.60 b	0.60 b	6.09 d	76.66 c	40.86 ab	30.67 abc	7.60 bc	2.50 de			84.0 de	81.6 bc	51 de	2.70 bc	780 b
NOCA	0.17 a	5.20 b	5.20 b	15.44 d	119.30 c	18.74 ab	12.92 abc	5.50 bc	2.19 cde		5.72 c	145.3 de	45.1 bc	76 a	4.07 abc	1960 b
OLYM	0.89 a	1.57 b	1.57 b	12.91 d	117.92 c	21.31 ab	43.33 ab	23.47 b	3.04 cde			134.9 de	91.2 bc	60 bcd	7.84 abc	2175 b
MORA	6.00 a		6.00 b	13.21 d	101.14 c	9.27 ab	20.84abc	9.67 bc	5.14 cde		2.96 c	126.4 de	47.9 bc	73 ab	6.18 abc	764 b
CRLA		4.37 b	4.37 b	57.63 bcd	205.38 bc	18.35 ab	14.98 abc	4.69 bc	12.04 bcd		10.88 c	271.8 cde	60.9 bc	82 abc	5.91 abc	1103 b
LAVO				75.00 bcd	101.98 c	10.90 ab	10.73 abc	3.58 bc	11.14 bcde	3.14 a	31.08 bc	177.0 de	70.6 bc	71 ab	4.04 abc	315 b
YOSE	1.88 a	19.83 a	19.83 a	204.67 a	227.57 bc	16.80 ab	6.93 abc	4.00 bc	13.85 abc		34.80 bc	473.8 bcd	76.4 bc	86 a	5.49 abc	2096 b
SEKI	0.94 a	19.33 a	19.33 a	169.75 ab	487.75 b	13.33 ab	9.24 abc	12.16 bc	19.84 ab	8.01 a	159.95 a	697.1 ab	222.5 a	76 a	6.48 abc	814 b
GLAC	1.00 a	5.28 b	5.28 b	242.61 a	775.34 a	55.06 a	45.00 a	65.06 a	9.15 cde		113.40 ab	1029.5 a	287.7 a	78 a	9.39 a	72758 a
GRTE	0.13 a	4.10 ab	4.10 ab	39.75 bcd	144.25 bc	11.85 ab	9.00 abc	5.30 bc	4.51 cde	1.45 a	16.50 bc	192.3 bcde	48.6 bc	80 ab	2.87 abc	571 b
ROMO				9.00 bcd	14.00 c	1.83 ab	2.01 abc	0.49 bc	1.12 cde			23.0 cde	5.5 bc	81 abc	0.42 abc	100 ab
GRSA	0.63 a			175.00 abc	536.00 ab	65.50 ab	32.00 abc	11.00 bc	28.25 a		71.79 abc	711.6 abc	208.5 ab	77 ab	11.60 ab	667 b
BAND	0.51 a	5.10 ab	5.1 ab	39.80 cd	138.35 c	10.99 ab	10.37 abc	5.78 bc	7.433 cde		29.98 bc	188.9 de	64.6 bc	75 ab	4.734 abc	190 b
BIBE				9.8d	190.00 bc	3.45 ab	2.50 abc	2.68 bc	2.06 cde		12.40 bc	199.8 bcde	23.1 bc	90 a	1.97 abc	484 b
Conifers	**Current-Use Pesticides**					**Historic-Use Pesticides**						**Total Pesticides**				
Park	Trifluralin	Triallate	Chlorpyrifos	Dacthal	Endosulfans	HCB	a-HCH	g-HCH	Chlordanes	Dieldrin	DDTs	CUPs	HUPs	%CUPs	PCBs	PAHs
DENA			0.86 b	0.09 bcd	0.69 bc	4.53 a	4.82 ab	0.80 a	0.15 bc			1.6 d	10.3 b	14 h	0.56 ab	96b
KATM			0.63 b	0.26 d	1.68 c	7.76 a	4.44 ab	1.15 a	0.17 bc			2.6 d	13.5 b	16 gh	0.13 b	59 b
WRST			0.61 b		1.16 c	6.15 a	1.93 b	7.42 a	0.15 bc			1.8 d	15.7 b	10 h		40b
GLBA			2.35 b	0.10 d	1.63 bc	7.40 a	5.38 ab	32.76 a	0.44 bc			4.1 d	46.0 ab	8 h		131b
STLE			0.81 b	0.44 d	1.66 c	9.09 a	4.69 ab	16.63 a	0.33 bc			2.9 d	30.7 ab	9 h	0.18 b	227b
NOCA				9.36 bcd	42.52 b	26.00 a	31.80 ab	5.74 a	2.22 bc		6.61 ab	51.9 cd	72.4 ab	42 fe	1.66 ab	2429b
OLYM	2.31 a		1.62 b	3.36 d	19.99 bc	20.80 a	34.20 a	5.38 a	2.57 bc			27.3 d	63.0 ab	30 cde	2.33 ab	2462 b
MORA			1.68 b	9.11 bcd	93.57 abc	23.83 a	34.87 a	6.71 a	4.94 bc	5.56 a	2.13 b	104.4 bcd	78.0 ab	57 fg	3.89 a	1955 b
CRLA	0.27 a			21.12 bc	42.27 bc	21.36 a	16.58 ab	3.71 a	1.45 bc			63.7 bcd	43.1 ab	60 de	0.84 ab	826 b
LAVO			2.00 b	85.80 a	136.28 ab	14.60 a	16.80 ab	4.28 a	6.00 b		4.85 ab	224.1 ab	46.5 ab	83 a	1.31 ab	2170 b
YOSE			7.45 a	53.20 abcd	19.23 bc	14.63 a	6.30 ab		3.15 bc			79.9 bcd	24.1 ab	77 ab	1.10 ab	3787 b
SEKI			2.48 b	66.42 ab	191.72 a	12.61 a	13.79 ab	6.99 a	13.81 a	3.83 a	19.03 a	260.6 a	70.1 ab	79 ab	4.19 a	3255 b
GLAC		13.73 a	2.39 b	58.20 abc	132.09 abc	24.11 a	31.78 ab	27.45 a	2.28 bc		7.46 ab	206.4 abc	93.1 a	69 abc	3.46 ab	20044 a
GRTE		4.13 a	1.01 b	10.35 bcd	8.01 bc	6.91 a	5.80 ab	0.80 a	0.36 bc			23.5 d	13.9 b	63 bcd	0.73 ab	186b
ROMO			0.80 b	16.39 bcd	15.12 b	6.24 a	6.17 ab	8.36 a	1.12 bc		1.51 b	32.3 d	23.4 ab	58 cd	1.04 ab	242 b
GRSA				4.08 cd	6.06 bc	3.42 a	1.45 b					10.1 d	4.9 b	68 abcd	1.22 ab	134b
BAND				4.99 cd	2.69 c	3.26 a	2.22 b		0.09 c			7.7 d	5.6 b	58 cd	1.08 ab	221 b
BIBE			1.63 b	2.17 bcd	12.05 bc	5.27 a	2.47 ab		0.30 bc			15.9 cd	2.8 ab	85 abcd	0.12 ab	20 b

3. Pesticide concentrations in tundra lichens (*Cladina arbuscula* and *Flavocetraria cucullata*) collected at WRST and STLE appeared to be comparable to those in the non-buried lichen epiphyte, *Alectoria sarmentosa*, indicating that some tundra lichen species accumulate pesticides as well as some epiphtyes. *Alectoria sarmentosa* appears to be as poor an accumulator among the epiphytic lichens as *M. richardsonii* is among the tundra lichens (Figure 4-11; Appendix 4A.4).

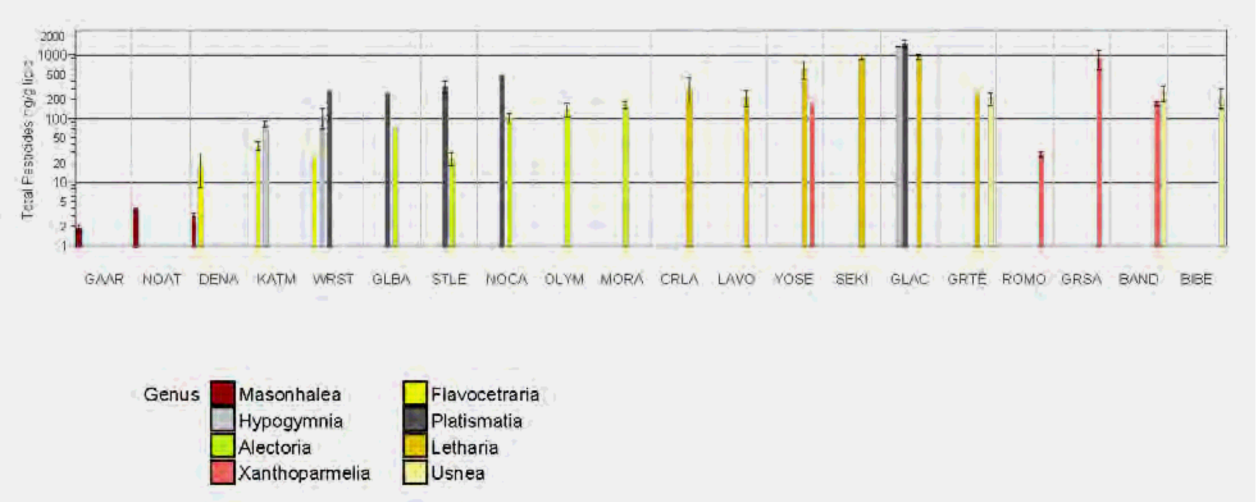


Figure 4-11. Comparison of Total Pesticide Accumulation in Lichen Species by Park from North to South along the Pacific Coast (GAAR to SEKI) and from North to South in the Rocky Mountains (GLAC to BIBE). Pesticide concentrations generally increased from north to south along the Pacific Coast and decreased from north to south in the Rocky Mountains (with the exception of GRSA, where intensive local agriculture might have influenced accumulation). Some lichens are better accumulators than others; of the tundra lichens, *Flavocetraria* accumulated more pesticides than *Masonhalea*; of the epiphytes, *Platismatia* accumulated more pesticides than *Alectoria*. Standardizing species can reduce noise in contaminant data.

In conclusion, inter-species differences in accumulation rates, and possibly snow burial, appear to account to some extent for low concentrations of pesticides in lichens from northern Alaska parks compared to those in lichens from parks in coastal Alaska and many conterminous 48 states. However, in any analysis disregarding (Table 4-2) or accounting for species differences (Appendix 4A.2), lichens from GLAC, SEKI, and sometimes YOSE and GRSA had higher pesticide concentrations than lichens in other parks.

4.2.3.1.2 Regional Patterns of Pesticide Accumulation in Conifer Needles

Regional patterns of pesticide accumulation in conifer needles were similar to patterns in lichens, except that the difference between samples from parks with lowest and highest concentrations was only about one order of magnitude (Appendices 4A.4 and 4A.7). Parks in the Arctic are largely treeless, and no conifer needles were collected there. The average total pesticide concentration in conifer needles from DENA was 11 ng/g lipid in needles. Concentrations of pesticides in conifer needles increased with southerly latitudes, maximizing in the Pacific Northwest and California and in GLAC in the northern Rockies at 100-200 ng/g lipid. Average total pesticide concentrations in conifer needles from parks of the central and southern Rockies were comparable to those in the Canadian Rockies (Davidson et al., 2003; Davidson et al., 2004) and coastal Alaska (20-30 ng/g lipid). Mean comparison tests disregarding (Table 4-2) or accounting for species differences between parks (Appendix 4A.5) support lichen data, in that conifer needles from SEKI, GLAC, and YOSE were most likely to have higher concentrations of SOCs than conifer needles in other parks.

The main discrepancy between vegetation sample types is the low concentration of total pesticides in conifer needles, compared to lichens, in the central and southern Rockies. The genus *Pinu*s, the only species collected in parks from the central and southern Rocky Mountains, appears to accumulate lower concentrations of nearly all SOCs than other coniferous species in parks (Appendix 4A.6). For example, if fir had been sampled instead of pine, SOC concentrations in needles in the southern Rockies parks (GRSA, BAND, and BIBE) might have been closer to concentrations in needles in the Pacific Northwest, as they were in lichens. It is also possible that the drier, warmer climates of the southern Rockies affect lichen and conifer uptake differently. Pine was also collected exclusively at YOSE, where needle SOC concentrations might otherwise have been intermediate to LAVO and SEKI (see subsection 4.2.3.2.3). Finally, it seems unlikely that snow burial can account for the magnitude of difference between northern Alaska and other WACAP parks, because SOC concentrations in conifer needles at the lowest elevations in DENA were substantially smaller than concentrations in samples from the highest elevation sites in other parks, which presumably are also buried under snow for many months of the year.

4.2.3.1.3 General Observations Regarding Pesticides in WACAP Vegetation

The current-use pesticides, endosulfans and dacthal, dominated total pesticide loading in vegetation samples from the conterminous 48 states (Figures 4-12 and 4-13, Table 4-2). This observation is consistent with the proximity of parks in the conterminous 48 states to large-scale agriculture, compared with Alaska parks. Agricultural intensity within 150 km of a park is strongly correlated with concentrations of these CUPs in vegetation. The Spearman’s Rho correlation for dacthal and agricultural intensity was 0.873 for conifer needles and 0.849 for lichens; the Spearman’s Rho correlation for endosulfan and agricultural intensity was 0.777 for conifer needles and 0.743 for lichens (see Table 5-15 in Chapter 5). Average regional concentrations of dacthal and endosulfans in lichens were 2 and 31 ng/g lipid, respectively, in Alaska parks and 82 and 243 ng/g lipid, respectively, in parks of the conterminous 48 states. Trifluralin and triallate in conifer needles and chlorpyrifos in lichens were below detection limits at all Alaska parks.

Historic-use pesticides, especially HCB, a-HCH, and g-HCH, comprised a larger fraction of the total contaminant concentration in Alaska parks, compared to parks in the conterminous 48 states, and concentrations were similar across parks, varying about one order of magnitude between lowest (NOAT, GAAR, DENA, ROMO, BIBE) and highest (GRSA, GLAC) measurements in both types of vegetation (Figures 4-12 and 4-13, Table 4-2). Endosulfan and dacthal comprised less than half of total pesticide concentrations in vegetation from Alaska parks, in contrast to parks in the conterminous 48 states. Dieldrin and DDTs were not detected in any Alaska parks in either conifer needles or lichens. Where they were detected in parks in the conterminous 48 states, mean dieldrin concentrations were < 20 ng/g lipid; DDT ranged up to 110 and 160 ng/g lipid at SEKI and GLAC, respectively.

Agricultural intensity, nitrogen availability as indicated by ammonium nitrate in fine particulates sampled by park IMPROVE monitors, and population density were positively correlated with SOC concentrations in vegetation. Many of the SOCs were also correlated with each other (i.e., parks with high concentrations of one SOC tended to have high concentrations of other SOCs). Agricultural intensity and population density were confounded (Spearman's Rho = 0.63 to 0.68), probably because many major western cities are built in valleys and at lower elevations where conditions are optimal for both habitation and agriculture (compare backgrounds of Figure 4-12 or 4-13 with Figure 4-19 later in this chapter). For lichens, stronger correlations were observed between SOC concentrations and agricultural intensity, but for conifer needles, correlation strength was comparable between agricultural intensity and population density. See Chapter 5 for a table (Table 5-15) and a discussion of strongest correlations.

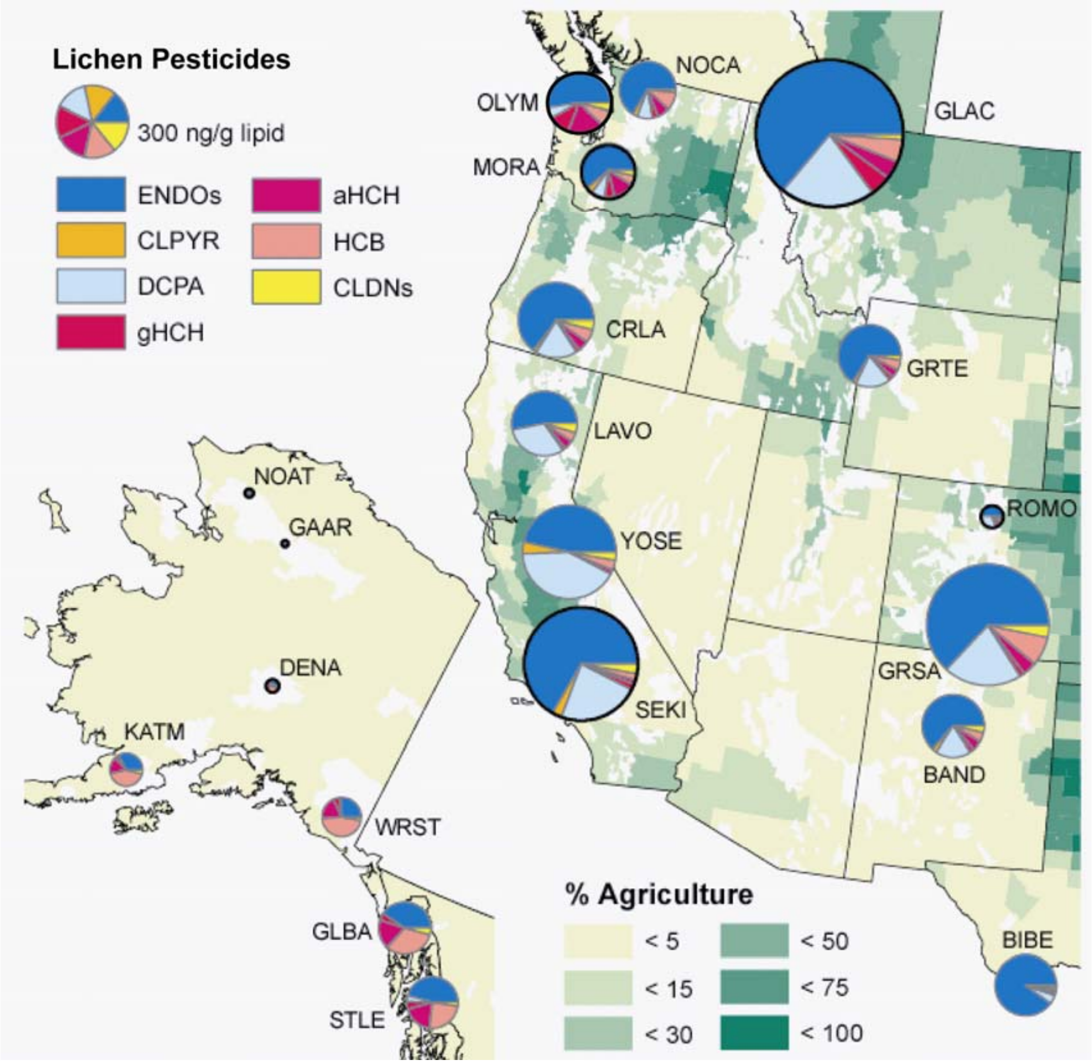


Figure 4-12. Pesticide Concentrations (ng/g lipid) in Lichens from Core and Secondary WACAP Parks Overlaid on a Map of Agricultural Intensity (US Department of Agriculture, National Agriculture Statistics Service, 2002). Circle area is proportional to total pesticide concentration. Light to dark green shading indicates increasing agricultural intensity. White shading indicates national forests or parks. Current-use pesticides endosulfan and dacthal dominate pesticide concentrations in parks in the conterminous United States, where most agriculture occurs. Historic-use pesticides comprise a relatively larger fraction of total pesticide concentrations in Alaska. Sites outlined in black are the core parks. Pesticide groups are endosulfans (ENDOs), chlorpyrifos (CLPYR), dacthal (DCPA), g-HCH and a-HCH (gHCH and aHCH), HCB, and chlordanes (CLDNs).

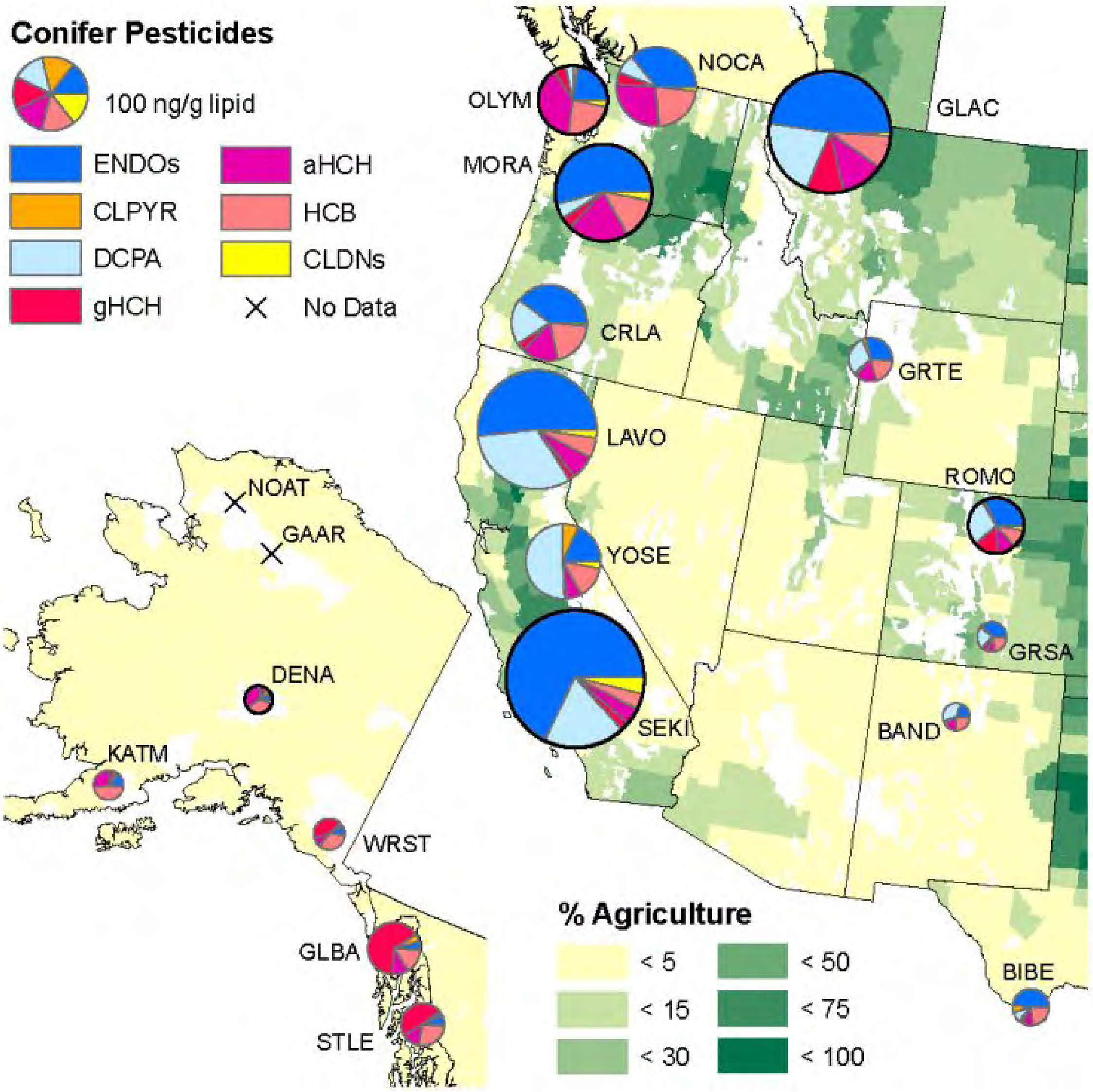


Figure 4-13. Pesticide Concentrations (ng/g lipid) in Conifer Needles from Core and Secondary WACAP Parks Overlaid on a Map of Agricultural Intensity (US Department of Agriculture, National Agriculture Statistics Service, 2002). Circle area is proportional to total pesticide concentration. Light to dark green shading indicates increasing agricultural intensity. White shading indicates national forests or parks. Current-use pesticides endosulfan and dacthal dominate pesticide concentrations in parks in the conterminous United States, where most agriculture occurs. Historic-use pesticides are relatively more important in Alaska, although total contaminant concentrations are lower. Conifers were not present in NOAT and GAAR. Sites outlined in black are the core parks. Pesticide coding is identical to that in Figure 4-12.

Concentrations of individual current-use pesticides in park vegetation appear to be markedly influenced by local usage. Because different types of crops are grown in different parts of the country, application rates (g/ha) of crop-specific insecticides and herbicides vary regionally across the United States. A visual comparison among maps of application rates of chlorpyrifos (Figure 4-14), dacthal (Figure 4-15), endosulfans (Figure 4-16), triallate (Figure 4-17), and trifluralin (Figure 4-18) in the western United States, with concentrations detected in vegetation, shows good agreement, especially if back trajectories are considered. In vegetation, application rate does not necessarily correspond with concentrations. For example, chlorpyrifos are applied at higher rates than endosulfans and dacthal but concentrations in vegetation were fairly low.

PAHs. Total PAH concentrations were lowest in the Arctic (<10 ng/g lipid) and in parks in central Alaska (<500 ng/g lipid), increasing in concentration and number of compounds with decreasing latitude along the Pacific Coast from southeastern Alaska (<5,000) to southern California (<20,000), peaking in GLAC (up to 200,000 ng/g lipid) and lower in the rest of the Rockies (<1,100 ng/g lipid) (see also Figure 4-19). The number of PAH compounds detected generally increased with total PAH concentration from 2 in the arctic to 17 in GLAC.

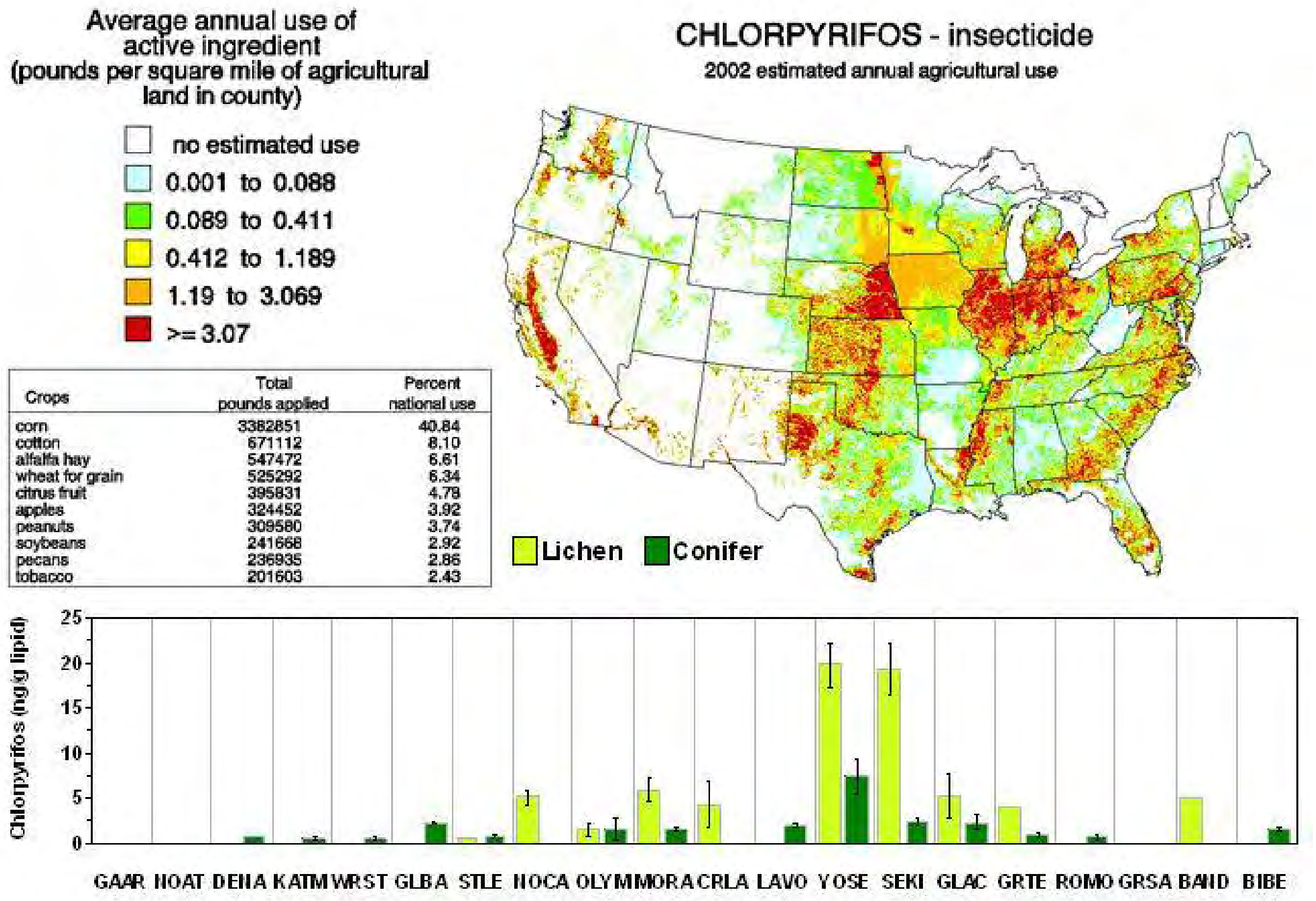
The PAHs detected in greatest concentrations (10 to 10,000 ng/g lipid) and in most or all parks were fluorene, phenanthrene, fluoranthrene, pyrene, retene, chrysene/triphenylene, and benzo(a) anthracene. The other PAHs detected in vegetation—acenaphthylene, acenapthene, anthraxcene, benzo(b)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthraxcene, and benzo(ghi)perylene—were detected in fewer parks, usually at concentrations < 100 ng/g lipid. One exception is the west side of the Continental Divide in GLAC, where concentrations of these PAHs were higher, but decreased with distance and elevation from Columbia Falls, Montana. Total PAH concentrations in vegetation reported in this document could be overestimated because of the co-elution of matrix interferences.

PCBs. Compared to the major herbicides and PAHs, concentrations of PCBs were very low in both lichens and conifer needles, and no discernable regional patterns were observed, either in total accumulation of PCBs or the relative proportions of PCBs detected (Table 4-2).

4.2.3.2 Effects of Species on SOC Concentrations in Vegetation

4.2.3.2.1 Conifer Needles vs. Lichens

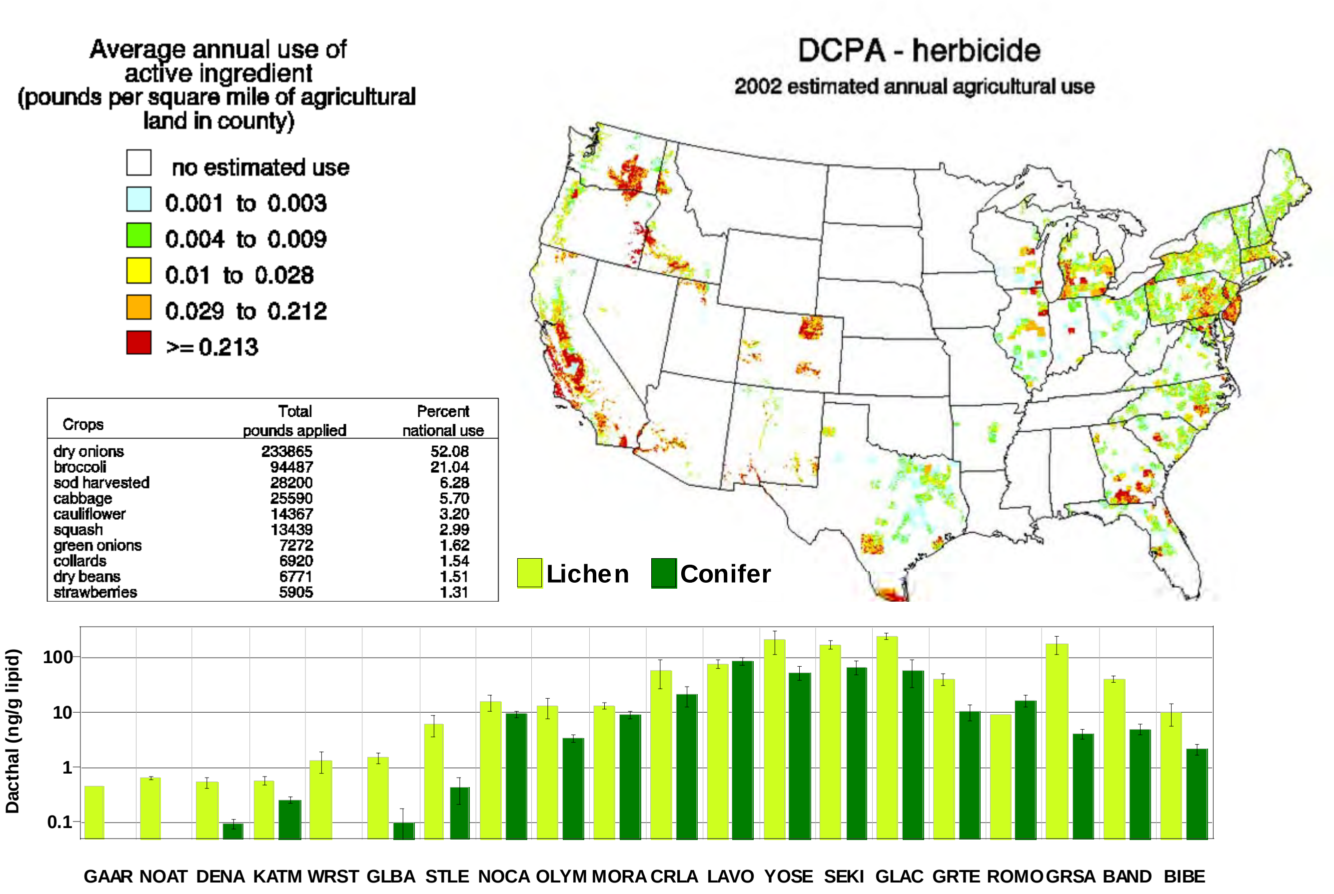
The relative contribution of individual SOCs to the total contaminant concentration in vegetation of the 20 WACAP parks was similar in conifer needles and lichens: PAHs > endosulfans > dacthal > HCB and a-HCH (Table 4-2). However, SOC concentrations were usually higher in lichens than in conifer needles, even after lipid normalization. Specifically, paired t-tests of conifer vs. lichen SOC concentrations at 69 WACAP sites where both vegetation types were collected provided evidence that mean concentrations of chlorpyrifos, dacthal, endosulfans, HCB, chlordanes, DDTs, PCBs, and PAHs were 2.6 to 9.0 times higher in lichens than in conifer needles (Prob > t < 0.05; see Appendix 4A.7). Only a-HCH and g-HCH concentrations did not differ among the vegetation types, and no compounds were higher in conifer needles than in lichens. Although there was no evidence that dieldrin, trifuralin, and triallate concentrations differed between vegetation types, statistical power was low because only 3, 1, and 7 of the 69 sites, respectively, had detectable concentrations of SOCs in both media.



Crops	Total pounds applied	Percent national use
corn	3382851	40.84
cotton	671112	8.10
alfalfa hay	547472	6.61
wheat for grain	525292	6.34
citrus fruit	395831	4.78
apples	324452	3.92
peanuts	309580	3.74
soybeans	241668	2.92
pecans	236935	2.86
tobacco	201603	2.43

Figure 4-14. Uses and Estimated Application Intensity in 2002 of the Current-Use Insecticide Chlorpyrifos in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng chlorpyrifos/g lipid conifer needles or lichens) from WACAP Parks. Chlorpyrifos were detected in vegetation in all parks except NOAT and GAAR, but highest concentrations were observed in SEKI and YOSE, close to the San Joaquin Valley in California, a particularly high use area. Error bars indicate one standard error.

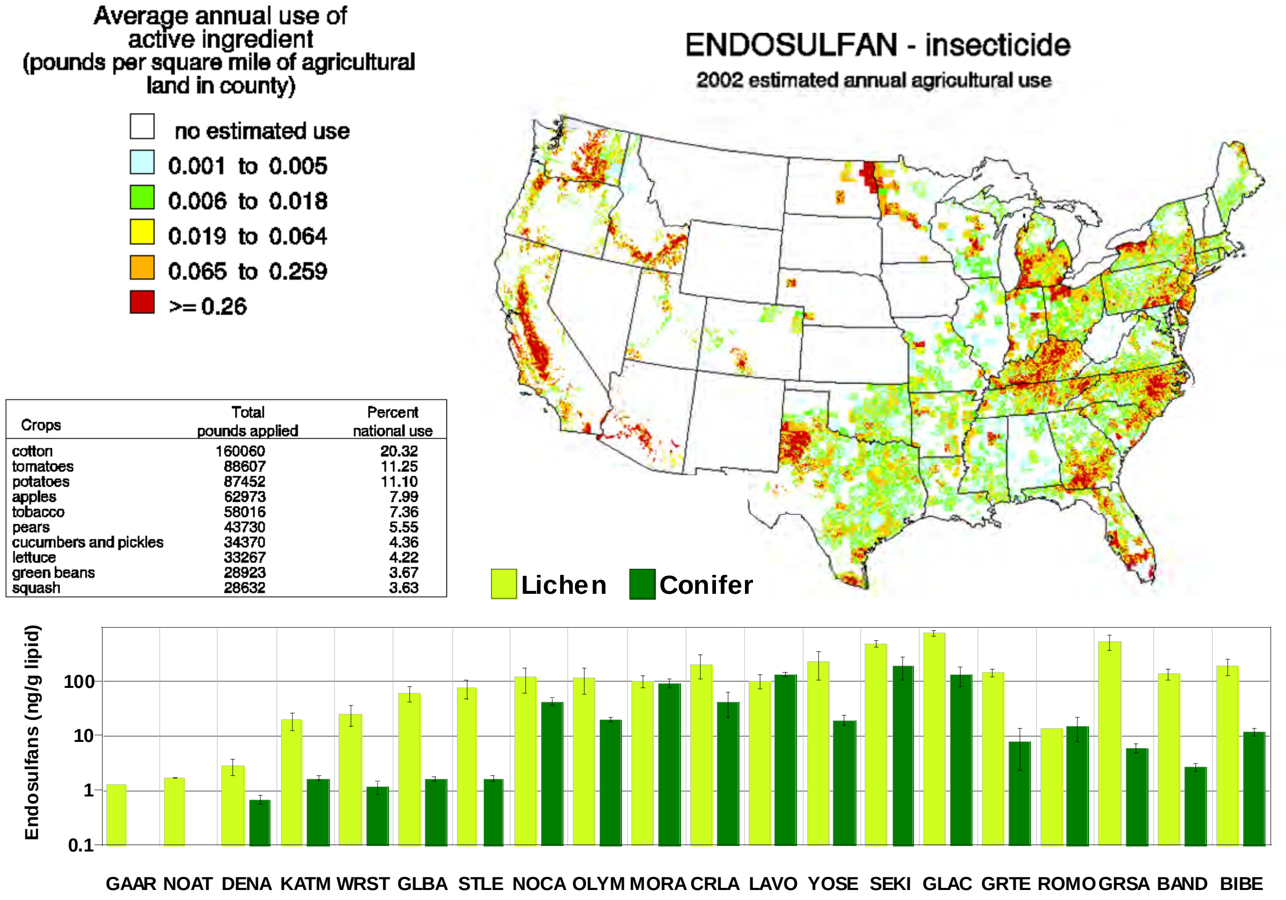
Source of chlorpyrifos data: http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m6009.



Crops	Total pounds applied	Percent national use
dry onions	233865	52.08
broccoli	94487	21.04
sod harvested	28200	6.28
cabbage	25590	5.70
cauliflower	14367	3.20
squash	13439	2.99
green onions	7272	1.62
collards	6920	1.54
dry beans	6771	1.51
strawberries	5905	1.31

Figure 4-15. Uses and Estimated Application Intensity in 2002 of the Current-Use Herbicide Dacthal in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng dacthal/g lipid conifer needles or lichens) from WACAP Parks. Dacthal was detected in vegetation in all parks, but the three parks with highest concentrations were YOSE and SEKI, downwind of the high-use San Joaquin Valley in California, and GRSA, in Alamosa County, Colorado (red patch in southeast Colorado). GLAC also had high concentrations; no data are available for Montana and Wyoming, but high-use areas in western Washington and northern Idaho are upwind of GLAC. Error bars indicate one standard error.

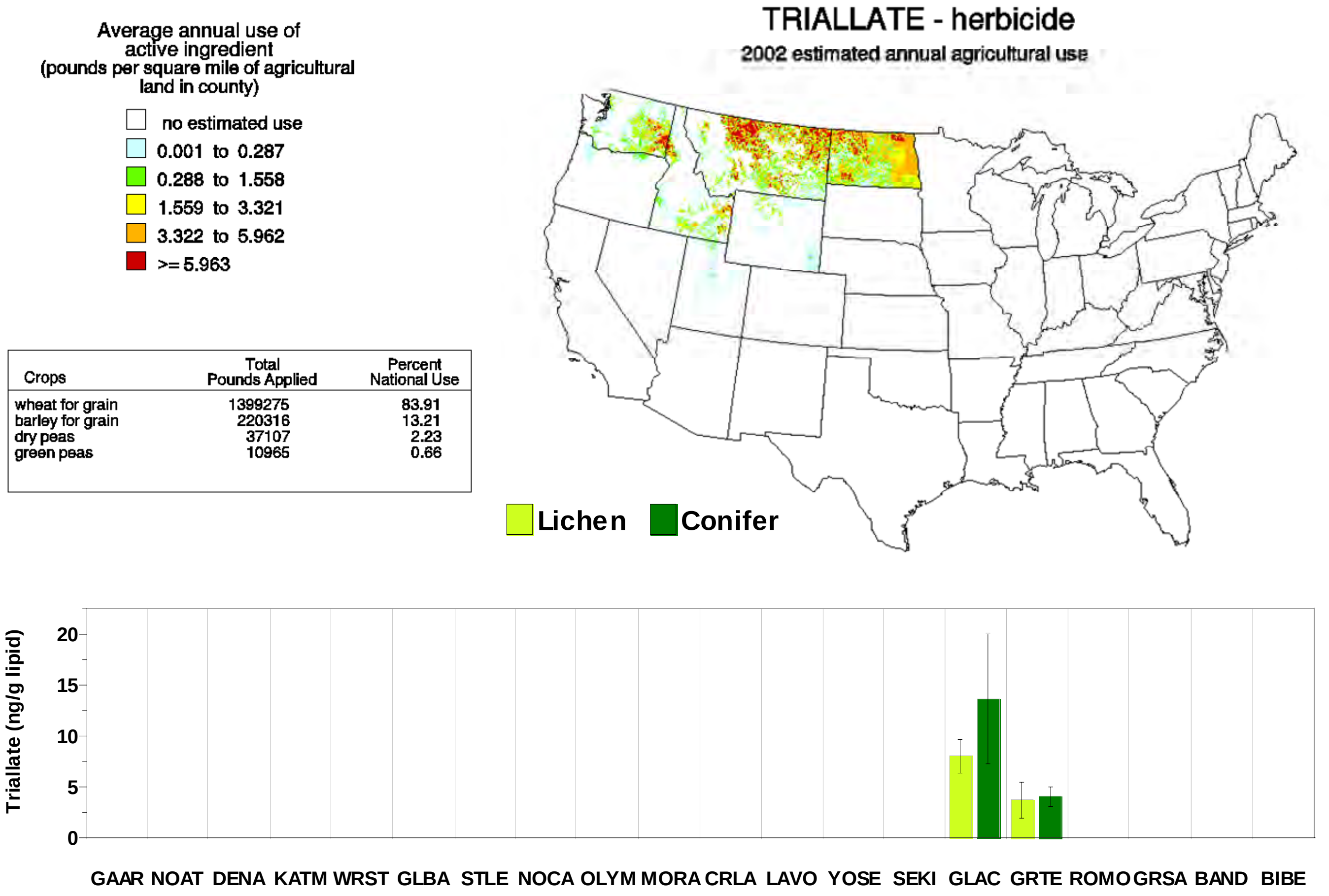
Source of dacthal data:
http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m1892.



Crops	Total pounds applied	Percent national use
cotton	160060	20.32
tomatoes	88607	11.25
potatoes	87452	11.10
apples	62973	7.99
tobacco	58016	7.36
pears	43730	5.55
cucumbers and pickles	34370	4.36
lettuce	33267	4.22
green beans	28923	3.67
squash	28632	3.63

Figure 4-16. Uses and Estimated Application Intensity in 2002 of the Current-Use Insecticide Endosulfan in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng endosulfan/g lipid conifer needles or lichens) from WACAP Parks. Endosulfans were detected in vegetation in all parks. No use data are available for Montana, Wyoming, New Mexico, or Mexico, hindering interpretation of results for GLAC, GRTE, BAND, and BIBE. But proximity to high-use areas appears to affect relative concentrations of endosulfans in other parks (NOCA, OLYM, MORA, CRLA, LAVO, YOSE, SEKI, ROMO, and GRSA). Error bars indicate one standard error.

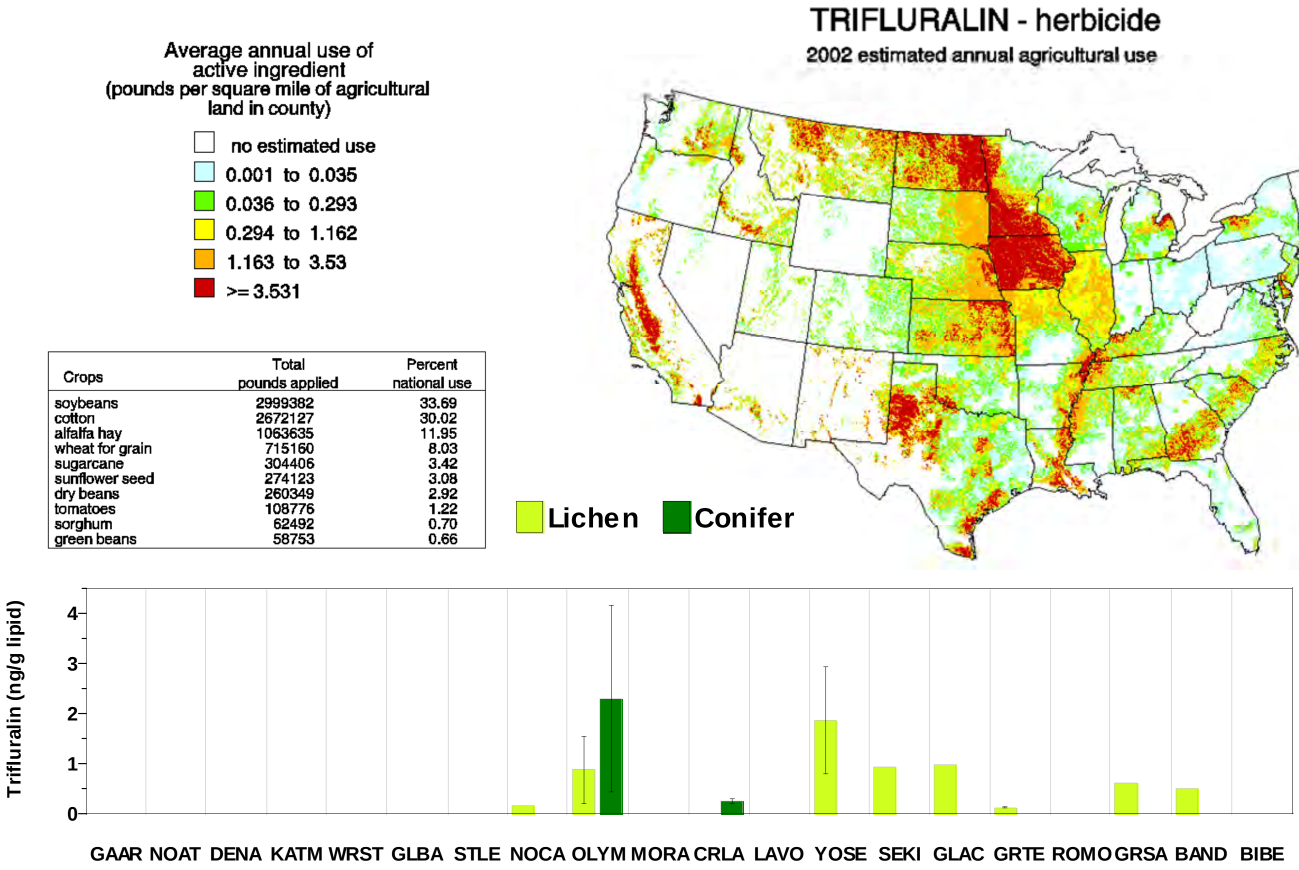
Source of endosulfan data:
http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m6019.



Crops	Total Pounds Applied	Percent National Use
wheat for grain	1399275	83.91
barley for grain	220316	13.21
dry peas	37107	2.23
green peas	10965	0.66

Figure 4-17. Uses and Estimated Application Intensity in 2002 of the Current-Use Herbicide Triallate in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng triallate/g lipid conifer needles or lichens) from WACAP Parks. Triallate is used most intensively in the northern states and was detected, correspondingly, only in vegetation from GLAC and GRTE. Error bars indicate one standard error.

Source of triallate data: http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m1790.



Crops	Total pounds applied	Percent national use
soybeans	2999382	33.69
cotton	2672127	30.02
alfalfa hay	1063635	11.95
wheat for grain	715160	8.03
sugarcane	304406	3.42
sunflower seed	274123	3.08
dry beans	260349	2.92
tomatoes	108776	1.22
sorghum	62492	0.70
green beans	58753	0.66

Figure 4-18. Uses and Estimated Application Intensity in 2002 of the Current-Use Herbicide Trifluralin in the Conterminous 48 States vs. Mean Concentration in Vegetation (ng trifluralin/g lipid conifer needles or lichens) from WACAP Parks. Trifluralin was detected in vegetation at low concentrations in nine parks, primarily in lichens. Parks where it was detected are downwind of high-use areas. Trifluralin was detected in OLYM (only at OLYM1) on the outskirts of Port Angeles, Washington. Error bars indicate one standard error.

Source of trifluralin data:
http://ca.water.usgs.gov/pnsp/pesticide_use_maps/show_map.php?year=02&map=m1361.

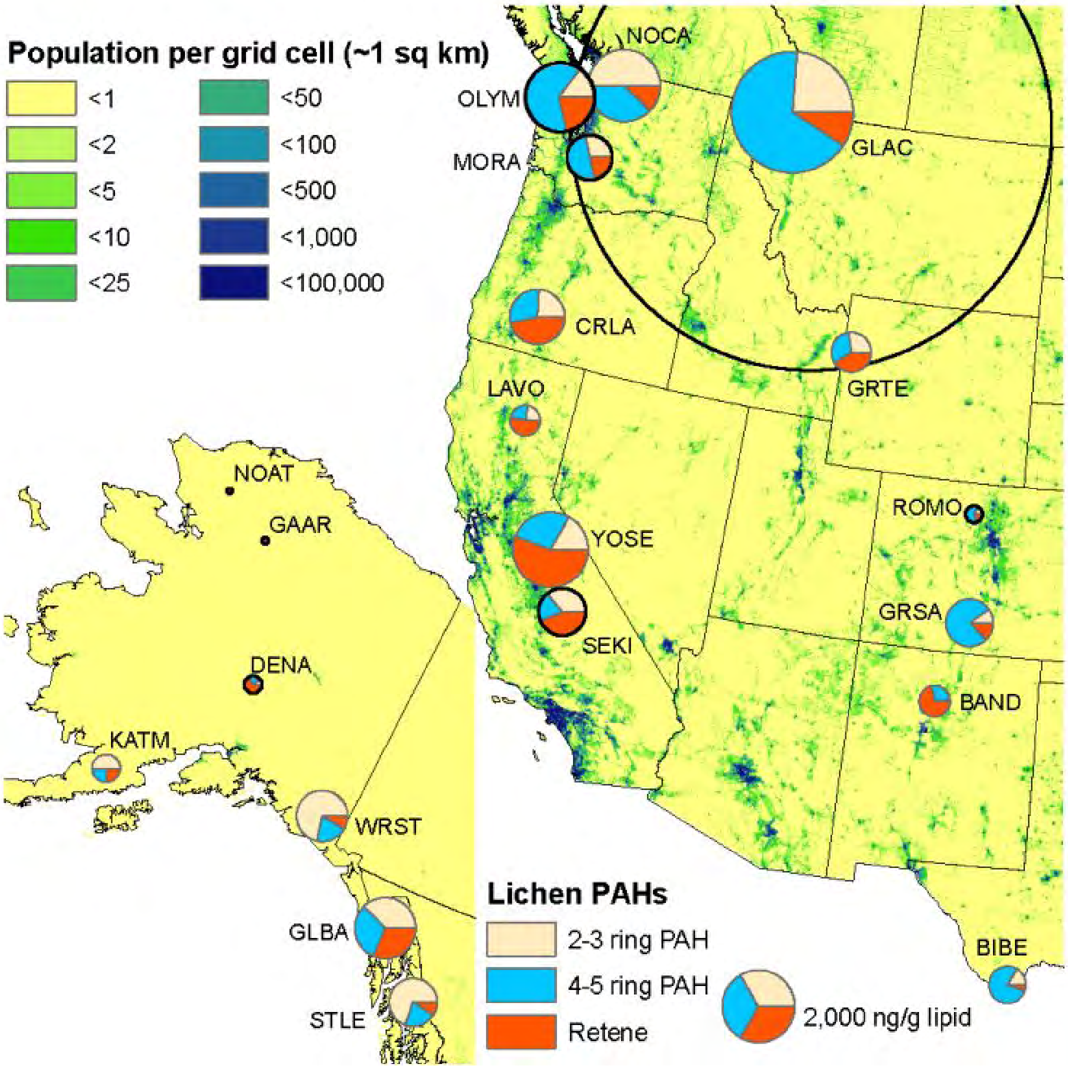


Figure 4-19. Concentrations (ng/g lipid) of PAHs in Lichens from Core and Secondary WACAP Parks Overlaid on a Map of Population Density. Circle area is proportional to total PAH concentration. Total PAH concentrations were lowest in Arctic Parks (< 10 ng/g lipid) and parks in central Alaska (< 500 ng/g lipid), increasing in concentration with decreasing latitude along the Pacific Coast from southeastern Alaska to southern California. Highest concentrations were in GLAC, where the black circle represents the true size of the total PAH concentration. Sites outlined in black are the core parks.

Possible explanations for greater SOC accumulations in lichens are:

1. Lichen material was on average older than conifer needles. Conifer needles were all sampled in the summer of their second year, whereas lichen samples were collected to represent the population on the site. Therefore, lichen samples, after homogenization in the laboratory, had a longer exposure and accumulation period than conifer needle samples. This explanation is valid only if SOCs in vegetation never equilibrate but continue to increase year after year; there is limited literature to suggest otherwise (see discussion in Chapter 5).
2. Epiphytic lichens were not buried under snow in wintertime, whereas conifer needles at higher elevation and higher latitude sites could be buried under snow from several weeks to many months of the year, reducing total exposure compared to lichens. The "lichen line" on trees demarcates the winter snow line; unlike conifer needles, epiphytic lichens usually do not survive extended burial.
3. Some physiochemical properties between lichens and conifer needles differed (e.g., surface chemistry or texture), predisposing lichens to more effectively accumulate some compounds or some forms of compounds (e.g., particulate vs. gas phase forms).

The chief advantage of sampling conifer needles is that their age is known and therefore, unless they are buried under snow in winter, their exposure period is also known. In contrast, lichen concentrations represent average concentrations in the lichen population that was sampled at the site, within which some individuals could be decades old and others only a few years old. Because coniferous forests cover an extensive land area in western North America and because the biomass of needles on a kg/ha basis is usually very much larger than lichen biomass, from an ecological perspective, conifer needle data are likely to be more relevant than lichen data. To the extent that contaminants concentrated in needles are deposited in litterfall or washed out in leachates, conifer needles must play a greater role than lichens in transferring contaminants to soils and soil organisms.

The chief advantage of sampling lichens is that their SOC concentrations are more likely to be above detection limits (e.g., PAHs at WACAP sites in GLAC) which makes it easier to detect differences between sites in mapping local contamination or elevation effects. In arctic and alpine ecosystems, where coniferous trees are absent, lichens can be a dominant component of the ecosystem and a good sampling choice. Analytically, the clean-up process was faster and instrument output was more readily interpretable for lichens than for conifer needles.

4.2.3.2.2 Differences in SOC Accumulation between Lichen Species

One of the assumptions of WACAP was that, within biological media types (i.e., lichens, conifer needles, or fish), differences between species could be minimized by lipid normalization. Although WACAP was not designed to specifically test this assumption, at the conclusion of the laboratory analyses, there were six sites (DENA5, WRST1, WRST5, OLYM5, and GLAC5) where SOC concentrations had been determined in multiple replicates of more than one species of lichen. A comparison of within-site means across species by one-way analysis of variance provided evidence that lipid normalization (i.e., reporting SOC concentration on a gram lipid basis) was largely successful in minimizing differences across species. Most comparisons showed no differences between species. However, significant differences between some species combinations for some SOCs did occur and the concentration differences were usually between 2- and 10-fold (Appendix 4A.1). For example, at WRST1, mean concentrations of HCBs and

PAHs were 2.5 times higher in the leafy epiphyte, *Platismatia glauca*, than in the leafy epiphyte, *Hypogymnia apinnata*. At WRST5, concentrations of dacthal, endosulfans, HCBs, a-HCH, g-HCH, chlordanes, PCBs, and PAHs were 5-17 times higher in *P. glauca* than in the pendant epiphyte, *Alectoria sarmentosa*. At OLYM5, concentrations of dacthal, endosulfans, and PCBs were 2.5-5 times higher in *Bryoria,* another pendant epiphyte, than in *A. sarmentosa.* Most notably, of the leafy tundra lichens, SOC concentrations were 7-50 times higher in *Flavocetraria cucullata* than in *Masonhalea richardsonii* for all SOCs except dacthal, which was not different. *Masonhalea* appears to be a very poor accumulator of SOCs.

When SOCs differed between species, they were usually consistently higher in one species than in another, but exceptions did occur. At GLAC5, concentrations of HCB, g-HCH ($p > F = 0.06$), chlordanes, DDTs, PCBs, and PAHs were 2-10 times higher in the leafy epiphyte, *Hypogymnia physodes*, than in the shrubby epiphyte, *Letharia vulpine*. However, *L. vulpina* had 2 times more g-HCH than *H. physodes*, and it also had detectable concentrations of chlorpyrifos, which was not detected in *H. physodes* at that site. Therefore, using the same species reduces error between sites by up to an order of magnitude. Because error among field replicates of the same species is fairly low (Appendix 4A.1), using the same species is an inexpensive way to improve detection of between-site differences. Based on WACAP results, *Masonhalea* should be avoided in future sample efforts. It is not a good accumulator of SOCs, nutrients, or metals, possibly because of its dense, glossy surface. *Flavocetraria cucullata* and *Cladina arbuscula* are better accumulators and could be comparable to epiphytes that are poor accumulators, such as *Alectoria sarmentosa* (Appendix 4A.8). *Flavocetraria cucullata* is readily recognizable and widespread in Alaska and in some moist, alpine areas of the northern conterminous 48 states.

In general, epiphytes are the best choice for sampling, but in dry, treeless areas of the conterminous 48 states, the rock lichen, *Xanthoparmelia,* appears to accumulate SOCs at concentrations similar to those in the epiphyte, *Usnea (*Appendix 4A.9). However, a higher proportion of total dry weight will be in soil mineral particles trapped between overlapping lobes of the lichen, some of which can be very time consuming, if not impractical, to remove. In addition, the burden of soil particulates in *Xanthoparmelia* might be magnified in windy or dusty sites, which might have happened in GRSA, because overlapping lobes trap soil particulates as the lichen grows.

4.2.3.2.3 Differences in SOC Accumulation between Conifer Species

The working assumption for the WACAP study design was that lipid normalization would minimize inter-species differences in SOC accumulation among conifers, as with lichens and fish. Unlike lichens (multiple species collected at some sites), only one species of conifer was collected at each site. Because conifer needles did not show elevation trends within parks, even when the same species were compared, mean SOC concentrations of different species from different sites within parks were compared. These means comparison tests (Appendix 4A.6) indicated that spruce (*Picea*), true fir (*Abies*), and Douglas-fir (*Pseudotsuga*) had fairly similar accumulation capacities, whereas western hemlock (*Tsuga*) was somewhat higher and pine (*Pinus*) was substantially lower, compared to the firs and spruce. See Figure 4-20 for a visual representation of these patterns.

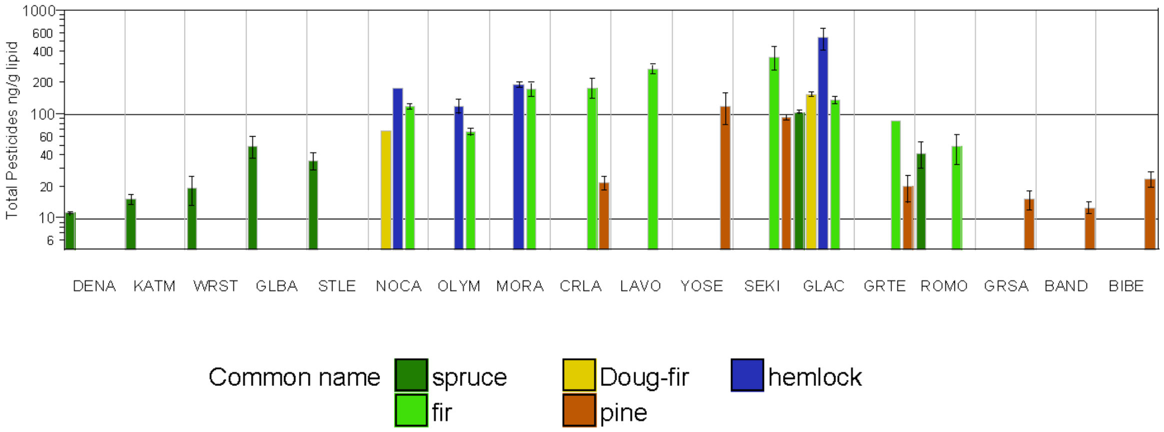


Figure 4-20. Comparison of Total Pesticide Accumulation in Conifer Needles by Species and Park. Although data were lipid normalized, intra-park differences among species indicate that some species are better accumulators than others (e.g., spruce and fir are comparable, hemlock is a somewhat better accumulator, and pine is the poorest accumulator). These differences might be attributable to needle morphology (see text for discussion). Mean concentrations in YOSE, GRSA, BAND, and BIBE would probably have been higher, had fir been sampled there instead of pine. Bar height indicates the mean; error bars indicate one standard error.

Specifically, firs usually accumulated substantially higher concentrations of SOCs than did pines, especially endosulfans (~10 × higher), dacthal (~2-5× higher), and historic-use HCHs and HCB (~ 3-5× higher). Western hemlock SOC concentrations were higher than those in fir by 1/3- to 3-fold. Douglas-fir was similar to true firs for most SOCs but was often 2-3 times lower in endosulfans and dacthal. Spruce was similar to fir and hemlock but tended to be ~5-10 times lower in endosulfans. These differences make sense from a needle morphology and tree architecture point of view (i.e., spruce, fir, and Douglas-fir needles have a similar flattened shape and size, whereas hemlock needles are shorter and pine needles are round and longer. Compared to fir and spruce needles, hemlock needles are more densely packed on the branches and pine needles are more loosely packed. All these factors could affect air circulation and needle surface area, and, together with differences in surface wax chemistry, affect absorption rates. Komp and McLachlan (1997) and Collins et al. (2006) have discussed these and other factors leading to interspecies variability. Figure 4-21 presents photos of the most commonly collected species of fir, spruce, and Douglas-fir in WACAP, compared with western hemlock and the most commonly collected pine.

The three genera that were most widely collected in national parks in the western United States were spruce in Alaska, fir in the Pacific Northwest, California, and northern Rocky Mountains, and pine in the southern Rocky Mountains. Although species differences after lipid normalization were lower (usually none to 5-fold) than park-to-park differences (up to 10-fold), species can nevertheless be an important source of error. To improve detection of differences among sites or parks, future researchers might choose to limit collections to a single genus, or to collect enough within-site replicates of multiple species to calculate a compensation factor for cross-species comparisons.

Figure 4-21. Needles of (A) Subalpine Fir, (B) Sitka Spruce, (C) Douglas-fir, (D) Western Hemlock, and (E) Lodgepole Pine. Similar morphology and arrangement on branches might help explain why SOC concentrations were usually similar among fir, spruce, and Douglas-fir. Hemlock tended to have higher concentrations of SOCs and pine had substantially lower concentrations of SOCs compared to spruce and fir; differences in needle length and density might partially explain this effect. Photos ©Susan McDougall (hemlock) and J.S. Peterson (all others) @ USDA-NRCS PLANTS database.

4.2.3.3 Elevational Gradients of SOCs in Vegetation

Several reasons explain why we might expect altitudinal gradients in SOC concentrations. First, many contaminants are present primarily because of regional sources (see Section 4.2.6). For such compounds, we would expect the greatest air concentrations, and therefore ecosystem exposure, to occur at the lowest altitudes. For contaminants associated with trans-Pacific/Asian sources (Jaffe et al., 2003; Killin et al., 2004), we would expect air concentrations and ecosystem exposure to occur at altitudes greater than 2,000 meters, because of the greater occurrence of transport at these altitudes (Jaffe et al., 2003). Finally, for contaminants that can undergo cold fractionation, we would expect an altitude gradient with highest concentrations at the highest and coldest elevations (Wania and Mackay, 1993; Blais et al., 1998; Simonich and Hites, 1995; Davidson et al., 2003; Davidson et al., 2004). It is also likely that several of these processes can operate simultaneously, thus complicating interpretation of the data.

Regression analysis of the combined WACAP lichen data provided strong evidence ($p \leq 0.014$) that concentrations of PCBs and the pesticides chlorpyrifos, dacthal, endosulfans, HCB, a-HCH, g-HCH, and chlordanes increased with elevation averaged across WACAP parks (Table 4-3). There was suggestive evidence ($p = 0.0875$) that DDT concentrations also increased with elevation.

Table 4-3. Linear Regression Model Results. Data are from all WACAP parks that met criteria*, for the fit of lichen SOC concentrations to increasing elevation after accounting for differences between parks.

SOC	Slope	SE	P-value	R^2	Estimated Ave. % Change in Concentration from 500 to 1,000 m
Chlorpyrifos	0.0035	0.0013	0.0117	0.5338	218
Dacthal	0.0010	0.0002	0.0001	0.9654	165
Endosulfans (sum)	0.0009	0.0002	0.0001	0.9541	157
Endosulfan I	0.0009	0.0001	0.0001	0.9454	157
Endosulfan II	0.0008	0.0002	0.0011	0.9297	149
Endosulfan sulfate	0.0009	0.0002	0.0001	0.9541	157
HCB	0.0012	0.0002	0.0001	0.9368	124
a-HCH	0.0013	0.0002	0.0001	0.8793	192
g-HCH	0.0016	0.0002	0.0001	0.8970	153
Chlordanes (sum)	0.0009	0.0002	0.0003	0.7878	156
Trans-Chlordane	0.0018	0.0005	0.0005	0.7684	217
Cis-Nonachlor	0.0009	0.0002	0.0001	0.7595	364
Trans-Nonachlor	0.0017	0.0005	0.0007	0.6971	236
DDTs (sum)	0.0004	0.0002	0.0875	0.9321	122
PCBs (sum)	0.0030	0.0009	0.0009	0.6174	165
PCB 118	0.0006	0.0002	0.0141	0.3786	135
PCB 138	0.0011	0.0003	0.0007	0.6589	161
PCB 153	0.0006	0.0002	0.0042	0.5345	150
PCB 183	0.0002	0.0001	0.0049	0.4552	178
PAHs (sum)	-0.0009	0.0002	0.0007	0.9374	-64
Fluorene	-0.0007	0.0002	0.0001	0.9479	-70
Phenanthrene	-0.0006	0.0001	0.0001	0.9754	-74
Retene	0.0015	0.0001	0.1443	0.4881	n.s.
Chrysene/Triphene	-0.0005	0.0002	0.0219	0.9271	-78
Benzo(a)anthracene	-0.0014	0.0003	0.0001	0.8998	-50

*Parks in models: BAND, CRLA, DENA, GLAC, KATM, LAVO, MORA, NOCA, SEKI, and STLE. Values for concentration change represent the average across all parks in the models. See Chapter 3 and Appendix 4A.11 for regression model details.

n.s. = not significant

By contrast, all the PAHs tested, except retene, decreased with elevation ($p \leq 0.0219$) (Table 4-3). The absolute change in ng/g lipid (non-transformed data) or percentage change (natural log transformed data) per 500 m increase in elevation varied by park, contaminant, and lichen species within park (Table 4-4). The bar charts in Figure 4-22 and Appendix 4A.10 show the concentration increases (or decreases) from lowest to highest elevations within each park and portray the magnitude and consistency of concentration changes across vegetated elevations of the WACAP parks.

Table 4-4. Simple Linear Regression Results of Lichen SOCs on Park and Elevation. Values represent concentration changes per 500 m elevation increment in ng/g lipid (non-transformed data) or percent change (natural log-transformed data) calculated for individual parks.

Compound	PARKS											
	BAND	**CRLA**	**DENA**	**GLAC**	**KATMF[1]**	**KATMH[2]**	**LAVO**	**MORA**	**NOCA**	**SEKI**	**STLEA[3]**	**STLEP[4]**
Chlorpyrifos	ND	7.20	ND	-1.40	ND	ND	ND	3.10	1.40	ND	ND	ND
Dacthal	156%	547%	128%	212%	332%	105%	182%	149%	165%	128%	192%	191%
Endosulfans	201%	386%	223%	182%	192%	547%	173%	192%	135%	116%	157%	105%
Endosulfan I	173%	521%	223%	173%	142%	234%	173%	157%	122%	142%	192%	128%
Endosulfan II	192%	426%	ND	259%	ND	ND	182%	149%	128%	111%	100%	173%
Endosulfansulfate	212%	349%	223%	182%	234%	605%	173%	223%	142%	111%	142%	100%
HCB	0.81	10.24	1.69	0.12	0.49	-0.42	0.12	0.64	0.00	0.16	0.06	0.56
a-HCH	192%	406%	300%	165%	165%	-90%	173%	300%	135%	182%	192%	100%
g-HCH	0.64	2.72	0.20	2.10	0.04	0.06	0.12	1.56	0.09	1.00	0.16	0.06
Chlordanes	0.01	8.41	ND	1.69	0.06	1.96	0.72	0.56	0.00	0.16	0.02	-0.06
t-Chlordane	0.10	6.30	ND	2.70	0.00	0.70	1.55	1.05	0.05	0.90	0.10	-0.50
c-Nonachlor	0.40	2.35	ND	1.55	0.10	0.60	0.55	0.35	0.10	0.50	0.10	-0.05
t-Nonachlor	0.35	5.60	ND	3.25	-0.20	1.20	1.25	0.80	-0.05	0.95	0.10	-0.75
DDTs	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
PCBs	1.25	11.3	ND	0.15	0.35	1.95	1.95	4.85	0.75	0.5	0.8	-0.25
PCB 118	NS	NS	NS	NS	NS	NS	NS	246%	NS	NS	NS	NS
PCB 138	0.35	4.40	ND	0.05	0.10	0.50	0.80	1.60	0.40	0.15	0.20	0.05
PCB 153	0.25	2.60	ND	0.20	0.20	0.60	0.50	1.20	-0.10	0.10	0.15	-0.15
PCB 183	0.15	0.20	ND	0.00	0.00	0.05	0.05	0.30	0.05	0.05	0.00	-0.05
PCB 187	0.30	1.25	ND	0.30	0.00	0.30	0.30	0.50	0.10	0.15	0.05	0.00
PAHs	-19.2%	-74.1%	-52.2%	-60.6%	-315.8%	-77.9%	-23.5%	-86.1%	-54.9%	-95.1%	-30.1%	-81.9%
FLO	ND	ND	ND	-74%	ND	-17.4%	-30%	105%	-52%	-86%	-44%	-74%
PHE	ND	-0.74	38.47	-0.70	1.16	-0.95	-0.33	1.00	-0.58	-0.78	-0.50	1.05
Retene	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
CHR/TRI	-60.6%	-90.5%	-182.2%	-60.6%	-258.6%	-28.7%	-5.0%	-81.87%	-81.9%	-81.9%	-22.3%	-60.6%
B(a) A	-40.7%	-33.3%	-173.3%	-54.9%	ND	ND	-36.8%	-19.2%	-60.6%	-74.1%	-9.07%	-35.0%

Note: Negative trends indicate decreasing concentration with increasing elevation. See Methods chapter and Appendix 4A.11 for model details. ND = no data, all samples below EDLs; NS = fitted line not a significantly better fit than the mean for this park ($p > 0.05$).

[1]KATMF = KATM *Flavocetraria cuculata*. [2]KATMH = KATM *Hypogymnia physodes*. [3]STLEA = STLE *Alectoria sarmentosa*. [4]STLEP = STLE *Platismatia glauca*.

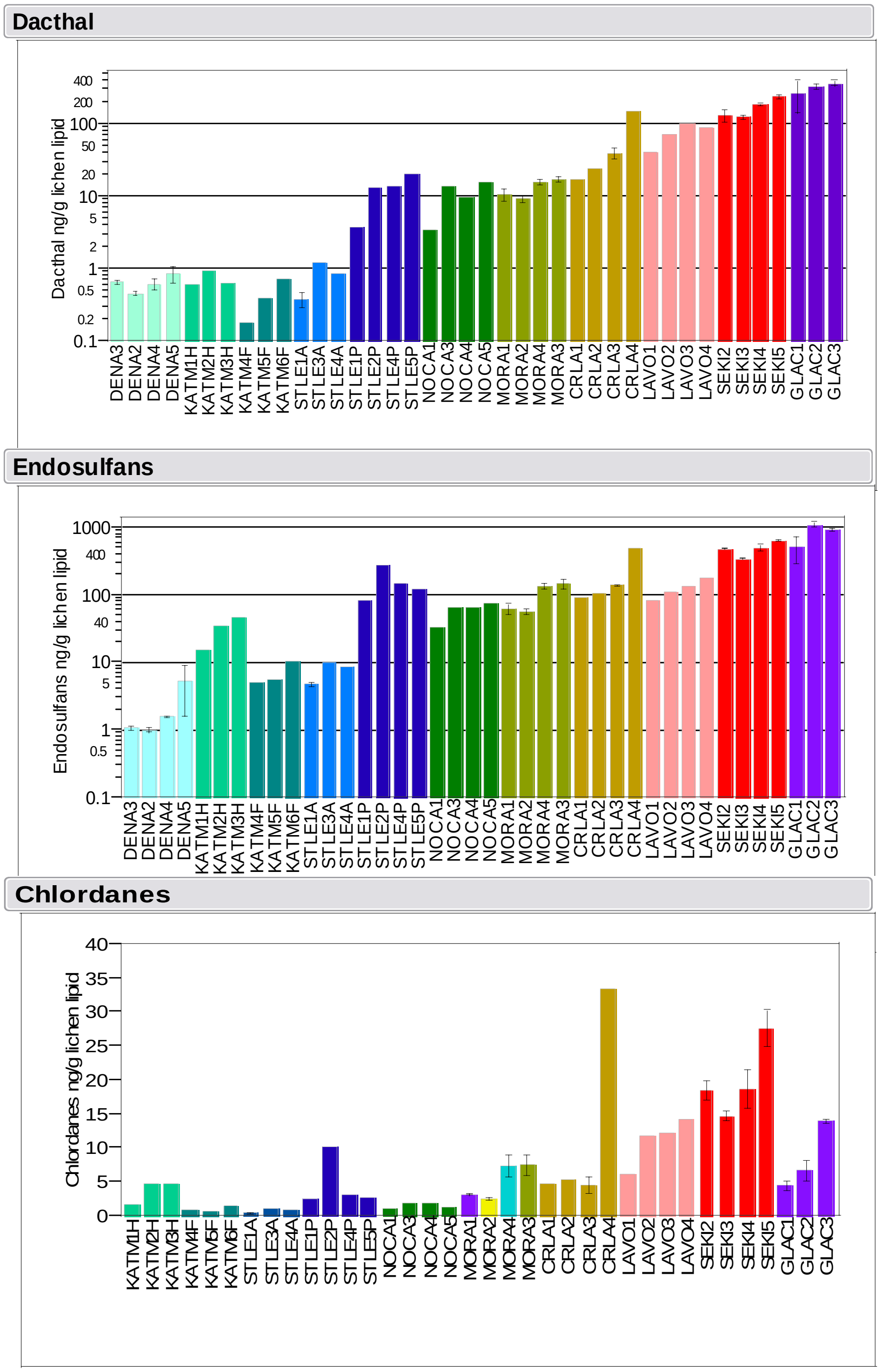


Figure 4-22. Elevational Gradients for Sum Dacthal, Sum Endosulfan, and Sum Chlordane Concentrations in Lichens. Within each park, sites are listed in order of increasing elevation. Codes H, F, A, and P refer to lichen species sampled (see Table 4-4). Bars show the standard error. Statistical analyses of elevational gradients are reported in Tables 4-3 and 4-4. Additional graphic displays for other SOCs are given in Appendix 4A.10. See Chapter 3 for data selection criteria for elevational trends analyses.

In general, changes in SOC concentration per unit change in elevation were within the same order of magnitude across parks (Table 4-4). Parks with similar percentage increases might have different absolute increases in SOC concentrations per unit increase in elevation. For example, endosulfan concentrations in the lichen *Flavocetraria cucullata* from KATM increased 192% per 500 m, with the lowest elevation averaging 0.13 ng/g lipid, whereas endosulfans in GLAC lichens increased nearly the same percentage, 182%; however, samples from the lowest elevation averaged ~ 500 ng/g lipid (Table 4-4, Figure 4-22). Doubling the latter concentration is more likely to have adverse ecological effects, especially if the total quantities of contaminants accumulated in vegetative biomass/ha are considered (see discussion in Chapter 5).

For the two parks, KATM and STLE, where two species were collected, the change in SOC concentration per unit elevation increase was as variable across species as it was between parks (Table 4-4). In KATM, we expected smaller SOC concentration changes in the tundra lichen, *Flavocetraria cucullata* (KATMF), compared to the epiphytic lichen *Hypogymnia physodes* (KATMH). Presumably the ground lichen would be buried under snow more days per year, whereas the epiphyte would be exposed to the air a greater number of days per year. Concentrations of SOCs were consistently higher in *H. physodes* (Figure 4-22, Appendix 4A.10), whereas elevational differences were often larger in *F. cucullata* (Table 4-4). Similarly, in STLE, *Platismatia glauca* (STLEP) appeared to be a better accumulator of SOCs than *Alectoria sarmentosa* (STLEA) (Figure 4-22; Appendix 4A.10) but changes in concentration per unit elevation increase were consistently larger for *A. sarmentosa*.

It is important not to over-interpret Table 4-4 because the slopes used to calculate percent change within individual parks are based on only 3-5 elevations; also, in the secondary parks, only one sample (three for the core parks) was collected per elevation. In contrast, the general models shown in Table 4-3 were developed from the combined WACAP dataset, providing better statistical power. Very high R-squared values and low standard errors for many compounds (e.g., dacthal, endosulfans, HCB, PAHs) indicate that concentrations of these important SOCs can be predicted accurately from elevation with general models (see Appendix 4A.11 for regression model details). For most PCBs and pesticides, concentrations at 1,000 m were 150-220% of concentrations at 500 m. PAHs were 50% to 80% lower at 1,000 m, compared with 500 m.

4.2.4 SOCs in Fish

Figures 4-1 to 4-4 and 4-6 show the concentrations of SOCs in fish; the data are reported in ng/g lipid. The dominant SOCs in fish were p,p′-DDE, dieldrin, PBDE 47, PBDE 99, PCB 153, PCB 138, dacthal, trans-nonachlor, HCB, and endosulfan sulfate. Dieldrin, p,p′-DDE, dacthal, and endosulfan sulfate concentrations were highest in fish from SEKI, ROMO, and GLAC. PBDE concentrations in fish across the WACAP parks (Figure 4-6) varied less than most other SOCs, both within and between lakes, and were highest in MORA fish, and lowest in fish in the Alaska national parks. Concentrations of the five major PCB congeners were comparable among fish from Alaska and Pacific coast parks (SEKI, OLYM, and MORA), and lower in fish from the Rocky Mountains (GLAC, ROMO) (Figure 4-4). Dacthal concentrations were highest in fish from SEKI, followed by ROMO and GLAC (Figure 4-1), and lower in parks in the Pacific Northwest (OLYM, MORA) and Alaska (DENA, NOAT). For most compounds, the variation in fish SOC concentrations within lakes was as large as the variations between lakes.

When compared to similar fish species collected from high-elevation lakes throughout Europe (Vives et al., 2004a), PBDE concentrations measured in fish in national parks in the western United States were, on average, approximately three times higher in concentration, after adjusting for differences between muscle and whole tissue concentrations (USEPA, 2000). Concentrations of most historic-use SOCs (HCB, DDTs, and HCHs) in fish in the western United States were comparable to or 2- to 9-fold lower than those in European mountain fish (Vives et al., 2004b). Because the European mountain fish and the WACAP fish studied included similar fish species collected from cold, oligotrophic lakes, within 3 years time, it is unlikely that the observed differences in the SOC concentrations are a result of fish accumulation differences or rapidly changing SOC emissions. Even a rapid PBDE doubling time of 6 years could not account for the 3-fold higher PBDE concentrations in fish in the western United States. This finding suggests that fish in national parks in the western United States are exposed to higher PBDE concentrations than similar European mountain fish, which is consistent with PBDE concentrations measured in other North American and European environmental compartments (Hites, 2004), and more recent European fish samples (Gallego et al., 2007).

Compared to fish collected from several alpine lakes in Canada (Demers et al., 2007), WACAP fish were significantly lower in HCHs and chlordanes (only ~ ¼ of the concentration) and comparable in concentrations of DDTs and HCB; dieldrin concentrations were approximately 3 times higher. Because the fish sampled in Canada and the western United States were of similar species and the lakes had similar productivity, these differences probably reflect differences in SOC exposure. Other than these, there are few observations of broad-ranging mountain fish DOC loads (particularly for CUPs) with which we can compare the WACAP fish data.

4.2.5 SOCs in Sediments

4.2.5.1 Spatial Distribution of SOCs in Sediments

Sediment cores provide information on the temporal changes of contaminant loadings in WACAP parks over the last ~150 years. Cores were collected from the lake sites in each core park by means of the methods described in Section 3.4.6.1. Because sediment data reflect an annual accumulation of material, they are reported as a flux (ng/m^2/yr), rather than a concentration. The sediment flux data have been corrected by lake “focusing factor,” as described in Section 3.4.6.2, which adjusts for differences in sediment accumulation for each watershed.

Figures 4-1 to 4-6 show the SOC fluxes in the WACAP lake surficial sediments corrected for sediment focusing. In these figures, we used the most recent year of sediment data to represent the surficial flux. Figures 4-23 to 4-29 show the temporal trends in SOC fluxes.

The most common CUPs detected in the surficial sediments were the endosulfans and dacthal. Endosulfans have the highest recent sediment flux of all CUPs. GLAC, OLYM, and MORA all had fluxes near 60 ng/m^2/yr. ROMO and SEKI were a factor of 5-7 higher at 290 and 420 ng/m^2/yr, respectively. Endosulfans at NOAT, GAAR, and DENA were at or below detection limits (see Figure 4-1). The most frequently detected groups of HUPs in the WACAP lake surficial sediments were the chlordanes and dieldrin (see Figure 4-3). Chlordanes were detected in every park, and concentrations were a factor of 40 higher at SEKI than at NOAT and GAAR. Sum DDTs were frequently detected at ROMO and SEKI. Surficial sediment fluxes of DDTs at these parks were 2,500 and 760 ng/m^2/yr, respectively.

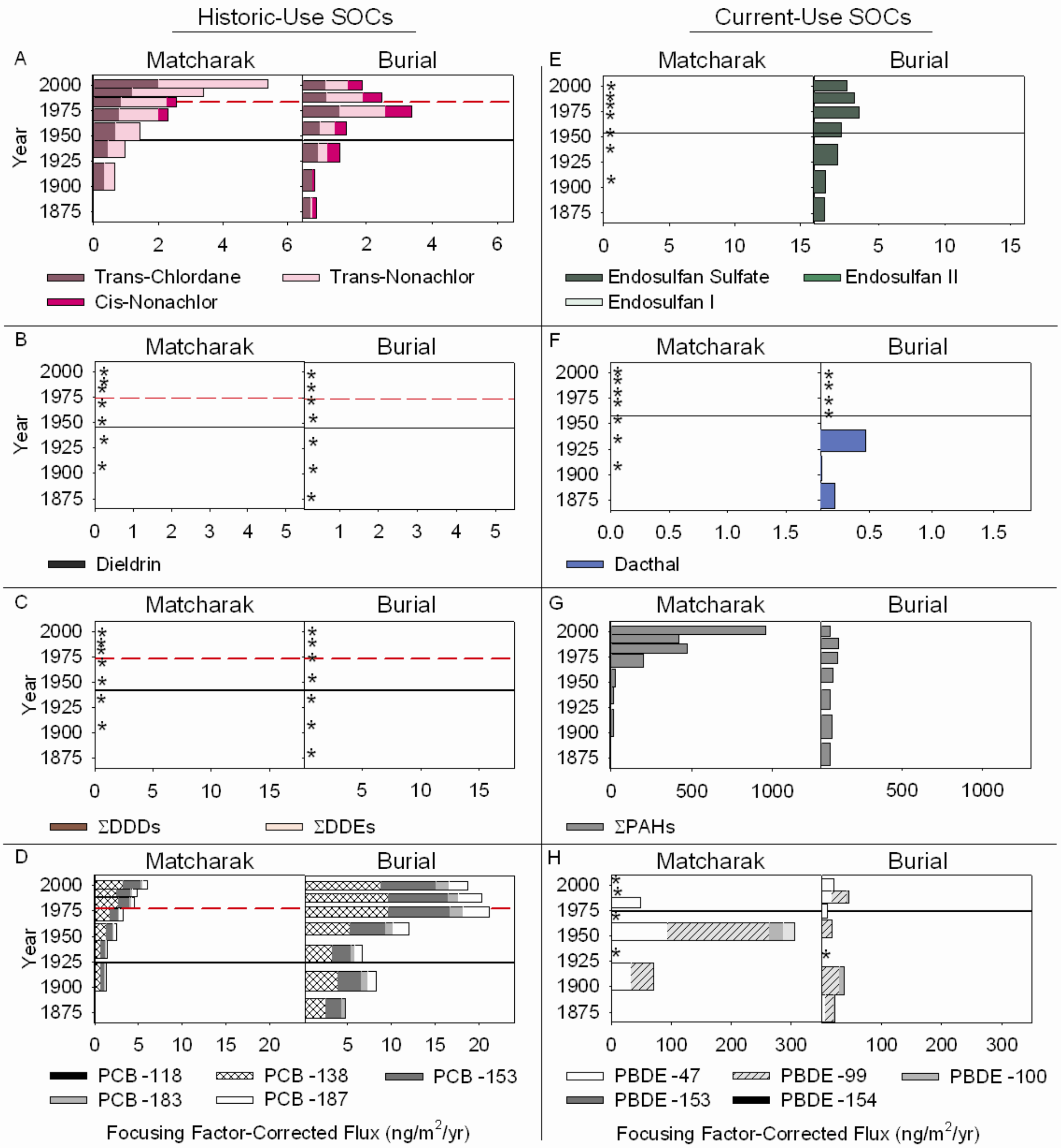


Figure 4-23. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in Matcharak Lake and Burial Lake Sediment Cores at GAAR and NOAT. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗) indicate below method detection limit.

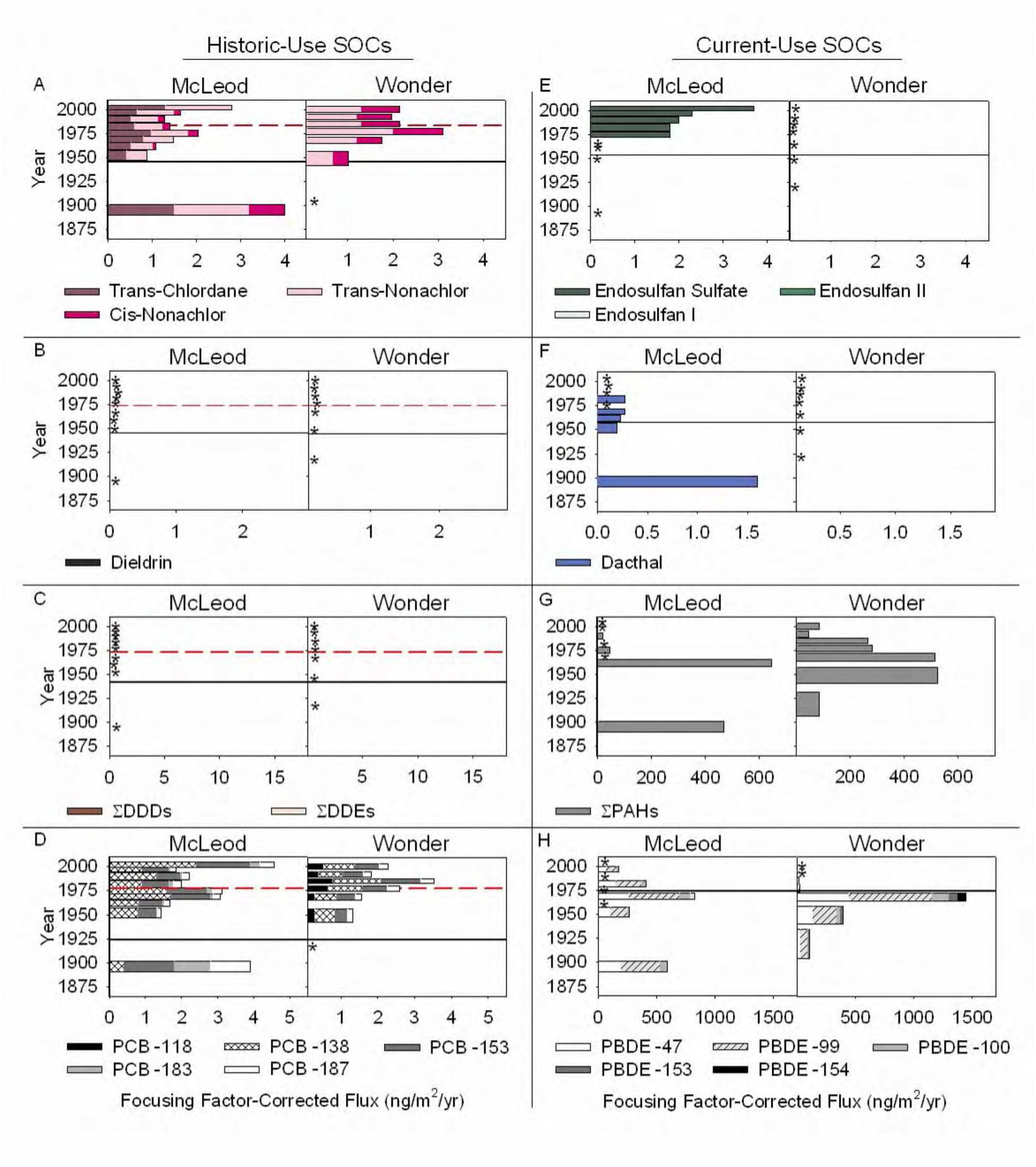


Figure 4-24. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in McLeod Lake and Wonder Lake Sediment Cores at DENA. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗)indicate below method detection limit.

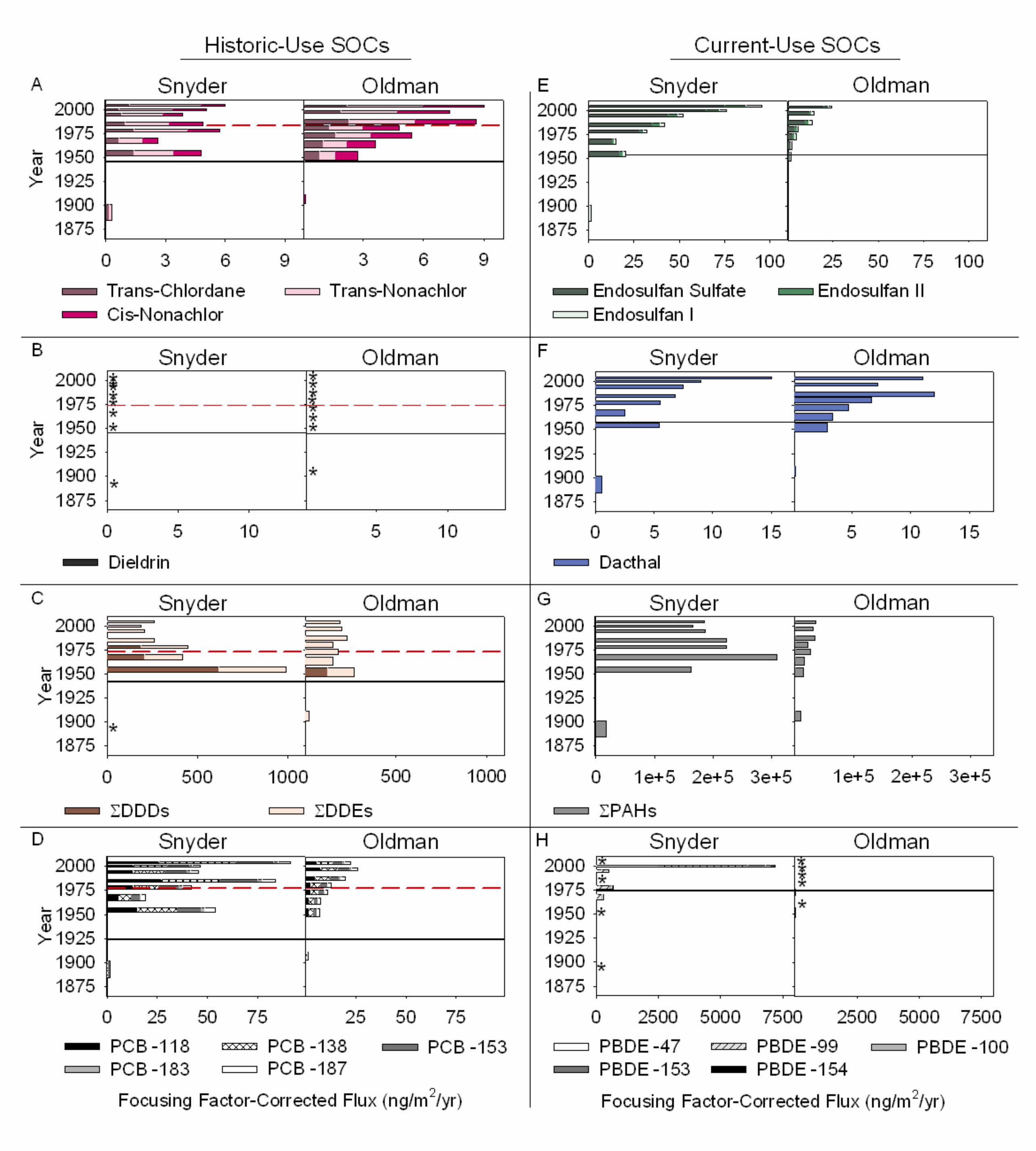


Figure 4-25. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in Snyder Lake and Oldman Lake Sediment Cores at GLAC. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗)indicate below method detection limit.

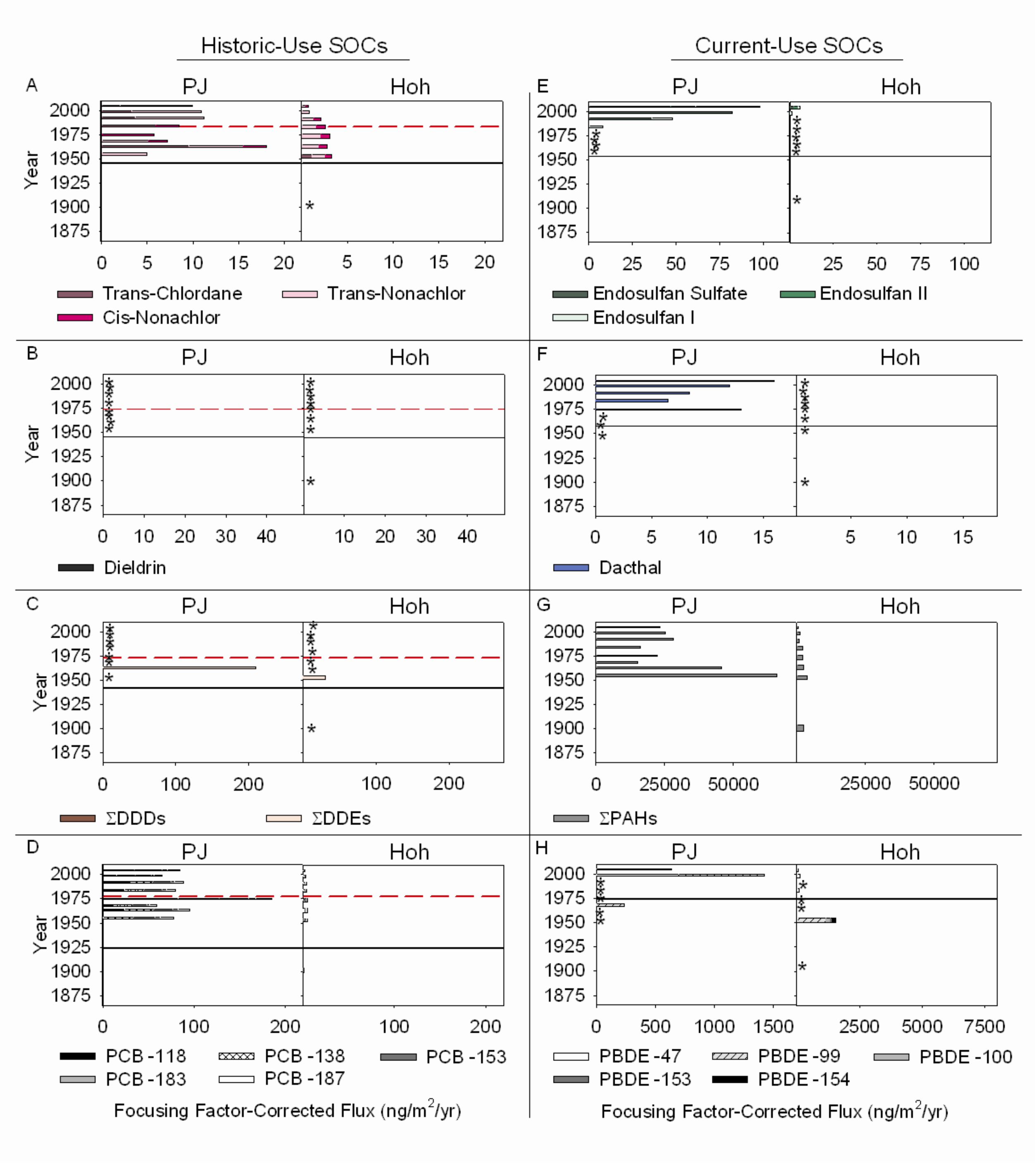


Figure 4-26. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in PJ Lake and Hoh Lake Sediment Cores at OLYM. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗)indicate below method detection limit.

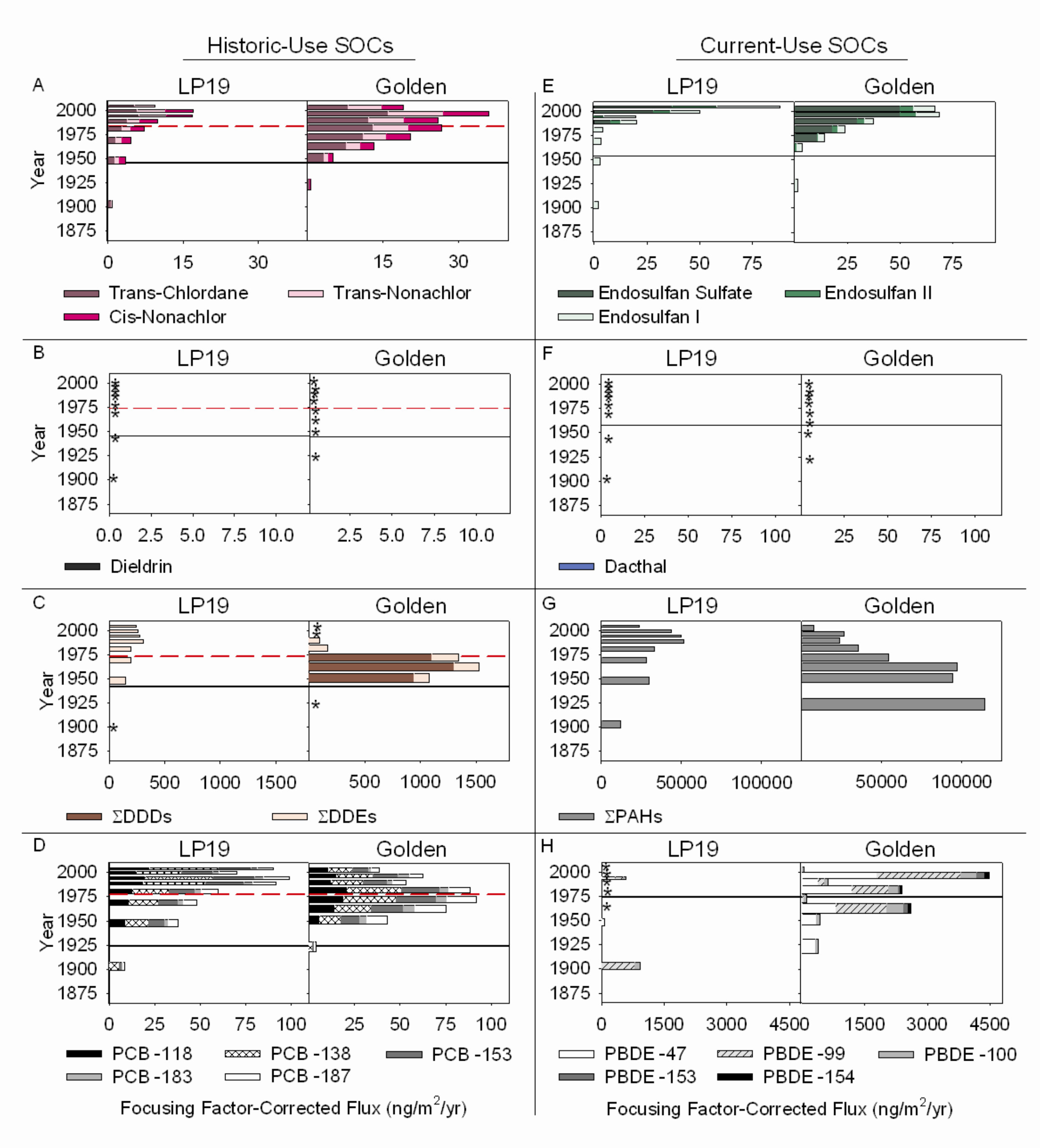


Figure 4-27. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in LP19 and Golden Lake Sediment Cores at MORA. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗)indicate below method detection limit.

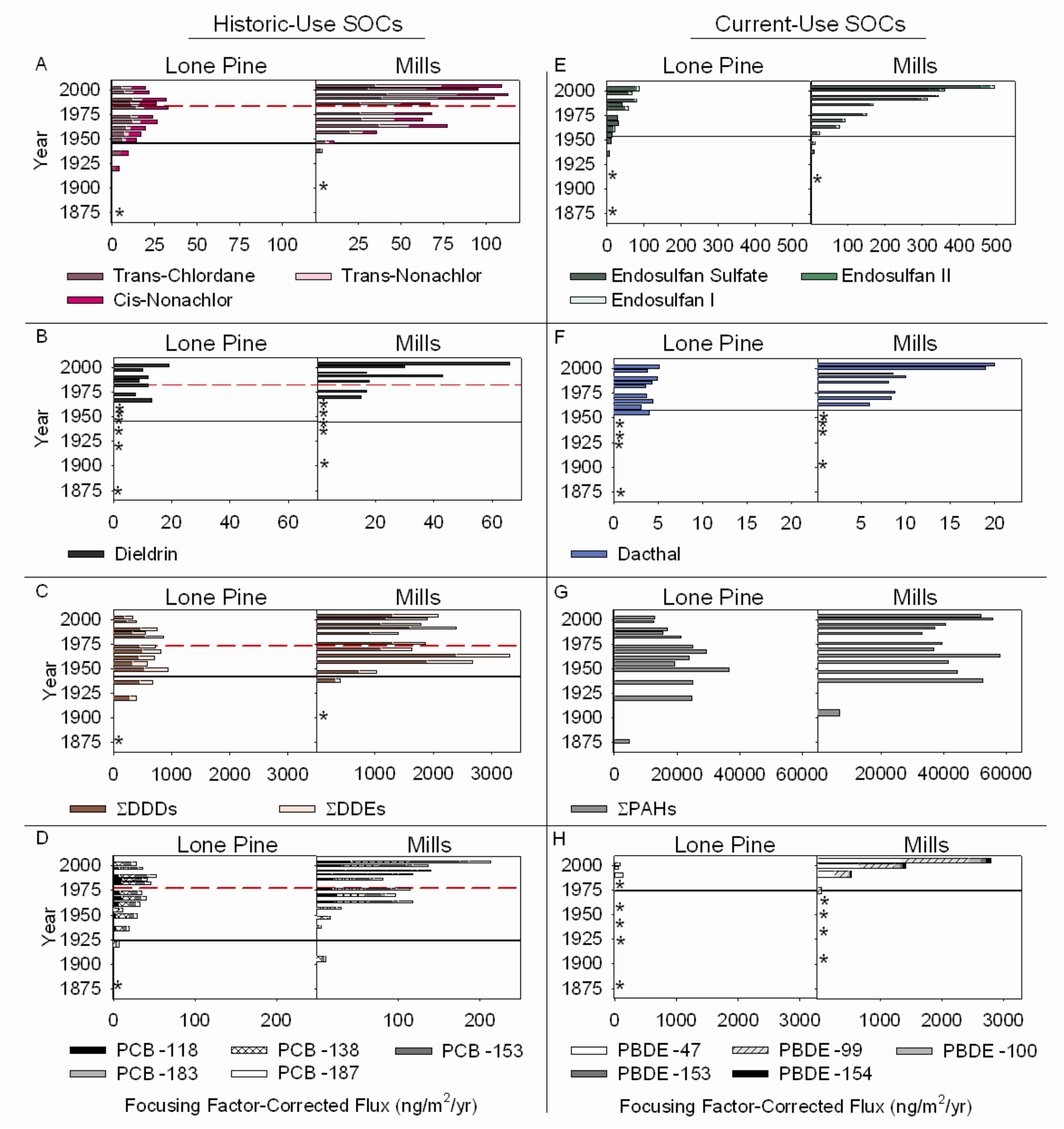


Figure 4-28. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in Lone Pine Lake and Mills Lake Sediment Cores at ROMO. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (∗)indicate below method detection limit.

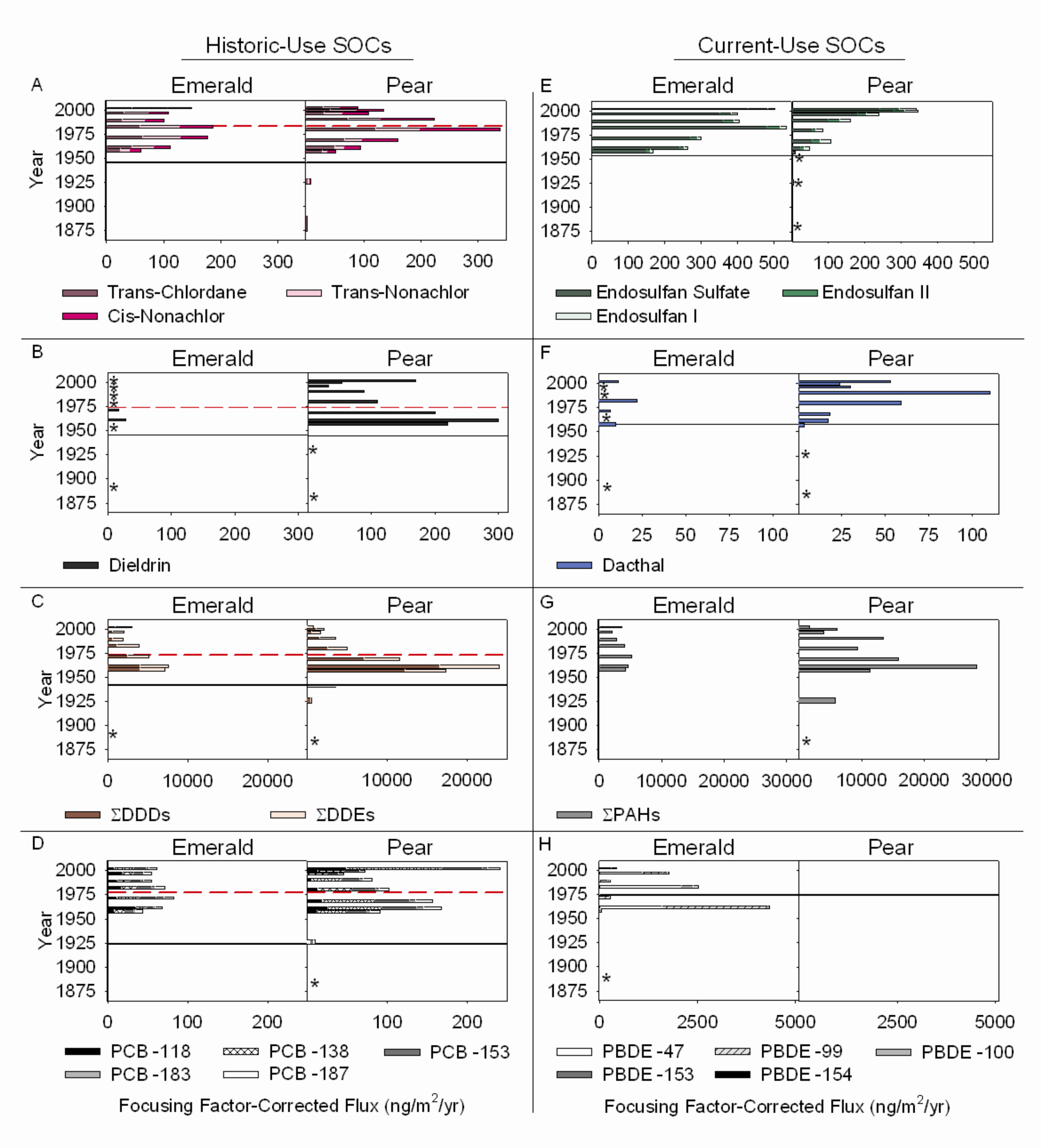


Figure 4-29. Focusing Factor-Corrected Flux (ng/m^2/yr) Profiles of Current- and Historic-Use SOCs in Emerald Lake and Pear Lake Sediment Cores at SEKI. Solid lines (——) indicate US registered use dates, dashed lines (– – –) indicate US restriction dates, and asterisks (*)indicate below method detection limit.

PCBs were detected in all surficial sediments, and were highest at low latitude sites. The lowest focusing factor-corrected fluxes were at DENA, NOAT, and GAAR. The highest fluxes were found at SEKI and ROMO (see Figure 4-4).

PBDE fluxes were above the method detection limits in the surficial sediment only from ROMO. Within ROMO, Mills Lake, located on the east side of the Continental Divide, had PBDE focus-corrected flux an order of magnitude greater than Lone Pine Lake, which is located on the west side of the Continental Divide. This finding is discussed further in Section 4.2.6.3.

PAHs had the highest surficial sediment flux of all SOCs in the WACAP sites. As it did for the vegetation and snow samples, GLAC (Snyder Lake) had the highest surficial sediment PAH flux. This finding is discussed further in Section 4.2.6.2.

4.2.5.2 Temporal Distribution of SOCs in Sediments

Lake sediment analysis can be an extremely useful tool for evaluating the history of contaminant loading to a lake, but its utility is dependent upon several key assumptions: (1) the constituent of interest is stable (i.e., the compound is persistent and does not move appreciably as a result of diagenesis within the sediment) and (2) the sediment dating profile can be reasonably established through appropriate isotopic dating techniques. The WACAP sediment analysis meets both of these objectives for the target contaminants (both SOCs and selected elements). The fairly short gravity cores that were obtained from each lake typically penetrated to a depth going back to at least 1850. Some cores from lakes with very slow sedimentation rates penetrated much further back in time. We collected two cores from each lake, and if the first core dated out well with the radioisotope techniques, we accepted it for further analyses. If the first core could not be clearly dated, or if other concerns were apparent, we examined the second core and then selected the most appropriate of the two for further analysis. In all cases, one of the two cores displayed an acceptable dating profile.

For SOCs, given the expense of the analytical measurement, we carefully selected the exact slices of sediment for which we would perform analyses. These slices were selected and analyzed incrementally so that we would end up with a profile that maximized depiction of trends from pre-industrial times to the present. In general, we allocated approximately eight core slices per core for a complete SOC analyses. The results of this work are displayed in Figures 4-23 to 4-29). Each figure shows the pair of lakes for a particular WACAP park side by side, and the most prevalent SOCs are displayed by date. All figures use focus-corrected flux, so that comparisons among the lakes can readily be made. The solid horizontal lines in each figure represent the registration date for the specific SOC and the dashed lines represent the date of US restriction, if appropriate. The asterisks (*) indicate values below the method detection limit.

In most cases, the sediment SOC profiles are as expected with regard to the history of SOC use and regulation in the United States. Most do not appear in the sediment profiles until the date (sediment depth) that they were registered. After US restriction, most SOC concentrations began to decline; however, they have not reached zero because of revolatilization from various ecosystem sinks (including agricultural soils) and subsequent atmospheric deposition. For those cases in which the compound appears before the time of registration, we suspect that bioturbation and/or diffusion of the chemical within the sediment profile are responsible.

An examination of all seven figures reveals three groupings, with respect to the overall flux of SOCs to the lake sediments: high (ROMO, GLAC, SEKI), intermediate (OLYM, MORA), and low (DENA, NOAT, GAAR). Sediment profiles of SOCs from SEKI and ROMO have the highest flux for most SOCs. Most of the SOC profiles for these two parks show an increase in specific SOCs near the time of registration. For SEKI lakes, there is often a decrease after the time in which the use of the specific compounds was restricted in the United States. In the ROMO lakes, there is good agreement within the sediment cores concerning the appearance of the compounds with time of US registration, but there has been virtually no decrease in deposition since use was restricted in the United States. This pattern might be a result of SOCs re-volatilizing from historic sources and undergoing atmospheric transport and deposition to remote ecosystems. A similar result was observed by Donald et al. (1999).

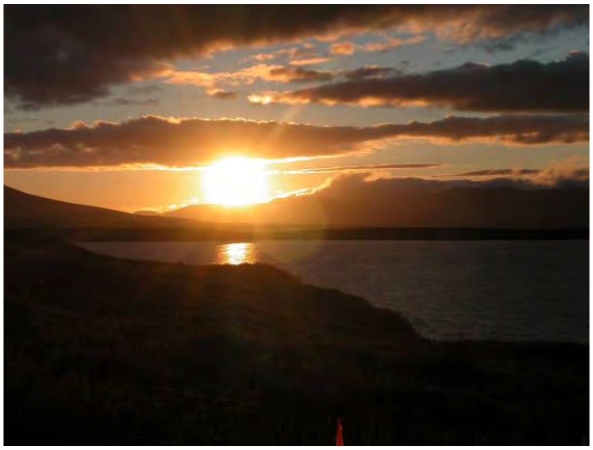
The profiles for specific SOCs from the paired lakes from each park generally show the same temporal pattern; however, the magnitude of flux to the sediments is frequently quite different. The differences in flux between sites in the same park could result from a variety of factors, including actual differences in airborne concentrations and deposition, differences in precipitation type and rate, differences in the way the watershed processes these compounds, and differences in mobility and delivery from the watersheds to the lake sediments themselves. Examining these issues for all sites is beyond the scope of WACAP, but will be addressed for ROMO as part of this work (Usenko et al., in press).

Several of the SOC sediment profiles stand out with much higher concentrations. Endosulfans and chlordanes are much higher at Emerald Lake (SEKI) and Mills Lake (ROMO), compared with all other sediment profiles, even those for the other lake in the same park. PAHs are significantly greater at Snyder Lake (GLAC) compared with all other lake profiles. This finding is consistent with PAH results at GLAC in other media, and is discussed further in Section 4.2.6.2.

For other SOCs, some concentrations were below our detection limit. This was the case for the entire profile of dieldrin, and for sum DDD and sum DDE, for all six lakes in MORA, OLYM, and GLAC. PCBs were lower in the intermediate lakes than in the high group, but are detectable throughout all profiles. Trends in PCB concentrations appeared to be stabilized or declining in the intermediate lakes, whereas two of the four lakes in the high group clearly had the highest PCB value at the surface of the core, which suggests a recent increase in flux of PCBs to the highest group.

SOC fluxes were lowest at the sites in Alaska (DENA, NOAT, GAAR), throughout their profiles. This is undoubtedly a result of the fact that these sites are long distances from major urban, industrial, and agricultural activities, and that precipitation, an important vector of SOC deposition, is generally lower at these sites. Chlordane and its major constituents, along with PCBs, were detectable in all Alaska lake sediment profiles, but at very low concentrations.

The group of contaminants most abundant in the sediments differed from those most common in snow and fish, primarily because of the different affinities SOCs have to partition among water, particulates, and lipid. Snow typically contains hydrophilic compounds, and some hydrophobic compounds can be associated with particulate deposition. Fish tend to accumulate compounds that are lipophilic. Lake sediments are a mix of organic and inorganic particles. Therefore, the contaminant histories in the sediments are influenced strongly by the watershed and lake processes leading to sedimentation, and would not be expected to have the same dominant suite of SOCs as snow and fish. It is difficult to compare SOC patterns across matrices; nonetheless, the sediments give information on the temporal changes in exposure to these contaminants.



Lake Matcharak

McLeod Lake

Wonder Lake

Burial Lake

4.2.6 Source Attribution for SOCs

4.2.6.1 Sources of Pesticides

Some of the pesticides detected in both annual snowpack and in surficial sediment in WACAP lakes include dacthal, endosulfans, dieldrin, and chlordanes. SEKI, ROMO, and GLAC had the highest pesticide concentrations in 3 years of annual snowpack measurements and surficial sediment fluxes.

In an analysis of the first year of WACAP snow data (collected in 2003), Hageman et al. (2006) found a correlation between regional agricultural intensity and the concentration of several pesticides in WACAP snow, including both current-use and historic-use pesticides. They used the linear relationship between percent of regional agriculture and log concentration to estimate the fraction of each pesticide attributable to regional sources (within 75, 150, and 300 km). This model assumes that the amount of pesticide present in the snow in the Alaska parks was entirely from global sources and that the global contribution was constant at all parks. We have updated this analysis to include all 3 years of WACAP snow data. Figure 4-30 shows the percentage of pesticides related to regional sources, within 150 km of each park, by means of this method.

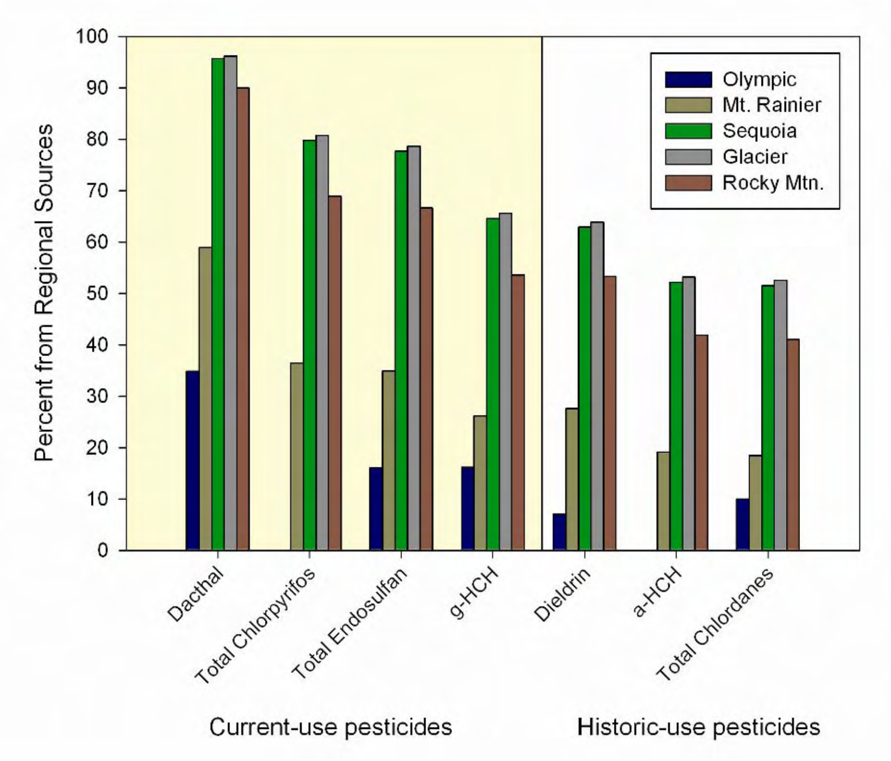


Figure 4-30. Percentage of Total Pesticide Concentration Related to Regional Sources. Regional is defined as within 150 km. Calculations use snow data collected from the springs of 2003-2005.

A small amount of agriculture occurs in Alaska, but for this analysis, the percentage of cropland intensity is insignificant. For GLAC and SEKI, the calculated contribution attributable to regional sources and transport is 80-100% for current-use pesticides, such as dacthal, total chlorpyrifos, and endosulfans. Even for some HUPs, such as dieldrin, a-HCH, and HCB, the pattern suggests a significant influence from historical regional agriculture. Presumably, this is a result of revolatilization of persistent SOCs that were applied to soils before the United States bans on agricultural usage.

Figures 4-12 and 4-13 show plots of SOC concentrations in lichens and conifer needles, respectively, overlaid on a map of agricultural intensity. For both lichens and conifer needles, the highest concentrations were measured in parks adjacent to the most intensive agricultural regions. In addition, parks with highest SOC concentrations were dominated by CUPs, usually endosulfans (see also Figure 4-31). At SEKI, the highest SOC concentrations in vegetation were endosulfans, but dacthal was the dominant SOC in snow (see Figures 4-1 and 4-7). This finding might reflect seasonality of sources, usage, or differences in uptake by snow and vegetation.

At parks with lowest overall concentrations of SOCs, HUPs made a larger contribution to total pesticide concentration. Concentrations of HUPs in Alaska parks were not very different from concentrations in parks in the conterminous 48 states. The results of Hageman et al. (2006) suggest that even for HUPs, regional agricultural sources are a good predictor for concentration in snow, presumably because the pesticide burden has revolatilized from soil and other sinks. For HUPs, regional agriculture explains 20-80% of the snow concentrations, with presumably global sources accounting for the remainder (see Figure 4-30).

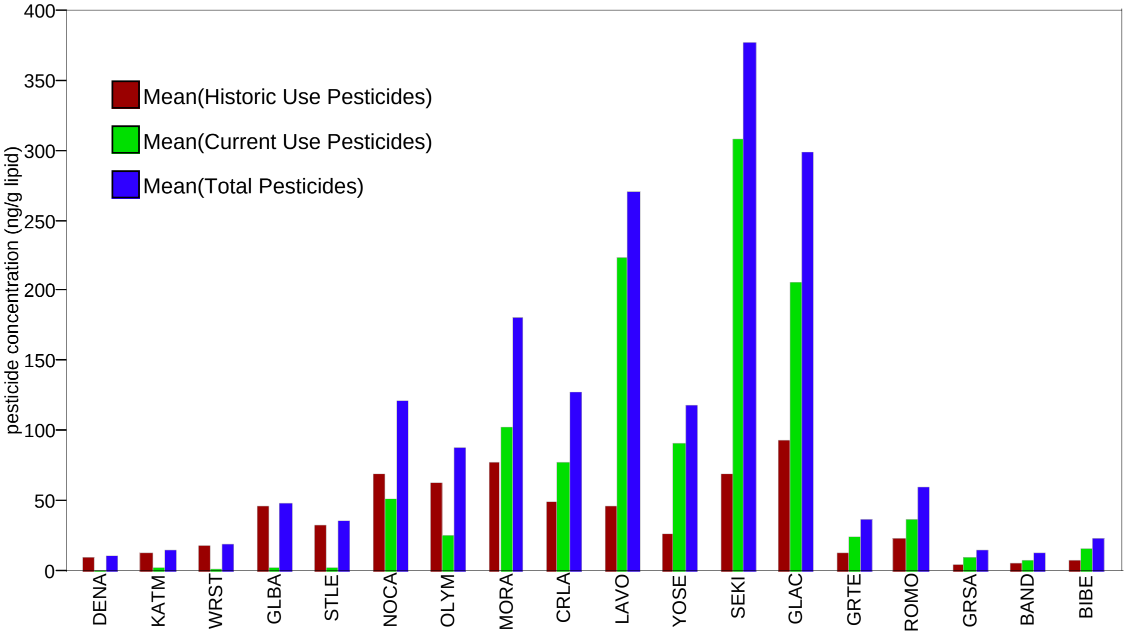


Figure 4-31. Mean Concentrations of Historic-Use (HCB, HCHs, Chlordanes, DDT, Dieldrin) and Current-Use (Trifluralin, Triallate, Chlorpyrifos, Dacthal, Endosulfans) Pesticides in Two-Year-Old Conifer Needles from WACAP Parks. Parks are ordered, left to right, from north to south along the Pacific Coast (DENA → SEKI), and from north to south in the Rocky Mountains (GLAC → BIBE). Current-use pesticides were not detected often in Alaska parks, comprised about one-third to one-half the total pesticide concentrations in northern Washington, and most of the pesticide burden elsewhere. Conifer needles were not sampled in NOAT and GAAR. Total pesticide burdens (current use + historic use) were highest in national parks of Washington, Oregon, California, and Montana.

Some specific pesticides in park vegetation could be influenced by regional and local application rates. Because different types of crops are grown in different parts of the United States, application rates of crop-specific insecticides and herbicides varies across the country.

Comparison of maps of application rates of chlorpyrifos, dacthal, endosulfans, triallate, and trifluralin in the western United States (Figures 4-14 to 4-18, respectively) and concentrations measured in vegetation suggest a relationship, especially if air mass back trajectories are considered (see Section 4.5).

Pesticide application rate does not correspond to pesticide concentrations in vegetation. For example, chlorpyrifos is applied at higher rates than endosulfans and dacthal, but concentrations in vegetation were low, probably as a result of the differences in the physico-chemical properties of these pesticides and their relative affinities to accumulate in vegetation. In addition, pesticide use data is missing for some western states and counties, limiting our ability to identify source regions.

4.2.6.2 Sources of PAHs at Glacier National Park

Previous studies have identified a relationship between PAH concentrations and proximity to urban regions (Garban et al., 2002; Hafner et al., 2005). Figure 4-5 shows the concentration of sum PAHs in vegetation, snow, and sediments. Concentrations of PAHs at GLAC were 1 to 2 orders of magnitude greater than at any other site, in these matrices. Figure 4-19 shows the concentration of sum PAHs in lichen at core and secondary parks, overlaid on a plot of population density. In contrast to the previous studies mentioned, a correlation with population is not present in the WACAP data, in large part because of the high PAH concentrations and low population density near GLAC.

However, the PAH concentrations in GLAC are not uniform across the park. Measurements in the watershed (Snyder Lake) closest to Columbia Falls showed significantly higher PAH concentrations. The sum PAH concentrations in snowpack, lichens, and surficial sediment were a factor of 7.7, 32.8, and 5.3 greater, respectively, in the Snyder Lake catchment (west of the Continental Divide) than in the Oldman Lake catchment (east of the Continental Divide). The PAH concentrations at Snyder Lake were the highest among all WACAP sites, whereas concentrations at Oldman Lake were comparable with those at sites in other parks. Referring to Figure 4-25, we see also that the PAHs in the Snyder Lake sediment core increased substantially in the early-mid 1950s. We believe the presence of high concentrations of PAHs at GLAC are related to the aluminum smelter in Columbia Falls, Montana, which came on-line in 1955 (Usenko et al., in press).

The electric-powered aluminum smelter in Columbia Falls operates with Söderberg aluminum smelting technology (Columbia Falls Aluminum Company, 2007). The smelter resides on the Flathead River (west of the Continental Divide), approximately 10 km southwest of GLAC and approximately 45 km southwest of Snyder Lake. Outflow from Snyder Lake forms a tributary of the Flathead River. Aluminum smelters that use Söderberg technology are known emitters of fluoride and PAHs, and can be significant local PAH sources in rural areas (Booth and Gribben, 2005; International Aluminum Institute, 2007). According to the USEPA, this specific smelter has been releasing hydrogen fluoride to the atmosphere at a rate of ~65 tons per year from 1999 to 2004 and PAHs to the atmosphere at a rate of ~14 tons per year from 1999 to 2005 (USEPA, 2007a). A previous study (National Park Service, 1998) suggests that fluoride, emitted to the atmosphere from the smelter, undergoes atmospheric transport and deposition to Snyder Lake catchment. These same upslope winds likely also transport PAHs from the aluminum smelter.

PAH ratios can be used to identify potential sources (Schauer et al., 2002; Yunker et al., 2002; Killin et al., 2004). The ratio of indeno[1,2,3-cd]pyrene concentration to indeno[1,2,3-cd]pyrene concentration + benzo[e]pyrene concentration (IcdP/(IcdP+BeP)) should remain fairly constant from emission sources to deposition in the environment, because these PAHs are typically sorbed to the particulate phase in the atmosphere and have similar physical and chemical properties. The IcdP/(IcdP+BeP) ratio from gasoline combustion in motor vehicles is 0.74 (Schauer et al., 2002), whereas the ratio from combustion of pine wood in a fireplace is 0.53 (Figure 4-32; Schauer et al., 2001). Aluminum smelters that use Söderberg aluminum smelting technology have been shown to emit an IcdP/(IcdP+BeP) ratio of 0.39 (Booth and Gribben, 2005; Sanderson et al., 2005).

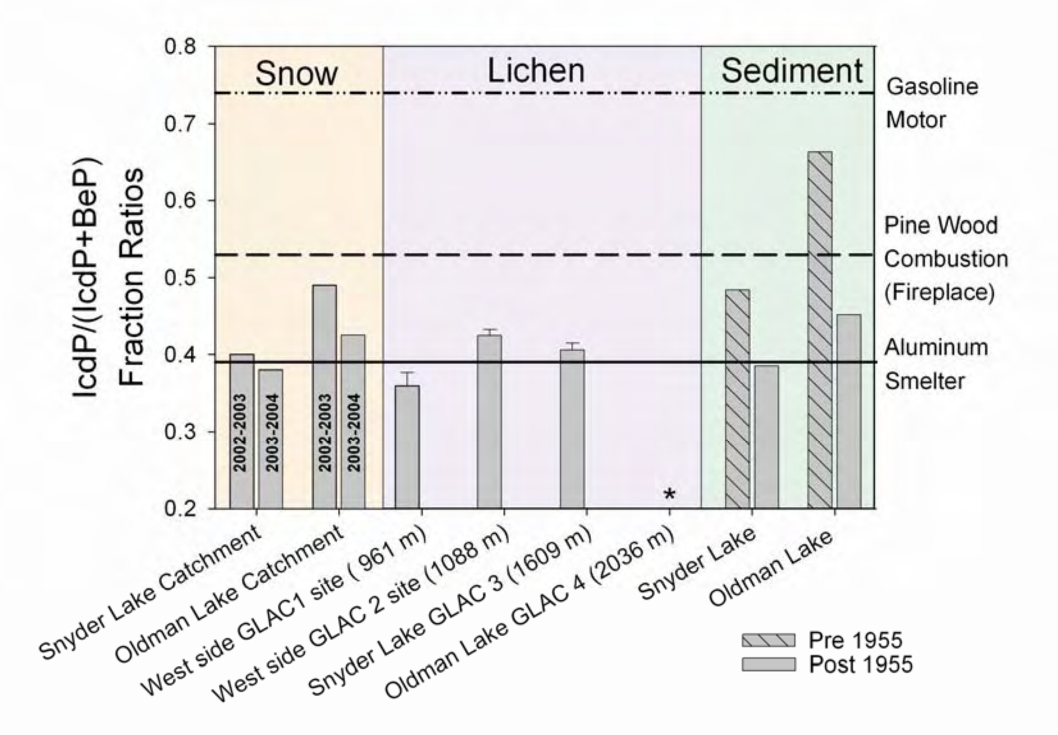


Figure 4-32. Fraction Ratios of IcdP/(IcdP+BeP) (average ± standard deviation) Calculated from Snow, Lichen, and Pre- and Post-1955 Sediment in Snyder and Oldman Lake Catchments in GLAC Compared to Measured Ratios. Measured ratios for gasoline motors from Schauer et al. (2002), pine wood combustion from Schauer et al. (2001), and an aluminum smelter from Sanderson and Farant (2005). " * " indicates values were below detection limits.

Figure 4-32 shows the measured IcdP/(IcdP+BeP) in snow, lichen, and sediment from the Snyder Lake and Oldman Lake catchments. The IcdP/(IcdP+BeP) ratio measured in the 2003 seasonal snowpack from Snyder Lake was 0.40, which closely matches the ratio previously seen for Söderberg aluminum smelter emissions; the ratio in the 2003 snowpack from Oldman Lake was 0.49. In addition, although the concentrations of PAHs in Snyder Lake vary considerably, the IcdP/(IcdP+BeP) ratio was fairly constant during the years of snow sampling.

The sum PAH flux in the Snyder Lake 2003-2004 snowpack was significantly lower than it was in the 2002-2003 snowpack. From March 2003 until 2007, the aluminum smelter reduced operations from 60% to 20% (Jamison, 2003). In 2002 (60% capacity), the aluminum smelter released 15.1 tons of PAHs to the atmosphere and in 2004 (20% capacity), the plant released 5.0 tons of PAHs (USEPA, 2007a). Although it is difficult to compare quantitatively, because a detailed timeline of smelter emissions is lacking, the reduction in PAH emissions is corroborated by a decline in PAH concentrations in the snowpack over this timeframe. The 2003-2004 snowpack PAH concentrations measured were approximately one-third of the 2002-2003 concentrations, similar to the reported emission reduction. At the same time the IcdP/(IcdP+BeP) ratios measured in the seasonal snowpack samples remained fairly constant from 2003 to 2004 (Figure 4-32), indicating that the smelter was still the dominant source of PAHs. BeP was not detected in lichens from Oldman Lake catchment, so the IcdP/(IcdP+BeP) ratio could not be calculated.

In the sediment cores at Snyder Lake, the IcdP/(IcdP+BeP) ratio was 0.49 before 1955, when the smelter came on line. From 1955 to the present, the IcdP/(IcdP+BeP) ratio has been fairly constant in the Snyder Lake sediment core, with an average and standard deviation of 0.35 ± 0.05. The IcdP/(IcdP+BeP) ratio measured in the Snyder Lake surficial sediment was 0.38. In Oldman Lake, IcdP was detected only in the 2005 (surficial sediment) and 1906 intervals. In 1906, the fraction ratio of IcdP/(IcdP+BeP) in the Oldman Lake sediment core was 0.66; in the surficial sediment of Oldman Lake, the IcdP/(IcdP+BeP) was 0.45 (Figure 4-32). In addition, the retene sediment flux over time was not significantly correlated with sum PAH, BeP, IcdP, or BghiP flux over time in Snyder Lake ($p > 0.05$), suggesting biomass combustion was not a major source of PAHs to the Snyder Lake catchment.

Taken together, we believe the data strongly suggest that the Snyder Lake watershed is influenced by the Columbia Falls aluminum smelter. The sources of PAHs for the Oldman Lake watershed are not as certain. The much lower concentrations and the IcdP/(IcdP+BeP) ratio are not consistent with an influence from the smelter, and the concentrations overall differ little from those in other parks.

4.2.6.3 Possible Urban/Regional Influences at Rocky Mountain National Park

At ROMO, a different issue emerges, related to observations at two sites across the Continental Divide. Mills and Lone Pine lakes are only 10 km apart, but they are on different sides of the Continental Divide. Mills Lake is on the east side and Lone Pine Lake is on the west side. Considering the impact that the Continental Divide has, it is possible that these two lakes receive different contaminant exposures.

Evidence of differences in atmospheric deposition within the Colorado Front Range has been reported in a number of studies (Burns, 2003, and references therein). Deposition of NO_3^- (nitrate) and NH_4^+ (ammonium) are greater on the east side of the Continental Divide than on the west side during summer. These two contaminants are associated with urban and agricultural sources. The elevated concentrations of these two contaminants might have resulted from summer upslope winds, or transport from the eastern lowlands up the Front Range of the Rocky Mountains, a wind pattern that is counter to the prevailing westerly winds (see Section 4.5).

Snow and sediment SOC data from ROMO suggest that these upslope winds might also be important in transporting PAHs and agricultural SOCs in higher concentrations to Mills Lake (Usenko et al., in press). Together, these matrices suggest year round differences in atmospheric concentrations between the two lakes. Figure 4-28 shows the SOC sediment flux profile for Mills and Lone Pine Lakes. For all compound classes, the sediment flux to Mills Lake was greater than the flux to Lone Pine (Usenko et al., in press).

A similar trend is true for the snow flux of SOCs. Table 4-5 shows the ratio of SOC fluxes, and concentrations, in the snowpack for Mills Lake compared with Lone Pine Lake for 2003 (Usenko et al., in press). The Mills Lake flux is always higher by a factor of from 1.6 to 4.1. However, much of the enhancement in snow flux at Mills Lake results from more snowfall in the Mills Lake basin, rather than higher atmospheric concentrations of contaminants. At Mills Lake, the 2003 snow water equivalent (SWE) was 90 cm; for Lone Pine Lake, it was 40 cm. The enhancement in snow concentrations between Mills and Lone Pine lakes is less than the fluxes. In fact, for dacthal, chlordanes, and PAHs, the snow concentrations are the same or greater in Lone Pine Lake than in Mills Lake (Usenko et al., in press).

SOC concentrations in air, conifer needles, and fish do not show a clear enhancement on the east side of ROMO. Conifers, in particular, do not provide evidence that the east side of ROMO has higher concentrations of pesticides than the west side. Although there is a suggestion of an east-west difference in SOC deposition at ROMO, not all of the WACAP data provide clear evidence for this effect. A more focused study, with many more sampling locations, would have to be conducted to address this question.

Table 4-5. Comparison of SOC Data from Mills and Lone Pine Lakes. The values in the table show the ratio of the Mills/Lone Pine Lake results for snow fluxes and snow concentrations.

	Mills to Lone Pine Ratio	
	Flux	**Concentration**
Endosulfans	3.2	1.4
Chlorpyrifos	NA	NA
Dacthal	2.5	1.0
g-HCH	4.1	1.8
a-HCH	4.1	1.8
HCB	NA	NA
Dieldrin	3.7	1.6
Chlordanes	1.6	0.7
PAHs	2.2	0.9

4.3 Trace Metals, Including Mercury

Figure 4-33 shows mean total mercury (Hg) concentrations in lichens, snow, fish, and sediments across all parks. Snow data are provided, both as concentrations and as fluxes. Hg concentrations in lichens are highest in parks in the conterminous 48 states. The same is true for Hg snow deposition fluxes. However, in fish, highest concentrations were found in samples taken in NOAT and GAAR. Detailed discussion of Hg concentrations in each medium follows.

4.3.1 Mercury and Trace Metals in Snow

Total Hg was measured in 60 snowpack samples, with park median concentrations ranging from 0.94 ng/L in MORA to 4.1 ng/L in GLAC. Mercury concentrations showed considerable spatial and temporal variability. Much of the Hg in snow is associated with particulate matter, which shows much greater variability at all scales, compared to dissolved constituents in melted snow (Turk et al., 2001). Hg was correlated with particulate carbon, and both were found at higher concentrations in snow samples from forested sites compared with samples from open meadows. In general, Hg concentrations in snow were lowest in the west coast parks, intermediate in the Alaska parks, and highest in the Rocky Mountain parks (Figure 4-33). The exception was OLYM, where concentrations and fluxes were fairly high. However, only a single year is represented because of poor snowpack conditions in 2003 and 2005.

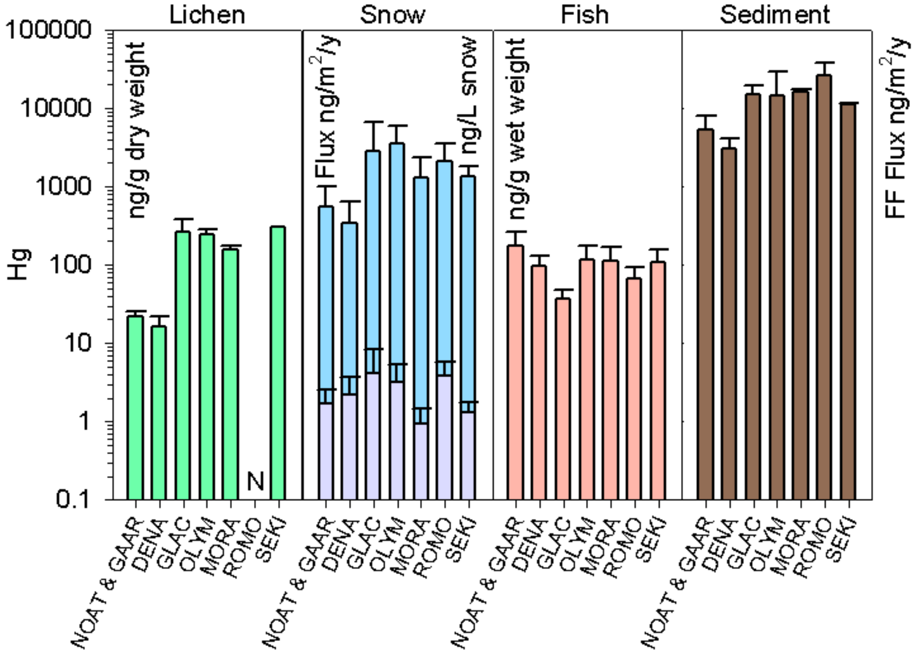


Figure 4-33. Average Concentrations and Fluxes of Mercury across Parks and Media. Snow data include fluxes (ng/m^2/yr) in blue and concentrations (ng/L) in gray. Fish data are for whole fish. Sediment data are reported as focusing factor-corrected (FF) flux for surficial sediment only. N = no data.

Deposition fluxes of Hg ranged from 336 ng/m^2/yr at DENA to 3,600 ng/m^2/yr at OLYM, with spatial and inter-annual variability driven largely by the variability in SWE. The Alaska parks had moderate concentrations but low SWE; OLYM had high concentrations and high SWE, and thus the highest Hg flux. MORA and SEKI had low concentrations and high SWE, and GLAC and ROMO had high concentrations and moderate SWE (see Figure 4-33). The Hg flux in OLYM was surprisingly high, but the median was calculated from only a few samples collected in a single year. Because warm-season deposition was not measured in this study, total annual deposition of mercury to the parks is higher than the snow fluxes reported here, especially in parks such as ROMO that receive substantial summer precipitation (Mast et al., 2005).

Concentrations of unfiltered methyl-mercury were measured in snowpack samples collected in 2005 only. Most values were below the detection limit of 0.04 ng/L; seven samples had values ranging from 0.05 to 0.59 ng/L; all of these had high particulate carbon concentrations as well.

Trace metals are often used as markers of source emissions types (see Section 4.2.6). We investigated the relationship between snow Hg concentrations and trace metals associated with coal combustion (Table 3-4). We found no significant correlations ($p < 0.1$) between Hg and these metals by linear regression or multiple linear regression, even if we accounted for the relationship between Hg and particulate carbon. We also analyzed the relationship between Hg and these metals by normalizing to Al concentrations to calculate an enrichment factor; again, we found no significant relationships. We hypothesize that the strong interaction between Hg and particulate carbon in snow overwhelms any relationship between Hg and other metals present in emissions from coal combustion.

4.3.2 Mercury and Particulate Carbon in Snow

We found a strong correlation ($R^2 = 0.63$, $p < .0001$) between total mercury and particulate carbon concentrations in the snowpack (Figure 4-34). The underlying mechanisms that control this relationship are uncertain. It is possible that mercury and particulate carbon become associated in the atmosphere and are deposited to the snowpack together. Or they could be deposited separately and become associated within the snowpack. This association could provide a mechanism to bind atmospherically deposited reactive mercury and prevent its reduction and subsequent evasion to the atmosphere (LaLonde et al., 2002). Thus, particulate carbon might act to sequester more of the deposited Hg from the winter deposition period, increasing the net flux of Hg to the watershed when the snowpack melts. Otherwise, Hg in the snowpack that is not bound to particulate carbon might be lost through revolatilization to the atmosphere. Thus, the WACAP Hg concentrations reflect complex biogeochemical cycling with natural and anthropogenic components.

Mercury in the snowpack is associated with particulate carbon

At Lake Irene in ROMO, snowpack sampling was conducted at paired sites approximately 200 m apart. The forest site was in a forest clearing about 10 m in diameter on a northwest-facing 20-degree slope; the meadow site was in an open meadow on a southeast-facing 5-degree slope (see photo). A single pair of samples (one from the forest site, one from the meadow site) was collected in 2002, 2004, and 2005, and two pairs were collected in 2003. Unfiltered total Hg averaged 2.7 ng/L greater (28%) at the forest site than at the meadow site for the five sample pairs. Particulate carbon was also higher at the forest site. Various processes could contribute to the difference. The greater surface area and more favorable depositional substrate of the forest canopy relative to the open snow-covered meadow probably enhances dry deposition of mercury and carbon in the forest (St. Louis et al., 2001). The northerly slope and shading from the canopy would also reduce solar radiation to the snowpack surface in the forest, limiting photo-reduction and evasion of mercury from the snowpack. The combined effects of particulate carbon and forest canopy on Hg concentrations in snow contribute to the large temporal and spatial variability in Hg deposition at all scales, as discussed in Section 4.3.1.

Higher mercury concentrations were found in the forest than in an adjacent meadow.

4.3.3 Trace Metals in Vegetation

Fifty-two lichen samples were analyzed for 45 elements, excluding nitrogen, representing 6 species for the 8 core parks. In addition, 105 samples representing 13 lichen genera from all 20 WACAP parks were analyzed for nitrogen. Because lichens differ in their elemental profiles, lichen element concentrations were considered separately by taxon (i.e., species when known, genus otherwise). Summary statistics for WACAP element concentrations by park and taxon are provided in Appendices 4A.12 and 4A.13.

Overall, metals were within expected background ranges in the WACAP parks.

To determine the enhancement of the nitrogen and sulfur nutrients and the toxic metals cadmium (Cd), nickel (Ni), and lead (Pb) in lichens of WACAP parks, relative to other remote sites in the western United States, we calculated the upper limit for the background range for public lands. To do this, we queried the national databases for the National Park Service [NPElement (Bennett, 2007)] and the US Forest Service [USFS Lichens and Air Quality Database (US Forest Service, 2007)] for lichen element concentrations from Montana, Wyoming, Colorado, New

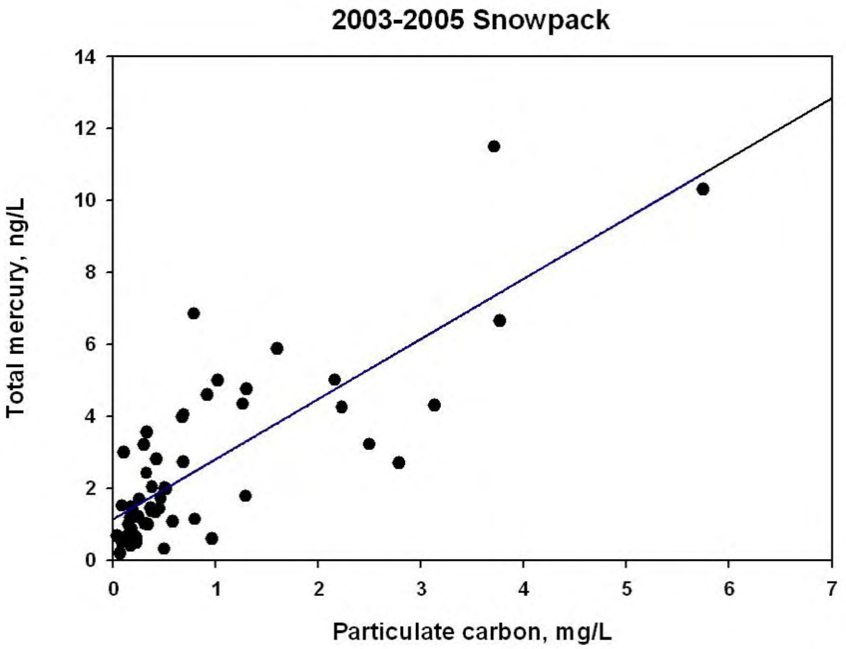


Figure 4-34. Unfiltered Total Mercury vs. Particulate Carbon Concentrations for All WACAP Snowpack Samples, 2003-2005.

Snow sampling crew digging a snow pit at the meadow site near Lake Irene in ROMO. The paired forest site is in the background.

Mexico, and Texas westward (excluding Hawaii), and all lichen species and elements targeted in WACAP parks.

To augment comparison data for the Arctic lichens, *Masonhalea richardsonii* and *Flavocetraria cucullata*, we added 2004 and 2005 data from the NPS Arctic Parks database from NOAT (Peter Neitlich, pers. comm.) to the resulting database. This combined WACAP Western States Lichen Element Database contains data for 7,953 lichen samples from 76 national forests, parks, and other federally managed lands for 60 elements representing all WACAP target lichens and includes the WACAP lichen element data. See Appendix 4A.15 for a list of public lands encompassed in the database.

To specifically examine the relative enhancement of nitrogen, sulfur, mercury, cadmium, nickel, and lead, we calculated the 0, 2.5, 10, 25, 50, 75, 90, 97.5 and 100% distribution quantiles by lichen genus and element for the WACAP Western States Lichen Element Database, excluding the WACAP data to determine background ranges that were independent of the WACAP data (Appendix 4A.14). Because not all parks are in pristine locations, we chose the 90% quantile, rather than a higher quantile, as the upper limit for background values. This limit is arbitrary, being based on a perusal of distribution histograms which indicate that values below the 90% quantile tend to follow a normal distribution typical of a background population. Ideally, comparisons at the species level would be desirable, but in this analysis, species in the WACAP target genera examined were similar morphologically and had similar element profiles, justifying assessment at the genus level. Also, comparing genera simplifies calculations by reducing the number of comparisons.

The same lichens that were best accumulators of SOCs—*Platismatia*, *Usnea*, *Xanthoparmelia*, and *Hypogymnia*—also accumulated larger concentrations of metals and nutrients, than did the poorer SOC accumulators—*Alectoria*, *Cladina*, *Flavocetraria*, and *Masonhalea* (compare 50% quantiles across species in Appendix 4A.14). This finding underscores the desirability of using a single species where possible, choosing species with similar element profiles, or overlapping target species sampling so that a system for comparison can be developed.

To evaluate how the samples in each park compared with background ranges for remote sites in the western United States, we expressed each sample as a percentage of the background range by dividing element concentrations of each WACAP sample by the upper limit of the background range for the relevant lichen genus and element. Results are presented as percent enhancement in Figure 4-35. The chief advantage of this approach is that it allows samples from different species within and across parks to be compared.

Overall, metals were not noticeably elevated in any of the WACAP parks (Appendix 4A.12). The GAAR site at Matcharak Lake had high concentrations of many of the rare earth elements [dysprosium (Dy), erbium (Er), europium (Eu), gallium (Ga), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), antimony (Sb), terbium (Tb), thulium (Tm), uranium (U), yttrium (Y), ytterbium (Yb)], compared to other WACAP core parks. Rare earth elements are typically associated with soils and probably represent local dust. Evidence of this association is the rather high aluminum concentrations in the *Flavocetraria cucullata* samples from GAAR. In general for lichen samples, the higher the aluminum and iron concentrations the higher the concentrations of the rare earth elements. Of the elements identified for comparison with other public lands of the western United States, mean concentrations of cadmium, nickel, and lead were well under thresholds at all parks (Figure 4-35).

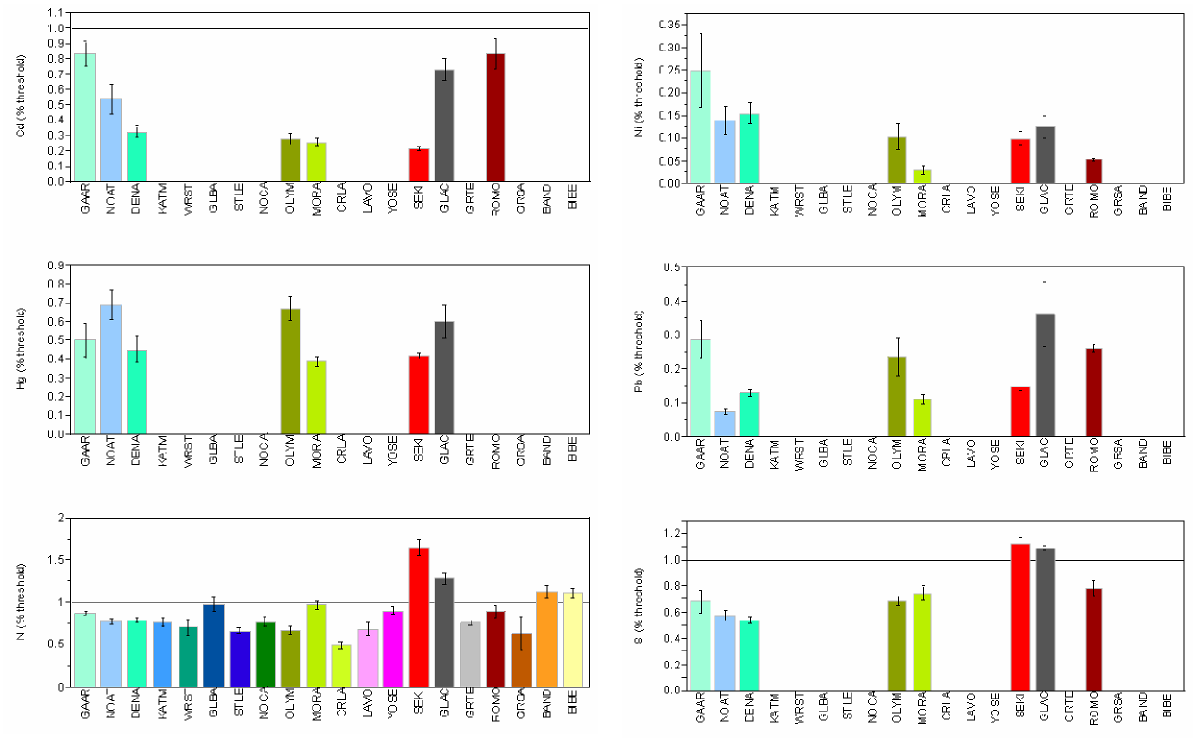


Figure 4-35. Comparison of Selected Elements in Lichens of WACAP Parks with Elements in Other National Parks and Forests in Western North America. Thresholds are the 90th percentile of element concentration distributions in lichens from remote sites. In general, lichen element concentrations indicate that metals were within expected ranges, sulfur deposition was elevated in SEKI and GLAC, and nitrogen deposition was elevated in SEKI, GLAC, BAND, BIBE. Error bars indicate one standard error.

Highest mercury concentrations in lichens among western parks in the NPElement database were measured in samples from BIBE in 2002: 39% of *Usnea* samples and 25% of *Xanthoparmelia* samples collected there in 2002 were above the 90% quantile of the background range for these species. (Lichen samples were collected at all WACAP parks and are currently archived at UMNRAL, but were analyzed only for sulfur, mercury, and metals at the core parks). Although mercury concentrations are not higher in the WACAP core parks than we would expect for western forests and parks, because the biomass of needles is so high on a per hectare basis, forest fire is a significant source of mercury release into the atmosphere (e.g., Friedli et al., 2003). Mercury is an emerging element in lichen biomonitoring of air quality, and historic data for trends analysis is nearly non-existent. The oldest data in NPElement and the USFS Lichens and Air Quality databases are from 1990 and 1995; only in recent years have researchers been more systematic about including mercury in lichen biomonitoring studies (Bennett, 2007; US Forest Service, 2007). On a global scale, mercury emissions are predicted to increase with increased human population and concomitant development of coal resources for energy production, especially in China. Continued monitoring of mercury in vegetation can assess the effects of implementing emission controls vs. increased energy production.

In contrast to mercury, most lichen elemental concentration studies on public lands have included measurements of lead and sulfur (Bennett, 2007; US Forest Service, 2007). Significant reductions have been observed in study areas where re-measurements have occurred. For example, lead concentrations in *Alectoria sarmentosa* collected in 1983 from Golden Lake in

MORA averaged 5.45 ± s.d. 2.62 ppm. WACAP samples of *A. sarmentosa* from Golden Lake collected in 2005 averaged 1.29 ppm ± s.d. 0.12 ppm. In SEKI, 27 samples of *Letharia vulpina* sampled at 8 sites in 1984 had concentrations ranging from 3.11 to 24.12 ppm (average 8.58). The 2004 WACAP samples of *L. vulpina* from Emerald Lake basin in SEKI ranged from 1.22 to 1.77 (average 1.39).

In summary, metal concentrations in WACAP core parks were within background ranges for remote sites in the western United States. Mercury is likely to be the metal of highest concern because it is re-released to the atmosphere during forest fires. Comparisons of WACAP data with historic data in the NPS lichen element database, NPElement (Bennett, 2007), indicate that lead is decreasing in MORA and SEKI. Although lichen sulfur and metal concentrations were not analyzed in the secondary parks, historic data from NPElement indicates mercury concentrations could be elevated in BIBE. Analysis of archived WACAP lichen samples could provide trends data for some secondary WACAP parks and establish baselines for parks currently lacking lichen data.

4.3.4 Mercury and Trace Metals in Fish

Unlike lipophilic SOCs (contaminants stored in lipids), Hg in fish is mainly in the form of methyl-Hg, which accumulates in muscle tissue (Munthe et al., 2007). Although fish Hg concentrations (shown in Figure 4-33) are measured in the whole fish, the bulk of the Hg is tied up in muscle tissue. Incorporation of Hg into the food web and into fish tissue is generally limited by rates of methylation, which in turn can be limited by nutrient availability (St. Louis et al., 2004). Therefore, some areas can have fairly high Hg deposition, but low methylation rates and hence low fish tissue Hg (Bloom, 1992). This limitation probably explains the fish concentration data at ROMO, where Hg flux to the snow and sediments is fairly high, yet fish Hg concentrations are fairly low (see Figure 4-33). Data from NOAT and GAAR show the opposite pattern—low Hg in snow and sediment fluxes, but high Hg concentrations in fish. On this basis, it appears that even though atmospheric deposition is a primary source of Hg to these ecosystems, the linkage between snow deposition and fish concentrations is weak. Other factors, as already mentioned, must also be important in explaining the Hg uptake and bioaccumulation in fish. More attention to this topic is given in Section 5.6 of Chapter 5.

> The complex processes that control mercury accumulation in fish include atmospheric deposition, methylation and bioconcentration in the food web, and bioaccumulation as fish age.

In a comprehensive study at Voyageurs National Park in Minnesota, Wiener et al. (2006) investigated the factors associated with Hg concentrations in fish. These authors concluded that high dissolved sulfate, low lake water pH, and high organic carbon favored methyl-Hg accumulation in the fish. Lake temperature has also been implicated in methylation (Schindler et al., 1995; Lambertsson and Nilsson, 2006). These results indicate that we should not expect a direct relationship between Hg concentrations in vegetation, snow, and fish in the WACAP parks, and indeed we see no simple relationship.

For trace metals in fish, we analyzed concentrations in both fillets and livers. A comparison of concentrations in the fillets with those in the livers showed significantly higher concentrations in the livers. For Cd, Cu, Ni, Pb, and zinc (Zn), concentrations in the livers were elevated by factors of 20, 60, 10, 900, and 230, respectively, compared to those in the fillets. On average, vanadium (V) did not show an enhancement. Because the concentrations in the fillets are very low, and close to the limit of detection for the various metals, small differences in concentration are not easily observed, whereas these changes are clearly indicated in the liver concentration data.

For all metals except V, the liver compositional analysis shows stronger influence from bioaccumulation than did the corresponding fillet tissue analysis.

Figure 4-36 shows the distribution of trace metals in the liver of fish from the core WACAP parks. The highest concentrations of lead in fish livers were observed in fish from Snyder Lake in GLAC (Figure 4-36). The next highest concentrations were observed for fish from Burial Lake (NOAT), Wonder Lake (DENA), and Emerald Lake (SEKI). There was always a significant difference in lead concentrations among lakes within a park, except at ROMO, where concentrations between Lone Pine and Mills Lakes were similar.

The Cd concentration in fish liver was highest in Emerald Lake (SEKI), followed by similar concentrations in Burial Lake (NOAT), Wonder Lake (DENA), Mills Lake (ROMO), and Pear Lake (SEKI). However, the fish specimens sampled in Burial and Wonder lakes were considerably older than specimens from the other lakes. Therefore, this observation could include an age/bioaccumulation effect or a species effect.

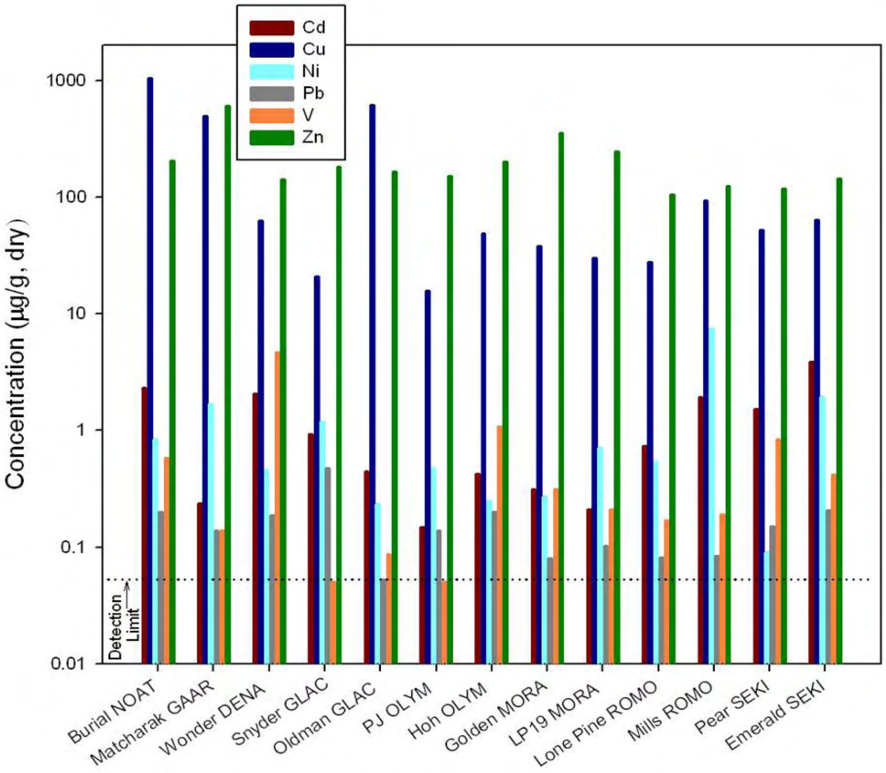


Figure 4-36. Trace Metals in Fish Liver. Distribution of Cd, Cu, Pb, Ni, V, and Zn average concentrations in fish livers from 2- to 8-year-old specimens collected from western national park lakes in GLAC, OLYM, MORA, ROMO, and SEKI, and 18- to 28-year-old specimens from lakes in NOAT, GAAR, and DENA. Because of the small sample size, no fish from McLeod Lake (DENA) were analyzed for trace metals.

Concentrations of Cu were highest in the livers of fish from Burial Lake, Matcharak Lake, and Oldman Lake, compared with fish livers from the other lakes studied. Copper concentrations in fish livers are similar in the other national park lakes, with the lowest concentration observed in PJ Lake (OLYM).

Concentrations of Zn in fish liver were highest in Matcharak Lake (GAAR), which represents older fish specimens that might exhibit bioaccumulation. The second highest concentration occurred in Golden Lake (MORA). Zinc concentrations were similar in magnitude in all other national park lakes—between 100 µg/g (dry basis) and 150 µg/g (dry basis).

All Ni and V concentrations in fish liver were below 10 µg/g (dry basis), with most below about 1 µg/g (dry basis). The detection limit for all metals was about 0.6 µg/g (dry basis).

4.3.5 Mercury, Trace Metals, and Spheroidal Carbonaceous Particles in Sediments

4.3.5.1 Mercury, Trace Metal, and SCP Focus-Corrected Fluxes

Temporal patterns of mercury, trace metals, and spheroidal carbonaceous particles (SCPs) were determined from the dated sediment profiles at the core parks. These have been corrected by the focusing factor as described in Chapter 3. Figures 4-37 to 4-43 show the focus-corrected fluxes for a selected set of metals and SCPs for both lakes in each park. In addition to atmospheric deposition, watershed processes influence the delivery of mercury to the lake sediments. Some of the more important factors are the watershed-to-lake area ratio, total organic carbon (TOC) in the lake water, and the wetland area associated with the lake (Wiener et al., 2006). In nearly all lakes, Hg fluxes are larger now, compared to pre-industrial values. The one exception is Hoh Lake, where the Hg flux showed a large increase between 1910 and 1930, and then decreased to pre-industrial values.

Figures 4-37 to 4-43 also show the focus-corrected fluxes for Ni, Cu, Pb, V, Zn, and Cd in µg/m^2/yr. These metals display a complex and closely matched pattern with some metals generally rising and falling together in the same lake. We know that many of these variations are related to watershed processes such as erosion, avalanches, and landslides, which is discussed in more detail later in this section. In most lakes, there were generally increasing fluxes of Pb and Cd toward the surface, which we believe to be associated with greater anthropogenic sources. But at some lakes, a different trend appeared, with metals increasing and decreasing together in a complex pattern. In most lakes in parks in the conterminous 48 states, the order of flux was approximately Zn > V > Pb > Cu > Ni > Cd > Hg. In a few sediment cores, V was greater than Zn. In the Alaska parks, Cu and Ni were much higher than the Pb flux. The highest flux for most metals was observed at PJ Lake (OLYM). PJ Lake shows a very complex pattern, with multiple peaks in the flux of all metals between 1920 and 1970. The Pb fluxes were highest in Snyder Lake (GLAC), Mills Lake (ROMO), and Emerald Lake (SEKI). These same lakes were also high in SCPs, suggesting a strong influence from regional combustion sources. Although the spatial pattern for Cd is similar to that of the other metals, the magnitude of the flux is lower than most other metals by a factor of 100 or more.

SCPs result from high temperature combustion of fossil fuels (see Chapter 3). Because SCPs range from 5 to 50 µm in diameter, transport of these large atmospheric particles is limited by their atmospheric lifetime (a few days to one week). Thus SCPs provide a measure of exposure to fossil fuel combustion within a range of a few hundred to approximately 1,000-2,000 km.

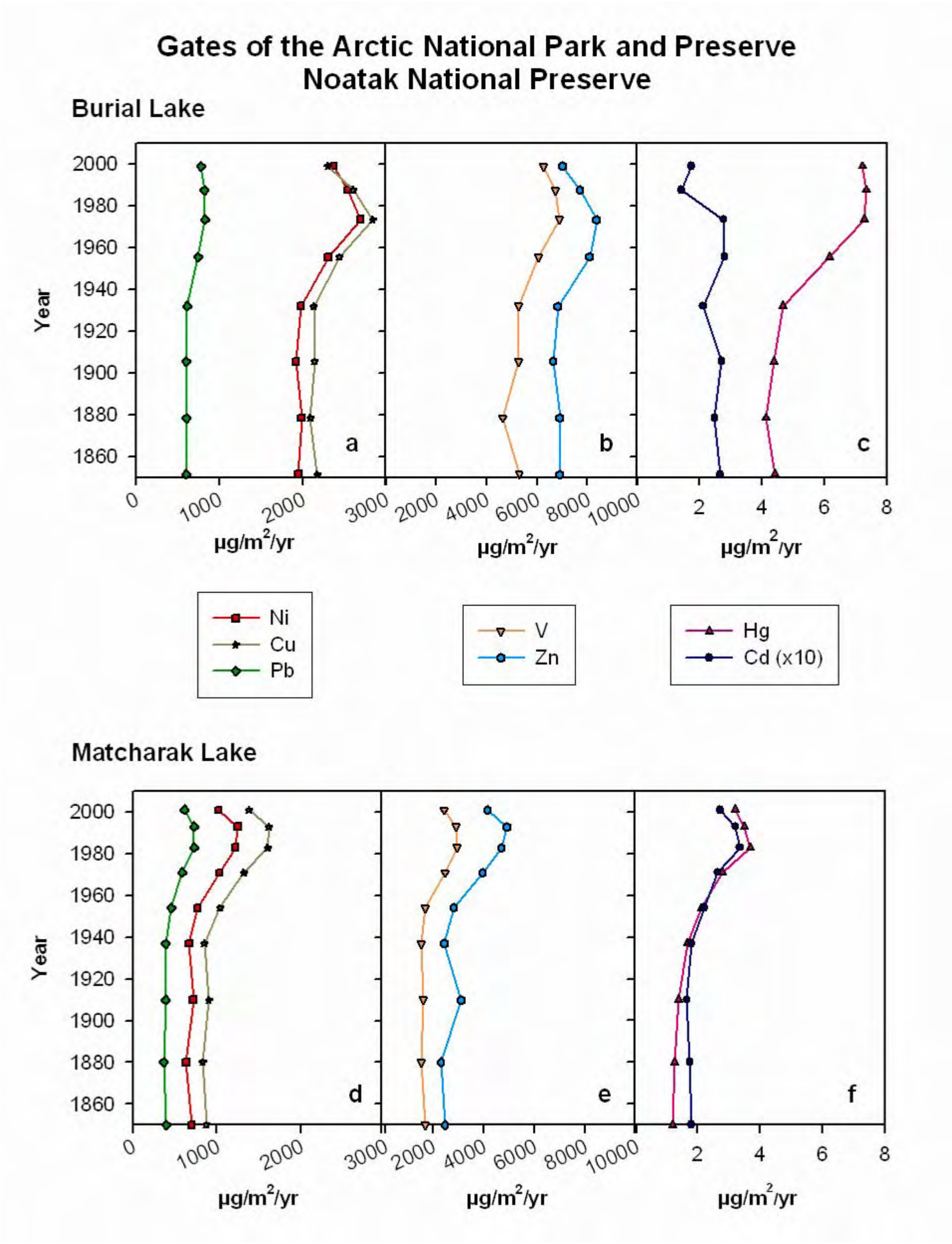


Figure 4-37. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (μg/m^2/yr) in Sediment Cores from Burial Lake (NOAT) and Lake Matcharak (GAAR). Cd flux has been reduced by a factor of 10. No SCPs were detected in the sediment cores from these lakes.

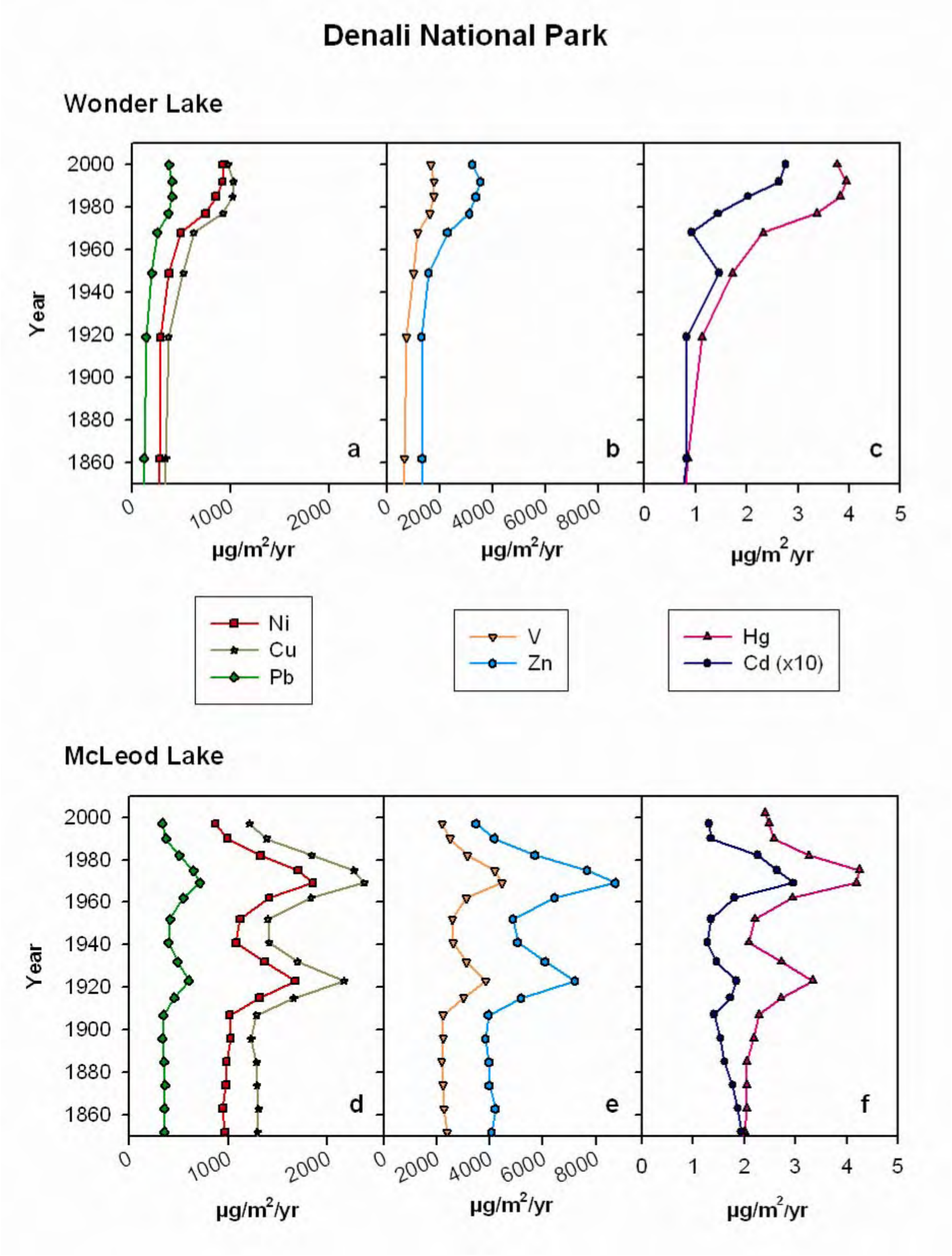


Figure 4-38. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg ($\mu g/m^2/yr$) in Sediment Cores from Wonder and McLeod Lakes (DENA). Cd flux has been reduced by a factor of 10. No SCPs were detected in the sediment cores from these lakes.

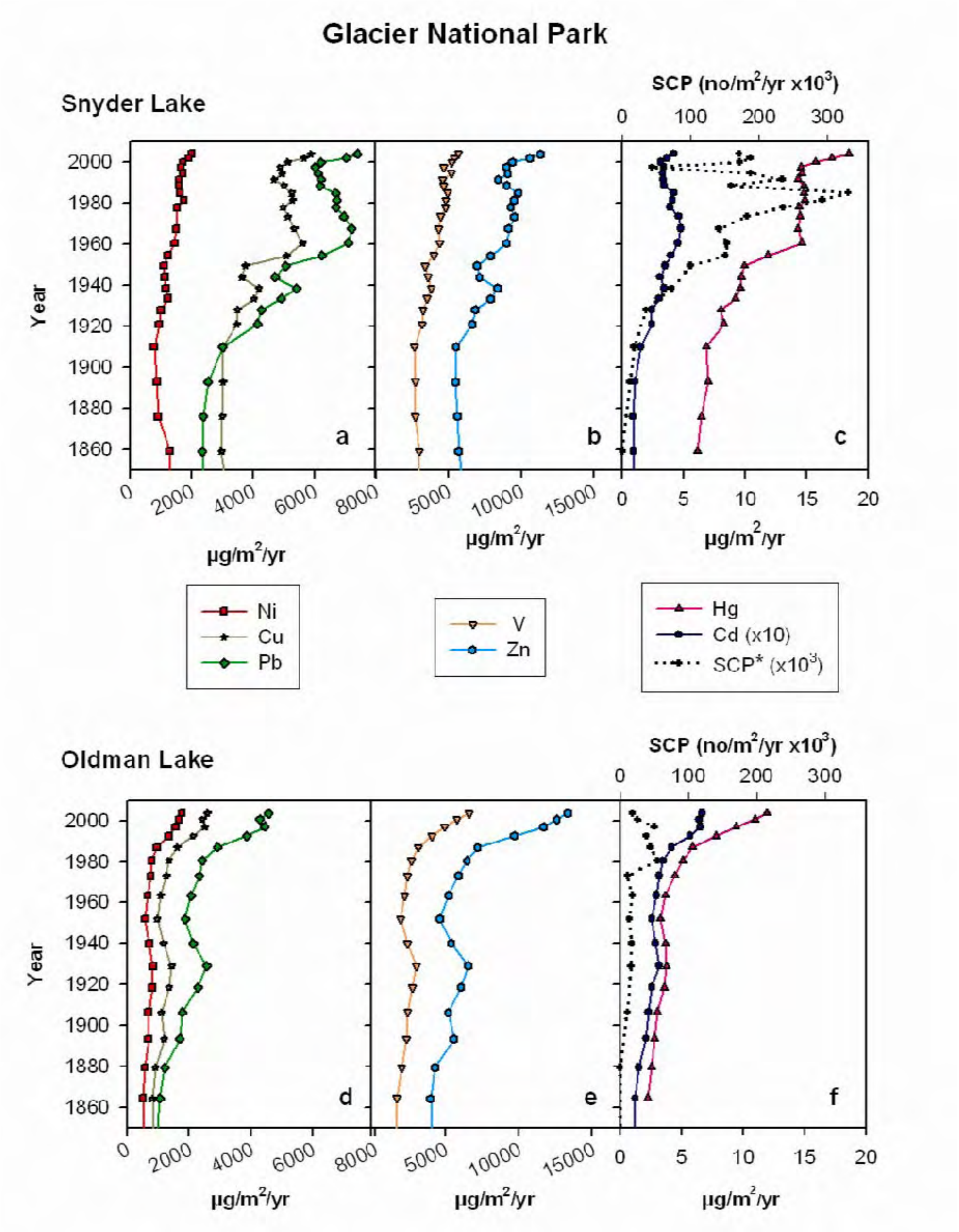


Figure 4-39. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (μg/m^2/yr) and SCP (number/m^2/yr, reduced by a factor of 1,000 and shown in the top axis) in Sediment Cores from Snyder and Oldman Lakes (GLAC). Cd flux has been reduced by a factor of 10. SCP flux for Snyder Lake is from the secondary core from this lake.

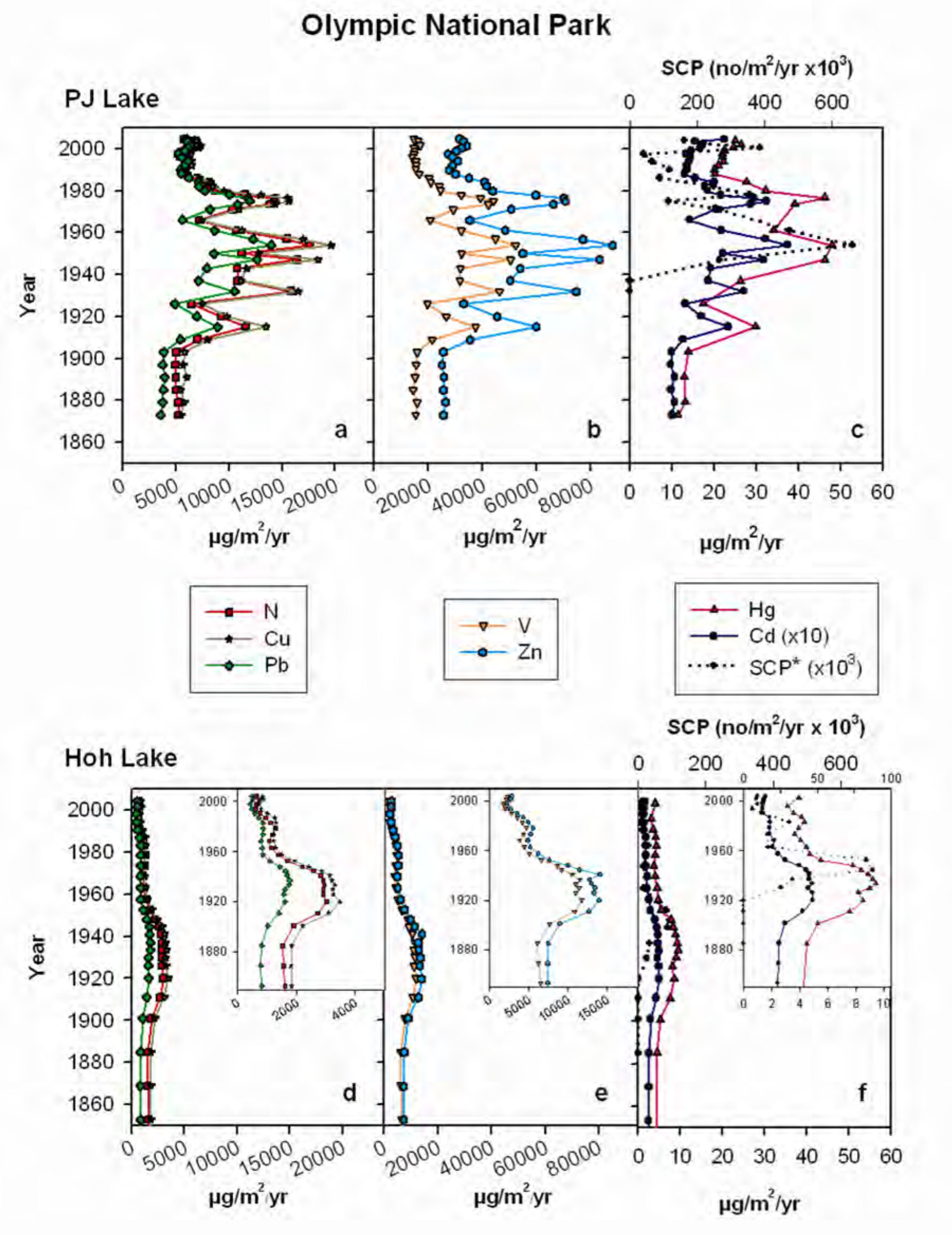


Figure 4-40. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (μg/m²/yr) and SCP (no/m²/yr, reduced by a factor of 1,000 and shown in the top axis) in Sediment Cores from PJ and Hoh Lakes (OLYM). Cd flux has been reduced by a factor of 10. Inset boxes for Hoh Lake have expanded flux scale. SCP flux is from the secondary cores from these lakes.

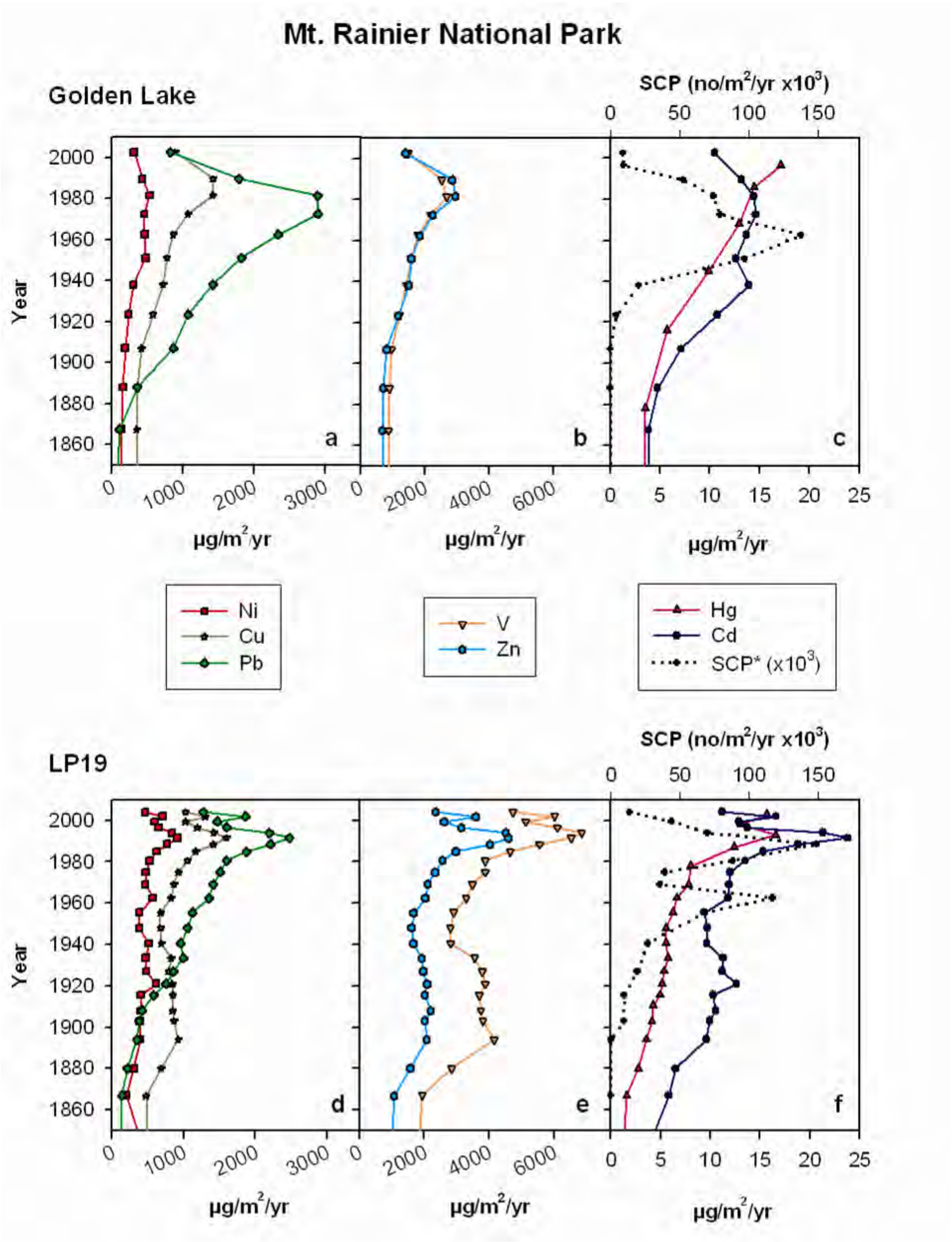


Figure 4-41. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (µg/m²/yr) and SCP (number/m²/yr, reduced by a factor of 1,000 and shown in the top axis) in Sediment Cores from Golden Lake and LP19 (MORA). SCP flux is from the secondary cores from these lakes.

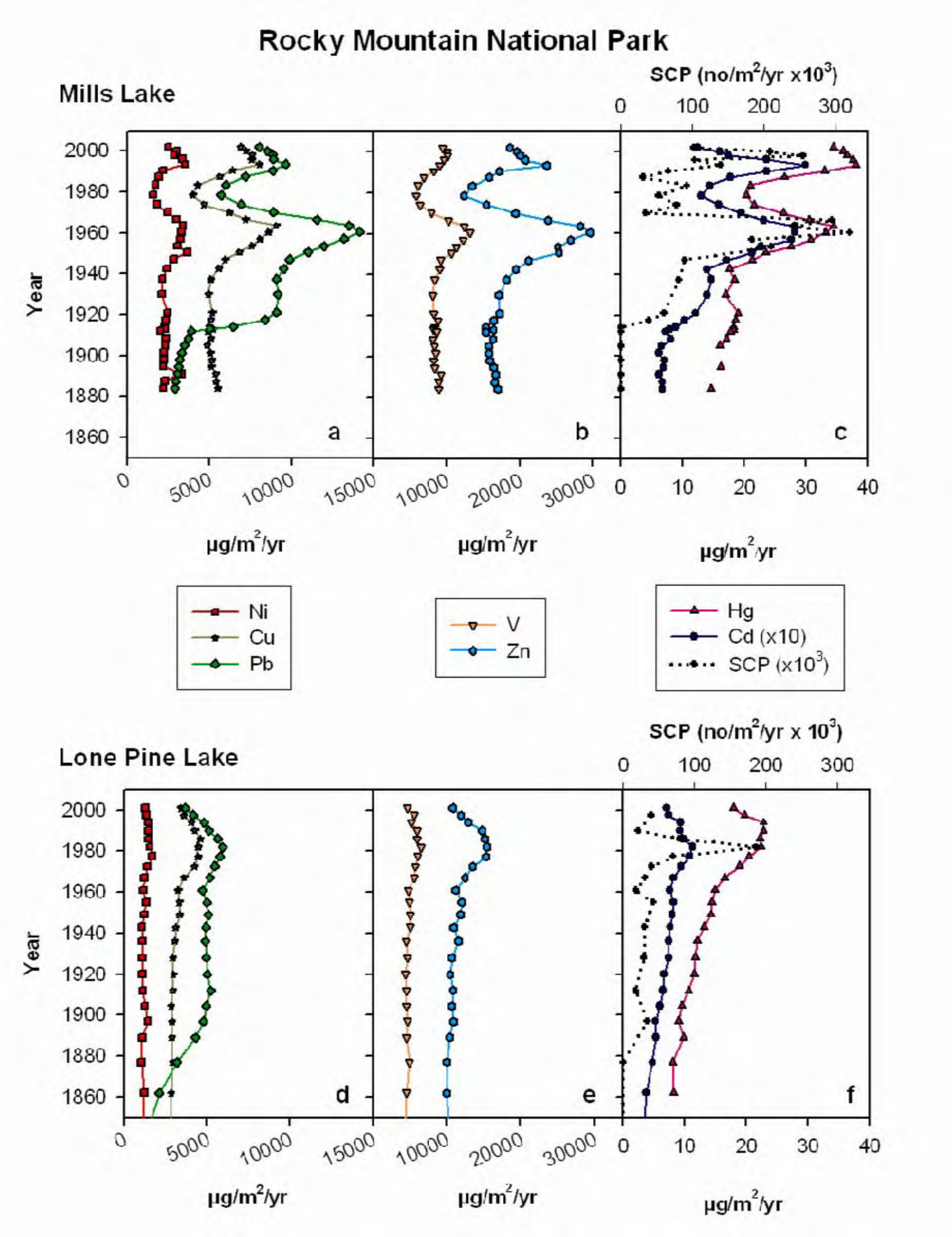


Figure 4-42. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (μg/m²/yr) and SCP (number/m²/yr, reduced by a factor of 1,000 and shown in the top axis) in Sediment Cores from Mills and Lone Pine Lakes (ROMO). Cd flux has been reduced by a factor of 10.

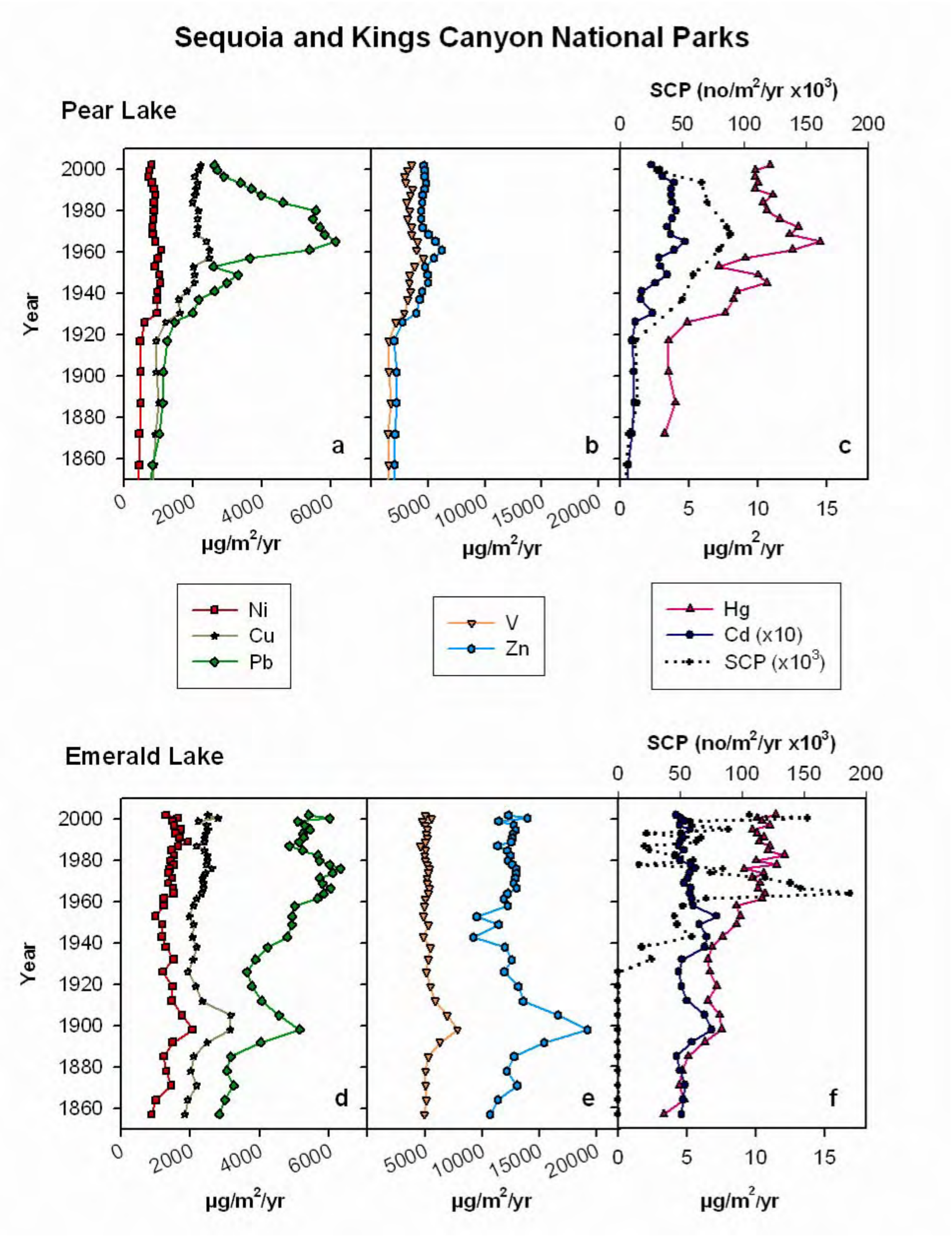


Figure 4-43. Focusing Factor-Corrected Flux of Ni, Cu, Pb, V, Zn, Cd, and Hg (μg/m²/yr) and SCP (number/m²/yr, reduced by a factor of 1,000 and shown in the top axis) in Sediment Cores from Pear and Emerald Lakes (SEKI). Cd flux has been reduced by a factor of 10.

Table 4-6 shows the accumulated SCP totals for each lake sediment core, in units of particles per $m^2 \times 10^5$. In terms of total deposition over the industrial period, the data show a general decline from south to north. Highest values occur for Emerald and Pear lakes in SEKI, while the four sites in Alaska are below the limits of detection. The results from sites in Alaska in themselves suggest very low concentrations of contamination from high-temperature combustion—equivalent to, or below, concentrations observed in sites in the European Arctic, the Falkland Islands, and even sites on the South Orkney Islands to the north of the Antarctic Peninsula (Rose, pers. comm., unpublished data). In GLAC, SCPs are higher at Snyder Lake than at Oldman Lake, which might be because of the proximity of regional sources (see Section 4.2.6). Similarly, PJ Lake (OLYM) shows considerably more SCP contamination than Hoh Lake, which might reflect greater local contamination. In terms of overall contamination, the SCP totals for SEKI are the highest among all WACAP parks and comparable to those observed in similarly affected European mountain lakes (in southern Spain, southern Norway, and the northwest UK (Rose, pers. comm. unpublished data).

Figures 4-37 to 4-43 also show the SCP flux profiles in the WACAP lake sediments (SCPs were not detected in the Alaskan lakes). In some cases, the SCPs were not analyzed on the same cores as the other compounds, but instead on parallel cores taken at the same time (in close proximity in the same lake). Although assumptions are made in transposing dates in this way, at present this is the best chronology available for SCPs in the sediment cores. It could explain some of the offsets seen in the SCP profiles, compared to the metals. The SCP dates can be updated when a better correlation between cores becomes available (e.g., with metal flux).

Table 4-6. Total Integrated SCPs in WACAP Lake Sediment Cores.

Park	Lake	Total Number of SCPs in the Core (x 10^5 m^{-2})[1]
NOAT	Burial	< DL
GAAR	Matcharak	< DL
DENA	McLeod	< DL
DENA	Wonder	< DL
GLAC	Oldman	100.4
GLAC	Snyder	143.3
OLYM	Hoh	51.3
OLYM	PJ	141.6
MORA	Golden	46.0
MORA	LP19	77.5
ROMO	Lone Pine	91.0
ROMO	Mills	168.6
SEKI	Emerald	193.8
SEKI	Pear	280.3

[1] This gives the total integrated number of SCPs in the entire core and can therefore be used to indicate the overall exposure to anthropogenic fossil fuel combustion over the entire temporal record of the sediment core.

4.3.5.2 Mercury and Trace Metal Enrichment Factors

The sediment profiles clearly indicate that watershed processes complicate the interpretation. Therefore, to better isolate and evaluate the human (anthropogenic) influence from atmospheric deposition over time, we normalized the sediment metal fluxes to titanium (Ti), a conservative element measured with high precision in the cores (Cowgill and Hutchinson, 1966; Engstrom, 1984). This procedure corrects for watershed disturbances and processes, such as catchment instability (e.g., avalanches, rapid snow melt) and erosion. The resulting enrichment is reported as the percent enrichment (PE) by subtracting the pre-industrial background concentrations from more recent metal concentrations as a modification of Kemp et al. (1976), as follows:

$$\text{Percent Sediment Enrichment} = \frac{(M_x/Ti_x) - (M_b/Ti_b)}{(M_b/Ti_b)} \times 100 \qquad [4\text{-}1]$$

where:

M_x = metal concentration (ng/g) at interval depth ×

Ti_x = titanium concentration (ng/g) at interval depth ×

M_b = metal concentration (ng/g) at interval closest to year 1870

Ti_b = titanium concentration (ng/g) at interval closest to year 1870

Figures 4-44 to 4-50 show the PE in the sediment cores for V, Cu, Zn, Pb, Cd, Ni, and Hg for each lake in the core WACAP parks. A PE value above zero indicates that that element is enriched in the sediment, relative to titanium and compared with the pre-industrial background (1870). For an element with a recent anthropogenic increase, we would expect its enrichment to go from zero (pre-industrial) to positive values after industrialization. Several patterns are apparent in the enrichment plots, compared to the un-normalized fluxes (Figures 4-37 – 4-43). All lakes in the conterminous 48 states show significant enrichment in Pb, Cd, and Hg. For all other metals, enrichment is either zero or fairly small. In the Alaska parks, there is recent enrichment in Hg at all lakes, but no other consistent patterns.

Atmospheric Pb is found primarily on fine particulate matter (less than 10 microns in diameter). Thus, deposition of Pb is related largely to sources within about 1,000-2,000 km. Pb deposition was heavily influenced by the introduction of leaded gasoline in the 1920s. Pb in gasoline was drastically reduced in the United States starting in the 1970s (Thomas, 1995). Other sources of lead to lake sediments shown to be important include lead mining, smelting, logging, and other industrial activities (see Table 3-4 in Chapter 3).

In the four Alaska lakes (Figures 4-44 and 4-45), only Wonder Lake shows a modest increase in Pb enrichment toward the surface, beginning in about 1920. In parks in the conterminous United States, Pb shows significant enrichment in all sediment profiles, and most of these lakes show a peak between 1960 and 1980, with a decrease afterwards. The PE values are by far the largest at both lakes in MORA. At LP19, Pb PE reached 400% and at Golden Lake, it reached 800%. At Mills Lake in ROMO, the Pb PE sharply increased in the early 1900s, possibly because of its proximity to historic lead mines and/or smelting operations. It is worth observing that the Omaha and Grant lead smelter was built in Denver in 1892 and the stack was the tallest structure in the world for some time thereafter.

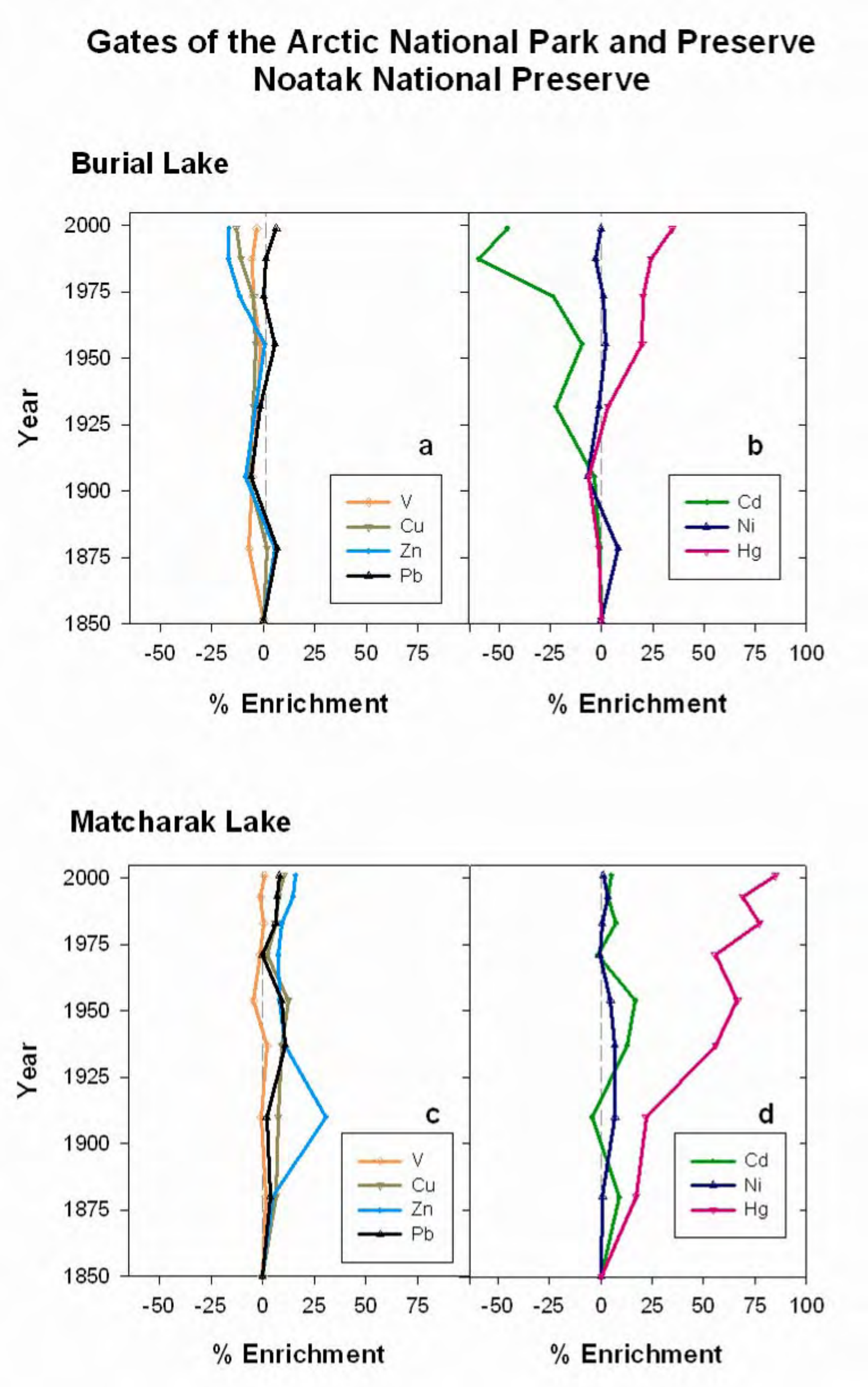


Figure 4-44. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Burial Lake (NOAT) and Lake Matcharak (GAAR). Sediment Ti values were used to normalize to a conservative crustal element to reduce the effects of watershed processes on the contaminant profiles.

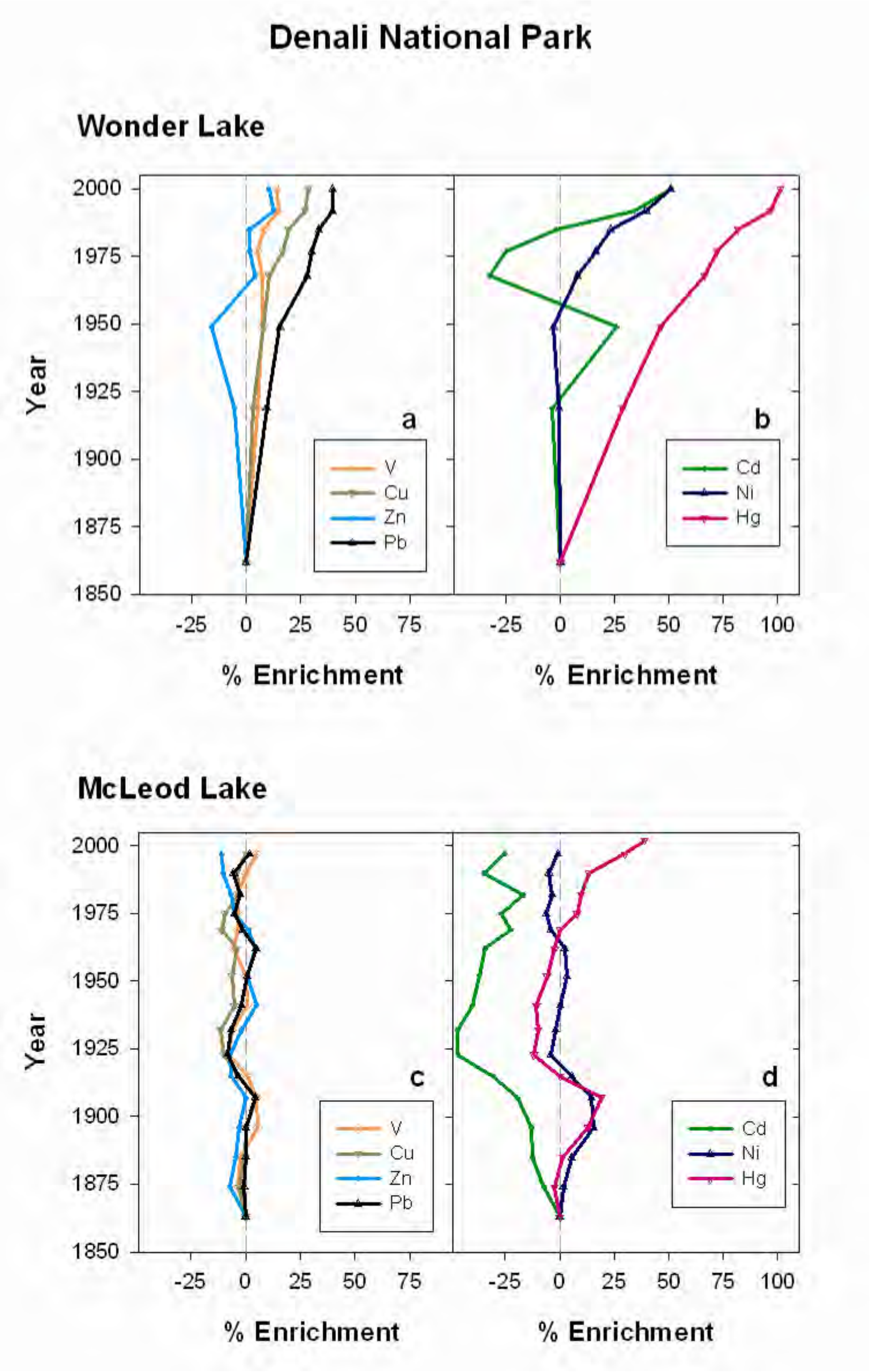


Figure 4-45. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Wonder and McLeod Lakes (DENA). See Figure 4-44 for more information.

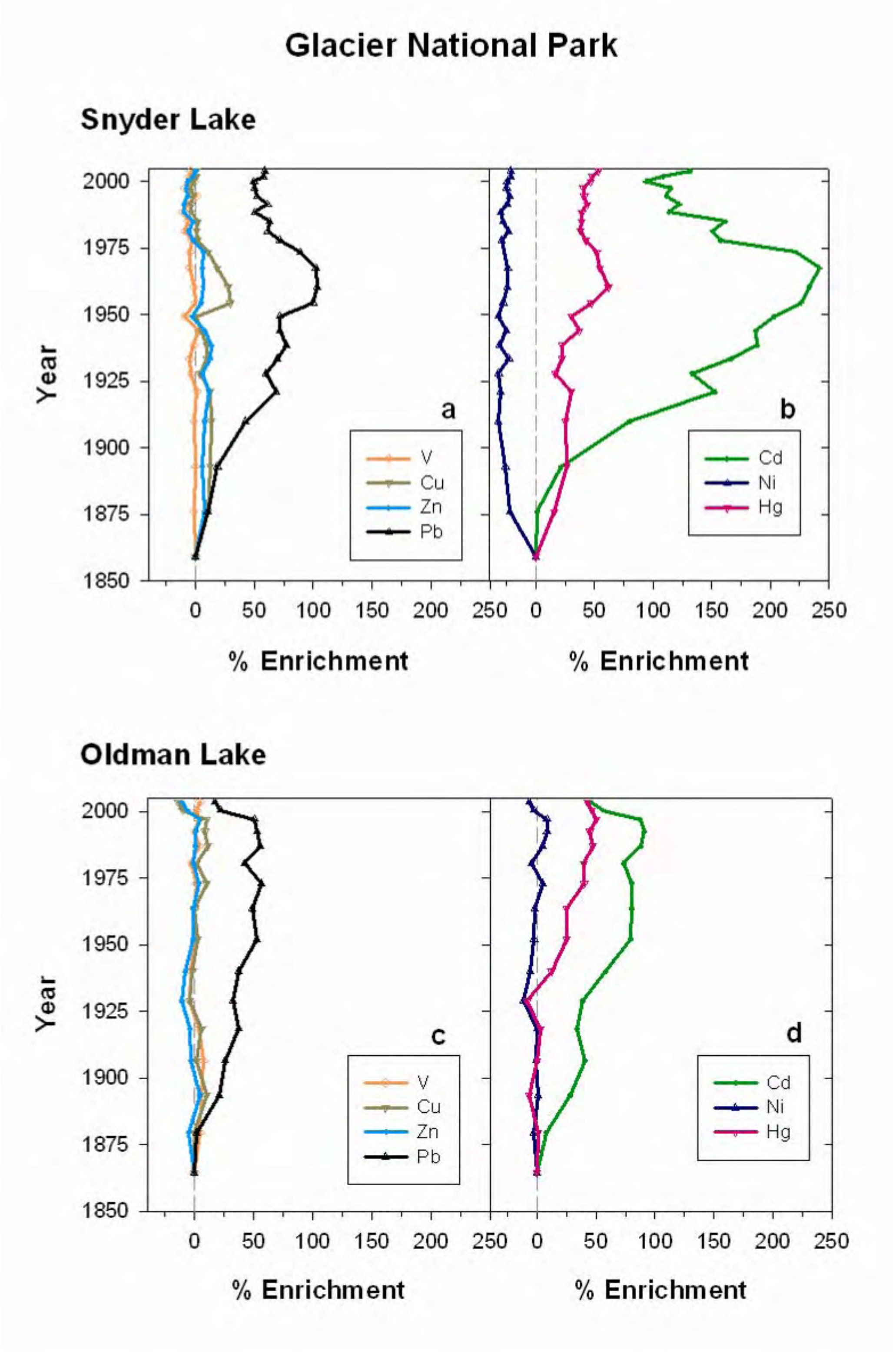


Figure 4-46. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Snyder and Oldman Lakes (GLAC). See Figure 4-44 for more information.

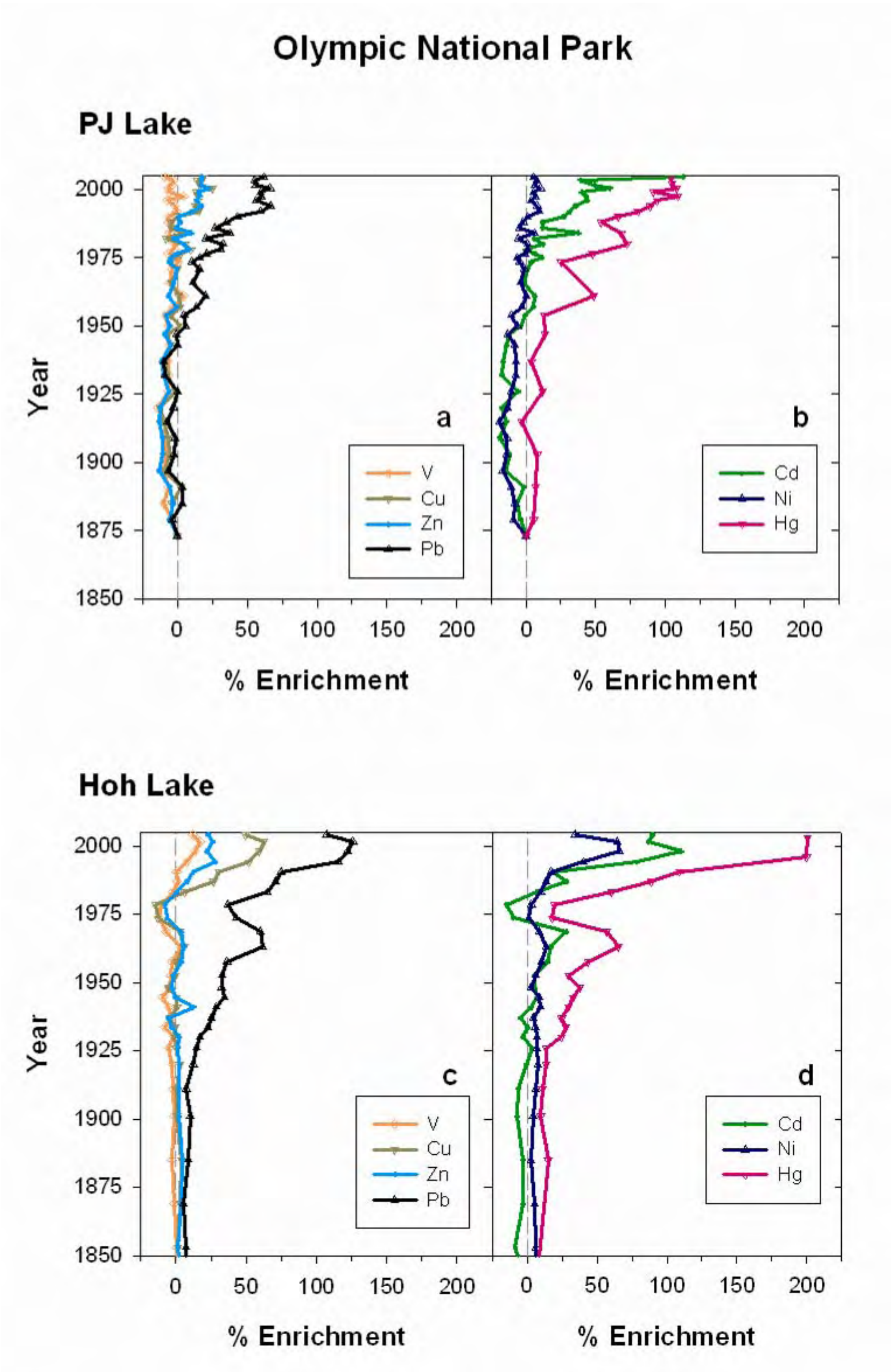


Figure 4-47. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from PJ and Hoh Lakes (OLYM). See Figure 4-44 for more information.

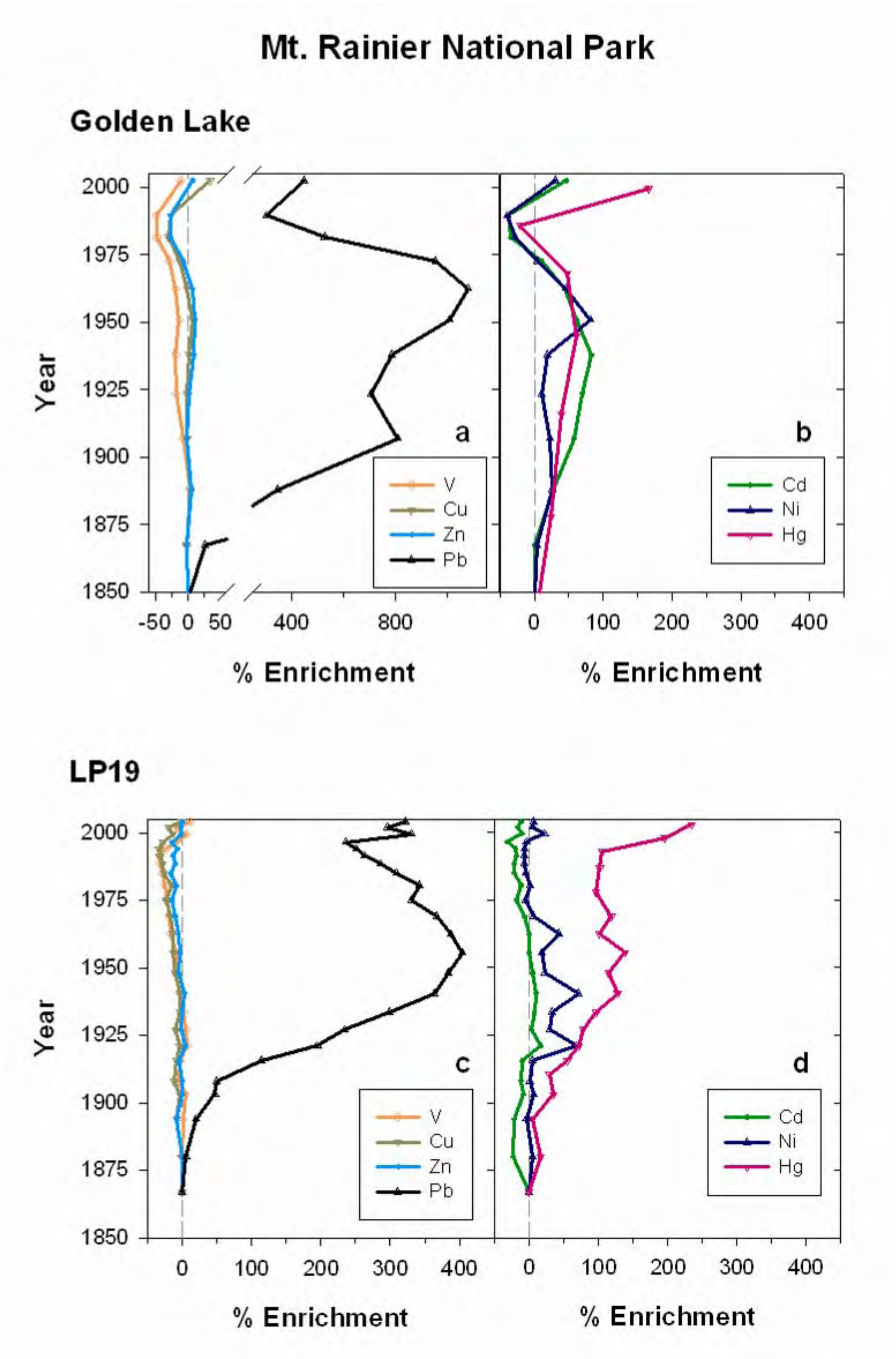


Figure 4-48. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Golden Lake and LP19 (MORA). See Figure 4-44 for more information.

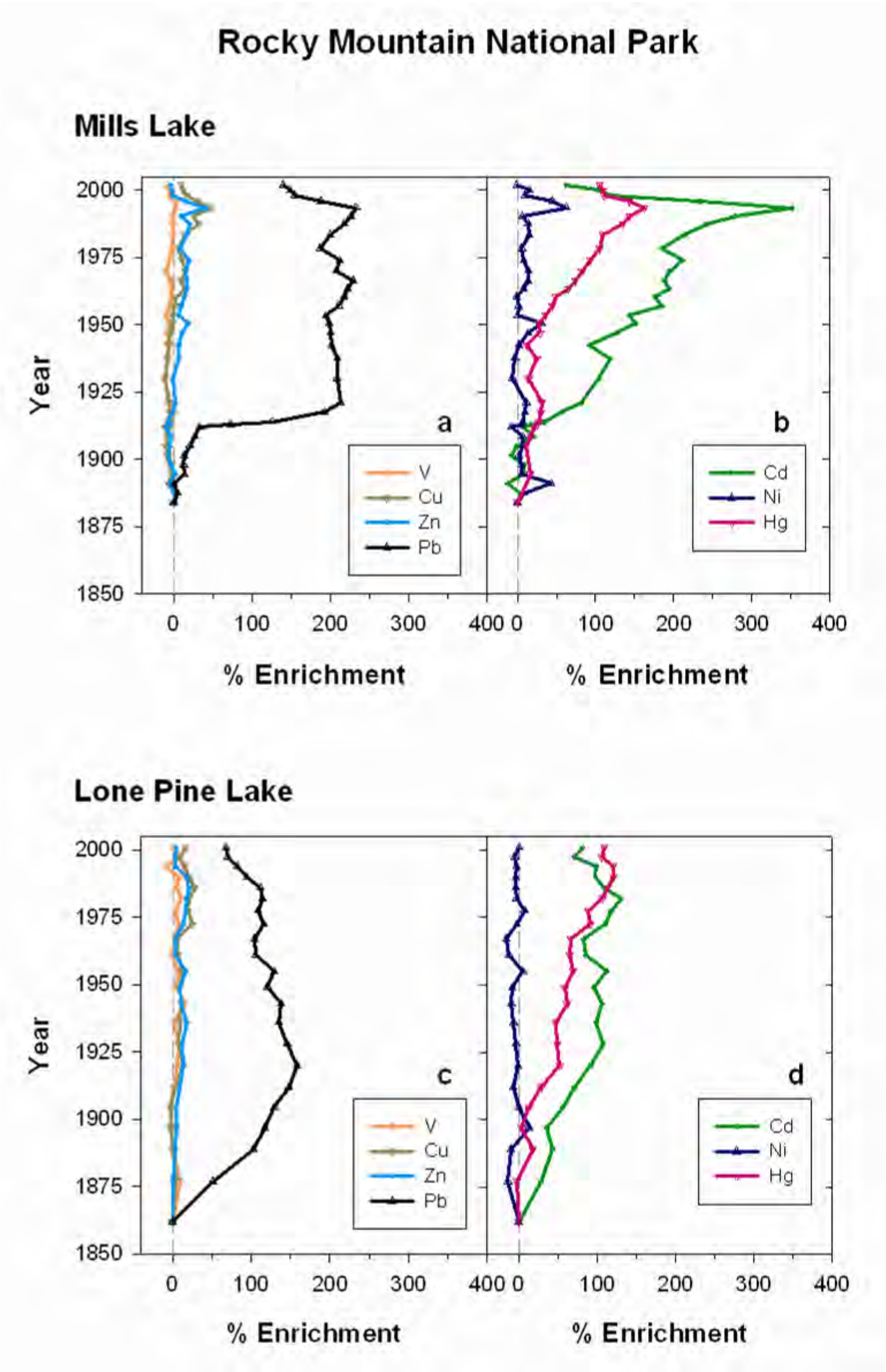


Figure 4-49. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Mills and Lone Pine Lakes (ROMO). See Figure 4-44 for more information.

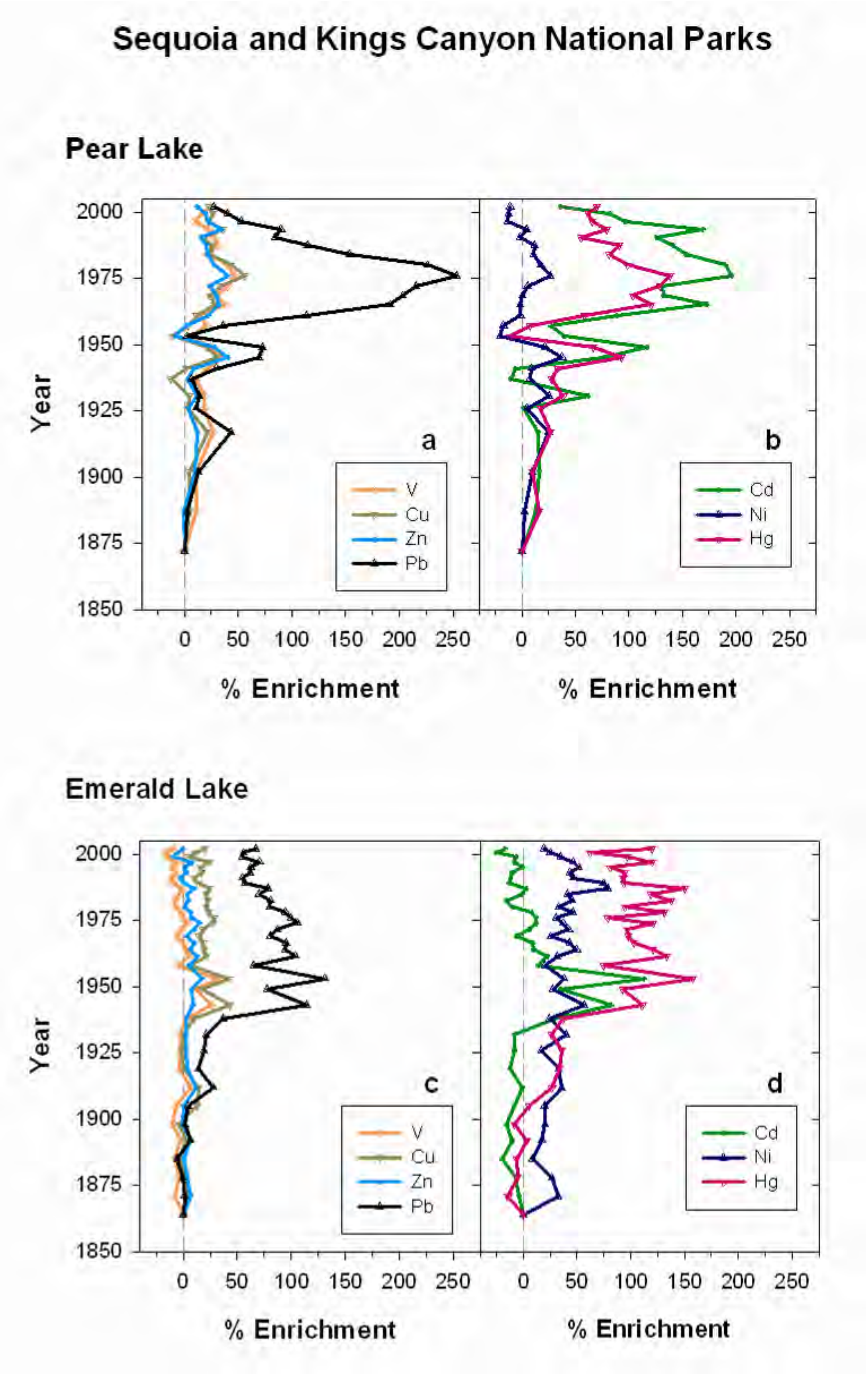


Figure 4-50. Percent Enrichment of V, Cu, Zn, Pb, Cd, Ni, and Hg in Sediment Cores from Pear and Emerald Lakes (SEKI). See Figure 4-44 for more information.

Like Pb, Cd is found on fine atmospheric particulate matter. The element is derived from many different anthropogenic and natural sources (see Table 3-4). Cd enrichment is a result of increasing anthropogenic sources of the metal. Significant Cd enrichment was not seen uniformly, but was seen at Snyder and Oldman Lakes (GLAC; Figure 4-46), PJ and Hoh lakes (OLYM; Figure 4-47), Mills and Lone Pine lakes (ROMO; Figure 4-49), and Pear Lake (SEKI; Figure 4-50). The largest PE increase for Cd was seen at Mills Lake (Figure 4-49), with a temporal pattern similar to that of Pb. Thus, sources associated with Pb mining and smelting in the area could be contributing both elements.

For mercury, all parks show an increase in PE starting around the late nineteenth or early twentieth century, which is consistent with other sediment and ice core data and is attributed to the increasing emissions of mercury from human sources. At most parks, the PE values reached 50-100% in the most recent sections of the sediment cores. At Hoh Lake (OLYM; Figure 4-47), Golden Lake (MORA; Figure 4-48), and LP19 (MORA; Figure 4-48)), PE was much higher in the last few (top) sediment layers. Some caution is needed, however, in interpreting these results, because for these lakes, the PE value was much lower and then rose significantly in the top one or two sediment sections. At Hoh Lake, although the PE value increased, the Hg flux values were low and generally decreasing.

For two of the Alaska lakes, Matcharak and Wonder (Figures 4-44 and 4-45), we see an increase in Hg PE beginning in the early 1900s that continues to the surface, with no leveling off or decline. Both lakes currently have Hg PE values of 85-100%. Burial and McLeod lakes (Figures 4-44 and 4-45) show a smaller increase in Hg PE, beginning in about 1970 for McLeod Lake and 1935 for Burial Lake. These two lakes had the lowest Hg PE (~35-40%) for recent sediments among all WACAP lakes. Because no SCPs were observed in any of the Alaska lake sediments, we suspect that these Hg increases result entirely from an increase in anthropogenic global background of Hg, rather than regional sources.

Oldman Lake and Snyder Lake (GLAC; Figure 4-46) show both differences and similarities in their Hg PE profiles. Hg in Snyder Lake began to rise in the late 1800s, along with Pb and Cd, whereas the Oldman Lake profile shows Hg PE beginning to increase about 1930, well after the increase in Pb and Cd. For both lakes, the Hg PE values increase steadily up to the surface, where values are fairly low, about 50%, similar to the Alaska lakes with the lowest values. At Snyder Lake, the SCP flux began earlier than it did at Oldman Lake, supporting the notion of a regional high temperature combustion source for the earlier rise in Hg PE. SCPs were higher at Snyder Lake, similar to the results for PAHs (see Section 4.2.6.2).

Both OLYM lakes (Figure 4-47) show similarity among Hg, Pb, Cd, Cu, and Zn PE profiles, suggesting that they might share a common source for all of these elements. The Hg focus-corrected fluxes for Hoh Lake were some of the lowest among all WACAP lakes, yet the PE values increased to very high values. For PJ lake, all metals had much higher fluxes (including Hg), yet the Hg enrichment values were not as high as those at Hoh Lake.

In the MORA lakes (Figure 4-48), the Hg PE profile for Golden Lake began a very slow increase in the late 1800s. At LP19, the increase began at about the same time, but the magnitude is much larger. At the surface, the PE values for LP19 were over 100% for most of the 1900s, and over 200% in the most recent sediment layers. As already mentioned, the top one or two sediment slices show significant enrichment in Hg, whereas SCPs are declining. This enrichment could be related to an increase in Hg deposition from global/Asian sources and decreasing SCPs as a result of controls on particulate emissions associated with regional high temperature combustion sources.

In the ROMO lakes (Figure 4-49), recent Hg fluxes were some of the highest among all WACAP parks (20-40 $\mu g/m^2/yr$), and the PE profiles are broadly similar to one another. Hg PE values for Lone Pine Lake show an increase starting around 1900, whereas values for Mills Lake began to increase somewhat later. The PE value at both sites reached maximum values of 100-150% in the late twentieth century and have declined slightly since. At Mills Lake, the SCP profile is broadly similar to the Hg profile, but at Lone Pine Lake, the SCP profile is rather different. This early increase in Hg is mirrored by Cd and Pb in both Mills and Lone Pine lakes, suggesting a possible common source. In both lakes, the SCPs have declined considerably in the recent decades. These patterns are broadly consistent with a decrease in regional emissions from high temperature fossil fuel combustion, metal smelting, or other industrial sources. These patterns are also influenced by an increase in global background Hg concentrations, not associated with SCPs, that have supplanted the regional sources. An increase in global sources (e.g., Wu et al., 2006) could be replacing Hg deposition that was previously from regional sources.

In SEKI (Figure 4-50), both lakes show an increase in Hg PE in the early 1900s, reaching values of 100-150%. Hg PE values in Emerald Lake reached this value very quickly between about 1940 and 1955. The concentrations have declined only slightly since then. At Pear Lake, the values are more variable, peaking around 1975, and have dropped considerably since then. At both lakes, the Cd and Pb enrichment pattern is similar to the Hg pattern. In Pear Lake, this pattern is similar to the SCP profile, suggesting a role for regional fossil fuel sources. But in Emerald Lake, the SCPs have a different pattern, suggesting that the sources are more complex. The fact that SCPs and Hg in both lakes now appear to be moving in different directions suggests that other Hg sources (i.e., increasing global background, transpacific, local/regional sources not associated with SCP) are now affecting these sites.

4.3.6 Source Attribution for Mercury, Trace Metals, and SCPs

Most metals and SCPs reside on, and are transported with, other fine particulate matter. As mentioned previously, detectable SCPs are in the range of 5-50 µm in diameter. Metals are found primarily on particles less than 10 µm diameter. These particles are produced from a variety of sources, including fossil fuel combustion, metal smelting, and other industrial processes. SCPs are produced only from high temperature combustion. Transport of the fine and larger particulate matter is generally limited to distances of no more than about 1,000-2,000 km. Starting in the late 1970s, the Clean Air Act mandated controls on many industrial sources in the United States. These controls initially applied only to new sources, but over time, nearly all large sources have installed, or are in the process of installing, scrubbers or other technologies to capture most particulate matter. Over the same time frame, Pb in gasoline was also phased out in the United States. Thus for SCPs, Pb, and Cd, we see a clear decline in fluxes to the sediments for nearly all WACAP sites in the conterminous 48 states. In Alaska, the SCPs were non-detectable and Pb and Cd were generally much lower than at sites in the conterminous 48 states; thus we do not observe the same decline in the Alaska sediment cores.

For Hg, source attribution is more complex. There are both natural and industrial sources and, once deposited, Hg can be re-emitted to the atmosphere. Mercury can be transported to the WACAP parks, both on fine particulate matter as well as via several gaseous compounds. While particulate mercury and gaseous Hg(II) compounds have short atmospheric lifetimes, gaseous elemental mercury [Hg(0)] has a lifetime up to one year or more, which results in a fairly uniform global reservoir of elemental mercury in the atmosphere. Gaseous elemental mercury is slowly oxidized to Hg(II), which is then quickly removed via wet or dry deposition. The oxidation is believed to be driven by UV light, which results in a latitudinal gradient in the depositional flux (Selin et al., 2007). Thus, in regions with significant industrial sources of particulate Hg or gaseous Hg(II) compounds, such as from coal combustion or waste incineration, there can be a significant contribution to regional deposition. The complexity of the Hg cycle suggests that the relative contribution from global vs. regional sources for any location is complex, and depends on numerous factors. In addition, there are large uncertainties in the sources and overall cycling of Hg in the atmosphere (Lindberg et al., 2007).

Mercury in the WACAP parks comes from both regional and global sources. As a result of the Clean Air Act, scrubbers and other control technologies were installed for removal of particulate matter, sulfur dioxide (SO_2), and nitrous oxides (NO_x) beginning in the 1970s. As an unintended benefit, these scrubbers also remove some of the mercury, mainly particle bound and Hg(II) compounds. These forms of Hg are also the forms that are most important for regional deposition. Gaseous elemental Hg is much more difficult to remove from the waste stream. According to the USEPA, between 1990 and 1999, US industrial emissions of Hg dropped by 44%, from 220 tons to 115 tons per year (see http://www.epa.gov/mercury/control_emissions/emissions.htm).

Using both global (Selin et al., 2007) and regional models (Seigneur et al., 2004), several groups have simulated Hg deposition patterns. Although there are significant uncertainties, these two models get broadly similar results: US industrial sources dominate Hg deposition in the eastern United States, whereas natural and global sources dominate deposition in the western United States. This largely reflects the greater emissions from coal-fired plants in the eastern United States. The WACAP results are broadly consistent with this current understanding, but they also demonstrate the complex biogeochemical pathways of Hg that result in our observations in sediments, vegetation, snow, and fish.

For the four Alaska WACAP lakes, the average Hg flux to the sediments since 1950 was 4.8 $\mu g/m^2/yr$, whereas the mean highest flux determined for WACAP lakes in the conterminous 48 states during the same period of accumulation was approximately 21 $\mu g/m^2/yr$. Thus, in the last 50 years, WACAP lakes in the conterminous 48 states accumulated approximately four times more Hg in their sediments. This large difference in Hg flux probably results from a combination of factors, including greater regional anthropogenic sources in the conterminous 48 states and enhanced oxidation of atmospheric Hg(0) at lower latitudes (Selin et al., 2007).

The overall impact is that the aquatic environment in the WACAP lakes in Alaska appears to receive 80% less Hg from atmospheric sources than WACAP lakes in the conterminous 48 states. This finding is also confirmed by the snowpack Hg flux (see Section 4.3.1). Nonetheless, fish from the Alaska lakes had the highest Hg concentrations among fish from all WACAP sites, reflecting the poor relationship between atmospheric deposition and fish bioaccumulation in aquatic ecosystems, which probably reflects mainly the complexity of food web transfer of mercury and methylation, both of which play key roles in bioaccumulation.

Winter deposition of Hg to the snowpack in the Alaska, Washington, and California parks is probably dominated by the global pool of atmospheric Hg, because of relatively low Hg(0) oxidation rates and subsequent deposition during the winter months (Selin et al., 2007).

However, the high SCP flux in SEKI lakes suggests Hg from regional high temperature combustion sources is also a likely source. For MORA, some Hg deposition from the coal-fired power plant in Centralia Washington is also likely. At ROMO, local and regional upwind emissions sources, principally coal combustion, might also contribute. As seen in the sediment patterns (Figures 4-41 and 4-48), both lakes in ROMO are undergoing recent declines in Hg flux to the sediments, probably because of reductions in regional emissions. The Hg flux to the snowpack in OLYM was fairly high (see Figure 4-33), but this probably reflects a very high snowpack amount, as well as the fact that the average is calculated from only a few samples collected in a single year.

In summary, the WACAP data show that regional sources of Hg have declined, consistent with reductions in US emissions of Hg. The WACAP data also suggest that global sources are now contributing an ever increasing share of the total Hg deposition. Because of the potential for continuing increases in global mercury emissions (Wu et al., 2006), the NPS should continue to monitor mercury in some forms within the western parks.

4.4 Nutrient Nitrogen and Sulfur

4.4.1 Spatial Distributions of Nitrogen and Sulfur in Lichens

Mean dry weight (dw) concentrations of nitrogen and sulfur in lichens in the core and secondary WACAP parks are shown in Figure 4-35 (see Section 4.3.3). Lichen data are reported in Appendices 4A.12 and 4A.13, as well as in the WACAP database. Lichen nitrogen and sulfur concentrations indicate that deposition of atmospheric pollutants containing nitrogen and sulfur is enhanced in some WACAP parks. Mean nitrogen and sulfur concentrations were well above the upper limit for the background range for public lands in the western United States at SEKI and GLAC, and nitrogen concentrations were also above these background ranges at BAND and BIBE (see Section 4.3.3 and Appendix 4A.14 for a description of how the background ranges were calculated). WACAP field lichenologists remarked in their notes that nitrophytic (nitrogen-loving) lichen species were abundant at these latter two parks. Because ammonium sulfate is a dominant fine particulate at the BIBE IMPROVE site, it is likely that sulfur deposition is also elevated in BIBE relative to other remote parks and forests in the western United States. Analysis of lichen samples collected during WACAP and currently archived at the University of Minnesota Research Analytical Laboratory could provide corroborative evidence.

4.4.2 Source Attribution for Nitrogen

Lichens generally accumulate nitrogen from atmospheric sources in the following order of preference: gaseous ammonia, particulate ammonium, particulate nitrates, gaseous nitric acid, and gaseous nitrogen oxides. Therefore, lichen nitrogen is highly responsive to agricultural sources, especially ammonia, as well as NO_x emissions from fossil fuel combustion. High N deposition is associated with adverse effects to vegetation. NO_x-nitrogen emissions come mainly from fossil fuel combustion, although there is a small natural contribution from lightning and soils. NH_3-nitrogen sources are associated with agricultural applications (fertilizers), animal wastes, and industrial sources. Natural sources are much smaller. Thus nitrogen sources are fairly ubiquitous in the western United States. SEKI probably gets the greatest contributions from both NH_3 and NO_x sources, because of its proximity to large urban areas, agriculture, and animal husbandry.

4.5 Atmospheric Transport

(Refer to Section 3.4.1 in Chapter 3 for a discussion of the interpretation of atmospheric trajectories and the methods used.) Figures 4-51 to 4-57 show the air mass back-trajectory cluster plots for all sites. The back-trajectories for each park were generated by the NOAA-Hysplit trajectory model for the period 1998-2005. Clusters were generated with 1-, 5-, and 10-day back trajectories, which represent the airsheds of the WACAP parks at different scales of atmospheric motion. These differences represent local, regional, and long-range atmospheric transport and the climatology of each cluster, as shown by two parameters: precipitation and seasonal distribution of transport patterns. Although the WACAP parks cover a wide geographic range, many of them share similar climatological drivers (and similar patterns within the clusters). OLYM, MORA, SEKI, and GLAC all have winter precipitation maxima and summer minima that are driven by the Aleutian low pressure and Pacific high pressure systems, respectively.

The annual average precipitation at MORA was about 275 cm. For the 1-day clusters, ~50% of this amount comes from winter-dominated clusters E and F, whereas these same clusters contain only ~17% of the total trajectories (see Figure 4-55). Conversely, summer-dominated clusters A and C are responsible for ~17% of the precipitation, with ~45% of the trajectories. Although the 1-day clusters capture the climate of the Pacific Coast, the seasonality and precipitation graphs for the 5- and 10-day clusters show that the percentage of trajectories per cluster and the percentage of precipitation per cluster are similar. These longer clusters do a poorer job of describing regional flow patterns at MORA, a trend that was also seen at OLYM, GLAC, and SEKI. Precipitation patterns at these sites occur on a scale of a few hundred kilometers. The standard deviations about the cluster means are very high in this region for the 5- and 10-day clusters, suggesting that longer clusters do not accurately describe regional phenomena. This result implies that the longer transport patterns do not accurately reflect the transport of regional emissions to the parks. Instead, the 1-day clusters do a better job of describing the nearby transport pathways.

As demonstrated in Chapter 3 (SOCs), 50-100% of historic- and current-use pesticide concentrations in snow are believed to result from regional transport of less than 300 km. The 1-day clusters represent trajectories with lengths ranging from ~250 km for the shortest clusters and ~1,200 km for the longest clusters, indicating that the 1-day clusters are most representative of regional transport to the WACAP parks. The remainder of the transport occurs on scales ranging up to ~7,500 km within 5 days, and ~17,000 km within 10 days. For contaminants with long enough atmospheric lifetimes, such a distance implies that trans-Pacific sources are possible.

ROMO has a precipitation regime unique amongst the WACAP sites. It receives nearly equal amounts of precipitation in each season. The percentage of trajectories in each cluster is nearly the same as the percentage of precipitation from each cluster, regardless of season (see Figure 4-56). Winter precipitation comes from the Pacific, and summer precipitation from the Gulf of Mexico. The cluster plots for ROMO reflect this pattern, especially summer-dominated cluster A in the 10-day clusters. In addition to bringing precipitation from the Gulf of Mexico, cluster A could be responsible for transport of SOCs from the more heavily contaminated southeastern United States. Higher SOC concentrations are observed in multiple media on the east side of the Continental Divide at ROMO, with different atmospheric sources the likely culprit (see Sections 4.2.1 and 4.2.6). In addition, 1-day cluster A suggests significant local/regional influence during summer.

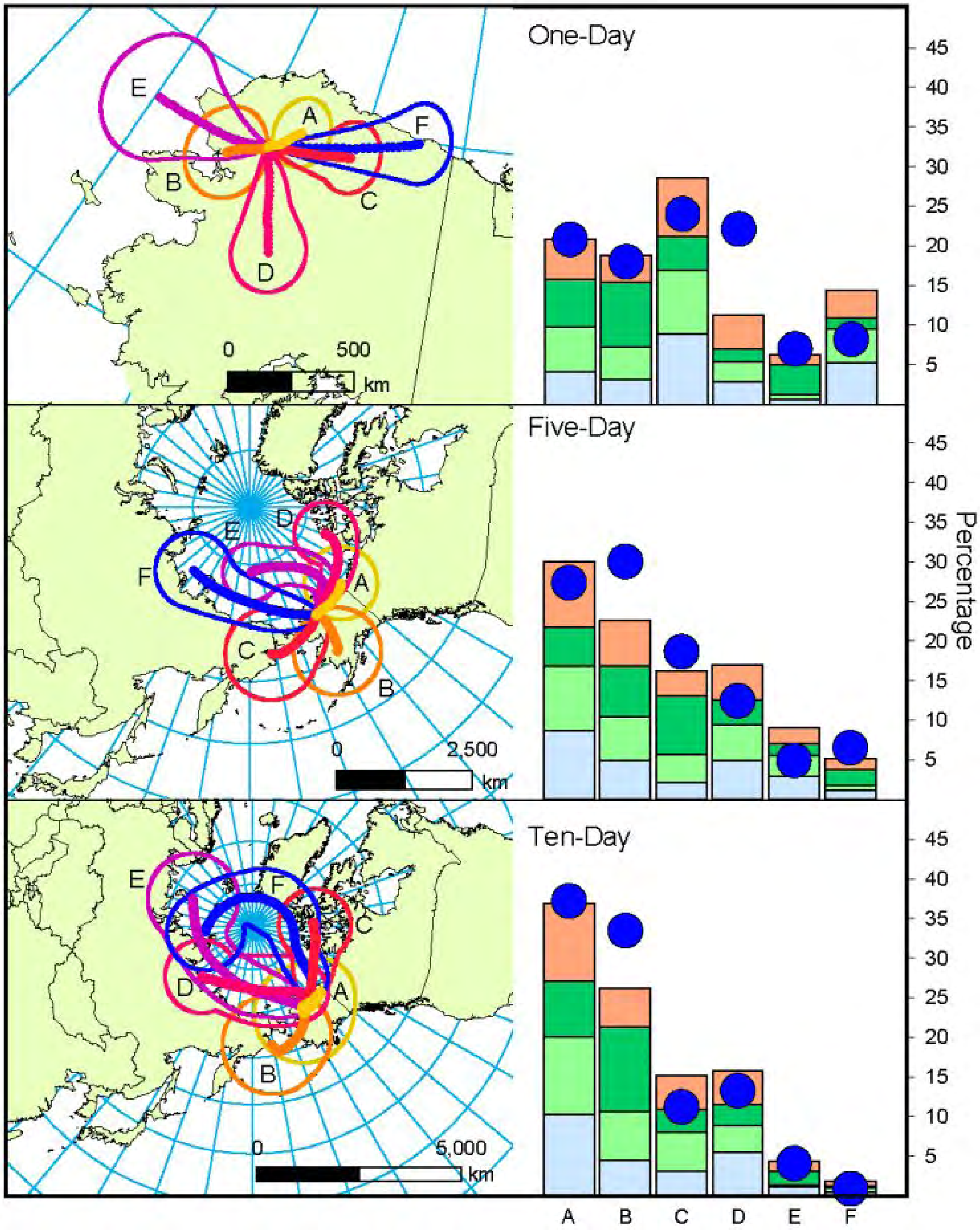


Figure 4-51. 1-, 5-, and 10-Day Cluster Plots for NOAT and GAAR. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories by season in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

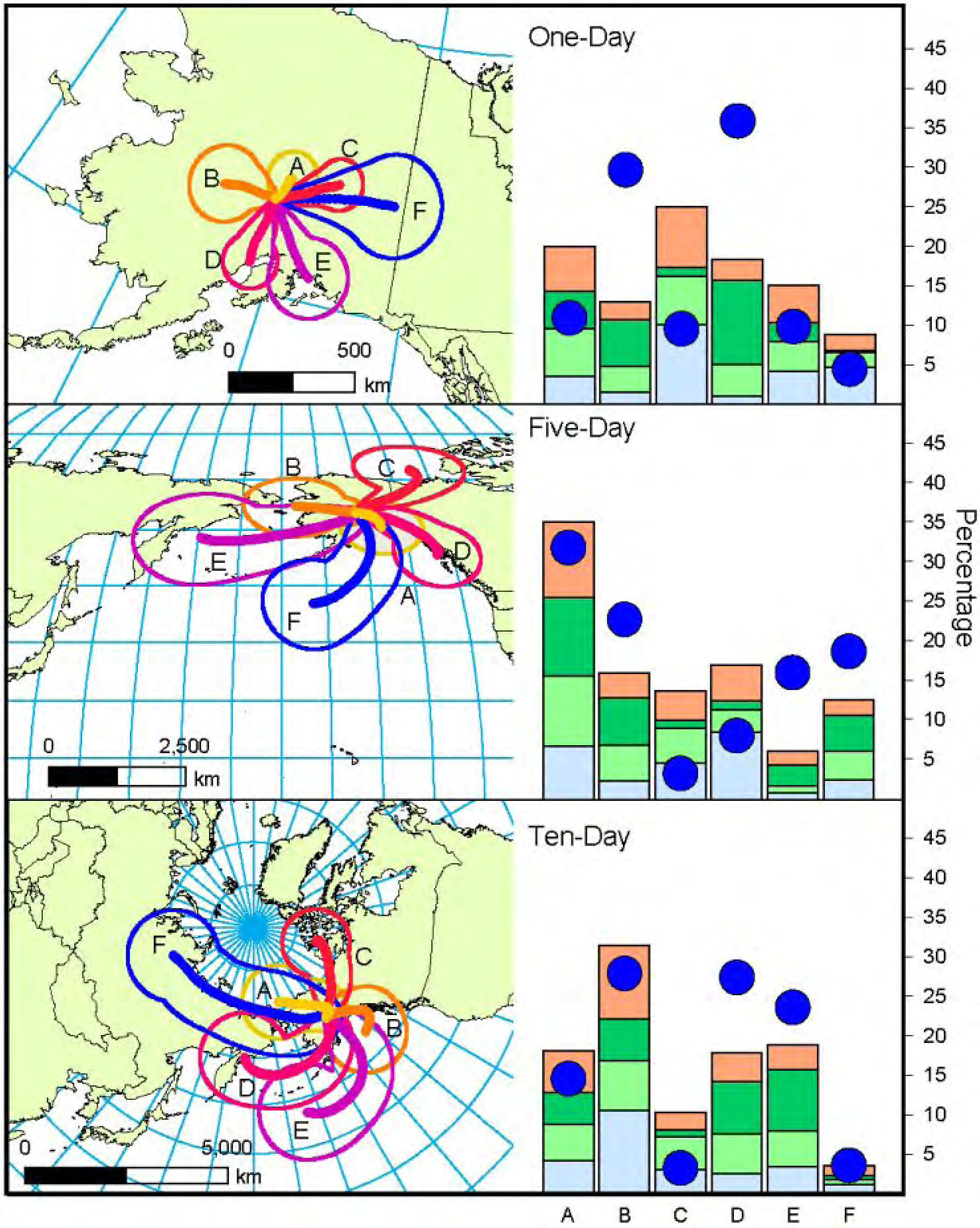


Figure 4-52. 1-, 5-, and 10-Day Cluster Plots for DENA. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

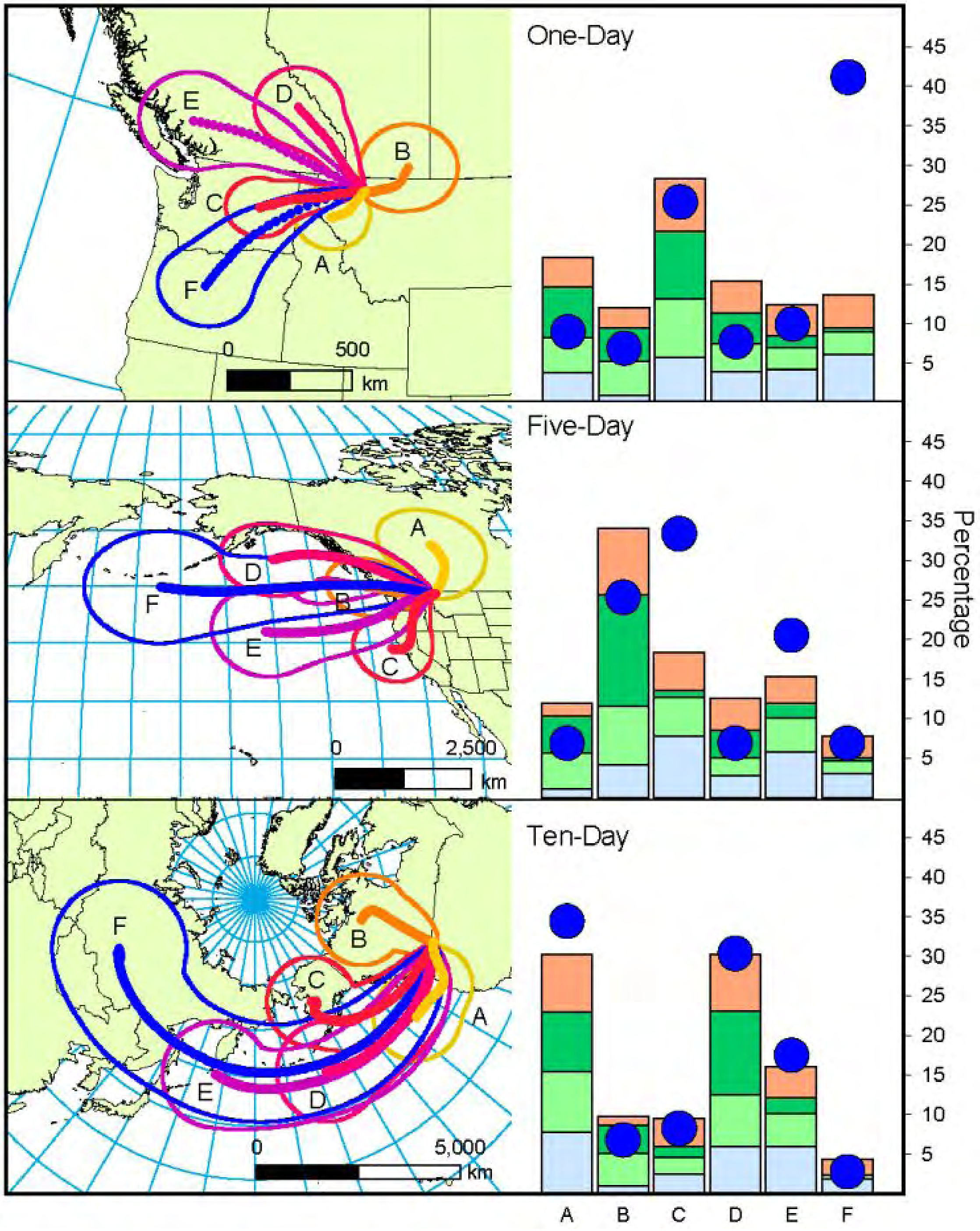


Figure 4-53. 1-, 5-, and 10-Day Cluster Plots for GLAC. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

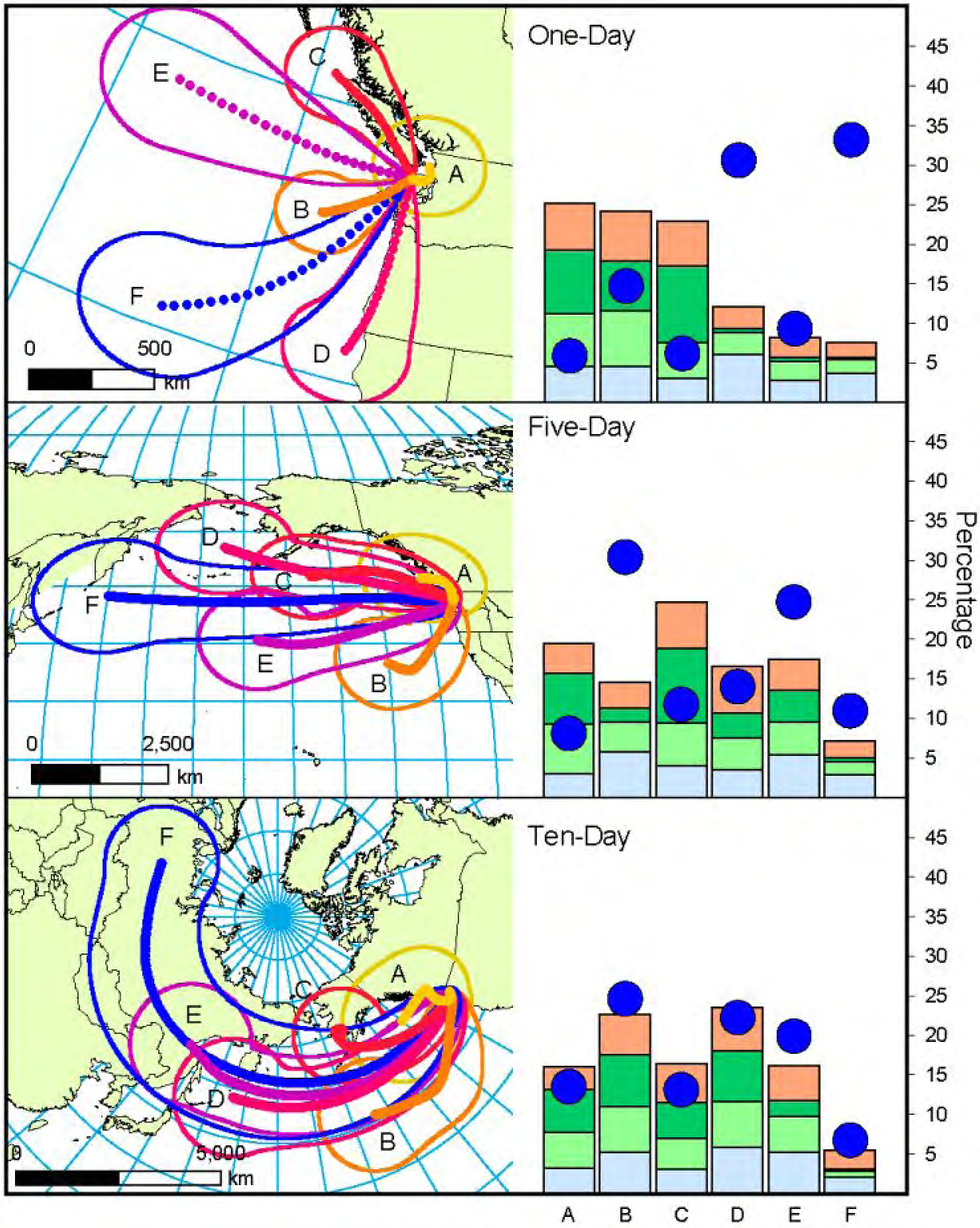


Figure 4-54. 1-, 5-, and 10-Day Cluster Plots for OLYM. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

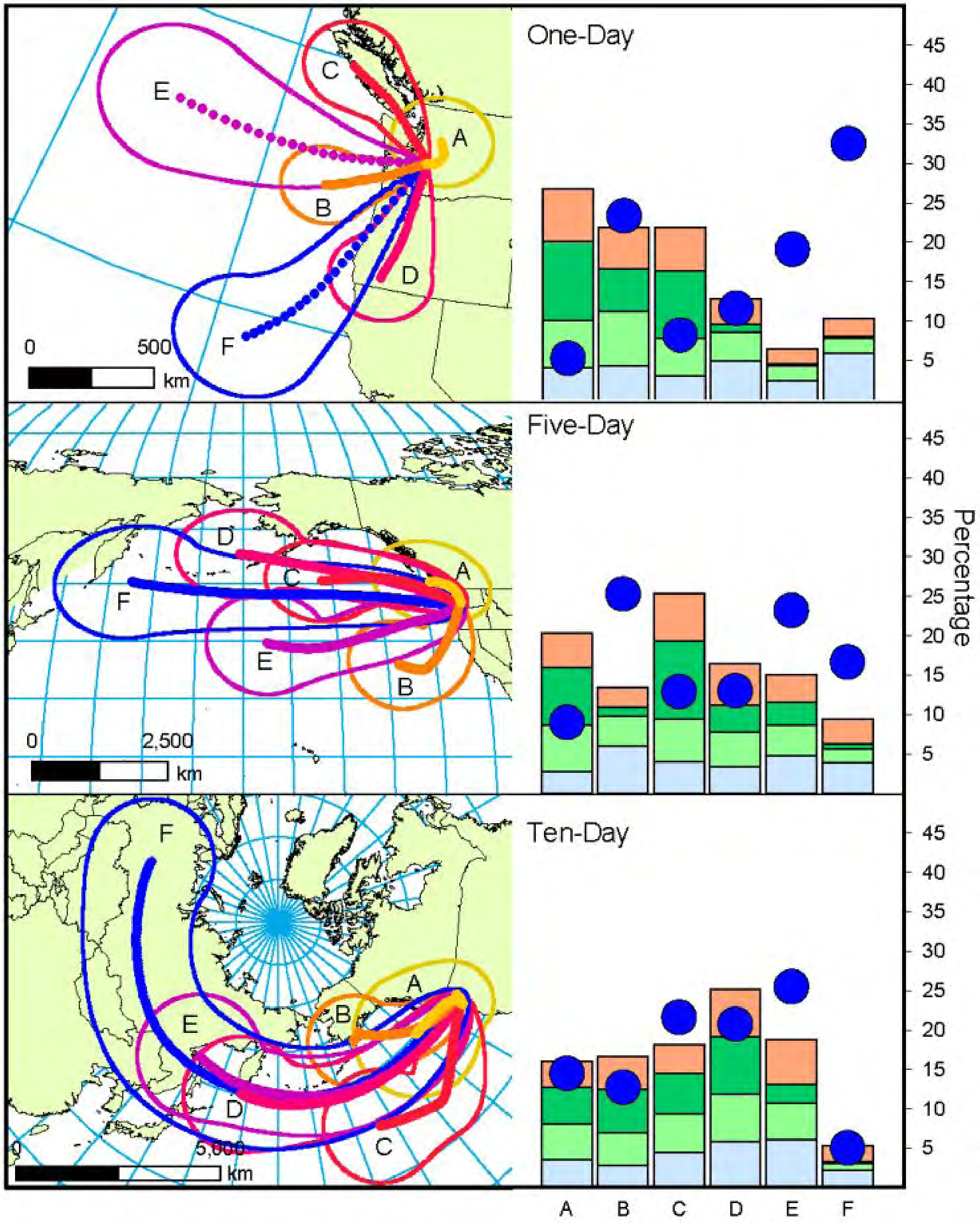


Figure 4-55. 1-, 5-, and 10-Day Cluster Plots for MORA. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

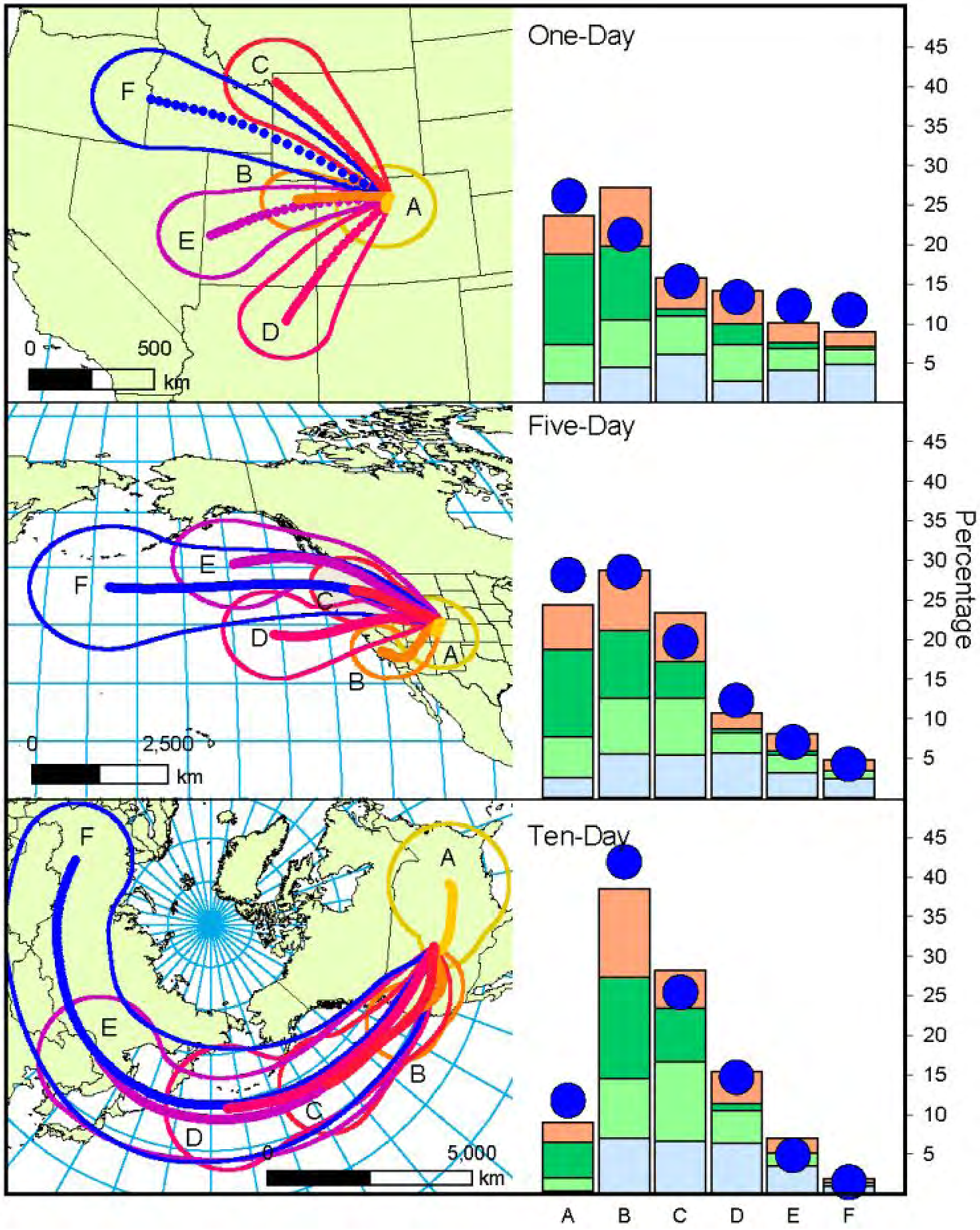


Figure 4-56. 1-, 5-, and 10-Day Cluster Plots for ROMO. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

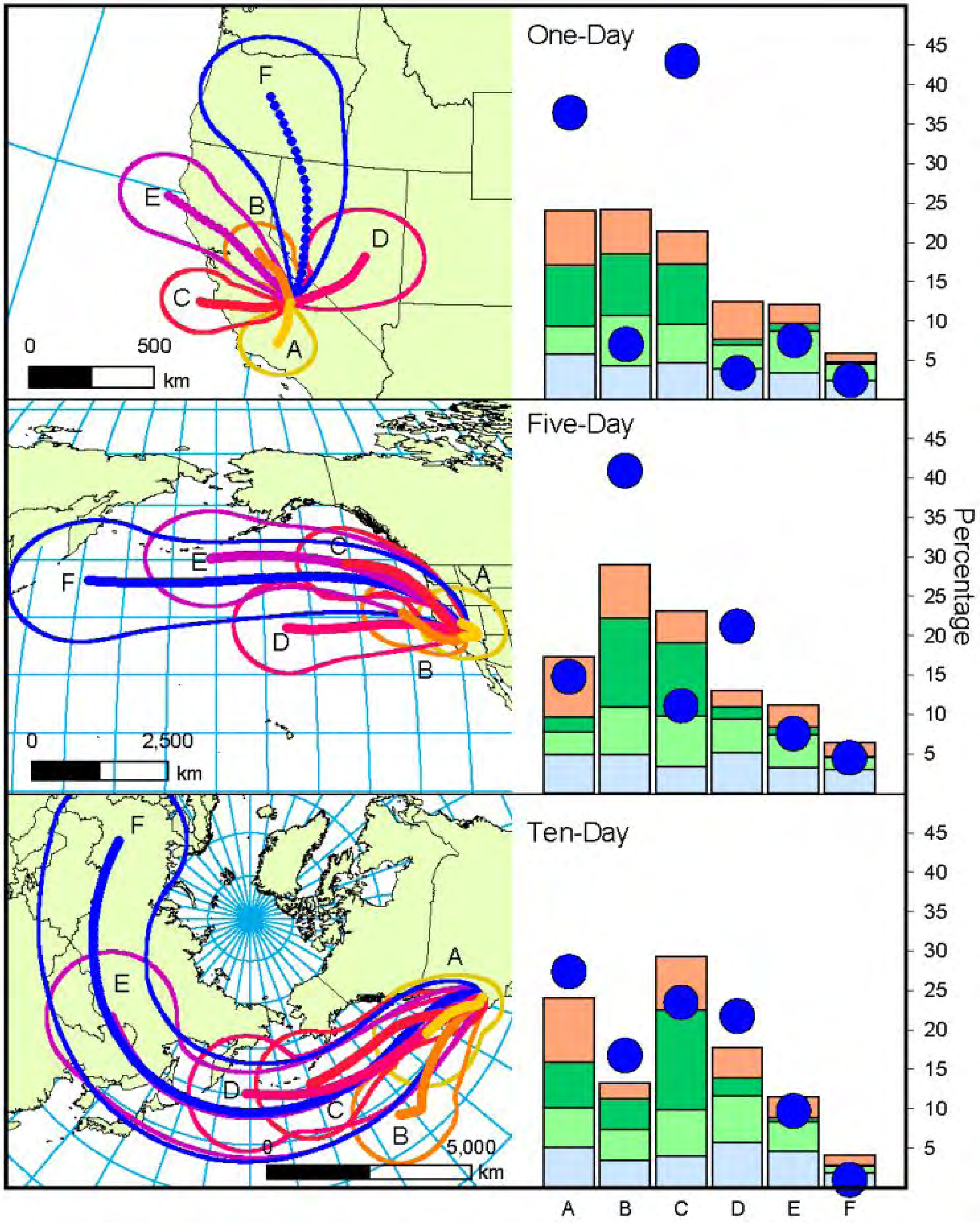


Figure 4-57. 1-, 5-, and 10-Day Cluster Plots for SEKI. Each cluster represents the average transport pathway for a group of individual trajectories. Clusters are sorted shortest to longest, A–F. Bars represent the percent of trajectories in each cluster out of 2,922 total (1998-2005). Light blue = winter; light green = spring; dark green = summer; orange = autumn. The dark blue dot is the percent of total precipitation for which each cluster is responsible.

SOCs measured in Alaska are attributed to background sources or long-range transport. Figure 4-52 shows the clusters for DENA. Within 5 days, likely sources include Siberia and coastal British Columbia. An important aspect of the Alaska clusters is that they are the shortest among clusters for all the sites. The WACAP sites at DENA and NOAT and GAAR are at low elevations, so these trajectories were calculated at ground level. The result was slower moving, less distinguishable air masses.

4.6 Summary

WACAP conducted extensive sampling in 8 core and 12 secondary parks in the western United States from 2003 to 2006. In the core parks, samples of lake water, snow, air, vegetation (lichen and conifer needles), fish, and lake sediments were collected from two watersheds in each park, except the Arctic parks NOAT and GAAR, where one watershed was sampled in each park. In the secondary parks, only lichen, conifer, and air samples were collected in 4-6 sites along an elevational gradient. Samples were analyzed for SOCs (current-use and historic-use pesticides, industrial compounds, and PAHs), mercury, and other metals. Lichen samples were also analyzed for nitrogen content. The data are presented and analyzed in this chapter. From these observations, we have drawn a number of conclusions, as follows:

1. Total SOC concentrations in snow were highest in interior (GLAC and ROMO) and in California (SEKI) parks. The highest SOC concentrations in vegetation were measured at SEKI, GLAC, YOSE, and GRSA.
2. At parks with the highest SOC concentrations in vegetation, the total SOC concentration was dominated by current-use pesticide residues, notably endosulfans and dacthal.
3. Lichen concentrations of PCBs and the pesticides chlorpyrifos, dacthal, endosulfans, HCB, a-HCH, g-HCH, chlordanes, and DDTs increased with elevation at most of the WACAP parks for which there were sufficient data, suggesting that these compounds are undergoing cold fractionation. Concentrations of PAHs decreased with elevation at most parks.
4. Similar SOC concentrations were detected in lichens and conifer needles, but lichens had concentrations 2-9 times greater, except for a-HCH and g-HCH, for which concentrations were similar. Despite lipid normalization, different species of lichens and conifers accumulated different concentrations of SOCs; sampling a single species aids site-to-site comparisons.
5. The magnitude of SOC concentrations in the seasonal snowpack varied substantially year to year, but the percent contribution of each SOC was fairly consistent from year to year for a given park.
6. Concentrations of flame retardants (PBDEs) and historic-use pesticides in WACAP fish were approximately 3 times higher and 2-9 times lower, respectively, than concentrations in fish from similar alpine environments in Europe. Concentrations of dieldrin in fish at some parks (notably ROMO and SEKI) were significantly elevated compared with concentrations in fish from similar Canadian studies.
7. At parks in the conterminous 48 states, good correlations were observed between concentrations of CUPs in snow and vegetation versus percent cropland within 150 km and, in the

case of vegetation, ammonium nitrate concentrations in ambient fine particulates measured by IMPROVE. Based on this relationship, we conclude that most of the CUP deposition comes from regional agricultural sources.

8. For some compounds (e.g., dacthal), pesticide application data are missing for significant regions of the western United States, limiting the ability to accurately identify sources.
9. PAH concentrations in snow, sediment, and vegetation in the Snyder Lake watershed at GLAC were higher than concentrations in the Oldman Lake watershed and in other WACAP parks. Several lines of evidence point to the aluminum smelter in Columbia Falls, Montana, as the most likely source.
10. The evidence suggests that SOC and Hg deposition to Mills Lake, on the east side of the Continental Divide in ROMO, is higher than deposition to Lone Pine Lake, on the west side. This finding might be because the Continental Divide serves as a topographic barrier for transport of SOCs and Hg from populated areas on the east side of ROMO to the west side. SOC concentrations in air, conifer needles, and fish show no clear evidence of an east side enhancement.
11. Snow, lake sediment, and vegetation data indicate that Hg flux to parks in the conterminous 48 states is greater than flux to the parks in Alaska. Despite this observation, fish in the Alaska parks had the highest concentrations of Hg. This finding could be a result of several factors, including fish age, Hg methylation rate, watershed biogeochemical characteristics, and foodweb efficiency as it relates to bioaccumulation.
12. Temporal records from sediment cores indicate that in nearly all parks, Hg deposition increased in the twentieth century because of anthropogenic sources. At some parks, Hg deposition fluxes have declined somewhat since the 1970-1980 time period, although at other parks, the Hg flux appears still to be increasing. This finding reflects a complex array of decreasing regional sources combined with increasing global contributions, complicated by the effects of watershed processes on the sedimentation record.
13. Pb, Cd, and SCPs indicate regional fossil fuel combustion sources. SCPs in lake sediments clearly show increasing contributions from industrial sources in the conterminous 48 states during the late twentieth century. In recent decades, Pb, Cd, and SCPs have declined substantially, reflecting source reductions resulting from the Clean Air Act and regulations on lead in gasoline. Lead concentrations in lichens at SEKI and MORA have decreased 5- to 6-fold since the 1980s.
14. In the Alaska lake sediments, SCPs were non-detectable and Pb and Cd showed little signs of a twentieth century increase. Only the Hg flux showed a consistent increase in the Alaska lake sediments, reflecting a primary contribution from global sources.
15. Nitrogen concentrations in lichens from SEKI, GLAC, BAND, and BIBE were elevated, indicating enhanced nitrogen deposition in these parks. Lichen sulfur concentrations indicated enhanced S deposition at SEKI and GLAC.

CHAPTER 5

Biological and Ecological Effects

5.1 Introduction

In this chapter, we present our assessment of the biological and ecological effects of anthropogenic semi-volatile organic compounds (SOCs), metals, and fixed nitrogen from atmospheric sources in national parks, preserves, monuments, and wilderness areas of the western United States. We begin with an assessment of the accumulation, magnification, and biological effects of contaminants in WACAP matrices (Section 5.2). We provide evidence for the *bioaccumulation* of SOCs and mercury (Hg) in fish and *biomagnification* of SOCs from the atmosphere to vegetation, and from lake water (and snow) to fish. For fish, abnormal endocrine responses in male fish, such as elevated estrogen-responsive protein, and the appearance of eggs in testes, suggest exposure to contaminants having estrogenic effects. Immune system reactions to stress, e.g., the density of macrophage aggregates (accumulations of immune cells), were also related to contaminant concentrations. These sub-lethal effects on fish could be related to contaminants, but other stressors cannot be ruled out with the current dataset.

Later in the chapter (Section 5.4), we discuss the potential ecological effects of current contaminant concentrations on the food web, including some piscivorous birds and mammals. We compare current contaminant concentrations in fish to EPA contaminant health thresholds to evaluate the potential human health effects of fish consumption for sensitive populations or for subsistence and recreational fishing in the parks.

Parks with enhanced nitrogen deposition are identified and the predictive values of various nitrogen indicators on SOC concentrations in vegetation are explored. Overall, the extent and effects of contamination and perturbation are demonstrated, focusing on the watershed level. The extremely diverse ecosystems at each national park are taken into account through identification of park-specific contaminants associated with measured or potential adverse effects on biological and ecological resources or visitor health.

5.2 Bioaccumulation and Biomagnification

5.2.1 Processes of Bioaccumulation and Biomagnification

The chief concerns regarding anthropogenic contamination of aquatic ecosystems are the processes of bioaccumulation and biomagnification of pollutants and metals. *Bioaccumulation* is the overall increase in contaminants in biota, compared to that of water, through time (Gobas and Morrison, 2000). This phenomenon depends on the rates of contaminant accumulation in the biota and the rates of metabolism of contaminants and eventual excretion, or other loss, from the biota. Chemicals not readily excreted from biota are most subject to bioaccumulation. They are often stored in body fat (lipophilic), and are often bio-active (mimic or stop the natural chemicals that control body systems). This is not to say that only lipophilic compounds bioaccumulate. Many metals bioaccumulate, but they are not necessarily lipophilic. *Biomagnification* is the overall increase in the contaminant concentrations beyond what is stored in food (Gobas and Morrison, 2000). For example, we can observe fairly low concentrations of contaminants in aquatic vegetation or phytoplankton, the organisms at the lowest trophic levels. The process of biomagnification is the increase in contaminant concentrations that occur in biota that ingest the vegetation, such as snails (*Gastropoda*). Subsequently, contaminants increase again in the fish that eat the snails, and in the birds or mammals (including humans) that eat the fish. Therefore, fairly low input of environmental contaminants to ecosystems can lead to high concentrations in the biota at the upper trophic levels. For clarification, *bioconcentration* is the uptake of chemicals from the water, and *bioavailability* refers only to the truly dissolved, bio-reactive fraction of any given chemical (Gobas and Morrison, 2000).

The relative solubility of chemicals in water or octanol (octanol-water partition) dictates, in part, how readily chemicals bioaccumulate. In general, octanol-water coefficients (K_{ow}) ranging from 4 to 7 have the greatest chance for bioaccumulation (Thomann, 1989). However, bioaccumulation also depends on biological and environmental factors that regulate the uptake and excretion of contaminants in biota (Mackay and Fraser, 2000). For example, toxico-kinetics of individual contaminants and chemical mixtures influence the bioavailability of contaminants to fish (van der Oost et al., 2003). The diet of the fish (food intake) is the main uptake mechanism for bioaccumulative compounds, whereas the metabolism of, and the individual organ sensitivities to, pollutants dictates how or if the contaminants are excreted from the biota. In addition, bioconcentration of contaminants from the water itself is another route of exposure for fishes (Barron, 1990).

5.2.2 Effects of Bioaccumulation and Biomagnification

5.2.2.1 Large Ecosystem Effects of Bioaccumulation

Bioaccumulation can negatively affect the physiological, endocrine, and immune systems of individual organisms exposed to contaminants (van der Oost et al., 2003). However, attributing changes in body systems to chemical concentrations should be done within a multiple stressor framework (Schreck, 2000a, b). That is, contaminants alone might negatively affect biota, but one should consider that additional stressors could be contributing to changes in the body systems.

Larger ecosystem effects occur through biomagnification of chemicals in the food web. That is, piscivorous birds and mammals usually have higher concentrations than fish, and the very top predators (e.g., polar bears), have the highest chemical concentrations (Mackay and Fraser, 2000). The significance of this dynamic is, first, that by the time population and ecosystem changes can be observed, the early biomarker signals either were not observed and measured or were not acknowledged and, second, that environmental contamination has been occurring for a long time (Figure 5-1) (van der Oost et al. 2003).

An example of large ecosystem effects is the eggshell thinning and population reductions that occurred among many bird species during the 1950s as a result of extensive use of the organochlorine insecticide dichlorodiphenyltrichloroethane (DDT). Until population and ecosystem changes were observed, the negative effects of DDT were either unknown or were not observed. Recovery of some bird populations, such as bald eagles, was largely successful, but required 40 years of extensive financial investment and the commitment of personnel from resource management agencies.

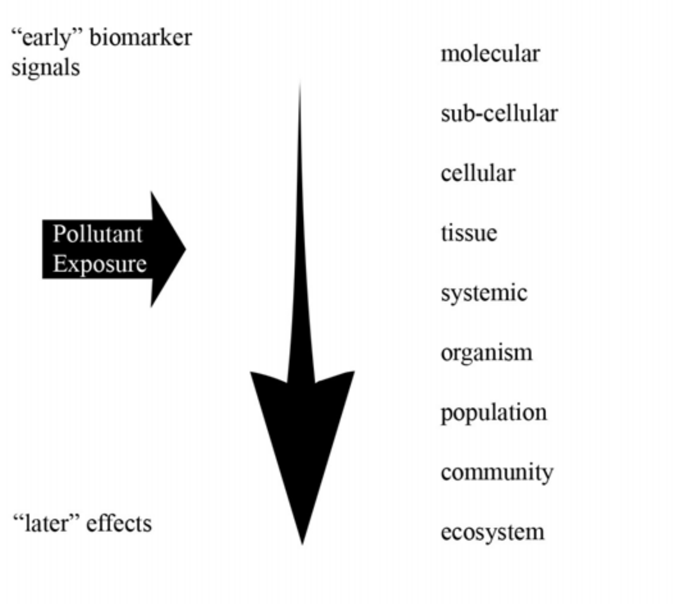


Figure 5-1. Diagram of Increasing Effects of Contaminants, from Individual to Ecosystem Level. Re-drawn from van der Oost et al. (2003).

Long-term concerns about bioaccumulation encompass both organism and ecosystem. Mercury, for example, is a highly persistent natural element and a global pollutant that readily bioaccumulates, biomagnifies, and affects nearly every body system in fish and other vertebrates, including humans. Because Hg is highly persistent, historic emissions (e.g., since the US industrial revolution) of Hg can potentially still be incorporated into the food web by the process of methylation. Furthermore, current emissions of Hg from anthropogenic sources, such as coal-fired power plants in the developed and developing worlds (e.g., the Asian industrial revolution), together with the documented long-range atmospheric transport of contaminants (Jaffe et al., 1999; Wania, 2003; Daly and Wania, 2005), indicate that Hg is likely to have a significant impact on aquatic and other ecosystems in the future.

Contaminants with short half-lives and non-bioaccumulative degradation products pose a lesser concern. Although the bioactivity of those compounds could still be of concern for individual organisms, they do not bioaccumulate and are unlikely to affect the entire food web.

The biota at most risk for adverse effects of bioaccumulation are long-lived, high trophic-level organisms. In the aquatic environments, adverse effects of bioaccumulation are usually observed in piscivorous fish, although insectivorous fish can also bioaccumulate contaminants. In terrestrial environments, birds and mammals that eat fish are susceptible to adverse bioaccumulation effects.

5.2.2.2 Evidence of Bioaccumulation in Fish

Of the many environmental pollutants known to bioaccumulate, Hg is significant because of the numerous and pronounced deleterious effects on fish, wildlife, and humans (Sweet and Zelikoff, 2001). Incorporation of Hg into the food web is highly complex; biota in lakes with similar limnological characteristics can exhibit very different Hg concentrations. For efficient incorporation of Hg into the food web, and for bioaccumulation and biomagnification to occur, Hg must be converted to an organic form by methylation. However, inorganic Hg can be absorbed across the gut of fish (Hoyle and Handy, 2005). Methyl-Hg is the predominant form found in fish tissues, ranging from 95% to 100% of the entire body burden (Bloom, 1992). Methylation is accomplished in the sediment and wetlands by micro-organisms (Ullrich et al., 2001) and is dependent on lake water pH, total organic carbon, dissolved sulfate (Wiener et al., 2006), temperature, and alkalinity (Ullrich et al., 2001). Mercury exists in three valence states; 0, 1, and 2; Hg^{2+} is the species that is methylated. Methylation of Hg requires a CH_3 donor; methylcobalamin is the most likely donor because it is found under anoxic conditions in micro-organisms and is the only natural compound capable of donating the carbanion (CH_3^-). Data suggest that in bacteria, methylation occurs intra- and extracellularly and that sulfate-reducing bacteria are the principal micro-organisms responsible for carrying out the methylation of inorganic Hg (Ullrich et al., 2001). The actual bio-transformation of Hg^{2+} to methyl-Hg by bacteria is poorly understood. Finally, there is also evidence of abiotic methylation of Hg.

Our observations of Hg accumulation in WACAP fish reflect the highly complex nature of Hg cycling in the environment. In the fish that we captured, Hg was age-dependent in all species up to approximately 15 years of age (Figure 5-2; Appendix 5A). In fish older than 15 years of age, the relationship disappears. In these older fish, Hg concentrations could be related to the trophic status of the fish, as has been demonstrated in other studies (Kidd et al., 1995; Evans et al., 2005). Another possibility is that metabolism and excretion of the Hg could occur, as has been modeled by Trudel and Rasmussen (1997). A third explanation is that Hg might increase steadily, until it eventually reaches toxic levels, and, in conjunction with the likely numerous other stressors, leads to senescence; as a result, only fish with fairly low concentrations of Hg reach old age. In our studies, only lake trout (*Salvelinus namaycush*) reached ages > 20 years, and lake trout were collected only in Alaska. Therefore, it is not known if the observed break-down in the relationship between age and Hg is unique to lake trout or is related to the food webs of which they are a part.

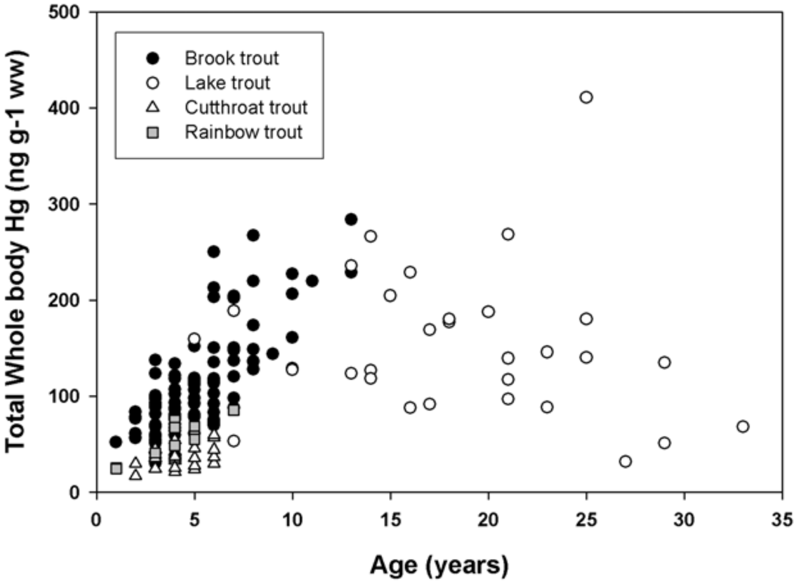


Figure 5-2. Relationship between Fish Age and Total Whole Body Hg in Trout from All Lakes. In fish ≤ 15 years of age, $F_{1,134} = 127.36$, $R^2 = 0.47$, $P = 1.61 \times 10^{-21}$.

Similarly, age was an important factor for SOC concentrations in fish, but not as important as the lipid levels of the fish. For most SOCs, percent lipid in the fish was the most reliable single predictor of SOC concentrations (average lake $R^2 = 0.29$), whereas fish age was the second most reliable predictor (average lake $R^2 = 0.22$) (Ackerman, 2007). Like Hg, some correlations for SOCs broke down among the oldest fish.

An important objective of WACAP is to provide the NPS with data on organic and trace element contamination in the western national parks in various environmental compartments. With these data, it is possible to make comparisons of contaminant concentrations in fish from these western parks to contaminant concentrations from studies published in the peer-reviewed literature. Through these comparisons, it is possible to determine the relative level of contamination in similar ecosystems around the world. In addition, data from the literature on highly affected ecosystems provide another perspective on the relative contamination of historically protected ecosystems in the national parks.

Data on organochlorine concentrations from selected publications from the United States, Canada, Africa, Asia, and Europe are compared to WACAP fish concentrations in Table 5-1. As expected, greatly affected areas such as the Ohio River (tributary of the Mississippi River, USA) and the Columbia River (Pacific Northwest, USA) have fish with organochlorine concentrations 10- to 10,000-fold higher than we report in fish from the national parks. It was surprising, however, that dieldrin concentrations were markedly higher in fish from SEKI, ROMO, and GLAC than in farmed Atlantic Salmon (*Salmo salar*) and wild Pacific salmon (*Oncorhynchus* spp.). The lake trout from GAAR and NOAT and brook trout (*S. fontinalis*) from OLYM represented the WACAP fish with lowest overall concentrations of SOCs; concentrations in these fish were generally lower than those reported in these selected studies.

All WACAP fish had lower polychlorinated byphenyl (PCB), hexachlorocyclohexane (HCH), and hexachlorobenzene (HCB) concentrations than the concentrations reported in the literature. However, we acknowledge that cumulative PCB concentrations might have been underestimated in this study because we targeted a limited number of congeners. A surprising finding was that concentrations of DDTs in fish from SEKI and ROMO were higher than those in many fish (including a piscivorous species) from Lake Malawi in East Africa, despite the current use of DDT in Africa for mosquito control.

Mercury concentrations by lake are presented graphically in Section 5.4.1.1; comparisons of fish in this study to concentrations in the peer-reviewed literature are presented in Table 5-2. In general, mercury concentrations in the trout from the parks in this study were lower than those reported for lakes in the Midwest and Northeast United States, including Lake Michigan and Lake Superior. In addition, mercury concentrations were lower in fish at all WACAP parks than in 1-year-old insectivorous yellow perch (*Perca flavescens*) at Voyageurs National Park in Minnesota. The same was true for lake trout and northern pike (*Esox lucius*) in northern lakes (50º N latitude and above) in Canada. But the opposite was the case for Arctic char (*Salvelinus alpinus*), grayling (*Thymallus arcticus*), and brook trout from northern lakes in Canada. Also, mercury concentrations were higher in WACAP lake fish than in brown trout (*Salmo trutta*) from similar mountain and sub-Arctic ecosystems in Europe. Juvenile sturgeon (*Acipenser transmontanus*) in the Columbia River, USA, had lower mercury concentrations than fish from the Arctic, Denali, Olympic, and Mount Rainier National Parks, although a 41-year-old adult female sturgeon had mercury concentrations well above all fish in this study.

Table 5-1. Comparison of Concentrations of Selected Organochlorines (OCs) in Fish from the Literature to Fish from WACAP Parks.

			Selected Organochlorines (range or mean ± error measure) Units [wet weight (ww) or lipid normalized (lip)] Measured Congeners or Metabolites						(↑ OC > in WACAP, ↓ OC < in WACAP, = OC similar to WACAP); Concentrations reduced 30% for comparisons to muscle							
Species Trophic Level	**Location**	**Tissue**	**DDTs (D)***	**PCBs (P)***	**Dieldrin (N)***	**Chlordane (C)***	**HCH (H)***	**HCB (B)***	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	**Ref.**
Salvelinus fontinalis Insectivorous	Kaweah River, California	Whole fish	40-66 ng/g ww p,p'-DDE	5-8 ng/g ww Sum 98 congener					↓	↓	↓	↓	↓	↓	↓	Datta et al., 1998
Esox lucius Piscivorous	Unspecified lakes, southern Sweden	Muscle	0.13-64 ng/g ww p,p'-DDE	0.32-64 ng/g ww Sum 24 congener					↓	↓	↓	↓	↓	↓	↓	Larsson et al., 1992
Salvelinus namaycush Piscivorous	Peter Lake, Northwest Territories, Canada	Muscle	57.9 ± 148 SD ng/g ww Sum	11.3 ± 23.7 SD ng/g ww PCB153		46.1 ± 112 SD ng/g ww Sum	2.16 ± 4.3 SD ng/g ww Sum		↓	↓	↓	↓	↓	↓	↓	Kidd et al., 1998
Salvelinus alpinus Piscivorous	Peter Lake, Northwest Territories, Canada	Muscle	4.62 ± 1.71 SD ng/g ww Sum	1.3 ± 0.63 SD ng/g ww PCB153		3.45 ± 1.65 SD ng/g ww Sum	1.68 ± 0.8 SD ng/g ww Sum		↓	↓	↑ D ↓PCH	↓	↓	= D ↓PCH	↑D ↓PCH	Kidd et al., 1998
Ctenopharynx pictus Planktivorous	Lake Malawi, Africa	Whole fish	2 ± 0.9 SD ng/g ww Sum p,p'-						↓	↓	↑	↓	↑	↑	↑	Kidd et al., 2001
Dimidiochromis kiwinge Piscivorous	Lake Malawi, Africa	Whole fish	2.9 ± 1.3 SD ng/g ww Sum p,p'-						↓	↓	↑	↓	↑	↑	↑	Kidd et al., 2001
Engraulicyprus sardella Planktivorous	Lake Malawi, Africa	Whole fish	5.2 ± 3.3 SD ng/g ww Sum p,p'-						↓	↓	↑	↓	↓	↑	↑	Kidd et al., 2001

Table 5-1. Comparison of Concentrations of Selected Organochlorines (OCs) in Fish from the Literature to Fish from WACAP Parks (continued).

Species Trophic Level	Location	Tissue	Selected Organochlorines (range or mean ± error measure) Units [wet weight (ww) or lipid normalized (lip)] Measured Congeners or Metabolites						(↑ OC > in WACAP, ↓ OC < in WACAP, = OC similar to WACAP); Concentrations reduced 30% for comparisons to muscle							Ref.
			DDTs (D)*	PCBs (P)*	Dieldrin (N)*	Chlordane (C)*	HCH (H)*	HCB (B)*	GAAR & NOAT	DENA	GLAC	OLYM	MORA	ROMO	SEKI	
Labeotropheus fuelleborni Herb-Insectivorous	Lake Malawi, Aftrica	Whole fish	1.2 ± 0.45 SD ng/g ww Sum p,p'-						↓	↓	↑	↓	↑	↑	↑	Kidd et al., 2001
Opsaridium microlepis Piscivorous	Lake Malawi, Africa	Whole fish	34 ± 16 ng/g ww Sum p,p'-						↓	↓	↓	↓	↓	↓	↓	Kidd et al., 2001
Synodontis njassae Insectivorous	Lake Malawi, Africa	Whole fish	58 ± 39 SD ng/g ww Sum p,p'-						↓	↓	↓	↓	↓	↓	↓	Kidd et al., 2001
Salmo salar Plankti-Piscivorous	Scotland fish farm	Muscle		~ 300 ng/g lip Sum	~ 30 ng/g lip				↓	↓	↓	↓	↓	↓P ↑N	↓P↑N	Hamilton et al., 2005
Salmo salar Plankti-Piscivorous	Norway fish farm	Muscle		~ 250 ng/g ww Sum	~ 25 ng/g lip				↓	↓	↓	↓	↓	↓P ↑N	↓P↑N	Hamilton et al., 2005
Salmo salar Plankti-Piscivorous	Chile fish farm	Muscle		~ 150 ng/g lip Sum	~ 10 ng/g lip				↓P =N	↓P = N	↓P↑N	↓	↓	↓P↑N	↓P↑N	Hamilton et al., 2005
Oncorhynchus nerka Plankti-Piscivorous	Southeast Alaska	Muscle		~ 100 ng/g lip Sum	~ 10 ng/g lip				↓P =N	↓P =N	↓P↑N	↓	↓	↓P↑N	↓P↑N	Hamilton et al., 2005

Table 5-1. Comparison of Concentrations of Selected Organochlorines (OCs) in Fish from the Literature to Fish from WACAP Parks (continued).

			Selected Organochlorines (range or mean ± error measure) Units [wet weight (ww) or lipid normalized (lip)] Measured Congeners or Metabolites						**(↑ OC > in WACAP, ↓ OC < in WACAP, = OC similar to WACAP); Concentrations reduced 30% for comparisons to muscle**							
Species **Trophic Level**	**Location**	**Tissue**	**DDTs (D)***	**PCBs (P)***	**Dieldrin (N)***	**Chlordane (C)***	**HCH (H)***	**HCB (B)***	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	**Ref.**
Oncorhynchus tschawytscha Plankti-Piscivorous	Oregon	Muscle		~ 100 ng/g lip Sum	~ 5 ng/g lip				↓P↑N	↓P↑N	↓P↑N	↓	↓P↑N	↓P↑N	↓P↑N	Hamilton et al., 2005
Salmo trutta Insectivorous	Ovre Neadalsvatn Norway	Muscle	0.74 ± 0.31 SD ng/g ww Sum	1.5 ± 0.57 SD ng/g ww Sum			0.28 ± 0.12 SD ng/g ww Sum	0.58 ± 0.21 SD ng/g ww	↑P ↓DHB	↑D ↓PHB	↓PH ↑DB	↓	↑D ↓HB	↑D ↓HB	↑D ↓HB	Vives et al., 2004
Salmo trutta Insectivorous	Ve'ke' Hincovo Slovakia	Muscle	36 ±13 SD ng/g ww Sum	17 ± 3.5 SD ng/g ww Sum			0.91 ± 0.44 SD ng/g ww Sum	0.3 ± 0.11 SD ng/g ww	↓DPH ↑B	↓DPH ↑B	↓DPH ↑B	↓	↓	↓	↓	Vives et al., 2004
Salmo trutta Insectivorous	Redon France / Spain	Muscle	19 ± 13 SD ng/g ww Sum	8.2 ± 4.8 SD ng/g ww Sum			1.6 ± 0.9 SD ng/g ww Sum	0.6 ± 0.36 SD ng/g ww Sum	↓	↓	↓DPH ↑B	↓	↓	↓	↓	Vives et al., 2004
Polyodon spathula Piscivorous	Ohio River USA	Muscle		50 – 3350 ng/g ww Arochlor 1260					↓	↓	↓	↓	↓	↓	↓	Gundersen and Pearson, 1992

Table 5-1. Comparison of Concentrations of Selected Organochlorines (OCs) in Fish from the Literature to Fish from WACAP Parks (continued).

Species			**Selected Organochlorines (range or mean ± error measure) Units [wet weight (ww) or lipid normalized (lip)] Measured Congeners or Metabolites**						**(↑ OC > in WACAP, ↓ OC < in WACAP, = OC similar to WACAP); Concentrations reduced 30% for comparisons to muscle**							**Ref.**
Trophic Level	**Location**	**Tissue**	**DDTs (D)***	**PCBs (P)***	**Dieldrin (N)***	**Chlordane (C)***	**HCH (H)***	**HCB (B)***	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	
Gymnocypris waddellii	Yamdro Lake Tibet	Muscle	~ 2.5 ng/g ww Sum				~ 1 ng/g ww Sum	~ 1 ng/g ww Sum	↓	↓	↑D ↓HB	↓	↑D ↓HB	↑D ↓HB	↑D ↓HB	Yang et al., 2007
Salvelinus fontinalis *Salvelinus confluentus* *Oncorhynchus mykiss* Pisci-Insectivorous	Mountain Lakes in Banff, Jasper, or Yoho National Parks	Muscle	4.5 ± 5.4 SD ng/g ww p,p'-DDE	7.7 ± 10.4 SD ng/g ww Sum 127 congen		61 ± 52 SD ng/g ww gama-chlor-dane			↓	↓	↑D ↓PC	↓	↓	=D ↓PC	↑D ↓PC	Demers et al., 2007
Salvelinus namaycush Piscivorous	Kusawa Lake Northwest Territories Canada	Muscle	26.66 ± 4.15 SD ng/g ww Sum	32.45 ± 3.66 SD ng/g ww Sum		3.01 ± 0.48 SD ng/g ww Sum	0.62 ± 0.08 SD ng/g ww Sum		↓	↓	↓	↓	↓	↓	↓	Ryan et al., 2005
Salvelinus namaycush Piscivorous	Quiet Lake Northwest Territories Canada	Muscle	0.53 ± 0.09 SD ng/g ww Sum	3.51 ± 0.62 SD ng/g ww Sum		0.62 ± 0.12 SD ng/g ww Sum	0.08 ± 0.02 SD ng/g ww Sum		↑DC ↓PH	↑DC ↓PH	↑DC ↓PH	=D ↓PCH	↑D ↓PCH	↑D ↓PCH	↑DC ↓PH	Ryan et al., 2005
Acipenser transmontanus Piscivorous	Columbia River Oregon	Liver	18,700 ± 7300 ng/g SE lip Sum		134 ± .45 SE ng/g lip Sum				↓	↓	↓	↓	↓	↓	↓	Feist et al., 2005

Table 5-1. Comparison of Concentrations of Selected Organochlorines (OCs) in Fish from the Literature to Fish from WACAP Parks (continued).

			Selected Organochlorines (range or mean ± error measure) Units [wet weight (ww) or lipid normalized (lip)] Measured Congeners or Metabolites						(↑ OC > in WACAP, ↓ OC < in WACAP, = OC similar to WACAP); Concentrations reduced 30% for comparisons to muscle							Ref.
Species Trophic Level	**Location**	**Tissue**	**DDTs (D)***	**PCBs (P)***	**Dieldrin (N)***	**Chlordane (C)***	**HCH (H)***	**HCB (B)***	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	
Salvelinus namaycush Piscivorous	Lake Superior, USA, 1990	Whole-fish	180 ± 50 ng/g 95% CI	450 ± 140 ng/g 95% CI Arochlor 1254	40 ± 4 ng/g 95% CI	100 ± 20 95% CI ng/g			↓	↓	↓	↓	↓	↓	↓	De-Vault et al., 1996
Salvelinus namaycush Piscivorous	Lake Huron, USA, 1992	Whole-fish	520 ± 20 ng/g 95% CI	1570 ± 90 ng/g 95% CI Arochlor 1254	60 ± 3 ng/g 95% CI	250 ± 10 ng/g 95% CI			↓	↓	↓	↓	↓	↓	↓	De-Vault et al., 1996
Salvelinus namaycush Piscivorous	Lake Michigan, USA, 1992	Whole-fish	3,490 ± 450 ng/g 95% CI	1,160 ± 180 ng/g 95% CI Arochlor 1254	190 ± 20 ng/g 95% CI	450 ± 30 ng/g 95% CI			↓	↓	↓	↓	↓	↓	↓	De-Vault et al., 1996
Salvelinus namaycush Piscivorous	Lake Ontario, USA, 1992	Whole-fish	2,650 ± 300 ng/g 95% CI	840 ± 120 ng/g 95% CI Arochlor 1254	80 ± 0.9 ng/g 95% CI	170 ± 90 ng/g 95% CI			↓	↓	↓	↓	↓	↓	↓	De-Vault et al., 1996
Sander vitreus Piscivorous	Lake Erie, USA, 1992	Whole-fish	2,200 ± 310 ng/g 95% CI	120 ± 10 ng/g 95% CI Arochlor 1254	30 ± 0.2 ng/g 95% CI	50 ± 0.2 ng/g 95% CI			↓	↓	↓	↓	↓	↓	↓	De-Vault et al., 1996

*In the column headings, letters in ( ) following compound names are codes used in the right side of the table to indicate the compounds.

Table 5-2. Comparison of Concentrations of Total Mercury in Fish from the Literature to Fish from WACAP Parks.

			Mercury Species (range or mean ± error measure) Units [wet weight (ww) or dry weight (dw)]	**(↑ Hg > in WACAP, ↓ Hg < in WACAP, = Hg similar to WACAP) Concentrations increased for comparisons to muscle following Peterson et al. 2007**							
Fish Trophic Level	**Location**	**Tissue**	**Total-Hg**	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	**Ref.**
Sander vitreus Piscivorous	Lakes in North-central Wisconsin	Muscle	120 – 1740 ng/g ww	↓	↓	↓	↓	↓	↓	↓	Wiener et al., 1990
Salmo trutta Insectivorous	Jorisee, Switzerland	Muscle	37 (18 – 56) ng/g ww	↑	↑	↑	↑	↑	↑	↑	Rognerud et al., 2002
Salvelinus alpinusi Piscivorous	Arresjoen, Svalbard Archipelago	Muscle	179 (39 – 441) ng/g ww	↑	=	↓	↑	=	↓	↓	Rognerud et al., 2002
Salmo trutta Insectivorous	Estany Redo, Spain	Muscle	68 (15-158) ng/g ww	↑	↑	↓	↑	↑	↑	↑	Rognerud et al., 2002
Salmo trutta Insectivorous	Stavsvatn, Norway	Muscle	44 (21-79) ng/g ww	↑	↑	↑	↑	↑	↑	↑	Rognerud et al., 2002
Salmo trutta Insectivorous	Gossen-kollesee, Czech Republic	Muscle	25 (16-39) ng/g ww	↑	↑	↑	↑	↑	↑	↑	Rognerud et al., 2002
Salmo trutta Insectivorous	Ovre Neadalsvatn, Norway	Muscle	21 (14-31) ng/g ww	↑	↑	↑	↑	↑	↑	↑	Rognerud et al., 2002
Salvelinus alpinus Insectivorous	Etang d' Aube, France	Muscle	55 (37-78) ng/g ww	↑	↑	=	↑	↑	↑	↑	Rognerud et al., 2002

Table 5-2. Comparison of Concentrations of Total Mercury in Fish from the Literature to Fish from WACAP Parks (continued).

			Mercury Species (range or mean ± error measure) Units [wet weight (ww) or dry weight (dw)]	(↑ Hg > in WACAP, ↓ Hg < in WACAP, = Hg similar to WACAP) Concentrations increased for comparisons to muscle following Peterson et al. 2007							
Fish Trophic Level	**Location**	**Tissue**	**Total-Hg**	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	**Ref.**
Salvelinus alpinus Insecti- Piscivorous	Lakes in Northern Canada (1971-2002)	Muscle	115 ± 237 SD ng/g ww	↑	↑	↓	↑	↑	↓	↑	Rognerud et al., 2002
Thymallus arcticus Insectivorous	Lakes in Northern Canada (1971-2002)	Muscle	53 ± 45 SD ng/g ww	↑	↑	=	↑	↑	↑	↑	Lockhart et al., 2005
Salvelinus fontinalis Insectivorous	Lakes in Northern Canada (1971-2002)	Muscle	106 ± 50 SD ng/g ww	↑	↑	↓	↑	↑	↓	↑	Lockhart et al., 2005
Lota lota Piscivorous	Lakes in Northern Canada (1971-2002)	Muscle	210 ± 135 SD ng/g ww	↑	↓	↓	↓	↓	↓	↓	Lockhart et al., 2005
Salvelinus namaycush Piscivorous	Lakes in Northern Canada (1971-2002)	Muscle	384 ± 351 SD ng/g ww	↓	↓	↓	↓	↓	↓	↓	Lockhart et al., 2005
Esox lucius Piscivorous	Lakes in Northern Canada (1971-2002)	Muscle	378 ± 298 SD ng/g ww	↓	↓	↓	↓	↓	↓	↓	Lockhart et al., 2005
Perca flavescens Planktivorous	Voyageurs National Park, USA	Whole fish	182-942 ng/g dw	↓	↓	↓	↓	↓	↓	↓	Wiener et al., 2006

Table 5-2. Comparison of Concentrations of Total Mercury in Fish from the Literature to Fish from WACAP Parks (continued).

			Mercury Species (range or mean ± error measure) Units [wet weight (ww) or dry weight (dw)]	**(↑ Hg > in WACAP, ↓ Hg < in WACAP, = Hg similar to WACAP) Concentrations increased for comparisons to muscle following Peterson et al. 2007**							
Fish Trophic Level	**Location**	**Tissue**	**Total-Hg**	**GAAR & NOAT**	**DENA**	**GLAC**	**OLYM**	**MORA**	**ROMO**	**SEKI**	**Ref.**
Perca flavescens Planktivorous	Northeast USA	Whole fish	230 (<0.50-3180) ng/g ww	↓	↓	↓	↓	↓	↓	↓	Evers et al., 2007
Salvelinus fontinalis Insectivorous	Northeast USA	Whole fish	310 (0.05-2070) ng/g ww	↓	↓	↓	↓	↓	↓	↓	Evers et al., 2007
Juvenile *Acipenser transmontanus* Piscivorous	Columbia River, Oregon	Muscle	170.54 ± 12.67 SE ng/g ww	↑	↑	↓	↑	↑	↓	=	Webb et al., 2006
Adult *Acipenser transmontanus* Piscivorous	Columbia River, Oregon	Muscle	1,094 ng/g ww, *N* = 1, Age = 41 y	↓	↓	↓	↓	↓	↓	↓	Webb et al., 2006
Salvelinus namaycush Piscivorous	Lake Michigan, USA	Whole fish	220 ± 80 SE ng/g (normalization not specified)	↓	↓	↓	↓	↓	↓	↓	Mason and Sullivan, 1997
Sander vitreus Piscivorous	St. Louis River Estuary, Lake Superior, USA (1979-1987)	Not specified	~ 250-1500 ng/g (normalization not specified)	↓	↓	↓	↓	↓	↓	↓	Glass et al., 1990
Esox lucius Piscivorous	St. Louis River Estuary, Lake Superior, USA (1979-1984)	Not specified	~ 250-600 ng/g (normalization not specified)	↓	↓	↓	↓	↓	↓	↓	Glass et al., 1990

Comparison of organochlorines and mercury in WACAP fish (Tables 5-1 and 5-2) with those reported in the literature indicate that contamination of WACAP watersheds by PCBs, hexachlorobenzene, hexachlorocyclohexanes, DDTs, and chlordanes is comparable to or lower than in similar mountain areas in Europe, Canada, and Asia, while dieldrin and PBDE contamination is higher than in similar mountain areas and in Pacific Ocean salmon (Ackerman 2007). In general, organochlorine concentrations are lower in WACAP fish than in other fish reported in the literature, but similar to or higher than values in the literature for mercury. Implications of this finding are unknown and some geographic areas reported in the literature have dramatically higher Hg than that observed for the national parks. The potential risk to consumers from fish in the WACAP parks is presented in Sections 5.4.1 and 5.4.2.

5.2.3 Evidence of Bioaccumulation in Vegetation

Bioaccumulation of SOCs in vegetation over time was observed in a subset of WACAP samples tested for this effect. First- and second-year lodgepole pine (*Pinus contorta*) and white fir (*Abies concolor*) needles from Emerald Lake basin in SEKI were analyzed for pesticides and PCB concentrations. Each pair of samples consisted of one set of branchlets that had been divided, with the terminal bud scars as year markers, into first- and second-year needles before analysis. Concentrations of the current-use pesticides endosulfan (sum of endosulfan 1, endosulfan 2, and the degradation product endosulfan sulfate) and dacthal were 2-3 times higher in second-year compared with first-year lodgepole pine needles (Table 5-3).

Although concentration values for second-year needles were all larger than those for first-year needles (except trifluralin in white fir) (Table 5-3), the small sample number and high variability among field replicates yielded insufficient statistical power to provide evidence of significant differences for the other SOCs. However, when all pairs of measurements for chlorpyrifos, endosulfans, dacthal, HCB, a-HCH, g-HCH, chlordanes, and PCBs were considered together (Table 5-4), there was good evidence that second-year needles had, on average, concentrations of these SOCs about 3 times higher than those in first-year needles and that SOC concentrations are strongly correlated with needle age.

Table 5-3. SOC Concentrations (ng/g lipid) in One- and Two-Year-Old Needles of White Fir (*Abies concolor*) and Lodgepole Pine (*Pinus contorta*) from the Emerald Lake Basin of Sequoia National Park. Nearly every value was larger in year 2 than year 1, but significant differences were demonstrated only for dacthal and endosulfans in pine (t-test, $p < t < 0.05$, equal variances). Statistical power was low because of high variability among field replicates and small sample sizes.

			Abies concolor				***Pinus contorta***			
Group	**SOC**	**Yr**	**N**	**Mean**	**s.d.**	**s.e.**	**N**	**Mean**	**s.d.**	**s.e.**
CUPs	Chlorpyrifos	1	2	**0.0**	0.0	0.0	1	**11.6**		
		2	2	**19.7**	26.1	18.5	2	**20.5**	17.7	12.5
	Dacthal	1	3	**1555**	1066	616	1	**530**		
		2	2	**2007**	1249	883	2	**1474**	1102	780
	Endosulfans	1	3	**2448**	963	556	1	**510**		
		2	2	**7573**	2419	1711	2	**1325**	176	124
	Triallate	1	3	**0.0**	0.0	0.0	1	**0.0**		
		2	2	**0.0**	0.0	0.0	2	**125.3**	177.2	125.3
	Trifluralin	1	2	**10.5**	14.9	10.5	1	**0.0**		

Table 5-3. SOC Concentrations (ng/g lipid) in One- and Two-Year-Old Needles of White Fir (*Abies concolor*) and Lodgepole Pine (*Pinus contorta*) from the Emerald Lake Basin of Sequoia National Park (continued).

			Abies concolor				*Pinus contorta*			
Group	**SOC**	**Yr**	**N**	**Mean**	**s.d.**	**s.e.**	**N**	**Mean**	**s.d.**	**s.e**
		2	1	**0.0**	.	.	2	**19.6**	26.5	18.7
		1	3	**95.2**	86.5	49.9	1	**32.4**		
		2	2	**145.5**	194.7	137.7	2	**38.7**	50.0	35.3
HUPs	Chlordanes	1	2	**64.7**	21.0	14.8	1	**80.9**		
		2	2	**188.5**	27.5	19.4	2	**148.1**	40.5	28.7
	HCB	1	2	**0.0**	0.0	0.0	1	**101.3**		
		2	2	**122.7**	173.5	122.7	2	**210.2**	97.3	68.8
	a-HCH	1	2	**0.0**	0.0	0.0	1	**0.0**		
		2	1	**0.0**	.	.	2	**79.2**	112.0	79.2
	g-HCH	1	3	**72.3**	84.3	48.7	1	**4.9**		
		2	2	**127.3**	41.6	29.4	2	**90.3**	123.6	87.4
PCBs	138, 153, 183, 187	1	3	**72.3**	84.3	48.7	1	**4.9**		

Table 5-4. Paired T-Test Results Comparing SOC Concentrations (ng SOC/g conifer needle lipid) in One- and Two-Year-Old Needles of White Fir (*Abies concolor*) and Lodgepole Pine (*Pinus contorta*)*. When all pairs of measurements were considered, the average SOC concentration was more than 3 times higher in second year than first year needles for both species (Prob > t < 0.05) and SOC concentrations were strongly correlated with needle age ($R^2 > 0.93$).

Statistic	***Abies concolor***	***Pinus contorta***
Year 2	1186	457
Year 1	360	127
Mean Difference	826	330
Increase (fold)	+3.3	+3.6
Std Error	473.9	167
Upper 95%	1830	709
Lower 95%	-178	-48
N	17	10
Correlation	**0.953**	**0.933**
t-Ratio	1.744	1.973
DF	16	9
Prob > |t|	0.1004	0.08
Prob > t	**0.0502**	**0.04**
Prob < t	0.9498	0.96

*Year 2 and Year 1 = Mean concentrations of the individual SOCs: chlorpyrifos, endosulfans, dacthal, HCB, a-HCH, g-HCH, chlordanes, and PCBs in field replicates of Year 2 and Year 1 conifer needles. Mean difference = average difference in individual SOC concentrations between first and second year needles. Increase (fold) = multiplicative increase in the mean difference between year one and year two. Std Error = standard error of the mean; Upper95% and Lower 95%= 95% confidence intervals around the mean; N = number of measurements; Correlation = correlation between concentrations of individual contaminants and year; t-ratio = t-test statistic; DF = degrees of freedom; Prob > |t| = probability of incorrectly rejecting the null hypothesis that there is no difference in SOC concentrations due to year (two-tailed test); Prob > t = probability of incorrectly rejecting the null hypothesis that year 2 concentrations are not greater than year 1 concentrations (one-tailed test); Prob < t = probability of incorrectly rejecting the null hypothesis that year 1 concentrations are not greater than year 2 concentrations (one-tailed test).

How many years of needles can be found on coniferous trees? Conifer needle retention varies across species and site conditions; maximum needle longevity is optimized by good site and micro-site conditions, including adequate nutrients, light, water, and heat, and low stress from pests, disease, and air pollution (Reich et al., 1994). Needles of most conifers reach at least 3-7 years in age (Li et al., 2006), and in the genus *Pinus*, often reach 15 years, or in the extreme case of the bristle cone pine (*Pinus longaeva*) even up to 45 years (Ewers and Schmid, 1981). Needle longevity generally increases with latitude and elevation, increasing the time that nutrients are resident in trees in less favorable environments and compensating for shorter growing periods in cold temperature (Li et al., 2006; Reich et al., 1996). A relevant example is black spruce (*Picea mariana*), collected for WACAP in DENA, central Alaska. Needle retention of this species varies from 5 to 7 years in its southerly boreal forest range in Quebec, to 13 years in central Alaska, and up to 30 years under subarctic conditions (Lamhamedi and Bernier, 1994).

Whether or not SOC concentrations in conifer needles continue to increase with needle age was not addressed by WACAP. Plant uptake of SOCs occurs primarily from the atmosphere via one of three processes: equilibrium partitioning between the vegetation and the gas phase, kinetically limited gaseous deposition, and wet plus dry particle-bound deposition. Each of these processes depends on different atmospheric concentrations, plant properties, and environmental variables (McLachlan, 1999).

It has been suggested that once the SOCs have been deposited, a two-compartment model for their storage in plant leaves applies (Tolls and McLachlan, 1994; Hauk et al., 1994), accepted also by Simonich and Hites (1995) and Collins et al. (2006). The two-compartment model consists of a fairly small surface compartment with rapid uptake and clearance kinetics (hours), and a larger reservoir compartment with slow chemical migration (months to years). At least some compounds are known to require many months to reach needle concentrations that are in equilibrium with the atmosphere. For example, Douglas-fir (*Pseudtsuga menziesii*) exposed to toluene, ethylbenzene, and xlenes for several years usually equilibrated within 5-6 months (Keymeulen et al., 1993). The composition of the larger reservoir compartment is believed to influence the retention of organic chemicals, but the physiological relationship between the two compartments has not been elucidated. Forces working against eventual equilibration include surface degradation of SOCs, such as the photo-oxidation of endosulfan I and II to endosulfan sulfate (Simonich and Hites, 1995) and seasonal variation in atmospheric concentrations of pollutants (Simonich and Hites, 1994). An interesting follow-up to WACAP would be to determine whether SOC concentrations equilibrate or continue to increase in conifer needles after year 2, especially at high elevations and northerly latitudes where a large percentage of needles are in older age classes.

Other ecologically relevant questions include how much SOC contamination of soils occurs during precipitation (i.e., directly from precipitation but also from the SOC concentration in particulates collected on the surface of needles between precipitation events that wash through the canopy during rain or snowfall) and how needle SOC concentrations change as needles senesce and finally drop to the forest floor. Both pathways are considered to be important sources of soil SOC contamination (Horstmann and McLachlan, 1998; Weiss, 2000; Nizzetto et al., 2006), although quantitative data for the western United States are scarce. Another ecologically important question is whether SOC contributions from litterfall and canopy leachates are sufficiently high, cumulative or long-lasting to adversely affect populations of arthropod, fungal, or microbial decomposers, or plant life, either as individual contaminants or synergistically. The answers to these questions require more research.

Although concentrations of individual SOCs are fairly small, ranging from ng (pesticides and PCBs) to µg (PAHs) per gram of needles, the total quantity of contaminants absorbed by conifer needles per hectare (ha) can be surprisingly high, especially considering that the exposure is passive. Table 5-5 shows calculation of annual needle production per ha across a wide range of site conditions in coniferous forests from New Mexico to British Columbia, using total above ground annual biomass production and stem:leaf ratios compiled by Hessl et al. (in press) and available on-line at http://ocid.nacse.org/research/ecophys/index.html.

Table 5-5. Estimates of Total SOC Concentrations (mg/ha) in Second-Year Needles from Western North American Coniferous Forests. Annual needle biomass production for each of 31 sites[1], representing xeric-continental to coastal-rain forests, was multiplied by average low and high needle SOC concentrations observed at WACAP parks to estimate per ha SOC concentrations. Needle biomass was more important than needle concentration; maximum estimated total pesticide and PAH concentrations were < 1 and <7 g/ha, respectively at all sites.

				Measure					
	Site Data			***Mean***	***St Dev***	***St Err***	***Median***	***Min***	***Max***
N = 31	Elevation (m)			886	771	267	500	200	2720
	Mean tree age (yrs)			103	91	32	72	22	450
	Carbon Allocation New Stem C: New Leaf C			1.87	0.89	0.31	1.69	0.20	3.32
	Net Above Ground Productivity (kg/m^2/yr)			1.55	2.48	0.86	0.84	0.12	10.50
	Annual Needle Production (kg/m^{2}yr)			0.634	1.156	0.400	0.286	0.100	5.000
	Annual Needle Production (g/ha/yr)			6,344,810	11,556,610	4,004,090	2,861,110	1,000,000	50,000,000
	Parameter	***Level***	***C***	***Mean***	***St Dev***	***St Err***	***Median***	***Min***	***Max***
SOC concentration (mg/ha) in second year needles*	Trifluralin**	high	1.29	0.54	0.98	0.34	0.24	0.08	4.24
	Triallate**	high	8.93	3.72	6.78	2.35	1.68	0.59	29.34
	Chlorpyrifos	low	1.45	0.61	1.1	0.38	0.27	0.1	4.77
		high	7.45	3.11	5.66	1.96	1.4	0.49	24.47
	Dacthal	low	8.76	3.65	6.65	2.3	1.65	0.58	28.78
		high	65.9	27.47	50.04	17.34	12.39	4.33	216.5
	Endosulfans	low	24.5	10.21	18.59	6.44	4.6	1.61	80.43
		high	138	57.7	105.09	36.41	26.02	9.09	454.69
	HCB	low	12.1	5.05	9.19	3.19	2.28	0.8	39.78
		high	12.6	5.23	9.53	3.3	2.36	0.82	41.24
	a-HCH	low	9.78	4.08	7.42	2.57	1.84	0.64	32.11
		high	14.7	6.11	11.13	3.86	2.76	0.96	48.16
	g-HCH	high	9.16	a-HCH	6.95	2.41	1.72	0.6	30.08
	Chlordanes	low	1.31		1	0.35	0.25	0.09	4.32

Table 5-5. Estimates of Total SOC Concentrations (mg/ha) in Second-Year Needles from Western North American Coniferous Forests (continued).

Parameter	*Level*	*C*	*Mean*	*St Dev*	*St Err*	*Median*	*Min*	*Max*
	high	13.8	g-HCH	10.49	3.63	2.6	0.91	45.37
Dieldrin**	high	4.70	1.96	3.56	1.24	0.88	0.31	15.42
DDTs	low	4.51	1.88	3.43	1.19	0.85	0.3	14.82
	high	9.49	3.95	7.2	2.5	1.78	0.62	31.17
CUPs	low		18.7			8.4	3	147.6
	high		92.5			41.7	14.6	729.2
HUPs	low		17.3			7.8	2.7	136.5
	high		26.8			12.1	4.2	211.4
Total Pesticides	low		36			16.3	5.7	284.1
	high		119.4			53.8	18.8	940.7
PCBs	low	1.13	0.47		0.3	0.21	0.07	3.7
	high	1.68	0.7		0.44	0.32	0.11	5.52
PAHs	low	1073	447		282	202	70	3525
	high	20044	8360		5270	3770	1320	65840
Total SOCs	low		483			219	76	3813
	high		8480			3824	1339	66786

[1] Data from the Western Forests Ecophysiology Database (http://ocid.nacse.org/research/ecophys/index.html)

[2] SOC (mg/ha) in 2nd year needles: = C ∗ .0657 ∗ annual needle production ∗ 1 x 10^{-6}, where C = mean conifer needle SOC concentration, ng/g lipid, among the WACAP parks in the lowest or highest group, 0.657 is the mean percentage of lipid in dry needles (converts ng/g lipid to ng/g dw), and Annual Needle Production is the dry weight (dw) of needles produced in one year in g/ha; dividing by 1 million converts SOC units from ng to mg. Values for the constant, C, were calculated from Chapter 4, Table 4-2 and are the mean conifer needle SOC concentrations in parks belonging to lowest and highest groups (i.e., least vs. most contaminated) assigned by the Tukey-Kramer test; parks that were in both highest and lowest groups were included in calculations for both low and high C.

[3] High estimates only are provided for triallate, trifluralin, g-HCH, and dieldrin as these SOCs were detected in only a few parks or concentrations did not differ between parks. Parks for which all samples were below detection limits for an individual SOC were not included in the analysis.

Means for parks in the lowest and highest needle SOC concentrations groups assigned by the Tukey-Kramer park means comparison tests (see Table 4-2 in Chapter 4) were calculated. The total accumulation of SOCs in second-year conifer needles per ha of forest were estimated by multiplying needle SOC concentration (ng/g dw) by the dry weight of needles produced each year (kg/ha) (see Table 5-5). So, in a park exposed to comparatively high concentrations of current use agricultural chemicals, such as SEKI, an estimate for endosulfan concentration in second-year needles might range from 80 to 450 mg/ha of forest, depending upon the productivity of the site, whereas the range for a more remote park might be 1.6 to 9.1 mg/ha. Because this value considers only second-year needles, and 3-7 years of needles are typically present, the total amount in live needles/ha at any point in time would be larger. This quantity obviously could be much lower, as (1) vegetation density varies across the landscape and with elevation from forest to woodland to krummholtz to bare rock and (2) vegetative productivity declines to zero. Productivity (i.e., needle biomass) varies much more across sites than needle SOC concentrations, which were generally less than 8-fold different among the WACAP sites and parks (i.e., from Alaska to Texas). Forest productivity is therefore a more important variable in predicting the total amount of SOCs removed from the atmosphere and potentially contributed to soils by vegetation.

Estimates of total quantities of historic use compounds accumulated by second-year needles per hectare tended to be lower than estimates of current use pesticides, but within the same order of magnitude (Table 5-5). For example, in the cleanest, most remote sites, a low productivity forest would accumulate about 3.0 and 2.7 mg/ha of current and historic use pesticides, respectively. In contrast, a high productivity forest close to important regional sources of pesticides could accumulate 729 and 211 mg/ha of current and historic use pesticides, respectively. PCBs were about 10-fold lower. Summed PAHs were 10 to 1,000 fold higher, or 70 to 65,840 mg/ha for low productivity remote forests compared with high productivity forests close to sources.

How well are forests scrubbing the air of pesticides relative to the amounts of pesticides applied? There are 125 million hectares of coniferous forest in the western United States and Alaska (US Forest Service, 1997; also see Chapter 1 ecoregion maps), of which 101 million hectares are publicly owned. If the second-year needles on each hectare scrubbed on average 3.65 to 27.5 mg of dacthal or 10.2 to 57.7 mg of endosulfans annually (from Table 5-5), multiplying by 125 million hectares, the total amount scrubbed per year could be between 456 and 3,430 kg of dacthal and 1,280 and 7,210 kg of endosulfans, or at most ~2 % of the reported total national commercial application in 2002 of dacthal and endosulfans, 198,000 and 284,000 kg, respectively (Figure 4-13 in Chapter 4).

Table 5-6. Endosulfans: Per Hectare Comparison of Estimated Annual Endosulfan Accumulation in Second-Year Conifer Needles and Typical 2002 Endosulfan Application Rates of This Pesticide in the Western United States. A hectare of forest can accumulate endosulfans at levels as high as medium regional application rates; total accumulation increases with forest productivity and proximity to sources. Background colors for conifer needle endosulfan accumulation are matched to regional application rates in the lower part of the table.

	Endosulfans Accumulated in Second-Year Conifer Needles (g/ha)*		
Forest location	**Low Productivity Forest**	**Average Productivity Forest**	**High Productivity Forest**
Remote	0.0016	0.010	0.080
Near Source	0.0091	0.058	0.45
2002 US Endosulfan Application Rates**	**(g/ha)****		
Not applied	0		
Lowest	0.0085 to 0.049		
Low	0.05 to 0.15		
Medium	0.16 to 0.55		
Highest	0.55 to 2.19		
Highest	≥ 2.20		

* Estimates from Table 5-1 rows (remote = low SOC concentrations, near source = high SOC concentrations) and columns (low productivity forest = minimum, average productivity forest = average, high productivity forest = maximum). Values in Table 4.1 were multiplied by 1000 to convert from mg/ha to g/ha.

**Average annual use of active ingredient in grams per hectare of agricultural land in county (converted from lbs/square mile) from Figure 4-14 in Chapter 4.

Because most of the national application occurs in the eastern half of the United States, and application in the western United States is uneven in distribution and intensity (see US map in Figure 4-13 in Chapter 4), perhaps a better way of approaching the question is to ask how well forests scrub the air under differing forest productivity and regional application rates. Table 5-6 shows endosulfans as an example.

A hectare of high productivity forest close to sources can absorb endosulfans in amounts that are equivalent to a medium application rate, or ≤ 25% of maximum per hectare application rates. At the other extreme, a hectare of remote, low productivity forest can be expected to absorb a very small total amount of endosulfans relative to a high productivity site near sources, which would still be about 10-20% of the amount applied per hectare in a very low use area but < 0.1% of the amounts applied per hectare in highest use areas. It seems reasonable to conclude that in addition to climatic factors discussed in Chapter 4 (notably temperature and precipitation), the capacity of a forest to scrub endosulfans from the air is a function of forest productivity (amount of leaf area—affected also by species-specific cuticular properties), its proximity to areas where endosulfans are applied, and the application rates in those areas. Pesticides other than endosulfans can be scrubbed by needles to a greater or lesser extent, depending on their physico-chemical properties, such as octanol-air partitioning coefficient (K_{oa}) and air-water portioning coefficient (K_{aw})(Su et al., 2007).

The importance of vegetation in scrubbing the atmosphere of organic contaminants has been discussed by other authors. For example Simonich and Hites (1994) estimated that as much as 24-72% of PAHs emitted in the atmosphere in the northeastern United States are removed by vegetation. More recently, Su et al. (2007) found extraordinarily high deposition velocities of PBDEs, PCBs, and PAHs in boreal and deciduous temperate forests in Canada and Germany. Model calculations suggest that the forest filter effect is most pronounced for SOCs with a log K_{oa} between 7 and 11 and a log $K_{aw} > -6$ (Wania and McLachlan, 2001). For such chemicals, uptake in forests can notably decrease air concentrations and markedly decrease the long-range transport of some SOCs, for example, to the Arctic (Su and Wania, 2005).

5.2.4 Evidence of Biomagnification

How do SOC concentrations in fish and vegetation compare with those in the media that transport contaminants to ecosystems (i.e., snow, lake water, and air)? The differences can be dramatic, and illustrative of the ability of biological organisms to accumulate molecules from the environment against astoundingly large concentration gradients. Figure 5-3 compares patterns and magnitudes of SOC concentrations in snow, lake water, sediments, lichens, conifer needles, and fish from Emerald Lake (SEKI). SOC compounds are listed in order of increasing K_{ow}, or decreasing polarity and solubility in water. Concentrations of all the media are displayed in picograms (i.e., trillionths of a gram) per gram wet weight, so they can be compared on the same (log) scale. SOC concentrations in XAD resin are not discussed; they were used to indicate relative differences between sites and were not converted to ambient air concentrations. The most striking observation in Figure 5-3 is that concentrations in biota and sediments are very much higher, by 3 to 7 orders of magnitude, than those in snow and, especially, lake water.

Another observation is that patterns of accumulation differed among media and among terrestrial and aquatic environments within the same watershed—evidence of different exposures, accumulation mechanisms, revolatilization rates, and, in the case of biota, the ability to metabolize and actively degrade and eliminate SOCs. For example, compared to sediments, fish had higher

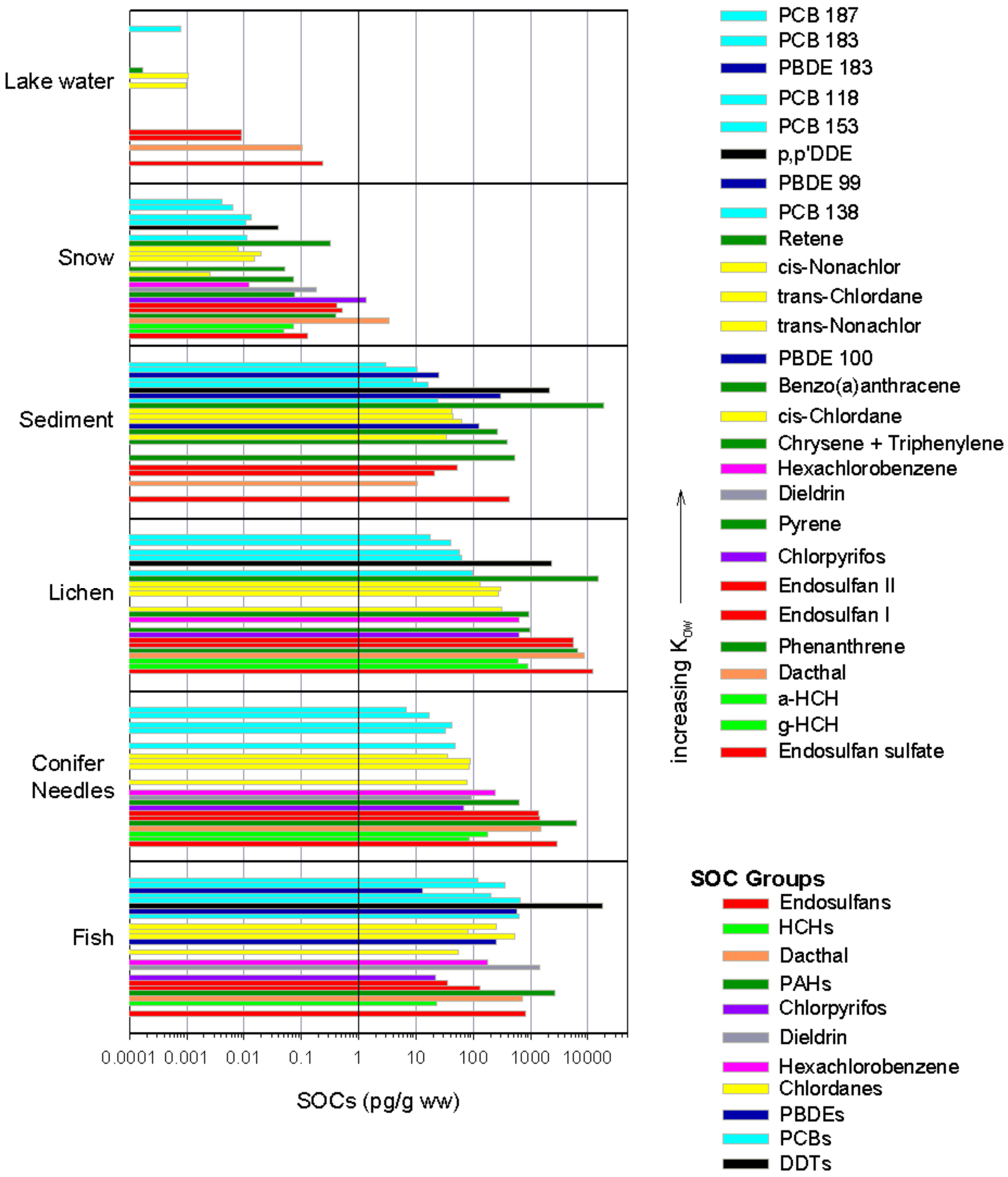


Figure 5-3. Mean SOC Concentrations (pg/g ww) in Lake Water, Snow, Sediments, Lichens, Conifer Needles, and Fish from Emerald Lake (SEKI). SOCs are ordered by increasing K_{ow}, or decreasing polarity and solubility in water, color-coded by group. SOC concentrations were 3 to 7 orders of magnitude higher in sediments and biota relative to snow and water. SOC concentrations in water, snow, and vegetation, but not sediments and fish, generally decreased with decreasing polarity. Compared to vegetation, fish were better accumulators of PCBs and dieldrin and poorer accumulators of PAHs, endosulfans, HCHs, dacthal, and chlorpyrifos. If no data are shown, all samples were below detection limits; PBDEs were measured in sediments and fish only. SOC concentrations (pg/g ww) are on $\log_{10}$ scale.

concentrations of PCBs and most pesticides. Compared to vegetation, fish had higher concentrations of PCBs, dieldrin, and DDTs, but lower concentrations of other pesticides and PAHs.

Fish and sediments concentrated compounds across the K_{ow} spectrum tested, which makes sense because of the complex organic and mineral chemistry of sediments and the presence of both lipids and water in fish and vegetation. In contrast, SOC concentrations in lake water, snow, and vegetation tended to decrease along the K_{ow} gradient, i.e., with decreasing solubility of SOCs in water. Although this is not surprising for snow and lake water, conifer needles and lichens had total lipid concentrations that were similar to those in fish. A possible explanation is that fish are able to accumulate lipophilic substances in fatty internal tissues and organs, whereas lipophilic SOCs absorbed by the waxy cuticles of conifer needles and by the lipid components of lichens might be partially revolatilized into the atmosphere during warm weather. Indeed, age and lipid concentrations were the best predictors of SOC concentrations in WACAP fish (subsection 5.2.2.2), whereas at least some research indicates that SOC concentrations in vegetation can equilibrate with the atmosphere over time (Keymeulen et al., 1993).

One of the air sampling objectives was to determine whether SOC concentrations in XAD resin can be used to predict concentrations in vegetation. All three media (i.e., air, lichens, and conifer needles) were sampled at four WACAP sites in core parks: Wonder Lake (DENA), Snyder and Oldman lakes (GLAC), and Lone Pine Lake (ROMO). Table 5-7 shows Spearman Rho correlations between concentrations of SOCs in XAD resin, conifer needles, and lichens at these sites. As a result of differential absorption abilities of SOCs across media, SOCs in vegetation could not be predicted from concentrations in XAD resin ($R^2 < 0.08$); however, concentrations in conifers and lichens were correlated ($R^2 = 0.63$). Comparison of the patterns of SOC accumulation across the three matrices (Figure 5-4) shows that the XAD resin appears to absorb compounds preferentially according to the K_{ow}, peaking at endosulfan I and then decreasing. Although not useful for predicting SOC concentrations in vegetation, PASDs are still a valuable and simple tool for comparing relative atmospheric concentrations across sites.

Table 5-7. Correlations (R^2 coefficients) between Total Pesticide Concentrations in XAD Resin (pg/g dry XAD), Conifer Needles (ng/g lipid), and Lichens (ng/g lipid) from Wonder, Snyder, Oldman, and Lone Pine Lake Watersheds.

	XAD	Lichens	Conifer Needles
XAD	1.000	0.053	0.073
Lichens	0.053	1.000	0.630
Conifer	0.073	0.630	1.000

5.3 Biological Effects

5.3.1 Effects of Contaminants and the Utility of Biomarkers

Many pollutants (e.g., Hg and especially dioxin) have long been known to be extremely toxic to biota, even at low concentrations. Toxicity occurs as both an acute response and a chronic or delayed response. The acute response, not necessarily applicable to WACAP because most contaminant concentrations are fairly low (0 - 10 ppb), is similar to that of a drug-overdose. Concentrations are elevated to the point of large-scale physiological shutdown. The chronic or delayed response is more applicable to WACAP, and more interesting biologically, from our perspective. For example, at low concentrations when the chemicals are not acutely toxic, endocrine and immune changes can occur that are measurable in the laboratory with biomarkers. Efforts can then be made to correlate those changes to contaminant concentrations. WACAP does not attempt to establish cause and effect, but looks for patterns that warrant future investigation.

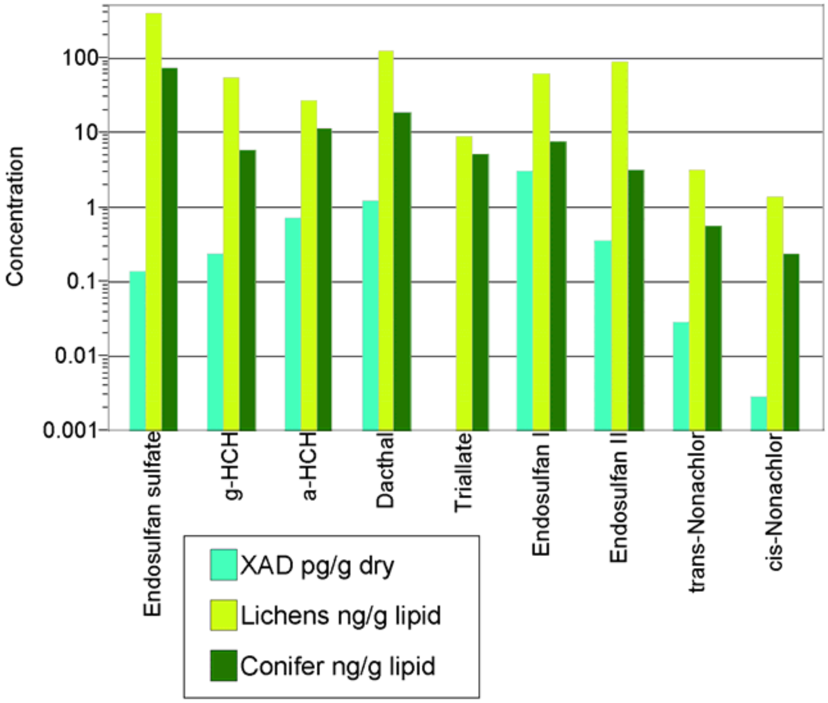


Figure 5-4. Pesticide Concentrations in Dry XAD Resin (used to sample air), Conifer Needles, and Lichens from Oldman Lake (GLAC). Compounds are ordered by increasing K_{ow} or decreasing polarity. Concentrations in vegetation decreased gradually with increasing K_{ow}; concentrations in XAD resin increased to Endosulfan I, then decreased. Differing affinities for SOCs might explain the poor correlations observed between SOC concentrations in XAD resin vs. vegetation (Table 5-7).

Fish are bioindicators of contaminant exposure because they are often top predators of aquatic ecosystems and accumulate organic and metal contaminants, usually via the diet (Thomann, 1989). Salmonids (*Oncorhynchus* spp. and *Salvelinus* spp. in this study), are often the keystone aquatic predators, yet they are prey to birds and mammals (Mackay and Fraser, 2000), where more significant effects of bioaccumulation (because of higher contaminant concentrations) can be observed. Measurement of contaminants in fish thus indicates impact to the part of the food web. Piscivorous animals are likely to have higher contaminant concentrations than the fish and the organisms forming the base of the food web are likely to have lower concentrations.

The potential effects of contaminants on the fish themselves can be determined by identifying changes in fish biomarkers. By extension, negative effects on fish can warn of harm to the ecosystem; therefore, changes in biomarkers are considered an early signal of negative effects (see Figure 5-1) (van der Oost et al., 2003). Fish biomarkers are tools that can be used to determine the relationship between contaminants and impaired health in individual fish (NRC, 1987). Biomarkers fall into three classifications: (1) markers of exposure, (2) markers of effect and, (3) markers of susceptibility (NRC, 1987). The biomarkers used in WACAP are markers of effect because they precede and can predict impaired health (NRC, 1987). The utility of biomarkers hinges on validating them by correlating exposure of chemicals to the change in the biomarker (NRC, 1987). Impaired health, for our purposes, refers to any relationships identified between contaminants and the biomarkers, as changes in biomarkers are considered to be an abnormal response. The difficulty lies in determining what is normal for the animal. Repeated sampling of the same water bodies over long periods of time in an effort to monitor changes in biomarkers was not possible. However, we did obtain samples for reproductive biomarkers for two different years from several of the WACAP sites, which in most cases replicated our initial results. The sampling strategy used by WACAP was unprecedented in geographic scale and ecological variability. As such, this strategy prohibited repeated sampling of the same locations for contaminant concentrations because of the extremely remote nature of the field sites and the time needed to complete the work.

Laboratory studies have documented the deleterious action of environmental pollutants on biota; however, the ecological significance or the significance to overall population health is still largely unknown and is recognized as a limitation on the use of biomarkers (Mills and Chichester, 2005). Results from laboratory studies are often limited by the fact that environmentally irrelevant concentrations of chemicals are often needed in laboratory studies to replicate observations obtained from the field. Recent work, however, has demonstrated that a mixture of environmental estrogens induced an estrogenic response, even though the individual contaminants were below the concentrations needed to induce a response on their own (Rajapakse et al., 2001, 2002). In addition, the “weak” xenoestrogens, dieldrin, endosulfan, and o,p′-DDT, induced estrogenic responses from 10^{-9} to 10^{-12} molar concentrations *in vitro* (Wozniak et al., 2005). In a recent study of trout in mountain lakes of Europe, Garcia-Reyero et al. (2007) found that HCB, PCBs, and DDTs were correlated with estrogenic activity in muscle extracts of the salmonids they examined.

We recognize that extensive laboratory studies testing the same chemicals and mixtures of chemicals identified in the field samples for estrogenic and reproductive effect would be desirable. However these experiments were beyond the scope of WACAP. Instead, we followed the approach used in the USGS Biomonitoring of Environmental Status and Trends Program (Schmitt and Detloff, 2000) and earlier argued by Ham et al. (1997) to use multiple biomarkers for ecotoxicology studies. With these guidelines, researchers can approach the topic of immune or endocrine disruption from a weight of evidence standpoint, by using multiple biomarkers and co-existent contaminant concentrations. To that end, we used macrophage aggregates, plasma vitellogenin (Vtg), 11-ketotestosterone, testosterone, estradiol, and gonad, kidney, liver, spleen, and gill histopathology to look for signs of abnormal changes in fish resulting potentially from contaminant concentrations. Appendix 5A provides a summary of all fish health measurements and biomarker values. In this chapter, we focus on results from macrophage aggregate analysis, plasma Vtg in male fish, and gonad histopathology, and draw upon the remaining biomarkers for supporting evidence when appropriate.

The rationale for choosing the biomarkers we did was guided by the following objectives.

1. Utilize accepted biomarkers that are sufficiently supported by the scientific literature.

2. Use biomarkers that can be attributed to a specific suite of contaminants for which the mechanism of action is established.
3. Use biomarkers that are cost effective, and suitable to current laboratory equipment.
4. Use biomarkers that do not affect other project objectives. For example, because biomarker and SOC analyses were performed on the same fish, it was desirable to remove as little tissue as possible from the animal so as to not dilute the contaminant signatures.
5. Identify numerous endpoints that can be measured in one tissue (e.g., sex steroids and Vtg can be quantified in the blood).

Satisfying these objectives is difficult and we acknowledge that all of our biomarkers do not satisfy every objective. The most important of these objectives were 1 and 4. In terms of number 1, we argue that efforts to develop biomarkers while simultaneously identifying relationships between those biomarkers and contaminants would have been difficult to achieve. Secondly, our foremost project objective was to provide fish intact enough to accurately assay contaminant concentrations. So biomarkers that destroy most of a tissue (e.g., the liver for mixed function oxidase analyses) would violate objective number 4. With these objectives in mind, we provide data on the biomarkers listed (see Appendix 5A for all of our measurements). We report in detail in the following sections on the biomarkers for which we found significant and plausible relationships from which some level of inference could be drawn. In addition, we report on biomarkers deemed to be of interest to the scientific community, the NPS, and the public.

5.3.2 Overview of General Fish Health

An important aspect of WACAP was that SOC and Hg concentrations would be determined in whole fish, as opposed to individual organs (e.g., liver), and that coincident changes in health could be determined in those same fish. With that in mind, a health-based necropsy procedure, similar to that used by Adams et al. (1993) was performed on every fish in the field to identify abnormalities that might or might not be related to contaminant concentrations. As discussed in Chapter 3, numerous tissues also were removed from the fish, successfully preserved in the field, and shipped to the laboratory for further microscopic and analytical procedures to assess the health of the fish. In general, our necropsy procedures did not reveal any gross abnormalities in the fish captured during these studies. However, numerous lake trout from GAAR were infected with nematode worms, later determined to be *Raphidascaris* spp. (Figure 5-5).

The definitive host is the northern pike (*Esox lucius*), one of which was captured as by-catch, so the presence of these parasites was not entirely unexpected. External copepod parasites were found on lake trout from Burial Lake, NOAT, and tapeworms and other unidentified nematodes were also found in Matcharak Lake fish (Figure 5-6). These parasitic infections probably did not result from contaminant concentrations. For complete descriptions of the pathologies identified in the lake trout from the Arctic and the other trout studied in WACAP, see Appendix 5A.

5.3.3 Biomarkers

5.3.3.1 Macrophage Aggregates (MAs)

Macrophage aggregates (MAs) are focal accumulations of pigmented macrophages occurring primarily in hematopoietic and hepatic tissues of fishes and other poikilothermic animals, and are thought to be the primitive analogs to mammalian lymph nodes (Wolke, 1992; Agius and Roberts, 2003). They can also occur in other organs, such as the gonads of fishes captured from

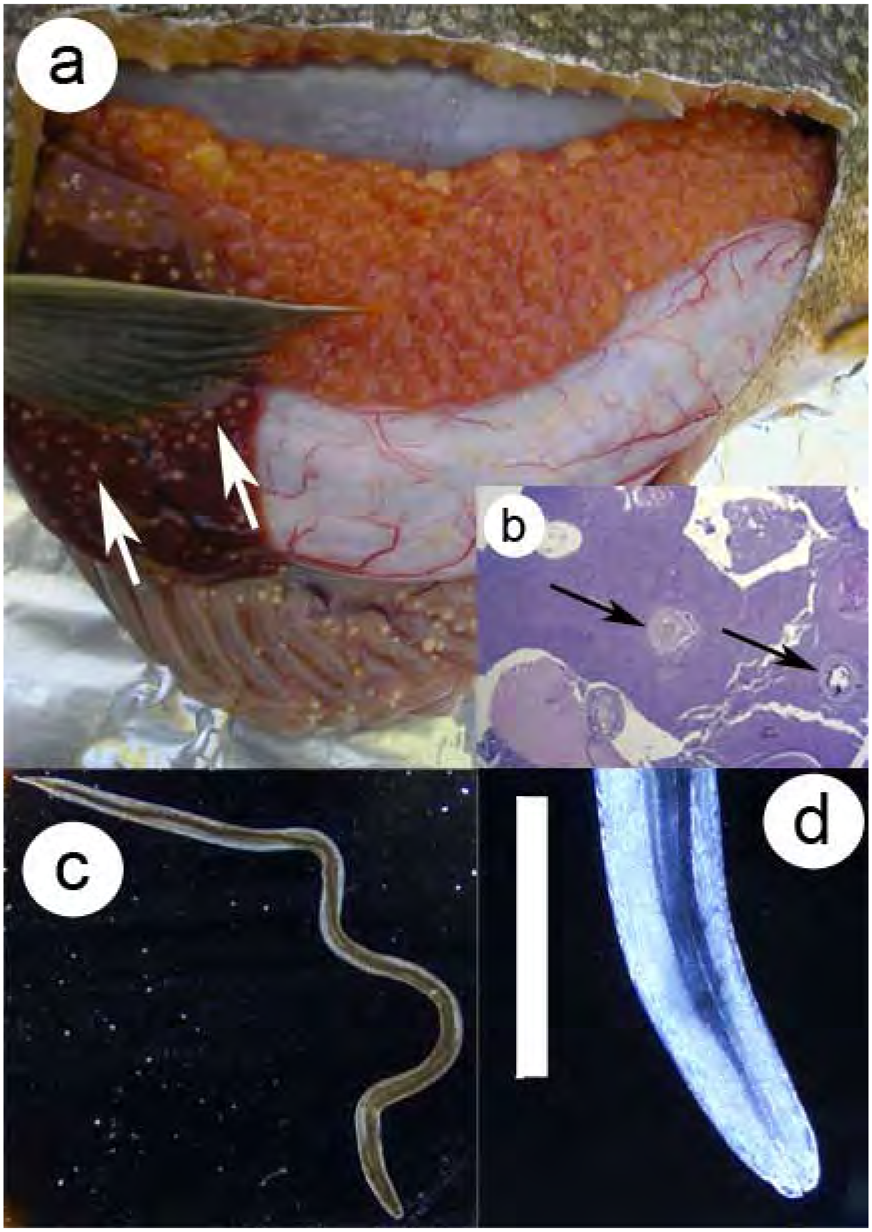


Figure 5-5. Incidental Pathology Affecting Multiple Organs from Multiple Lake Trout at Matcharak Lake (GAAR). Nodules on the liver [arrows in (a)] are encysted larval nematodes shown histologically [arrows in (b)]. Dissection of the nodules revealed numerous *Raphidascaris* spp. (Nematoda) wet-mount preparation shown in phase-contrast, bar = 1 mm (c, d). Hematoxylin and Eosin.

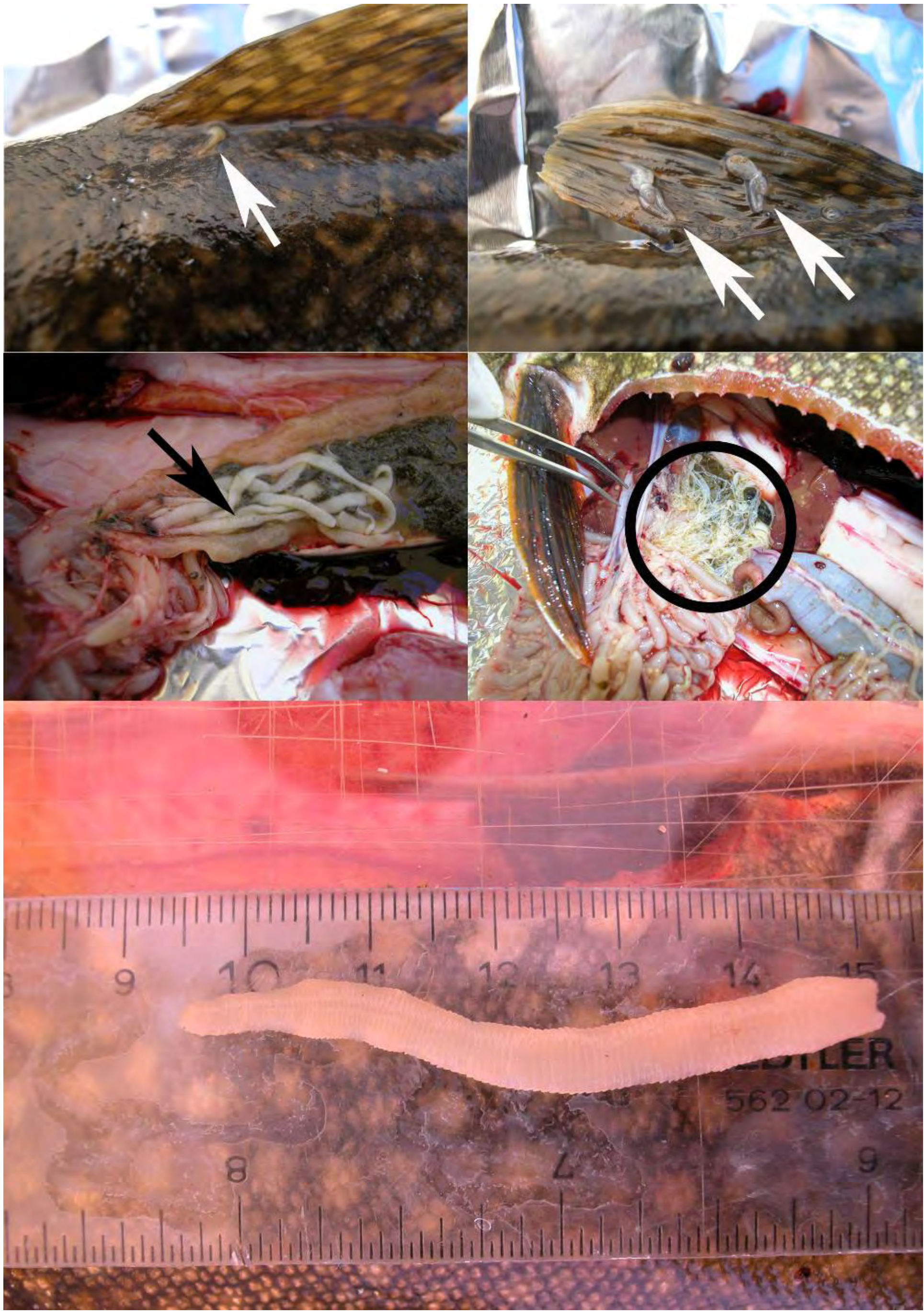


Figure 5-6. External (white arrows) Copepod Parasites and Internal (black arrow, circle) Parasites (tapeworms and roundworms) in Lake Trout from Burial Lake (NOAT) and Matcharak Lake (GAAR), Respectively. Tapeworm on the ruler is representative of the tapeworms denoted by the black arrow.

degraded environments (Blazer, 2002; Patino et al., 2003). Macrophage aggregates are thought to be storage centers for cellular debris (Wolke, 1992; Agius and Roberts, 2003); therefore, toxicants that induce tissue damage are likely to be associated with MAs. In terms of physical appearance, melanin, hemosiderin, and ceroid/lipofuscin are the pigments contained within the MAs, ranging in color from golden to brown to black in slides stained with hematoxylin and eosin (Wolke, 1992; Agius and Roberts, 2003) (Figure 5-7). Increases in pigment content are suggestive of catabolic, infectious, toxic, or otherwise stressful events or exposures (Wolke, 1992; Agius and Roberts, 2003). In a polluted river in Germany, Meinelt et al. (1997) found positive correlations between liver, kidney, and spleen MAs and mercury in individual pike (*Esox lucius*). Handy and Penrice (1993) induced MAs in the rainbow trout kidney by chronic *per os* exposure of 10 mg/kg $HgCl^-$ over 42 days. Although this is a high dose, it establishes the proof of concept that mercuric compounds can induce the formation of MAs in salmonid fishes. This broad application of MAs for assessment of fish and environmental health has been well documented in many fishes.

5.3.3.1.1 Data Analysis

Our objectives were to use MAs as potential indicators of age-dependent contaminants, such as Hg, where N = 10-25 per lake, but all contaminants were tested for association with MAs. We also intended to determine if potential among-lake differences in MAs could be associated with differences in contaminants in those lakes. Among-lake comparisons were made by ANOVA or Kruskal Wallis, followed by a Bonferroni post hoc at 95% confidence. Levene's test was used to determine if there was equal variance in MAs between the lakes. Distributions of MAs from the spleen and kidney of WACAP fish for which there was corresponding SOC and Hg data (N = 8-10 fish per lake) are shown, by lake, in Figure 5-8. Fewer data are available for these comparisons because SOCs were determined on a subset of the fish where Hg and biological data were also available. Relationships between contaminants and MAs were made with simple linear or log regression. Arcsine square-root transformations were used on the MA data and log10 transformations on the Hg data. Before we grouped and analyzed all brook trout for contaminant and MA relationships, we determined if potential co-variates (age, sex, maturation state, and condition factor) were different among lakes. Percent area occupied by MAs in the kidney, spleen, and liver was quantified following the method of Schwindt et al. (2006). Liver MAs are reported in Appendix 5A.

5.3.3.1.2 Results and Discussion

The following comparisons were made on trout where Hg, SOC, and biological data were available. In the brook trout (N = 9-10 fish per lake), no significant differences in kidney or spleen MAs among lakes were found, although a significant main effect suggested that overall there were differences among lakes in mean arcsine square root transformed spleen MAs (ANOVA $F_{6,62} = 2.84$, $P = 0.02$), as well as kidney MAs (ANOVA $F_{6,62} = 2.38$, $P = 0.04$). The *Oncorhynchus* spp. (N = 8-10 fish per lake) were analyzed together because different species or subspecies were captured at each lake. Any differences could be confounded by the potential differences between species, but at least the genus is the same. Both spleen ($F_{2,25} = 4.75$, $P = 0.02$) and kidney ($F_{2,25} = 6.84$, $P = 0.004$) MAs were higher in Snyder Lake fish than in Oldman Lake fish, and fish in both GLAC lakes were not different from rainbow trout (*Oncorhynchus mykiss*) at Mills Lake, ROMO. In the lake trout (N = 8-10 fish per lake), arcsine square-root transformed spleen MAs were significantly elevated in Wonder Lake fish compared to fish in Matcharak and Burial lakes ($F_{2,25} = 34.81$, $P = <0.0001$) and higher in Matcharak Lake fish than

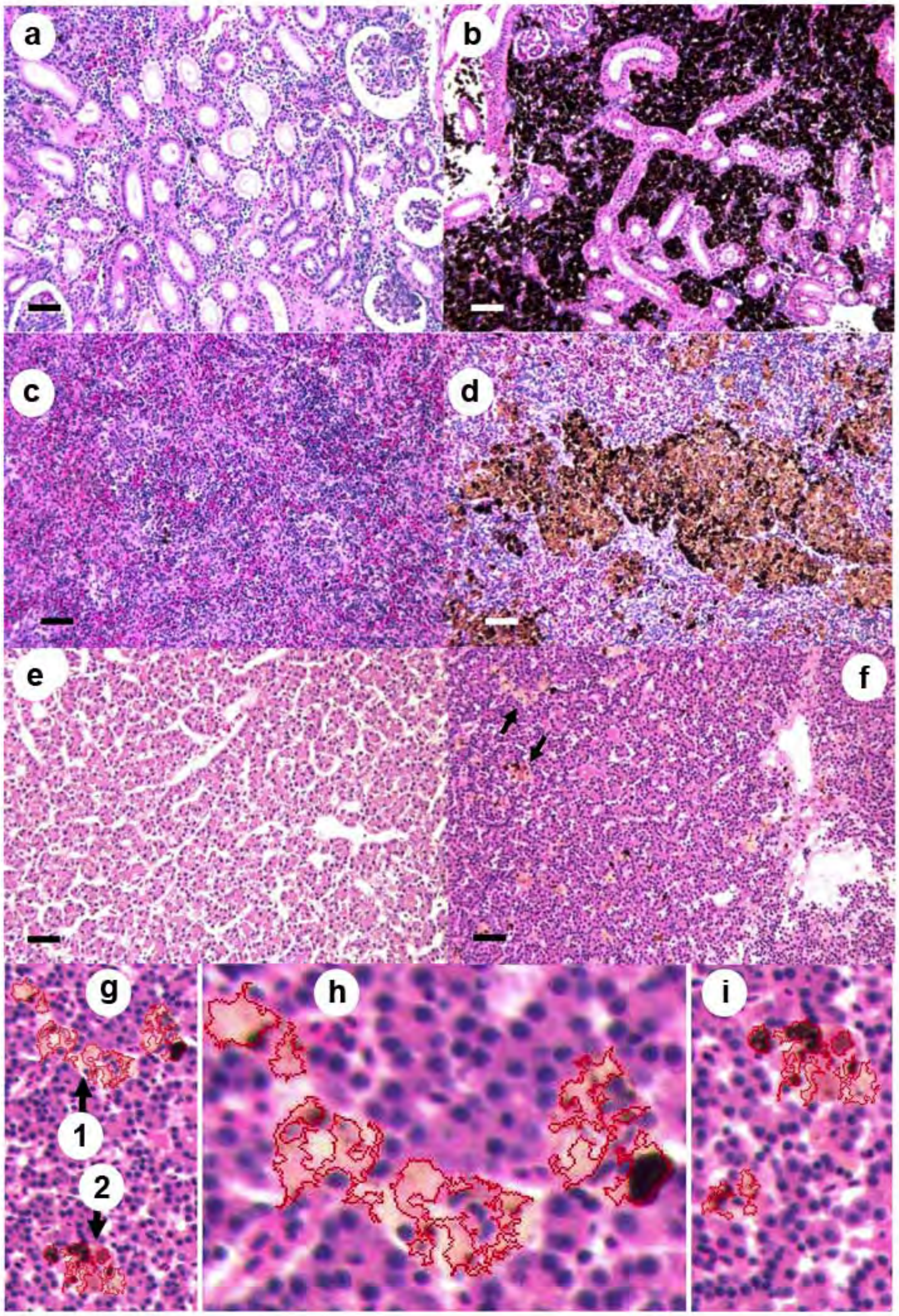


Figure 5-7. Representative Hematoxylin-Eosin Stained Brook Trout Organs Showing the Relative Difference between Fish with Very Few or No Macrophage Aggregates (MAs) and Extensive Accumulations of MAs (a-f) and Outlined High Magnification Hepatic MAs (g-i). Bars = 50 µm; (a) Kidney with a few MAs; (b) Kidney with extensive MAs; (c) Spleen with a few MAs; (d) Spleen with extensive MAs; (e) Liver with no MAs; (f) Liver with extensive MAs; (g) High magnification of liver MAs corresponding to MAs (arrows) in (f); (h) 2X magnification of the MA corresponding to arrow 1 in G; (i) 2x magnification of the MA corresponding to arrow 2 in (g). The outlined areas in (g) through (i) are the computer output of delineated MAs based on pigment selection by the computer program in the liver. Modified from Schwindt et al. (2006).

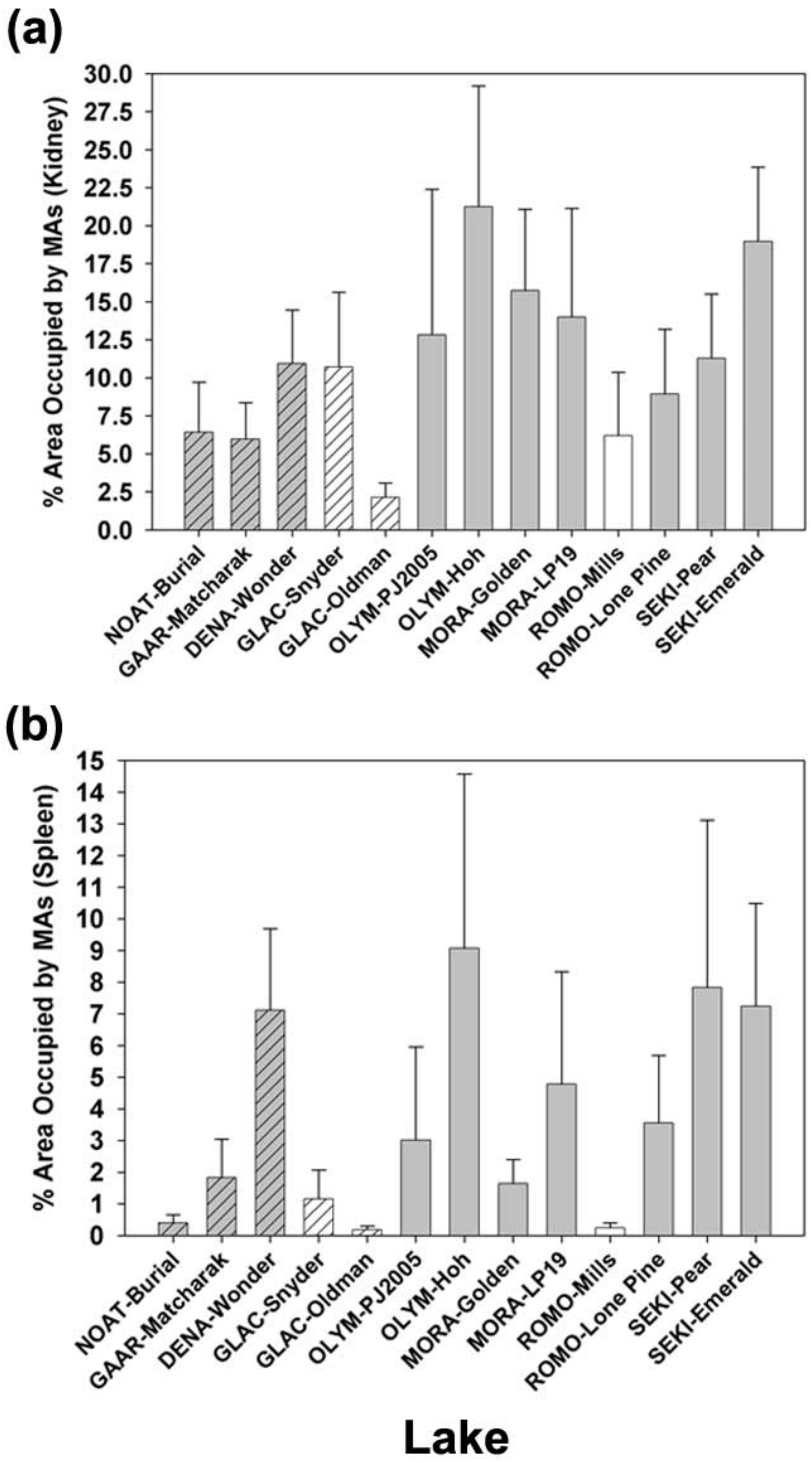


Figure 5-8. Mean Percent, %MAs + 95% Confidence Intervals, for Fish with Corresponding Hg and SOC Data: (a) Spleen, (b) Kidney. Gray bars = brook trout, White bars = rainbow trout, White hatched bars = cutthroat trout, and gray hatched bars = lake trout. *N* = 8-10.

in Burial Lake fish. The significance of these among-lake differences remains to be determined; no contaminant patterns emerged among lakes that could explain differences in the MAs.

In the WACAP lakes with brook trout, mean fish age and condition factor were not significantly different among lakes (ANOVA $p > 0.05$). Comparison of median (because of unequal variance) arcsine square-root transformed spleen MAs in brook trout for which there were biological and Hg data ($n = 10$-25 fish per lake) yielded a significant main effect (Kruskal Wallis Test Statistic $= 14.31$, $p = 0.03$), but differences between individual lakes were not detected (Bonferroni). Average Hg ($\log_{10}$ transformed to normalize data) was significantly elevated at LP19 (MORA) and Hoh Lake (OLYM), compared to Lone Pine Lake (ROMO) and Golden Lake (MORA) (ANOVA $F_{6,93} = 4.33$, $p = 0.0007$). The results from these analyses suggest that the observed among-lake differences in Hg were not consistently related to differences in MAs. Furthermore, sex did not appear to affect the regressions because there was no difference in MAs between the sexes ($T_{39\text{female}, 59\text{male}} = 1.12$, $p = 0.26$). Sexual maturation was not different between sites (ANOVA $p > 0.05$, Figure 5-9). Finally, the slopes of the among-lake regression lines were not different for MAs versus age ($F_{1,6} = 0.81$, $p = 0.56$) or MAs versus Hg ($F_{1,6} = 1.43$, $p = 0.21$). This suggests that MAs respond to age and Hg equally among lakes. Based on these results, we did not identify any confounding factors affecting MAs, Hg, or age among lakes. Therefore, we grouped the brook trout data for the following regression analysis.

The following results are based on all brook trout where Hg and biological data are available. Knowing that MAs are correlated with age in these fish (Schwindt et al., 2006), we identified a suite of contaminants thought to be associated with MAs based on their suspected age-dependence. Total whole body Hg was chosen because it was also associated with age, although all contaminants analyzed in WACAP were screened for potential associations to MAs. In our results, Hg was positively associated with spleen MAs and age, with the strongest relationships observed in brook trout ($F_{1,98} = 82.82$, $p < 0.0001$, $R^2 = 0.45$) (Figure 5-10a). In the brook trout, positive relationships were also found between MAs and the ∑PCBs ($F1,68 = 26.04$, $p < 0.0001$, $R^2 = 0.28$) and the ∑PBDEs ($F_{1,68} = 17.14$, $p = 0.0001$, $R^2 = 0.20$). As mentioned previously, MAs have been associated with pathogenic infections of microbes in fish. However, in our analysis of MAs in fish from WACAP, MAs were not influenced by the presence of parasites, or evidence of other infectious agents (e.g., bacterial kidney disease-like granulomas). That is, MAs were not concentrated around the parasites or granulomas, nor were they more abundant in fish with parasite infestations.

To further delineate the relationship between MAs and Hg, we searched for age-independent associations between MAs and Hg. To do this, we divided our datasets into age classes prior to regression analysis for every species of fish where data were available. The best relationships we found were in the 4- to 6-year-old brook trout with significant age-independent increases in MAs and Hg ($F_{1,46} = 26.27$, $p < 0.0001$, $R^2 = 0.36$) (Figure 5-10b). In the 1 to 3- and 7- to 13-year-old trout, only weak relationships, if any, were identified (see Appendix 5C). Dividing the 7- to 13-year-old classes further did not yield any significant relationships (data not shown). Appendices 5B and 5C contain tables of regression statistics for all permutations performed on the data to search for relationships between Hg, MAs, and age.

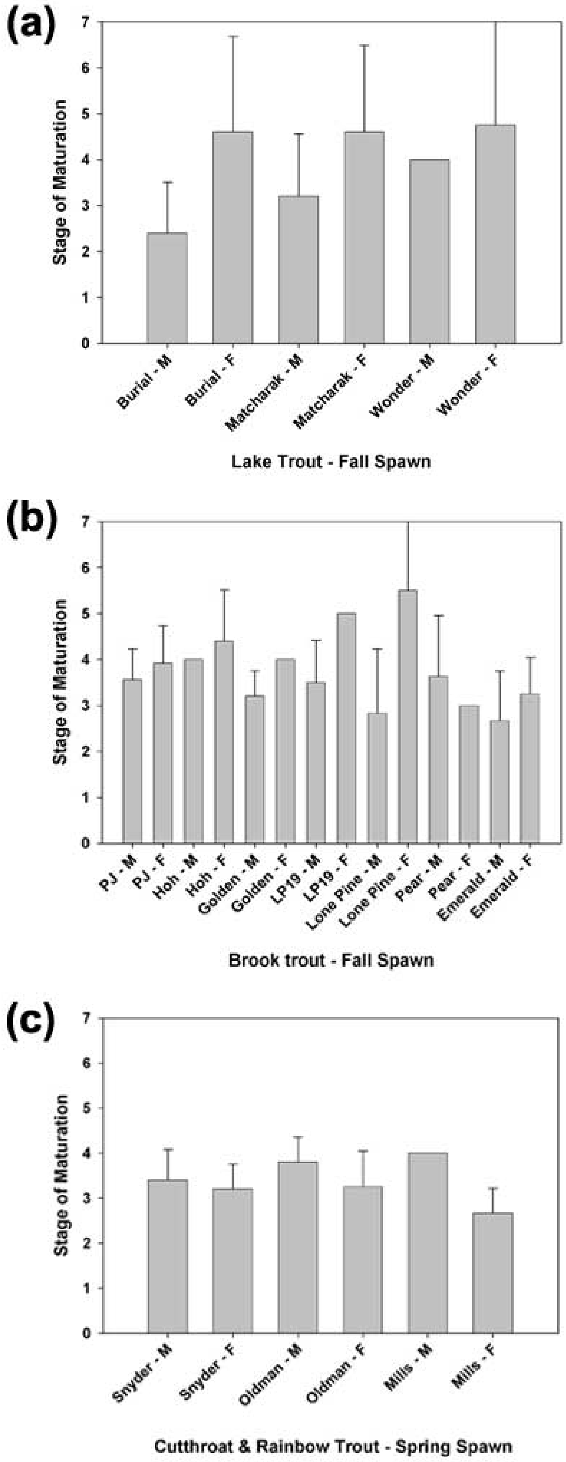


Figure 5-9. Average Stage of Gonad Maturation ± 95% Confidence Intervals in Trout for which Corresponding SOC and Hg Data are also Available. *N* = 2-11; M = male; F = female; (a) lake trout, fall spawn, (b) brook trout, fall spawn, (c) cutthroat and rainbow trout, spring spawn.

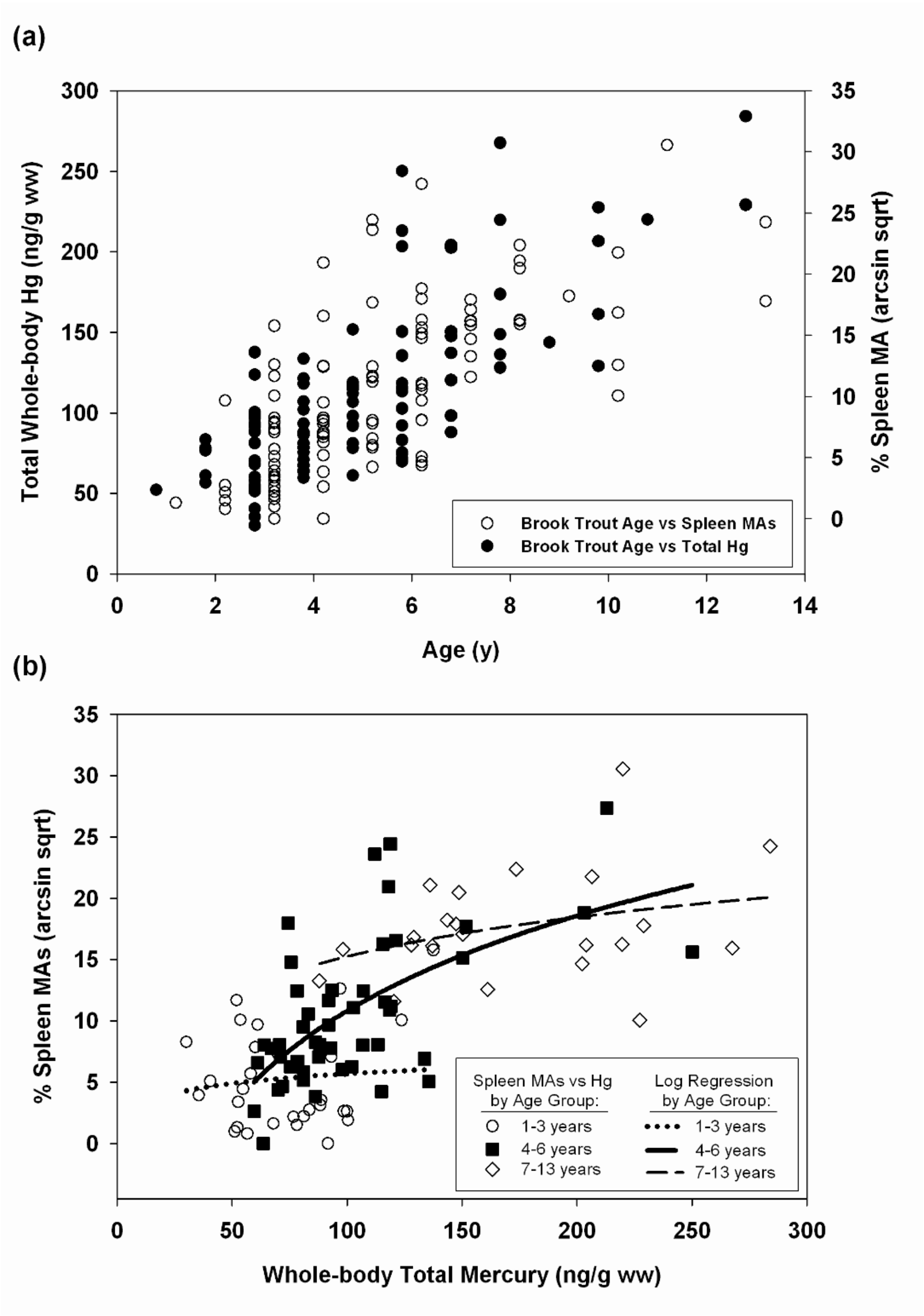


Figure 5-10. Co-Linearity between (a) Splenic MAs, Hg, and Age in Brook Trout, and (b) Log-Linear Relationships between Hg and Brook Trout (*Salvelinus fontinalis*) Splenic MAs. See Appendix 5C for regression statistics. Some data are overlapping and x-axis data in (a) are offset slightly.

Incorporation of Hg varies between life history stages of salmonid fishes (Mathers and Johansen, 1985). Mercury accumulates rapidly during periods of fast growth and increased food consumption (MacCrimmon et al., 1983). Mercury has been associated with MAs (Handy and Penrice, 1993); during periods of fast growth, MAs and Hg increase independently of age, as was observed in our results for 4- to 6-year-old brook trout. Nevertheless, the well-established fact that MAs increase with age has not been explained (for review see Agius and Roberts, 2003). Macrophage aggregates are more likely to result from the bioaccumulation of toxicants, and long-term multiple hits by acute stressors, than merely a side effect of aging and senescence alone. This phenomenon is comparable to the "liver spots" that form on fair-skinned humans. Liver spots (senile lentigines) develop in exposed regions of the skin of older persons because of long-term cumulative effects of UV radiation, not simply because of age itself (Porta, 2002).

Lake trout (from DENA, GAAR, and NOAT) represented a much smaller data set than brook trout, and their environment is considerably different from the lakes of the other trout species. The lake trout were captured from much larger lakes that contained more fish species than lakes in lower 48 states (see Table 5-2 for species). In addition, the lake trout were relatively older, with several individuals > 15 years. Significant relationships between Hg and MAs were found only in lake trout < 20 years old (Appendix 5C). Mercury concentrations decreased in lake trout > 20 years from the Arctic (GAAR and NOAT), yet, as with other fishes, MAs increased with age throughout the entire age structure (Appendix 5C).

Some data suggest a decline in MAs following exposure to contaminants (Payne and Fancey, 1989; Bucke et al., 1992). However, those results might have been confounded by movement of fish in and out of contaminated areas such as polluted bays or estuaries. Lakes in our study, aside from those in Alaska, were relatively small (< 20 km^2 surface area), and thus fish cannot migrate in or out of potentially contaminated areas. Therefore, changes in MAs in relation to contaminants are not confounded by migration and are more likely related to individual responses to the contaminants and/or other stressors. Several explanations, none conclusive, might account for the breakdown of the relationship between of MAs and Hg in older lake trout.

First, eventual sequestration of Hg in the muscle tissue might render Hg less "bioavailable" to the kidney, liver, or spleen, thus MAs decline subsequently. This observation holds, to a certain extent, for the fairly old brook trout as well. In 7- to 13-year-old brook trout, Hg was rather high, but no changes in MAs were observed (Figure 5-10b). Second, Hg is lethal to rainbow trout at exposures of 10-20 µg/g and toxic to fish at 1-5 µg/g (Niimi and Kissoon, 1994). It is conceivable that lake trout with higher Hg concentrations died disproportionately, and that the older fish are represented by those that have experienced less exposure to Hg. Third, ecology changes in food consumption might account for the rapid, non-age-associated changes in contaminant concentrations. To our knowledge, there are no studies that describe the fate of MAs after the stressor has been removed. Therefore, a fourth possibility is that MAs persisted long after the cause had ceased or declined in the old lake trout. Finally, these older fish might be subjected to a different MA-inducing stressor that younger fish that we are not aware of. We observed some interesting relationships when the lakes with lake trout were studied individually. In the lake trout from Wonder Lake, DENA, no relationship was found between MAs and age, thus the entire data set was used to determine positive correlations between MAs and Hg (Appendix 5C). In this case, MAs were significantly correlated with Hg.

Rainbow trout were collected only from Mills Lake, ROMO. The age distribution from this population was restricted; most of the fish were between 4 and 6 years of age, thus it was not possible to test other age classes. Nevertheless, the entire dataset was used, and MAs were significantly related to age, as demonstrated in an earlier publication (Schwindt et al., 2006), as well as to Hg (Appendices 5B and 5C) in this lake. Similarly, in the cutthroat trout (*O. clarki lewisi* and *O. clarki bouvieri*) from GLAC, it was not possible to test numerous age classes and MAs were related to both age and Hg (Appendices 5B and 5C).

Mercury is toxic to fish at relatively low concentrations (Niimi and Kissoon, 1994). Exposure of fishes to Hg affects numerous physiological endpoints, including histopathological indicators such as MAs. For example, Handy and Penrice (1993) illustrated numerous histological changes in addition to increased kidney MAs following Hg exposure in the laboratory. Corresponding Hg concentrations in the kidney ranged from approximately 2 to 9 µg/g (Handy and Penrice, 1993), which is within the realm of whole body concentrations found in WACAP. Mercury concentrations in individual organs and muscle tissue in the trout from this study would undoubtedly be much higher, as analysis of whole fish dilutes the Hg sequestered in target organs and skeletal muscle. In blue gourami (*Trichogaster trichopterus*) fed 9 ppb of methyl-Hg and exposed to viral and bacterial pathogens, the hemosiderin bodies, associated with MAs, were infiltrated by the white pulp of the spleen and decreased antibody production was also observed (Roales and Perlmutter, 1980). The reduction in hemosiderin was attributed to the infectious agents, not Hg, and the authors concluded that Hg induced immuno-suppression as indicated by reduced antibody production (Roales and Perlmutter, 1980). In the flounder (*Platichthys flesus*), Pulsford et al. (1992) observed localization of metals in splenic MAs, but no associations were made between the metals and changes in MAs.

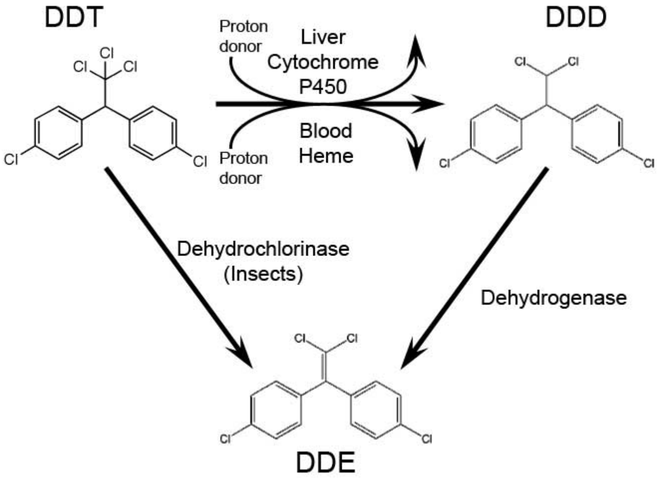
In summary, we demonstrate the association between MAs and Hg for brook trout, given the large geographic area sampled. This suggests that spleen MAs might be ideal sentinels for assessing the incorporation of Hg, or other largely age-dependent pollutants, into the food web. We do not generalize beyond brook trout, however, because of the small sample sizes and the limited geographic areas from which we collected the lake, rainbow, and cutthroat trout. Within lakes (other than those in the Arctic), Hg and age both explained significant amounts of variation in MAs. At present, we cannot explain why MAs were higher in lake trout from Wonder Lake, DENA, compared to the fish from the Arctic lakes (GAAR and NOAT). Nor can we explain why MAs were higher in fish from Snyder Lake, GLAC. We recommend continued Hg monitoring in whole fish. Sampling of fish for MAs could easily be conducted along with Hg sampling.

5.3.3.2 Vitellogenin in the Blood of Male Fish

Vitellogenin is an egg-yolk precursor protein synthesized in the liver of oviparous animals in response to estrogen, or xenoestrogen (Arukwe and Goksoyr, 2003). Male and immature female oviparous animals have the capacity to produce Vtg, but endogenous estrogens are rarely present in sufficient concentrations to induce appreciable amounts of plasma Vtg (Sumpter and Jobling, 1995). Thus, when Vtg is observed in the plasma of male or immature female fish, it suggests exposure and response to a xenoestrogen (Purdom et al., 1994; Jobling et al., 1996, 1998). These features have led to Vtg becoming a biomarker for environmental estrogen exposure and used as such in many studies (e.g., Purdom et al., 1994; Jobling et al., 1996, 1998; Harries et al., 1997; Christiansen et al., 1998; Gronen et al., 1999; Mills et al., 2001, 2003; Zaroogian et al., 2001; Palace et al., 2002; Sepulveda et al., 2002; Kavanagh et al., 2004; Feist et al., 2005).

Metabolism of DDT. It is apparent from these data that certain metabolites of contaminants are present in higher concentrations than the applied or active ingredient. For example, p,p'-DDE, one of the DDT metabolites, is present in higher concentrations in fish than DDT itself. The p,p'- and o,p'- isomers of DDT are metabolized in fish (and in the soil and lake sediment) to DDD and DDE. The most persistent of these is DDE and DDD is found only in very minute concentrations because is it rapidly metabolized.

In fish (and other vertebrates) DDT metabolism occurs in the liver, where many foreign and endogenous compounds are metabolized, as well as the blood. The liver contains the cytochrome P450 (CYP) enzyme family that is responsible for the oxidative metabolism of many substances, including DDT. There are many CYP enzyme sub-families and they reside in microsomes, which are vesicles that break off of cellular organelles. The CYP enzymes degrade DDT by dechlorination and dehydrogenation and eventually DDE (the most persistent metabolite) is broken down to the water-soluble DDA and is excreted from the animal. There is also evidence for non-enzymatic degradations.



Proposed Mechanisms of DDT Metabolism. Redrawn from Kitamura et al. (2002).

Environmental estrogens (xenoestrogens) are artificially produced chemicals that mimic the estrogens produced in animals. The proposed mechanism of action is similar to that of the native 17β-estradiol (E_2). That is, xenoestrogens bind to hormone receptors and either block or initiate the action that would otherwise be controlled by endogenous estrogens. The relative "strength" of xenoestrogens, measured by the concentration needed to displace endogenously produced E_2 from receptors, varies considerably. The birth control hormone, 17α-ethynylestradiol, is about 10 times stronger than E_2, and most other chemicals (e.g., DDT, bisphenol A, alkyphenol ethoxylates) are weakly estrogenic, requiring 10^3 to 10^6 times the E_2 to occupy the receptor (Zava et al., 1997; Kloas et al., 2000). Vitellogenin is the most abundant downstream product of estrogen receptor activation and is specific to E_2 and estrogen-like chemicals. The (in)activation of hormone receptors by anthropogenic chemicals is called endocrine disruption, the consequences of which are currently being debated in the scientific community. Recent evidence suggests that exposure to the birth-control hormone 17α-ethynylestradiol led to a population crash of the fathead minnow (*Pimephales promelas*) (Kidd et al., 2007).

Endocrine disruption is not limited to the actions of xenoestrogens; other hormonal pathways can be disrupted by different chemicals. For example, the brominated flame retardants affect thyroid hormone pathways (Legler and Brouwer, 2003; Jahnke et al., 2004). Polyaromatic hydrocarbons and other aryl-hydrocarbon receptor agonists (such as dioxin) are anti-androgenic (Safe, 1994). The banned organochlorine pesticide DDT (and its metabolites) is a well-known endocrine disruptor (Colburn et al., 1993) that binds to estrogen receptors and initiates cellular changes, such as the synthesis of proteins, such as Vtg. The degradation products of the current-use pesticides endosulfan and methoxychlor are also weakly estrogenic and have been detected in the fish in this study. Although not target analytes in WACAP, detergent additives, plasticizers, birth control hormones, food additives, phytoestrogens (Kuiper et al., 1998; Bennetau-Pelissero et al., 2004; Fox, 2004), and some personal care products are also weakly estrogenic.

5.3.3.2.1 Data Analysis

Our objectives for the use of blood plasma Vtg in WACAP were to screen male fish for potential response to estrogen-like compounds and relate the Vtg to the contaminant concentrations. We assumed that male fish do not normally produce Vtg because circulating levels of endogenous estrogens are very low (10s to 100s ppt) and are not thought to induce Vtg. For comparison, 10 to 100 times as much E_2 is needed in females to significantly increase Vtg levels. Despite this, all male fish in WACAP were analyzed for E_2 to be sure that endogenous estrogens were not influencing the Vtg levels. Indeed, in our results, male plasma E_2 fell within the above range (Appendix 5A), and was not different than the E_2 in male fish with low, or non-detectable Vtg, indicating that fairly high Vtg levels in some male trout were not caused by endogenous estrogens. Based on the ranges of concentrations in the literature from polluted and reference sites and laboratory studies, we consider Vtg above 1 ppm to be abnormal in male fish. To explore potential relationships between Vtg and suspected or known estrogenic contaminants identified within those same fish, we performed regression analysis on fish for which contaminant concentrations were available and >1 fish exhibited elevated Vtg. Regression analysis could not be performed on the fish from GLAC because only 1 fish from each lake displayed fairly high levels of Vtg and, therefore, one data point would anchor the regression line. Vitellogenin concentrations were determined following the method of Schwindt et al. (2007).

5.3.3.2.2 Results and Discussion

The National Park Service is concerned about contaminant effects (e.g., changes in biomarkers) on populations as well as on individuals. Therefore, we plotted the Vtg concentrations in male fish as a scatterplot and as a mean, so that individual concentrations could be easily visualized with respect to the average (Figure 5-11). Of note were numerous sites from parks in the Rocky Mountains that had appreciably higher levels of Vtg than the other sites, which were at least an order of magnitude lower if not non-detectable (Figure 5-11). Results from our samples obtained in 2003 from ROMO prompted a subsequent study to sample additional waters during the summers of 2005 and 2006, as well as to repeat the work performed in 2003. Additional waters, Sprague Lake in 2005 and Spirit Lake in 2006 (both in ROMO), with male fish displaying fairly high Vtg were discovered, and in 2006, we repeated the findings obtained at Lone Pine Lake in 2003. Spirit Lake is in the same drainage, but upstream from Lone Pine Lake, and does not have campsites, reducing the influence of localized use. Also, two male fish from GLAC and one male fish from Golden Lake, MORA, displayed elevated levels of Vtg (Figure 5-11). In lakes sampled in 2005, Vtg gene expression in the liver was also evaluated. No Vtg gene expression was evident (Biales, pers. comm.); therefore, it appears that the cause of the slightly elevated Vtg we found was probably exposure to something not active around the day of fish collection. Although the sample sizes were very small, significant correlations between known or suspected estrogenic contaminants and Vtg in both lakes sampled at ROMO in 2003 were found (Figure 5-12). Although statistical analysis could not be performed, the fish from Oldman Lake, GLAC, was the only fish in WACAP to have detectable concentrations of o,p′-DDT, as well as the highest concentrations of p,p′-DDT, well-known endocrine disruptors. These results suggest that not only are Vtg levels in certain trout elevated relative to within-lake counterparts, they are also related to concomitant increases in estrogen-like contaminants.

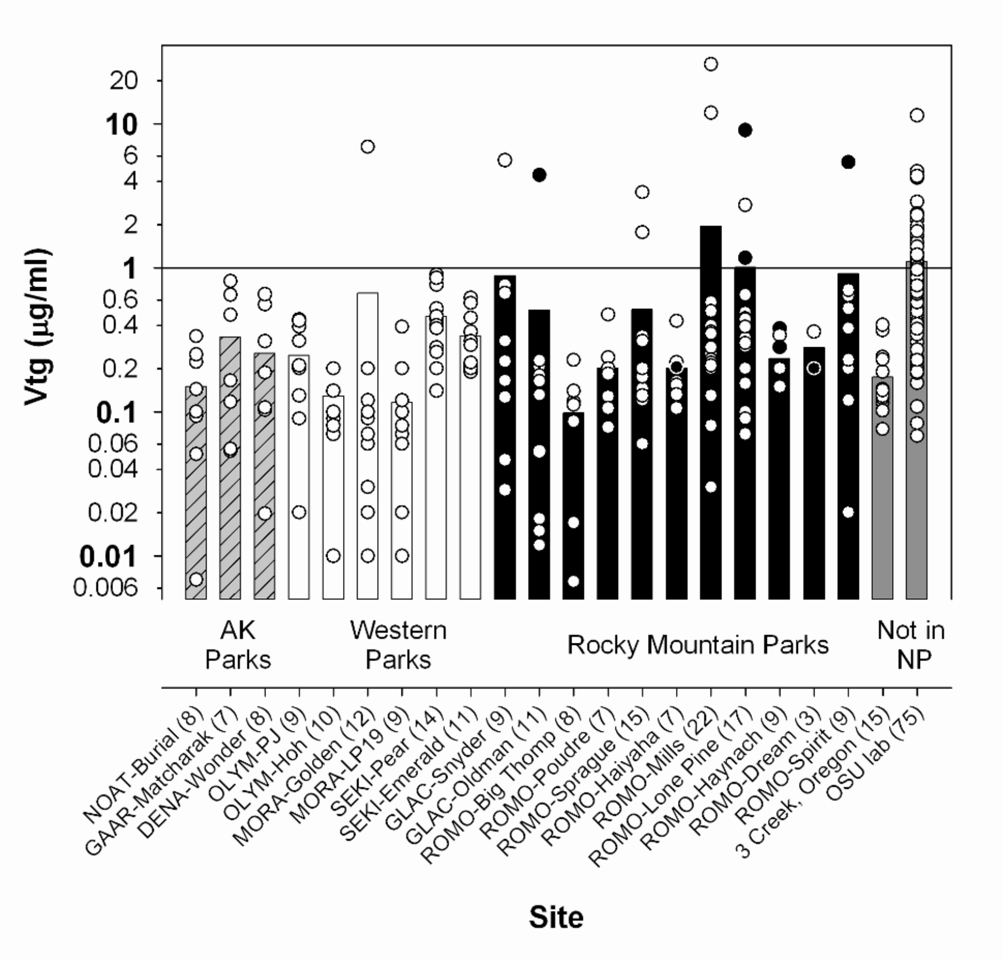


Figure 5-11. Mean Vitellogenin + 95% Confidence Intervals and Concentrations from Individual Male Trout from Lakes or Streams in National Parks in the Western United States and Other Sites. Bars are shaded to denote region. *N* = 3 to 75, depending on location, and is listed for each field site after the site name. Black data points are intersex males. Vtg concentrations determined following Schwindt et al. (2007). Data are plotted on a $\log_{10}$ scale and there is some data overlap.

5.3.3.3 Intersex in Male Fish

Intersex, the presence of both male and female reproductive structures in the same animal, is a commonly used biomarker of estrogen-like chemical exposure in gonochoristic fishes, such as salmonids. Many fishes are natural hermaphrodites. The process is essential to the reproductive life histories of numerous families of fish, and it has been argued that there is a “baseline” level of intersex, even in gonochoristic fishes (Devlin and Nagahama, 2002; Sumpter and Johnson, 2005). Regardless, the underlying assumption that trout, by genetic determination, are phenol-typically male or female implies that any deviation (i.e., intersex) from that is abnormal (Bortone and Davis, 1994). Although this might be true, the difficulty lies in attributing the abnormality to some random genetically or environmentally induced baseline level or to the effect of estrogen-like compounds, as in the case of reports of feminized male fish in the scientific literature (e.g., Jobling et al., 1998; Woodling et al., 2006). Even in the laboratory, consistent induction of intersex with “weak” estrogens is difficult (Carlson et al., 2000).

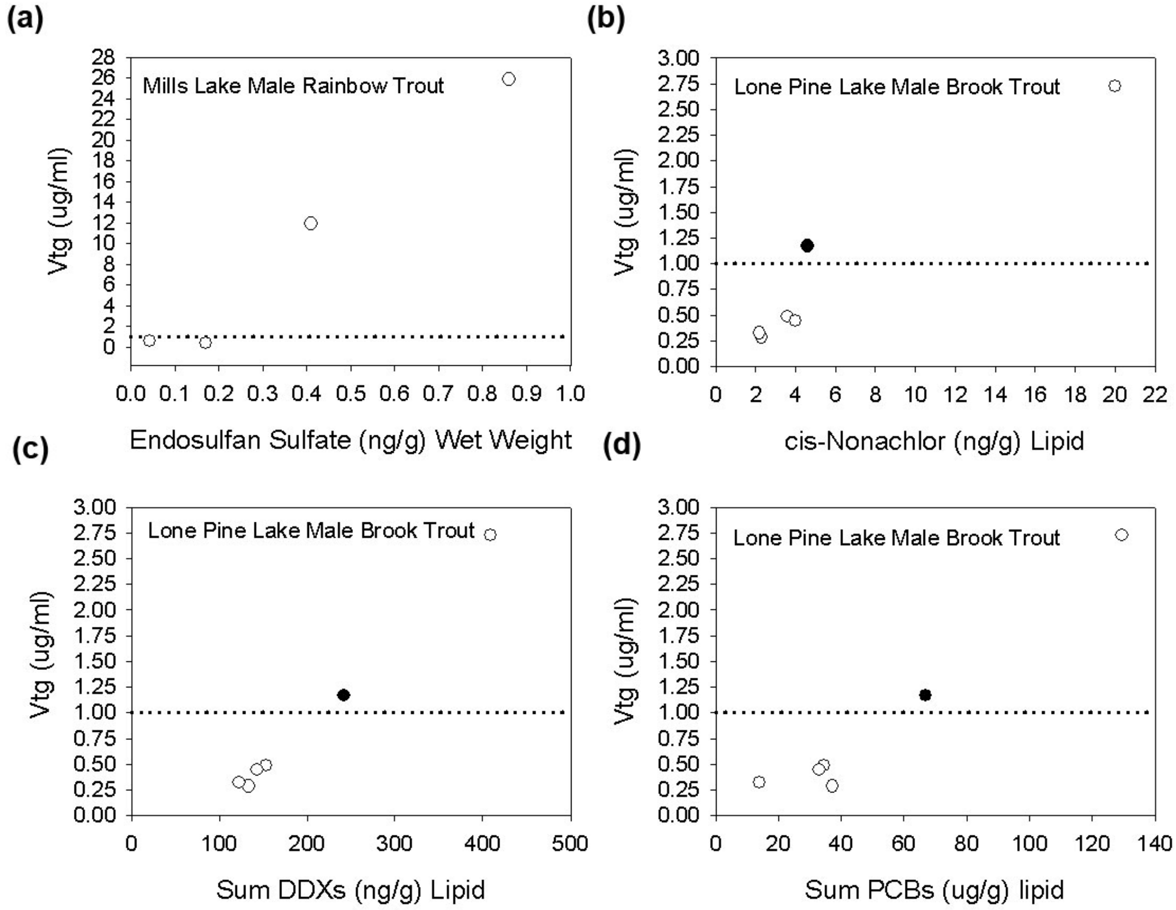


Figure 5-12. Scatterplots Comparing Suspected Endocrine Disruptors and Plasma Vitellogenin (Vtg), a Commonly Used Indicator of Estrogenic Contaminants in Male Trout. For the bottom two graphs, "Sum" indicates that individual contaminant concentrations were added together to arrive at the sum concentration. For DDT, the o,p′- and p,p′- isomers of DDT, DDD, and DDE were summed. For the PCBs, congeners 74, 101, 118, 153, 138, 187, and 183 were summed. The data point in black is an intersex male trout. The dashed line is the quantitation limit for the assay. $N = 4$ for Mills Lake and $N = 6$ for Lone Pine Lake. For Mills Lake, Vtg v. Endosulfan sulfate $F_{1,2} = 78.38$, $R^2 = 0.97$, $P = 0.012$. For Lone Pine Lake, Vtg v. cis-Nonachlor $F_{1,4} = 77.49$, $R^2 = 0.95$, $P = 0.0009$. Lone Pine Lake Vtg v. ∑PCBs $F_{1,4} = 100.66$, $R^2 = 0.96$, $P = 0.0006$. Lone Pine Lake Vtg v. ∑DDTs $F_{1,4} = 645.33$, $R^2 = 0.99$, $P < 0.0001$.

Yet, intersex has been used as a biomarker by numerous researchers (Vigano et al., 2001; Gercken and Sordyl, 2002; Kirby et al., 2004) and is considered the most reliable biomarker of reproductive abnormalities. This suggests that intersex should be validated, as well as possible, for study organisms. However, validation of intersex in trout is more difficult than for Vtg. It is a time-consuming endeavor and, to our knowledge, has not been attempted by other researchers. In an effort to validate the use of intersex in trout as a biomarker, we obtained trout from the University of Washington School of Fisheries in Seattle and from the California Academy of Sciences in San Francisco to determine if intersex could be observed in fish captured before the large-scale anthropogenic emission of the endocrine disrupting compounds (pre-1940s). The sites, species, sex ratio, and number intersex for every trout analyzed in these studies are shown in Figure 5-13 and Table 5-8.

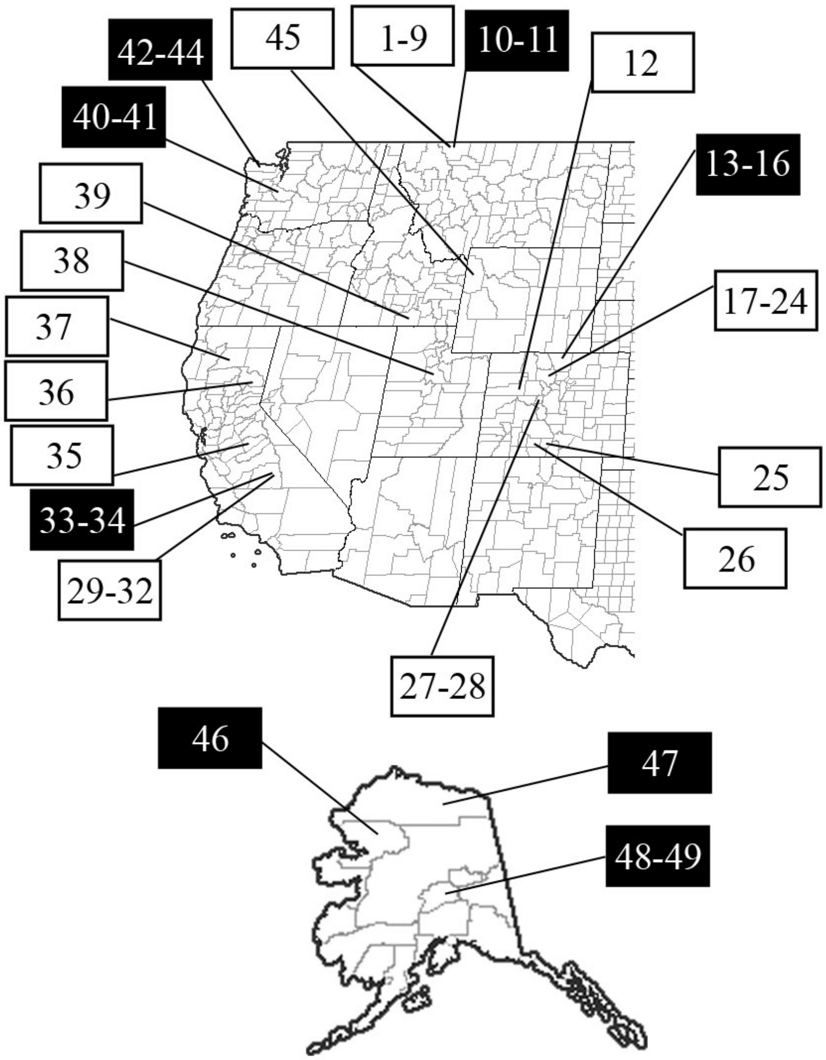


Figure 5-13. Counties or Boroughs (Alaska) Where Museum (white boxes) and/or WACAP (black boxes) Fish Samples Were Collected and Gonads Analyzed for Sex and Intersex. The key to the numbers on the map, and the numbers of male, female, and intersex fish is in Table 5-8.

Table 5-8. Characteristics of Intersex Trout Analyzed from Current and Historic Sampling.

Map #	State	County	Location	Park	Year	Species	M / F	Intersex
1	MT	Glacier	Middle Fork, Flathead River	GLAC	1934	*Oncorhynchus clarki* subsp.	0 / 1	0
2	MT	Glacier	Coal Creek	GLAC	1934	*O. clarki* subsp.	2 / 2	0
3	MT	Glacier	Fish Creek	GLAC	1934	*O. clarki* subsp.	1 / 2	0
4	MT	Glacier	Arrow Lake	GLAC	1934	*O. clarki* subsp.	2 / 0	0
5	MT	Glacier	Lincoln Creek beaver ponds	GLAC	1934	*O. clarki* subsp.	3 / 6	0
6	MT	Glacier	Trout Lake	GLAC	1934	*O. clarki* subsp.	3 / 2	0
7	MT	Glacier	Park Creek	GLAC	1934	*O. clarki* subsp.	1 / 2	0
8	MT	Glacier	Isabel Lake outlet	GLAC	1934	*O. clarki* subsp.	1 / 1	0
9	MT	Glacier	Lower Snyder Lake	GLAC	1934	*O. clarki* subsp.	5 / 2	0
10	MT	Glacier	Lower Snyder Lake	GLAC	2005	*O. clarki lewisi*	9 / 6	0
11	MT	Glacier	Oldman Lake	GLAC	2005	*O. clarki bouvieri*	11 / 4	1 Male
12	CO	Garfield	Trappers Lake		<1871	*O. clarki pleuriticus*	0 / 1	0
13	CO	Grand	Lone Pine Lake	ROMO	2003	*Salvelinus fontinalis*	7 / 8	1 Male
14	CO	Grand	Lone Pine Lake	ROMO	2006	*S. fontinalis*	10 / 20	1 Male
15	CO	Grand	Spirit Lake	ROMO	2006	*S. fontinalis*	9 / 6	1 Male
16	CO	Grand	Haynach Lake	ROMO	2006	*O. clarki bouvieri*	9 / 6	2 Male
17	CO	Larimer	Mills Lake	ROMO	2003	*O. mykiss / clarki*	6 / 9	0
18	CO	Larimer	Mills Lake	ROMO	2006	*O. mykiss / clarki*	16 / 11	0
19	CO	Larimer	North Fork, Big Thompson R.	ROMO	2005	*S. fontinalis*	8 / 7	0
20	CO	Larimer	Lake Haiyaha	ROMO	2005	*O. clarki*	7 / 8	1 Male
21	CO	Larimer	Poudre Lake	ROMO	2005	*S. fontinalis*	7 / 9	0
22	CO	Larimer	Sprague Lake	ROMO	2005	*S. fontinalis*	11 / 5	0
23	CO	Larimer	Sprague Lake	ROMO	2006	*S. fontinalis*	4 / 8	0
24	CO	Larimer	Dream Lake	ROMO	2006	*O. clarki stomias*	3 / 12	1 Male
25	CO	Alamosa	Conejos River		1889	*O. clarki virginalis*	2 / 1	0
26	CO	Rio Grande	Rio Grande		1889	*O. clarki virginalis*	2 / 0	0
27	CO	Lake	Twin Lakes		1889[1]	*O. clarki stomias*	3 / 0	2 Male
28	CO	Lake	Arkansas River		1889	*O. clarki stomias*	2 / 0	0

Table 5-8. Characteristics of Intersex Trout Analyzed from Current and Historic Sampling (continued).

Map #	State	County	Location	Park	Year	Species	M / F	Intersex
29	CA	Tulare	Volcano Creek		1891	*O. mykiss aguabonita*	1 / 0	0
30	CA	Tulare	Golden Trout Creek		1893[1]	*O. mykiss aguabonita*	7 / 1	0
31	CA	Tulare	Golden Trout Creek		1904	*O. mykiss aguabonita*	2 / 0	0
32	CA	Tulare	Cottonwood Lakes		1912	*O. mykiss aguabonita*	0 / 2	0
33	CA	Tulare	Emerald Lake	SEKI	2003	*S. fontinalis*	11 / 5	0
34	CA	Tulare	Pear Lake	SEKI	2003	*S. fontinalis*	14 / 3	0
35	CA	Mariposa	near Merced Lake	YOSE	1921	*S. fontinalis*	1 / 1	0
36	CA	Plumas	Gold Lake		1899	*O. mykiss*	1 / 0	0
37	CA	Shasta	Fall River		1898	*O. clarki*	1 / 1	0
38	UT	Utah	Provo River		1889[1]	*O. clarki virginalis*	1 / 1	0
39	ID	Cassia	Cottonwood Creek		1894	*O. clarki lewisi*	0 / 1	0
40	WA	Pierce	LP19	MORA	2005	*S. fontinalis*	9 / 6	0
41	WA	Pierce	Golden Lake	MORA	2005	*S. fontinalis*	12 / 3	0
42	WA	Clallum	PJ Lake	OLYM	2003	*S. fontinalis*	4 / 11	0
43	WA	Clallum	PJ Lake	OLYM	2005	*S. fontinalis*	5 / 10	0
44	WA	Clallum	Hoh Lake	OLYM	2005	*S. fontinalis*	10 / 5	0
45	WY	Teton	Pacific Creek		1891	*O. clarki*	2 / 0	0
46	AK	NW Arctic	Matcharak Lake	GAAR	2004	*S. namaycush*	7 / 8	0
47	AK	North Slope	Burial Lake	NOAT	2004	*S. namaycush*	8 / 7	0
48	AK	Denali	McLeod Lake	DENA	2004	*Lota lota*	2 / 0	0
49	AK	Denali	Wonder Lake	DENA	2004	*S. namaycush*	8 / 7	0

[1] Collection date is inferred from information associated with the specimens.

5.3.3.3.1 Data Analysis

Our objectives were to identify abnormalities in the gonads of male and female fish. In the event that abnormalities were identified, we searched for possible hypothesis-generating relationships to aid in interpreting the significance of the abnormalities. To find the intersex fish, evidenced by ova-testis, or other abnormalities, we scanned the entire gonad section, beginning with 100× total magnification, by compound light microscopy. When oocytes were visualized in the testis, we increased the magnification to 400× to confirm and capture digital images. In some instances, 25× or 50× total magnifications were sufficient to observe the maturing ova present in the testis. To determine the extent of testicular abnormalities, we developed a grading system, similar to that developed by Jobling et al. (1998), for the degree of abnormality observed in the male gonads. The testes observed in these studies are characterized as the following: (1) normal testis, (2) poorly developed testis for the size of the fish (i.e., does not show signs of reproductive maturity), (3) normally developing testis with primary or perinucleolar oocytes, and (4) poorly developed or degenerative testis with perinucleolar oocytes and/or vitellogenic oocytes (Figure 5-14). The numbers of fish we observed in each category, separated by geographic region and current or historic sampling, are listed in Table 5-9. The proportion of current and historic sites with intersex fish in the Rocky Mountains was compared with Fisher's Exact Test and the results are reported in Table 5-10.

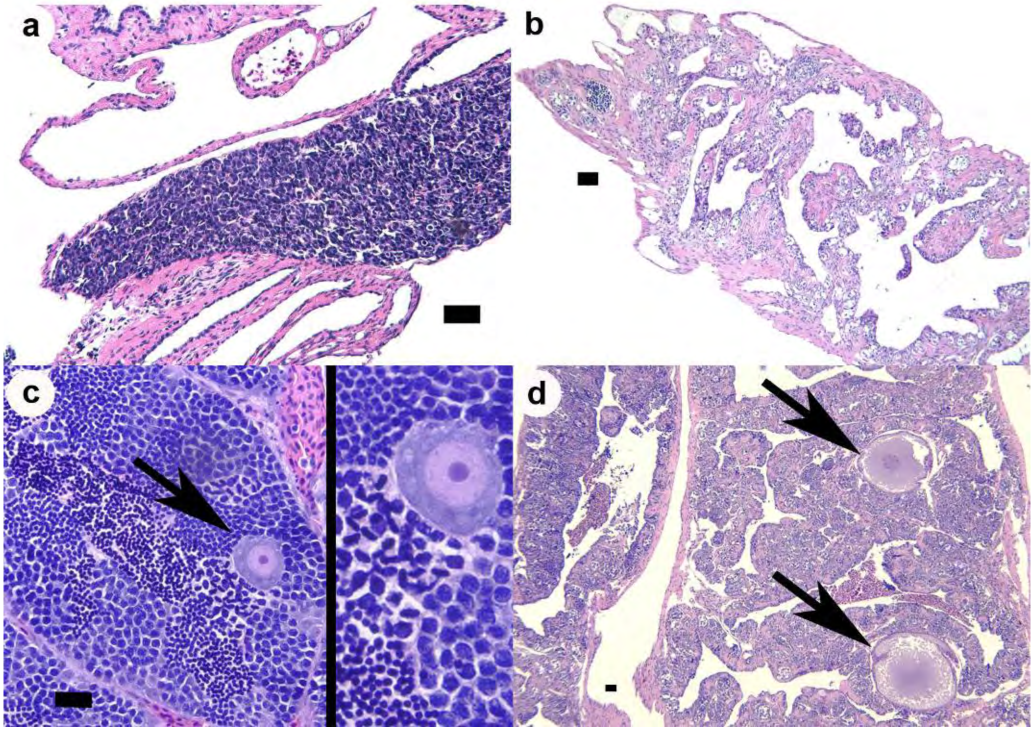


Figure 5-14. Categories of Relative Gonad Abnormality: (a) Normal immature testis, (b) Poorly developed testis or degenerative testis, for the size of fish, (c) Normally developing testis with primary or perinucleolar oocytes (inset is the magnified oocyte at the arrow), and (d) Poorly developed testis with perinucleolar oocytes and/or vitellogenic oocytes (arrows). Hematoxylin and Eosin; bars = 50 μm.

Table 5-9. Categorization of Trout Testes by Abnormality, Geographic Region, and Current or Historic Sampling.

Region	Sample	Total Males	Testis Category			
			a	b	c	d
Rocky Mountains	Current	117	107	2	5	3
	Historic	30	28	0	2	0
Sierra Nevada	Current	25	25	0	0	0
	Historic	12	11	0	0	0
Olympics/Cascades	Current	40	40	0	0	0
	Historic	1	1	0	0	0
Denali, Alaska	Current	10	10	0	0	0
	Historic	0				
Arctic Alaska	Current	15	15	0	0	0
	Historic	0				

Table 5-10. Comparison of Sites with Intersex Fish from the Rocky Mountains.

Dates	Intersex	Not Intersex	Proportion	*p* (Fisher's Exact Test)
1871-1934	1	13	0.07	
2003-2006	6	5	0.54	0.0213

5.3.3.3.2 Results and Discussion

In the historic samples, we dissected a total of 85 trout, finding 42 males, 28 females, 2 intersex males (counted as male), and 15 fish specimens for which we could not identify sex because of the poor quality of the specimen. Of note, we obtained westslope cutthroat trout samples from the University of Washington captured in 1934 from Lower Snyder Lake, the same lake we sampled from GLAC in 2005. In both the current and the museum samples, intersex trout from this lake were not found (Figure 5-13; Table 5-8). In the current samples, 207 total male fish were sampled and 8 of 117 male fish in the Rocky Mountains were intersex. The within-lakes frequencies ranged from 9% to 33%, and 50% of these intersex fish also produced elevated concentrations of Vtg.

We found two historic samples collected in the late 1800s from Twin Lakes, Colorado, in the Rocky Mountains that were intersex (Figure 5-15). This lake is quite close to ROMO. It is also in the vicinity of where extensive heavy metal mining took place in the 1800s. This is the earliest known intersex trout, to our knowledge, and a noteworthy finding in and of itself. We are unaware of the work showing that metals can lead to intersex among teleosts fishes, but there is evidence that cadmium has estrogenic properties (Johnson et al., 2003). There is also evidence that elevated concentrations of some heavy metals such as cadmium can cause testicular injury (Sangalang and O'Halloran, 1972, 1973). Our observations of intersex male trout in very old specimens, long before the manufacture of organic contaminants, warrants a more extensive investigation into the depth and breadth of this phenomenon, albeit it is beyond the scope of WACAP. Reeder et al. (2005) analyzed the gonads of 814 cricket frogs (*Acris crepitans*) dating from 1852 to 2001 and found that the frequency of intersex fluctuated with relative anthropogenic input to the environment.

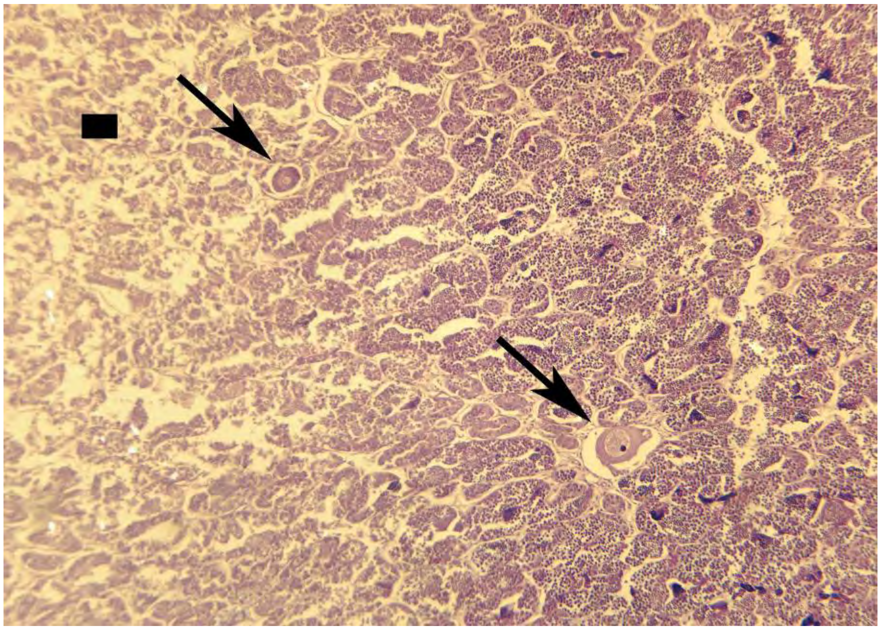


Figure 5-15. Intersex Male Greenback Cutthroat Trout from Twin Lakes, Colorado, Captured in the Late 1800s. Primary oocytes (arrows) are surrounded by normally developing testis, indicating category c gonad abnormality (see Figure 5-14). Hematoxylin and Eosin; bar = 50 µm.

While the frequency of intersex trout we found across the West and in Alaska is quite low, it appears concentrated in the Rockies where the sites with intersex fish today is significantly greater in number than in the past (Table 5-9). The severity of abnormalities observed in the current samples is also greater (Table 5-9). All three intersex trout from Lone Pine and Spirit Lakes displayed category 4 gonad abnormalities, and had low androgen and estrogen levels and elevated levels of Vtg during the time of year when the other trout were nearing sexual maturity. Based on this information, we argue that these individuals are incapable of reproduction, whatever the cause. Identifying the cause of these observations is impossible with the current dataset. If similar numbers of fish from the museums were sampled, then the possibility of finding similar numbers of category 4 testis abnormalities is definitely possible.

The intersex fish at Lone Pine Lake in 2003 (Figure 5-16a-c) had the second highest concentrations of p,p′-DDT and 10 to 100 times the dieldrin, both documented endocrine disruptors, of the other fish analyzed in WACAP. This finding implies that contaminants are at least influencing the reproductive health of that individual. Furthermore, that similar levels of disruption were found at Lone Pine Lake in 2003 and 2006 indicates that the observed abnormalities are not transient phenomena. The consequences of 1 in 7 and 1 in 10 males in 2003 and 2006, respectively, not reproducing, if indeed they cannot reproduce, are unknown. Long-term monitoring is needed to determine if the population is stable. The intersex fish at Oldman Lake, GLAC, was category 3 (Figure 5-16d), had elevated Vtg levels, and had the highest concentrations of chlordanes (*cis, trans, oxy* and nonachlors), the dioxin-like PCB 118, and was the only fish in the study with detectable concentrations of o,p'-DDT, also a confirmed xenoestogen. This fish also had normal levels of plasma androgens and, aside from being intersex, had normally developing gonads.

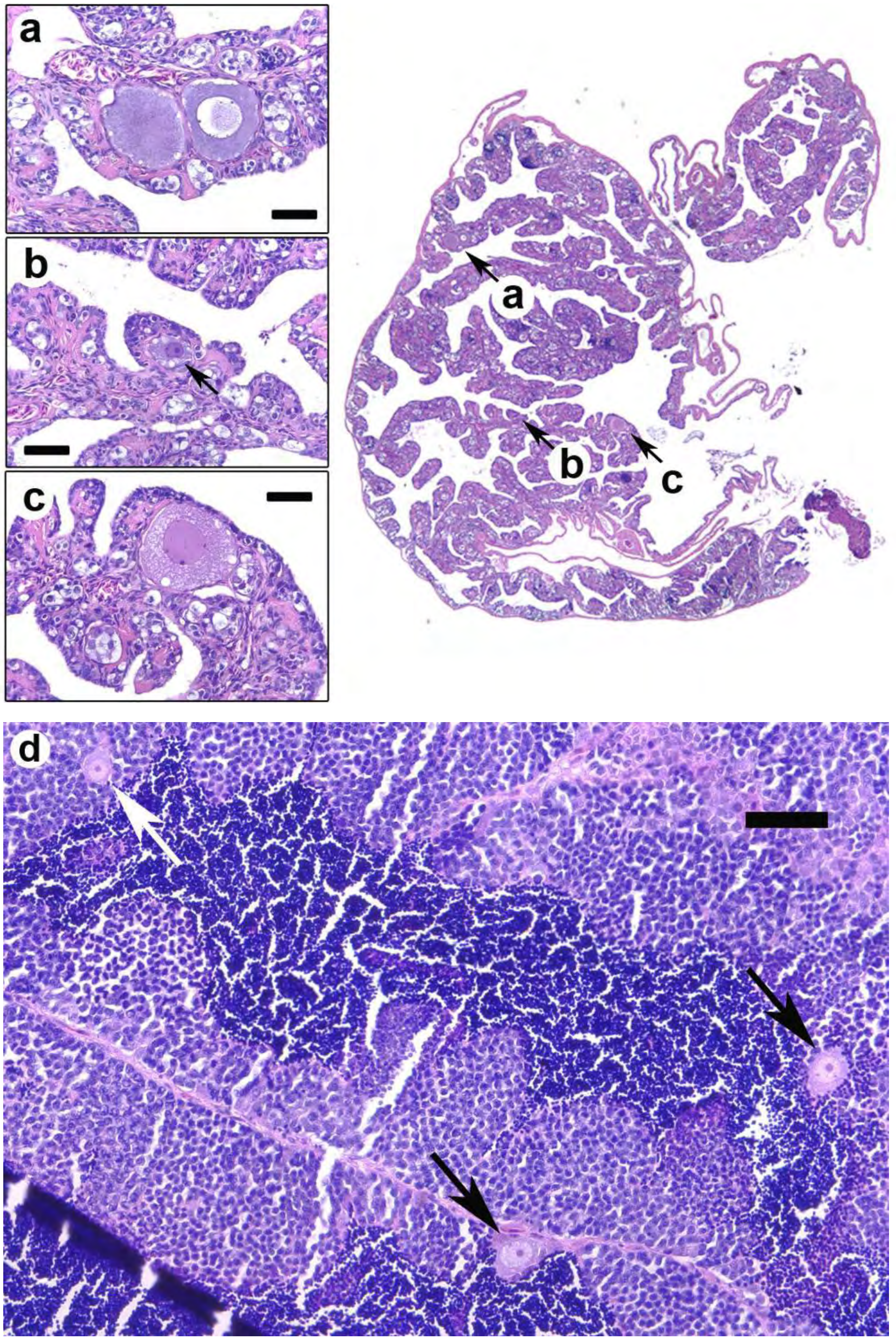


Figure 5-16. Intersex Male Trout from Lone Pine Lake, ROMO (a–c) and Oldman Lake, GLAC (d). The insets (a–c, 400x), areas denoted by the corresponding letters and arrows on the low magnification image (composite, 50x), depict perinucleolar oocytes surrounded by a poorly developed testis. In (d) primary oocytes (arrows) are surrounded by normally developing testis (composite, 400x). Hematoxylin and Eosin; bars = 50 µm.

In summary, the use of intersex as biomarker for endocrine or reproductive disruption is not perfect; however, our studies signify the importance establishing a baseline to which future sampling can be compared. Intersex had not been observed, to our knowledge, in trout from ecologically protected areas. In the scientific literature, increased frequencies or severity of intersex is highly suggestive, if not indicative, of reproductive dysfunction (Devlin and Nagahama, 2002), whatever the cause. Our recommendations are to continue monitoring lakes in the Rocky Mountains, including ROMO and GLAC, for Vtg, sex steroids, and gonad abnormalities. In addition, we recommend that sampling be expanded to include Grand Teton and Yellowstone National Parks, as they are roughly mid-way between ROMO and GLAC. Other parks in the Rocky Mountains could consider initiating similar monitoring programs. These future efforts, in coordination with expanded sampling of museum specimens, could help provide resource managers with the information necessary to determine if biomarkers of reproductive endocrine disruption are changing through time.

5.3.3.4 Interpretation and Integrated Analysis: Emphasizing Park and Regional Differences in Biomarkers and Contaminants

Our analysis of biomarker responses and their relationship to contaminant concentrations focused on effects on trout in general. That is, we identified relationships between MAs and Hg in brook trout from all the parks. However, we have not explained among-lake differences in MAs, for the lake trout and *Oncorhynchus* spp. and how they might relate to contaminant concentrations. The question that has not been addressed is: Are MAs higher in fish with higher contaminant concentrations? At present we cannot answer this question because no readily apparent statistical relationships emerged (because of small sample sizes). In other analyses, we have related contaminants suspected to have estrogenic action to biomarkers that respond to estrogenic contaminants. One question that arises from these analyses is: Why is the evidence for endocrine disruption (Vtg and intersex male fish) confined to parks in the Rocky Mountains? The following paragraphs are intended to address this question as best possible, considering the small sample sizes and subtle among-park and regional differences.

5.3.3.4.1 Biomarkers Related to Reproductive Disruption

Vitellogenin persists in the blood for about 2 weeks following an acute induction (Schultz et al., 2001), so the window of detectability is limited for this biomarker. For Emerald and Pear Lakes (SEKI), where some contaminant concentrations were higher than those of Lone Pine Lake (ROMO) and Golden Lake (MORA) (Figure 5-17), the absence of Vtg could be related to the absence of estrogenic contaminants in the blood. Without mobilization of contaminants from fat, or ingestion of contaminated food, it is unlikely that elevated Vtg would be observed, despite higher contaminant concentrations in SEKI. So, one reason for not observing elevated Vtg in SEKI is that the fish were sampled outside the window of sensitivity to the contaminants or the biomarker. The lakes with *Oncorhynchus* spp. (Mills Lake, ROMO, and both lakes in GLAC) all had fish with elevated levels of Vtg. Our analysis of contaminant sums by class (e.g., the chlordanes) revealed subtle differences in mean concentrations (generally higher at Oldman Lake, GLAC), but Vtg levels in the rainbow trout (from Mills Lake, ROMO) were generally higher than in the other species. This could be a result of the species-specific sensitivity to the chemicals, including the contaminants measured in WACAP, as well as those not measured. An alternative explanation is that the polyclonal antibody used in the assay was generated against rainbow trout Vtg (see Schwindt et al., 2007), so these antibodies might recognize more epitopes on the rainbow trout Vtg than on the Vtg in the other salmonids.

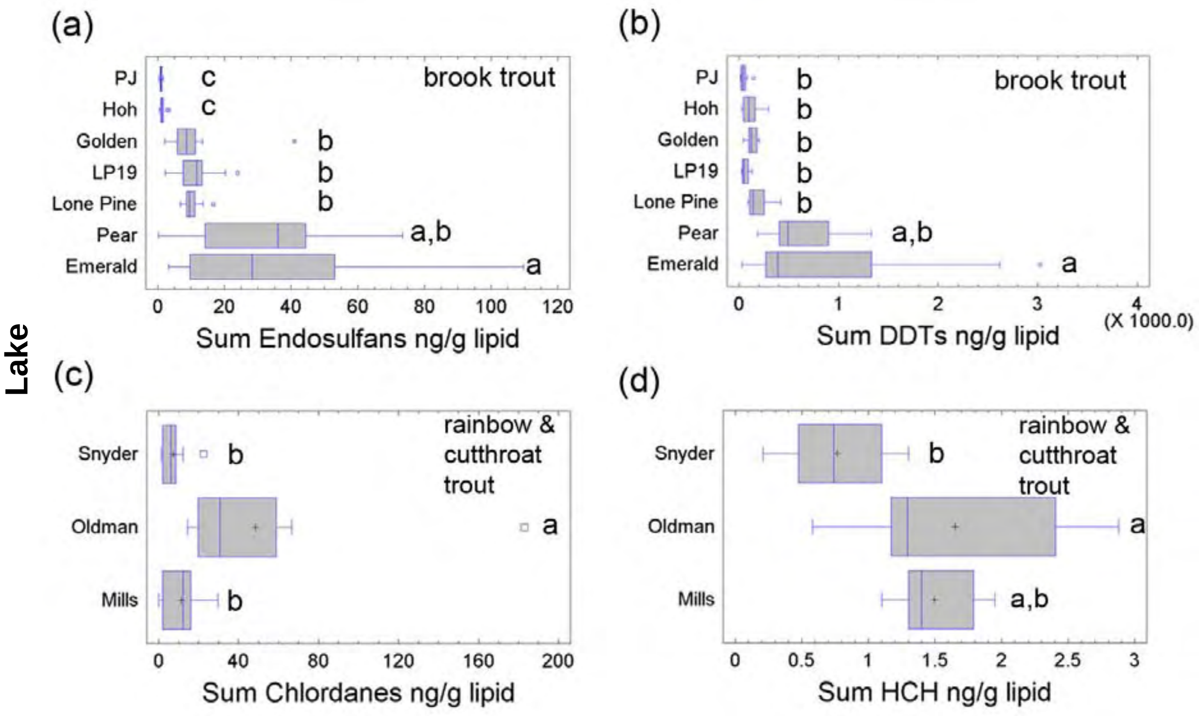


Figure 5-17. Box and Whisker Plots of Select Groups of Organochlorines Analyzed by Brook Trout (a,b) or *Oncorhynchus* spp. (c,d). Median sum endosulfans (a) and DDTs (b) are compared by Kruskal Wallis because of unequal variance. Sum chlordanes (c) and HCHs (d) are compared by ANOVA followed by a Bonferroni *post hoc* at 95% confidence. Different letters denote significantly different medians or means at $p < 0.05$. Boxes are the middle 50% of the data divided by the median (line); the "+" symbol represents the mean. Whiskers are the range of data and individual points are outliers. Sum endosulfans = endosulfan I, II, and sulfate. Sum DDTs = o,p′- and p,p′- isomers of DDT, DDD, and DDE. Sum chlordanes = *cis*, *trans*, *oxy*-chlordane, and nonachlor. Sum HCH = a-, d-, and g-HCH. Data below the detection limits are represented as ½ the EDL.

Alternative explanations for the presence of intersex fish and elevated Vtg include the presence of estrogens from human birth control, perhaps from humans swimming in the lakes. It is not known if the numbers of humans on birth control that would urinate in the lakes during a possible backcountry swim could excrete a quantity of estrogenic substance sufficient to be endocrine disrupting. Other sources of estrogenic substances could be from horses and wildlife that frequent the lakes, but several of these lakes in which intersex fish are present are not accessible to horses or mules. In addition, the unknowns mentioned for human excretions would apply to wildlife. One other possibility is that some lakes might contain fish that have fed on artificial baits introduced by anglers that contain endocrine disrupting substances to a sufficient amount. However, attributing the endocrine disruption to sources other than airborne contaminants appears considerably more speculative. In addition, the elevated Vtg evident in our laboratory population of trout is probably attributable to the presence of estrogenic substances known to be present in artificial fish feeds.

The intersex condition was found only in parks in the Rocky Mountains and the limited number of intersex fish prevents establishing statistical relationships with contaminants. However, dieldrin was much higher in the intersex brook trout from Lone Pine Lake, ROMO and o,p′-DDT was detectable only in the intersex Yellowstone cutthroat trout from Oldman Lake, GLAC. It could be purely coincidental that these estrogenic contaminants were higher in the intersex fish. At present there is no robust scientific explanation for the regional confinement of the intersex condition to the Rocky Mountains; however, our data suggest that the incidence is increasing. Perhaps if more fish were sampled from the lakes in SEKI, MORA, or OLYM, or if more lakes were sampled in SEKI or other parks in the Sierra Nevada, intersex fish would be found. The percentages of intersex fish we found in ROMO (9 to 33%) were fairly high, compared to those reported in the literature (range from 1% to 0.0002%). Therefore, it could simply be a matter of sampling enough fish from the other parks to increase the probability of finding intersex fish.

Six of 11 water bodies in ROMO had intersex fish. This is a remarkable occurrence that is biologically fascinating, and potentially alarming to resource managers and stakeholders. The established implications in the literature for high frequencies of intersex, is that endocrine or reproductive disruption is occurring. Whether these observations are caused by contaminants is impossible to say with the current dataset. We attempted to use a weight of evidence approach to establish some credible evidence for endocrine disruption (or lack of disruption). Our data show that some intersex fish also produce Vtg, have underdeveloped testis, and low sex steroids at a time of year when cohorts are nearing reproductive maturity. We even provide evidence that Vtg is related to some organochlorine concentrations. One would be hard pressed to find such compelling evidence for reproductive disruption based on observational data in the literature. To our knowledge, there is a paucity of studies in which contaminants and reproductive biomarkers have been measured in the same fish. Regardless, without experimental spiking of lakes in national parks with contaminants, measuring the contaminants in the fish, and finding statistically significant changes in the proportion of intersex fish, there is no way to attribute the intersex condition to contaminants, or anything for that matter. Intersex can be caused by genetic mutations, parasites, abrupt temperature changes, hormonal abnormalities, and contaminants. The fact that our observations occurred in two different genera, in three different species, and in allopatric populations reduces the possibility that endogenous factors (mutations and hormonal abnormalities) are at fault. Abrupt temperature changes are unlikely in these lakes and parasites were not found in the intersex fish (see Appendix 5A).

Finding intersex fish in the museum samples, prior to the manufacture of the organochlorines and other synthetic chemicals was indeed surprising. These results call to attention the possibility of some level of intersex in trout that is not associated with organic pollutants. The area around Twin Lakes was subjected to extensive ore mining. Perhaps metal contamination of waters resulting from natural or mining induced acid rock drainage was at fault. Or, the stocking of fish might have resulted in hybridization that induced a genetic abnormality (Metcalf et al., 2007). Clearly, more sampling of the museum specimens is necessary. Focusing on acquiring not only more fish from each water body, but from more water bodies in the western and northeastern parts of the USA is needed before definitive conclusions can be drawn.

In summary, there is strong inference that our results regarding intersex and Vtg in some populations in the Rocky Mountain parks can better be explained by endocrine disruption related to contaminants than by other potential causes. We also believe that it is the more responsible explanation from the perspective of conservation biology. The consequences to park resources would not be negatively affected if further investigation found this contention to be wrong. However, consequences could be negative if we do not take this contention seriously and it is indeed true, as we think.

5.3.3.5 Contaminant (SOCs and Metals) Accumulation in Moose and Potential Biological Effects on Moose in the Parks

The WACAP Research Plan included analysis of moose tissue samples for SOCs and metals in an attempt to make an explicit linkage between the Alaskan food web that WACAP was exploring for contaminants and the humans that use this food web for obtaining subsistence foods. Moose was chosen because Alaska NPS experts advised WACAP scientists that this subsistence animal was considered one of the most widely distributed and used terrestrial game animal in Alaska. Moreover, the range of an individual moose is generally small, compared to that of caribou, the other subsistence animal considered. The smaller range of the moose would tie the results of contaminant analysis to a smaller area of the Alaskan landscape. We intended to obtain moose muscle and liver samples from subsistence hunters in or near the three core WACAP sites in Alaska over a 3-year period. We allocated a total of 35 SOC and metal samples for this effort. We hoped to obtain at least three moose samples per year from each park for 3 years. At the time of the peer review, the reviewers recognized this component of WACAP as an attempt to link the more rigorous WACAP science effort to the life of the subsistence human. However, the peer review panel suggested that we not try to integrate this effort into the main WACAP science effort focused on explicit objectives and having a rigorous, controlled sampling design and schedule. Rather, understanding the interest in making the connection to the human component of the food web, they suggested we continue this as a minor effort in WACAP.

We worked through NPS personnel at DENA, NOAT, and GAAR toward the goal of obtaining moose samples from the three core Alaskan parks. We prepared information packets, tissue sub-sampling materials, and packaging and mailing items for the NPS contacts to give to potential moose hunters. In total, during the 3-year effort, we obtained tissue samples from only three animals, all collected in DENA. Two samples were obtained in 2004 and one in 2005. The moose samples were collected and delivered to the WACAP laboratory, generally following the simple procedures we outlined in a flyer distributed to subsistence hunters. Samples received at the WACAP laboratories arrived frozen solid and wrapped, and were accompanied by meta data regarding the location of the animal when it was harvested.

5.3.3.5.1 SOCs in Moose Tissue

The moose tissue analyses for SOCs revealed that few of the target compounds were detected in the tissues and, when present, the concentrations of the compounds were generally quite low (Table 5-11). Many of the compounds were below detection limits for the analysis, or were flagged for various reasons. As a general rule, when sample concentrations approach the detections limits for an analytical procedure, the number of flags tends to increase.

Fifteen SOC compounds were detected at least once in either muscle or liver tissue of the three moose. With three moose sampled, that means that we could have detected the presence of these 15 compounds 45 times for each of the 2 tissue groups, liver and muscle. For liver, 12 out of a possible 45 samples contained detectable concentrations of SOCs. In muscle, we detected SOCs in half that number, 6 of a possible 45 samples. One of the animals had a fairly high concentration of p,p′-DDD in its liver, at 340 ng/g lipid. On the other hand, many of the concentrations of detected SOCs were very low.

The generally low detection frequencies and the absence of any major patterns among SOC compound groups, among individual moose, or between moose tissue types suggest that moose for which we obtained samples were not biomagnifying SOCs to a level of concern at this time.

Table 5-11. SOC Concentrations in Moose Meat and Liver.

		Fish Tissue					
SOC	**Unit**	**Liver**	**Liver**	**Liver**	**Meat**	**Meat**	**Meat**
Endosulfans	ng/g wet wt	BDL	BDL	BDL	BDL	BDL	BDL
PCB 153	ng/g lipid	DF	0.025	DF	DF	0.48	DF
	ng/g wet wt	DF	0.0062	DF	DF	0.0037	DF
TFLN	ng/g lipid	X	X	X	BDL	0.62	X
	ng/g wet wt	X	X	X	BDL	0.0048	X
HCB	ng/g lipid	DF	0.72	DF	DF	X	DF
	ng/g wet wt	DF	0.18	DF	DF	X	DF
CLPYR	ng/g lipid	DF	BDL	BDL	1.2	BDL	BDL
	ng/g wet wt	DF	BDL	BDL	0.15	BDL	BDL
Dieldrin	ng/g wet wt	BDL	BDL	BDL	BDL	BDL	BDL
ACE	ng/g lipid	56	BDL	44	X	BDL	BDL
	ng/g wet wt	6.9	BDL	11	X	BDL	BDL
FLO	ng/g lipid	X	2	X	X	X	BDL
	ng/g wet wt	X	0.51	X	X	X	BDL
FLA	ng/g lipid	X	BDL	X	BDL	7.2	X
	ng/g wet wt	X	BDL	X	BDL	0.055	X
PYR	ng/g lipid	BDL	BDL	1.2	BDL	BDL	BDL
	ng/g wet wt	BDL	BDL	0.32	BDL	BDL	BDL
pp-DDD	ng/g lipid	340	BDL	32	BDL	BDL	BDL
	ng/g wet wt	42	BDL	8.4	BDL	BDL	BDL
	FLAG	b					
op-DDT	ng/g lipid	BDL	BDL	BDL	630	BDL	BDL
	ng/g wet wt	BDL	BDL	BDL	76	BDL	BDL
pp-DDT	ng/g lipid	DF	BDL	2.4	BDL	BDL	BDL
	ng/g wet wt	DF	BDL	0.63	BDL	BDL	BDL
MXCLR	ng/g lipid	DF	3.2	BDL	18	BDL	BDL
	ng/g wet wt	DF	0.8	BDL	2.2	BDL	BDL
CHR/TRI	ng/g lipid	BDL	BDL	0.46	BDL	BDL	BDL
	ng/g wet wt	BDL	BDL	0.12	BDL	BDL	BDL
B[b]F	ng/g lipid	BDL	BDL	1	BDL	BDL	BDL
	ng/g wet wt	BDL	BDL	0.26	BDL	BDL	BDL

SOC names: PCB = polychlorinated biphenyl; TLFN = trifluralin; HCB = hexachlorobenze; CLPYR = chlorpyrifos; ACE = Acenaphthene; FLO = fluorene; FLA = fluoranthane; PYR = pyrene; MXCLR = methoxychlor; CHR/TRI = Chrysene + Triphene; B[b]F = Benzo(b)fluoranthene

Flags: BDL = below detection limit; DF = detected, but flagged as not meeting QA Objectives; X = no value reported, lab blank > 33% of sample value; b = value is above the calibration range

However, this screening was based on only three animals taken from one national park (DENA). Notably, moose are herbivores, located quite low on the food web, and would not be expected to demonstrate biomagnification to the same degree as a predator.

5.3.3.5.2 Metals in Moose tissue

Moose liver and meat metal concentrations for the three animals sampled are provided in Table 5-12 for seven metals: Cadmium (Cd), Copper (Cu), Nickel (Ni), Lead (Pb), Vanadium (V), Zinc (Zn), and Mercury (Hg).

To consider the three WACAP moose samples from DENA in context with other moose sampled from North America, we present the mean and standard deviation for the WACAP moose liver and muscle tissue samples along with literature citations from Canada (Yukon), the Coville River area of Alaska, and “Other Alaska Killed Moose” (Gamberg et al., 2005; O’Hara et al., 2001) in Table 5-11.

We compared WACAP moose liver sample values to Cd, Cu, and Zn concentrations from the previously published studies. For Cd, Cu, and Zn, the mean WACAP moose sample concentrations were always lower. However, these differences were significantly different only at the 0.05 level for Zn in liver from Coville, Alaska. Although these general findings are good news for subsistence users of moose, these very low Cu concentrations in moose have been determined to adversely affect Fe adsorption mobilization, transformation, and incorporation into hemoglobin (Owen, 1982; Suttle, 1991). The WACAP mean moose liver Cu concentrations of 9.4 ± 4.9 µg/g ww were considered to be in the deficient range (from 5 to < 10 ppm ww) for Cu by Frank et al. (1994). Two of the three WACAP moose tissue samples analyzed in this study fell within this deficient range for Cu. This finding might be of interest to DENA wildlife biologists.

For the sparse data available from other studies for metals in moose tissue, the WACAP (DENA) moose tissue sample values were (1) lower than all values reported for Cd and Cu and (2) similar in Zn concentrations to the Coville (Alaska) moose but much less than the mean Zn concentrations for other Alaska moose (Table 5-11). However, as with liver samples, in only one instance was there a significant difference ($P \leq 0.05$) and that was for Cd in muscle from the Coville, Alaska, study.

5.4 Ecological Effects

5.4.1 Mercury

Mercury is a persistent bioaccumulating and biomagnifying non-essential metal. It is present in three forms in the atmosphere (elemental, reactive gaseous, and particulate), but it must be methylated to an organic form for efficient incorporation into the food web. Methylation is accomplished in the sediment or water column of a water body by microbial organisms (Ullrich et al., 2001). Source apportionment of Hg is difficult, because it does not degrade and is a global pollutant. Current thinking is that most Hg entering the national parks is via atmospheric deposition from local, regional, and trans-Pacific sources (Keeler et l., 2006; Wiener et al., 2006). It is estimated that up to 75% of the Hg entering the atmosphere is from anthropogenic sources (Nriagu, 1990) such as combustion; steel, iron, coke, and lime production; smelting; petroleum refining; and mercury cell chlor-alkali production (Keeler et al., 1995; Landis et al., 2004). Methyl-mercury affects the brain and nervous system, reproductive system, and immune system and is not readily excreted from animals. The concentrations of whole-body total Hg in WACAP

Table 5-12. Metal Concentrations in Moose Meat and Liver (μg/g wet weight).

Samples	Date Collected	Hg ng/g ww	Cd μg/g ww	Cu μg/g ww	Ni μg/g ww	Pb μg/g ww	V μg/g ww	Zn μg/g ww
Liver								
WACAP	9/13/2004	11.88	1.7	8.2	0.65	0.023	0.004	13
WACAP	9/27/2004	32.66	8.3	14.8	0.16	0.017	0.006	40
WACAP	9/23/2005	6.88	1.2	5.2	0.009	0.012	0.048	16
WACAP Mean	Mean ± s.d.	17.14 ± 13.67	3.8 ± 4.0	9.4 ± 4.9	0.27 ± 0.33	0.017 ± 0.006	0.019 ±0.025	23 ± 15
Yukon[1]	Mean ± s.d.	-	4.94 ± 3.52	40.3 ± 47.7	-	0.1 ±0.63	-	34.9 ±36.0
Coville R. Alaska[2]	Mean ± s.d.	-	3.13 ± 2.5	9.8 ± 12.7	-	-	-	66.5 ±58.1*
Other Alaska Killed Moose[2]	Mean	-	11.9	103.9	-	-	-	73.3
Meat								
WACAP	9/13/2004	25.82	0.010	1.7	0.004	0.008	0.003	69
WACAP	9/27/2004	4.56	0.022	0.8	0.019	0.029	0.001	47
WACAP	9/23/2005	2.06	0.006	1.3	0.080	0.011	0.030	71
WACAP Mean	Mean ± s.d.	10.81 ± 13.06	0.013 ± 0.008	1.3 ± 0.4	0.13 ±0.15	0.016 ± 0.011	0.011 ±0.016	62 ± 14
Yukon[1]	Mean ± s.d.	-	0.03 ±0.03	1.48 ± 0.53	-	0.03 ± 0.09	-	51.7 ± 27.9
Coville R. Alaska[2]	Mean ± s.d.	-	1.78 ±1.69*	-	-	-	-	
Other Alaska Killed Moose[2]	Mean ± s.d.	-	-	5.53	-	-	-	183.3

*Significant differences (P ≤0.05) between WACAP moose samples and the other studies based on the T-test

All concentrations based on wet weights.

Metals were analyzed on freeze-dried tissue, and Hg was analyzed on liquid nitrogen ground tissue, not dried.

Moose tissue collected on same date are from the same animal.

[1] Gamberg et al., 2005.

[2] O'Hara et al., 2001.

fish are shown in Figure 5-18. At numerous sites, mean lake concentrations were above contaminant health thresholds for piscivorous biota. The contaminant health threshold for humans is 300 ng/g wet weight (USEPA, 2001), and is based on methyl-Hg in the fillet for a general population of adults with 70 kg body weight and 0.0175 kg fish intake per day (approximately the same intake rate used for determining consumption thresholds for recreational fishers). We converted the threshold value to 185 ng/g whole-body total Hg based on (1) 95-100% of the Hg in fish being methyl-Hg (Bloom, 1992), and (2) conversion from fillet to w hole-body basis by the formula [log (fillet biopsy Hg) 0.2545 + 1.0623 log (whole-fish Hg)] developed by Peterson et al. (2007).

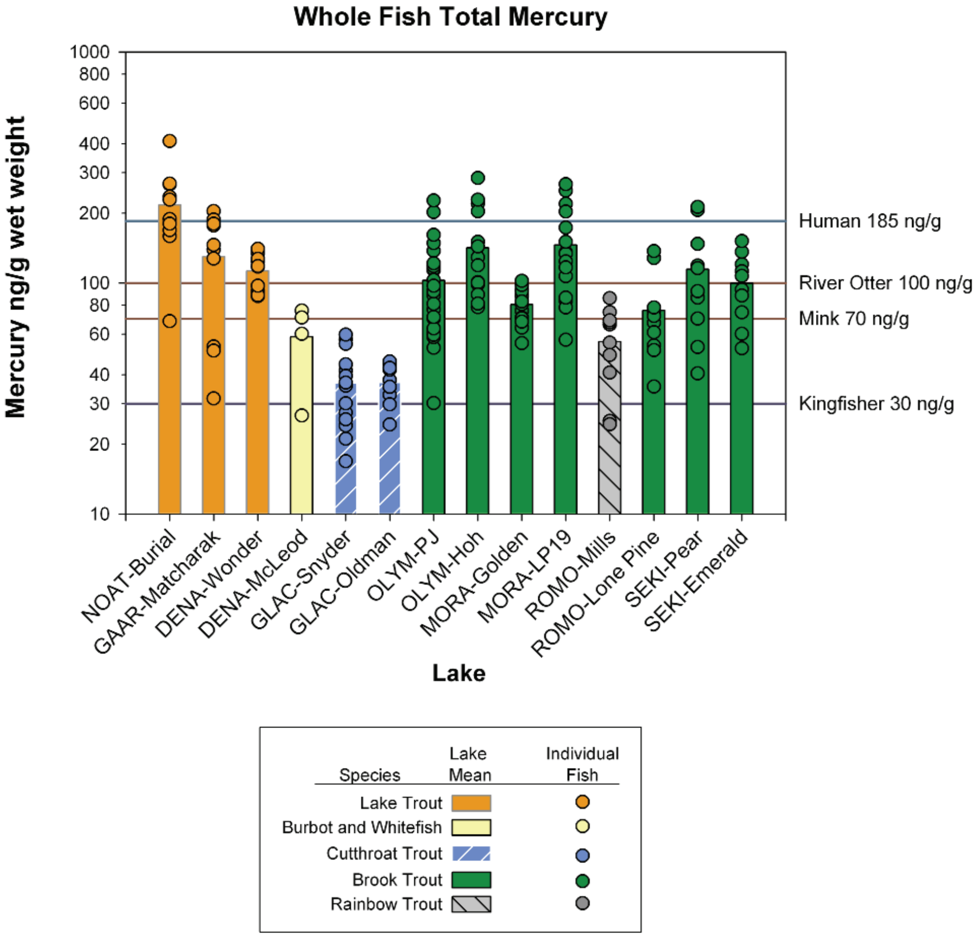


Figure 5-18. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Total Mercury and Contaminant Health Thresholds for Various Biota. The mean ng/g total Hg in fish at NOAT exceeds the human contaminant health threshold; the ng/g total Hg in some fish at GAAR (Matcharak), OLYM (PJ, Hoh), MORA (LP19), and SEKI (Pear) exceeds the human contaminant health threshold. The mean ng/g Hg concentration in fish at all parks exceeds the kingfisher contaminant threshold, and the mean at seven lakes exceeds all wildlife thresholds—NOAT (Burial), GAAR (Matcharak), DENA (Wonder), OLYM (PJ, Hoh), MORA (LP19), and SEKI (Pear). The human threshold is 300 ng/g wet weight (USEPA, 2001), and is based on methyl-Hg in the fillet for a general population of adults with 70 kg body weight and 0.0175 kg fish intake per day. 95-100% of Hg in fish is methyl-Hg (Bloom, 1992), and 300 ng/g in the fillet is equivalent to 185 ng/g ww whole body methyl-Hg (Peterson et al., 2007). Contaminant health thresholds in piscivorous animals (wildlife) are based on 100% fish in the diet for whole body total Hg, as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale; the y-axis starts at 10 ng/g.

5.4.2 Selected SOCs with Contaminant Health Thresholds for Piscivorous Biota

Potential risk to piscivorous biota from fish consumption is of concern. Lazorchak et al. (2003) developed SOC fish contaminant health thresholds for mink (*Mustela vison*), river otter (*Lutra canadensis*), and belted kingfisher (*Ceryle alcyon*) in the mid-Atlantic States, USA, and we used these values to identify national parks that contained fish with contaminant concentrations above the various criteria. Although the criteria were developed for the mid-Atlantic states, mink, otter, and kingfishers inhabit nearly all the field sites in this study (Table 5-13). As indicated by Lazorchak et al. (2003), deleterious effects on the wildlife can vary, because effects are contingent upon numerous other factors. Individual differences in responses to contaminants depend on sex, reproductive strategy and status, exposure to other stressors, and the overall health of the animal.

5.4.2.1 PCBs

Polychlorinated biphenyls were used for insulation and cooling of electrical transformers and capacitors, among many other uses. Being ring-structures, similar to cholesterols and steroid hormones, PCBs are highly bio-active inducing birth-defects, reproductive failure, liver damage, and tumors. Like mercury, PCBs are a global pollutant, are environmentally persistent, and they bioaccumulate and biomagnify in the food web. Because of the toxic nature of PCBs, legislation in the United States banned production and use in 1979; however, it is estimated that 82 million kg of PCBs remain in various forms. PCBs arrive at the national parks via regional and long range atmospheric transport (Eisler, 1986). The concentrations of the sum of PCBs in WACAP fish are shown in Figure 5-19; concentrations in all fish were below contaminant health thresholds for piscivorous biota.

5.4.2.2 DDT and Metabolites

DDT is an organochlorine insecticide and is similar to the PCBs in that it is bioactive because of the ring-structure. Also, as for the PCBs, legislation stopped the large-scale use of DDT in the United States in 1972. However, DDT is still used in the developing world. It is one of the few chemicals that effectively reduce numbers of *Anopheles gambiae*, the mosquitoes that carry malaria. In fact, the World Health Organization recently advocated that DDT be “painted” on the inside of dwellings in Africa to help curb the spread of malaria. DDT was used extensively in the United States from the mid-1940s to the early 1960s as an insecticide, after which Rachel Carson publicized the negative effects of DDT, and other organochlorines, on birds in the book, *Silent Spring*. Henceforth p,p′-DDT, the isomer o,p′-DDT, and the metabolites, o,p′-DDE and p,p′-DDE, have received extensive testing for various biological effects in the scientific literature. The effects range from acute toxicity to reproductive or developmental abnormalities, and endocrine and immune disruption. The concentrations of the sum of DDTs in WACAP fish are shown in Figure 5-20. The mean DDT concentration at Oldman Lake (GLAC) and the concentrations in some individual fish at Pear and Emerald Lakes (SEKI) are above contaminant health thresholds for piscivorous birds.

Table 5-13. Species Represented in Each Guild of the Loop Analysis.

Guild	Species in Each Guild		
Detritus	Not Specified		
Invertebrates	Numerous		
Fish	Salvelinus fontinalis OLYM, MORA, ROMO, SEKI	*Oncorhynchus mykiss* ROMO	*O. clarki* subsp. GLAC
	Thymallus arcticus NOAT, GAAR, DENA	*Cottus* spp. NOAT, DENA, MORA	Gasterosteidae spp. NOAT, GAAR
	Prosopium cylindraceum NOAT, GAAR, DENA		
	S. namaycush NOAT, GAAR, DENA	*Esox lucius* GAAR	*Lota lota* DENA
Mammals	*Lutra canadensis* NOAT, GLAC, MORA, ROMO	*Mustela vison* DENA, GLAC, OLYM, MORA	*Ondatra zibethicus* DENA, GLAC
	Sorex palustris OLYM, MORA	*Spilogale putorius* OLYM	*Mustela erminea* MORA
Birds	*Ceryle alcyon* DENA, GLAC, OLYM, MORA, ROMO, SEKI	*Anas* spp. NOAT, DENA, OLYM, MORA, ROMO	Scolopacidae spp. OLYM, ROMO
	Gavia spp. NOAT, GAAR, DENA, GLAC	Podicipedidae spp. GAAR, DENA, MORA,	*Mergus* spp. GAAR, OLYM, MORA, ROMO
	Larus spp. NOAT, GAAR, DENA	*Sterna paradisaea* NOAT, GAAR, DENA	*Pandion haliaetus* DENA, GLAC, OLYM, MORA, ROMO
	Ardea herodias GLAC, OLYM, MORA, SEKI	Strigidae spp. OLYM, MORA	*Haliaeetus leucocephalus* GLAC, OLYM, MORA, ROMO
	Aquila chrysaetos MORA, SEKI	*Buteo regalis* MORA	*Falco* spp. ROMO, SEKI
Aquatic Birds	*Cinclus mexicanus* DENA, OLYM, ROMO		

Notes:
NOAT = Noatak National Preserve
GAAR = Gates of the Arctic National Park and Preserve
DENA = Denali National Park and Preserve
GLAC = Glacier National Park
OLYM = Olympic National Park
MORA = Mount Rainier National Park
ROMO = Rocky Mountain National Park
SEKI = Sequoia and Kings Canyon National Parks

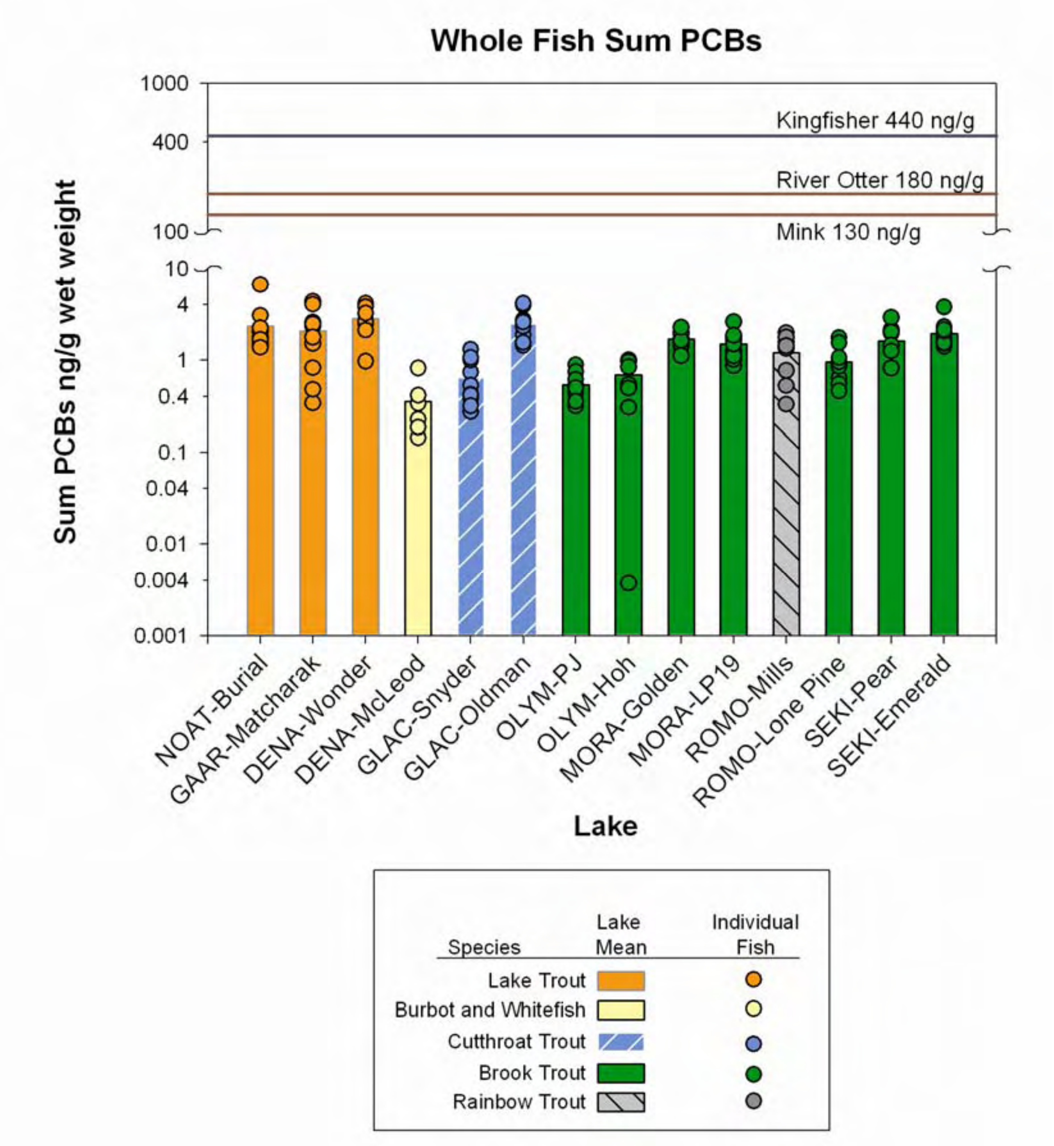


Figure 5-19. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Sum PCB Concentrations, with Contaminant Health Thresholds for Various Wildlife. *N* = 10, except *N* = 6 for McLeod Lake. Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet for whole body total PCBs as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale and below detection limit values are reported as ½ the EDL.

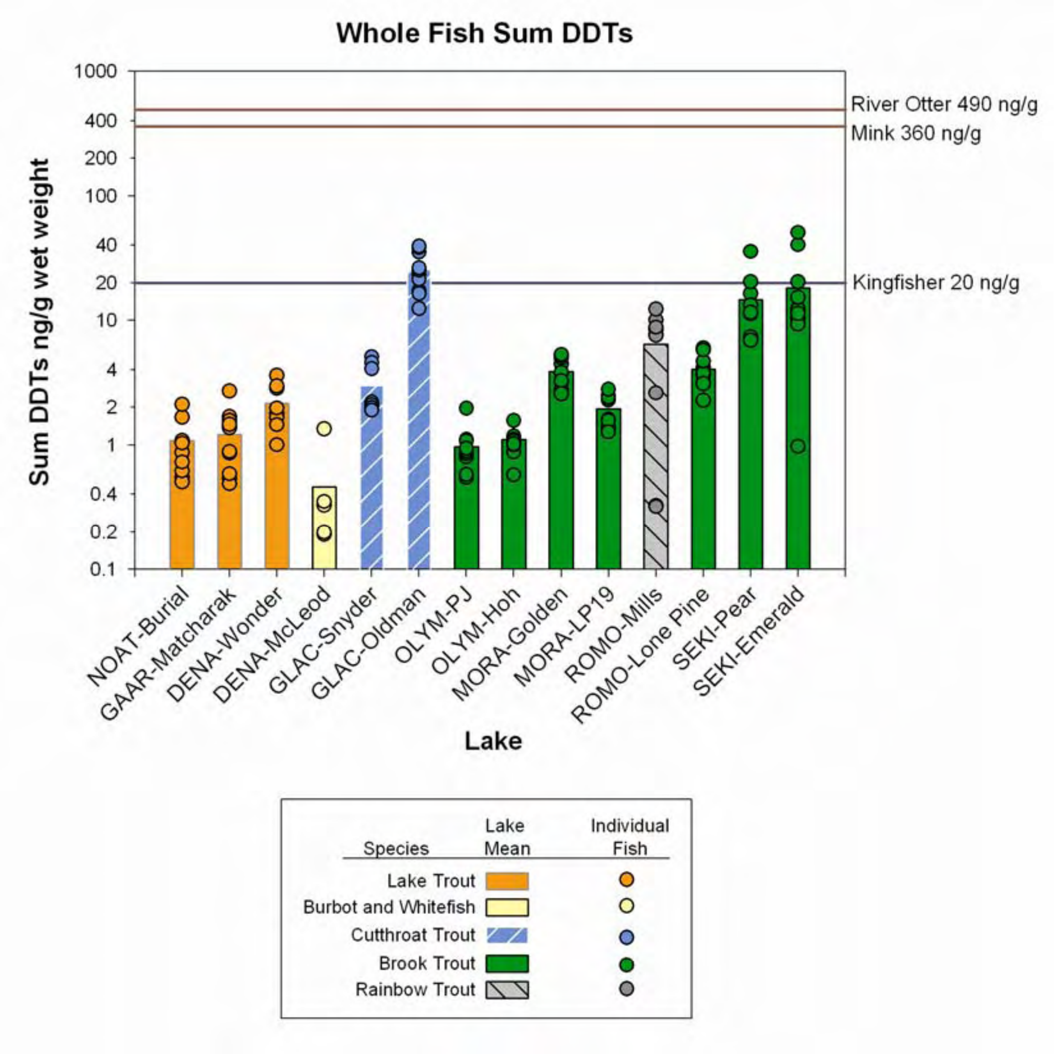


Figure 5-20. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Sum DDT Concentrations (DDT, DDD, and DDE), with Contaminant Health Thresholds for Various Wildlife. *N* = 10, except *N* = 6 for McLeod Lake. Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet for whole body total DDTs as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale. All lake means (bars) were derived from the sums of DDTs in individual fish in each lake; more than 50% of the DDT forms used in the sums were below detection limits and were replaced with values equal to ½ the estimated detection limit. The form of DDT most frequently detected in the fish was p,p′-DDE.

5.4.2.3 Chlordanes (cis- and trans-chlordane, and cis- and trans-nonachlor)

Chlordane is a broad use pesticide. The technical mixture contained some or all of the additional chemicals listed in the previous subsection. Chlordane is an organochlorine, like DDT, and concerns about potential carcinogenic effects led to banning chlordane in 1983. Chlordane in wildlife is highest in areas where the pesticide has been used to control underground termites. Highly lipophilic, chlordane accumulates in the fatty tissues of animals such as the gonads, liver, and brain. Chlordane differs from Hg, PCBs, and DDT in that it does not readily bioaccumulate, but high concentrations have been found in top marine predators.

Chlordane is transported to the national parks in the atmosphere and is widespread in the environment. It is a suspected carcinogen and endocrine disruptor (Eisler, 1990). Concentrations of the sum of chlordanes in WACAP fish are shown in Figure 5-21; the concentration sum in one fish in Oldman Lake (GLAC) was above contaminant health thresholds for piscivorous birds. The concentrations of chlordane are low enough to protect piscivorous mammals.

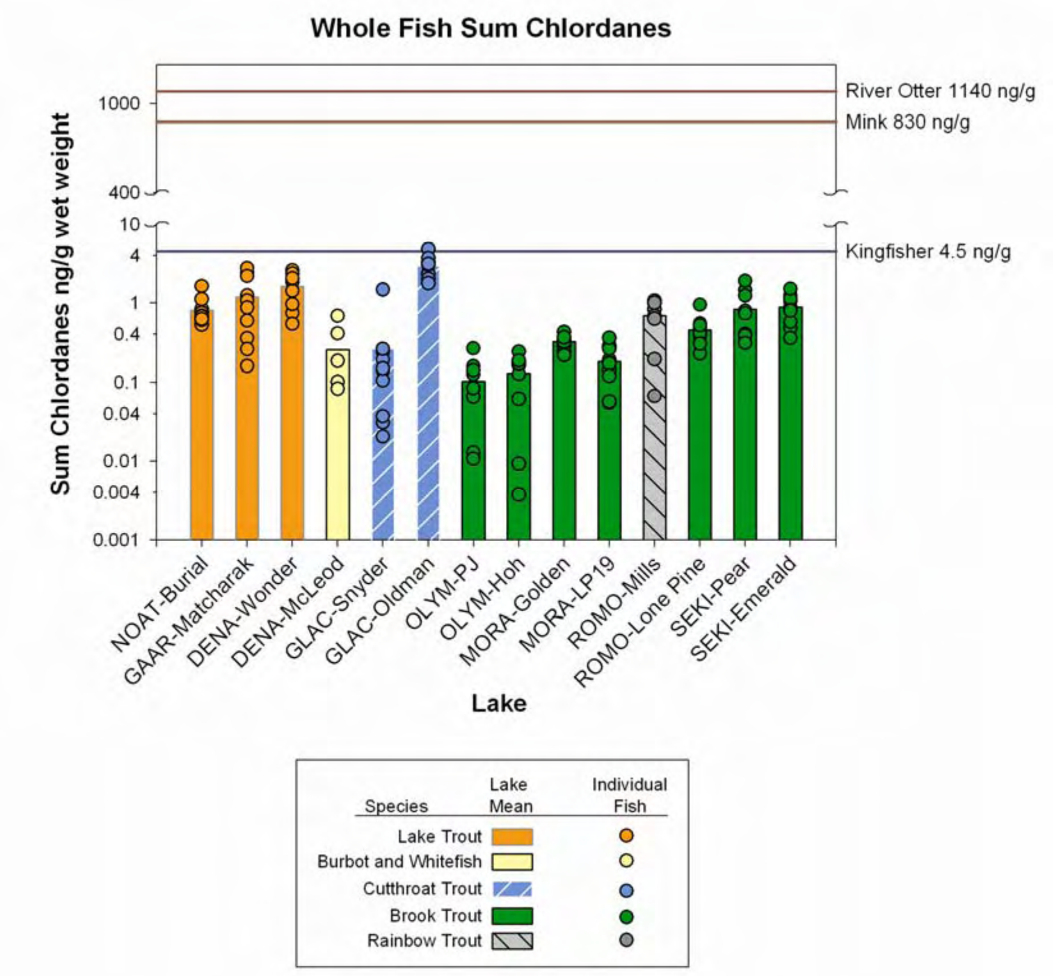


Figure 5-21. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Sum Chlordane Concentrations, with Contaminant Health Thresholds for Various Wildlife. *N* = 10, except *N* = 6 for McLeod Lake. Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale and below detection limit values are reported as ½ the EDL.

5.4.2.4 Dieldrin

Dieldrin is a breakdown product of the organochlorine pesticide aldrin, but once dieldrin itself proved to be an effective pesticide, it was produced along with aldrin. Dieldrin was produced in Denver, Colorado, from 1952 to 1973 (Walden Research Division of Abcor, 1975). In the United States, it was banned for agricultural use in 1974 and for most uses in 1987. Perhaps not coincidentally, some of the highest dieldrin concentrations in fish in this study were found in Rocky Mountain National Park, less than 160 km from Denver, where it was once manufactured. Like the PCBs, DDT, and chlordane, the aldrin/dieldrin/endrin family of pesticides are members of the so called "dirty dozen," a group of persistent bioaccumulative chemicals that have been largely banned from production and use. The bioaccumulation of dieldrin has been observed in piscivorous and non-piscivorous birds, and hatchling success is diminished in the former that have been exposed to dieldrin. The maternal transfer of dieldrin to fish eggs has also been documented. Acutely toxic, dieldrin is carcinogenic and is a suspected endocrine disruptor, with potential developmental and reproductive effects (Jorgenson, 2001). The concentrations of dieldrin in fish are shown in Figure 5-22; concentrations are low enough to protect piscivorous wildlife.

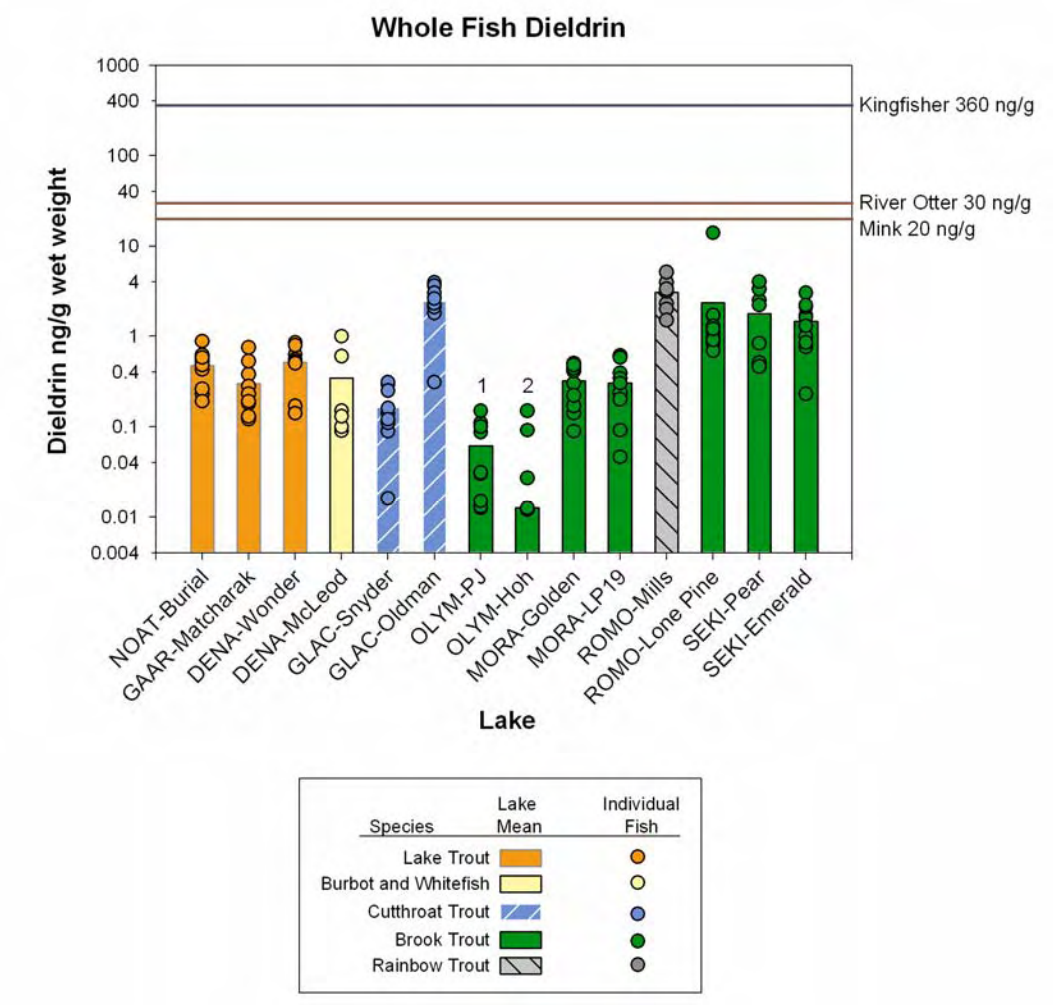


Figure 5-22. Fish Whole-Body Lake Mean (bars) and Individual Fish (symbols) Sum Dieldrin Concentrations, with Contaminant Health Thresholds for Various Wildlife. *N* = 10, except *N* = 6 for McLeod Lake. Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet as determined by Lazorchak et al. (2003). Data are plotted on a $\log_{10}$ scale and below detection limit values are reported as ½ the EDL. "1" indicates that dieldrin was detected in 50-70% of the samples (PJ Lake, OLYM); "2" indicates that dieldrin was detected in < 50% of the samples; the mean value on the graph is ½ the EDL (Hoh Lake, OLYM).

5.4.3 Human Health Risks from Consumption of SOCs in Fish

A formal human risk assessment for the consumption of SOCs in fish was beyond the scope and resources of WACAP. Instead, we used USEPA's (2000) "Guidance for Assessing Chemical Contaminant Data for use in Fish Advisories" to adjust contaminant health thresholds for recreational and subsistence fishers who eat fish only from WACAP lakes. The contaminant health threshold is the point at which a 70-kg person who consumes 17.5 g of fish per day (recreational fishing) or 142 g/day (subsistence fishing) would increase the lifetime risk of developing cancer by 1 in 100,000 for carcinogenic contaminants, or measurably increase the risk of chronic conditions from toxic contaminants. Concentrations of SOCs in individual fish and the average concentration (by WACAP lake) were then compared with the USEPA contaminant health thresholds (Figures 5-23 through 5-27). It is assumed that recreational fishers, but not subsistence fishers, reduce their contaminant exposure 32% by trimming and cooking their fish. Specifically, cancer slope factors and reference doses for the 13 SOCs that were detected in > 50% of WACAP fish were obtained from the EPA-ORD Integrated Risk Information System database (2007) and forward-multiplied to estimate individual contaminant concentrations in fish tissue sufficient to exceed EPA contaminant health thresholds for humans eating fish.

A total of 13 SOCs in 136 fish from the 14 WACAP lakes were compared with calculated contaminant health thresholds (Figures 5-23 through 5-27). Concentrations in fish ranged from <0.23 pg/g to 120 ng/g, and averaged 0.55 ng/g wet weight. Most contaminant concentrations in fish from the WACAP lakes fell below contaminant health thresholds calculated for recreational and subsistence fishing. However, over half (77 of 136) of the individual fish from 11 of the 14 lakes analyzed carried concentrations exceeding subsistence fishing contaminant health thresholds for dieldrin (Figure 5-23) and/or p,p′-DDE (Figure 5-25).

WACAP Adjustments for Contaminant Health Thresholds (Fish Consumption)

Consumption of fish offers many health benefits but can also increase exposure to environmental pollutants. Some pollutants are carcinogenic, teratogenic, and/or mutagenic; therefore, impaired health resulting from the consumption of contaminated foods is of concern. The EPA and other agencies (e.g., the World Health Organization) develop benchmarks for the consumption of fish in amounts that should not raise the risk of developing cancer or other chronic conditions. In this report, we call these benchmarks *contaminant health thresholds*. Their use is intended to provide an estimate of potential health risk resulting from the consumption of fish from lakes in the national parks we studied. The contaminant health thresholds do not consider the beneficial aspects of eating fish.

Different populations of humans consume fish at different rates; therefore, contaminant health thresholds are different for recreational and subsistence fishing. The values are calculated for 70-kg adults. For recreational fishing, it is assumed that 2.3 8-ounce fillets are consumed every month for a lifetime; for subsistence fishing, it is assumed that 19 8-ounce meals of whole fish are consumed every month. Based on these estimated amounts of fish consumed, the contaminant health thresholds are concentrations of contaminant exposure that would raise the risk of cancer above 1:100,000 (0.001%).

We adjusted the recreational fishing contaminant health threshold values upwards 32% to account for the estimated amount of chemical lost from fresh, whole fish during filleting and cooking. By making these adjustments, we were able to compare the benchmark, developed for cooked fillets, to our data, gathered from whole uncooked fish. In all the graphs, the concentrations were not adjusted; only the thresholds were adjusted to account for the difference between whole fish and filleted cooked fish. In the subsistence fishing scenario, no adjustment was made—per the EPA (2000) recommendation. Raw, whole-fish concentrations were compared with reference doses and cancer risk threshold values.

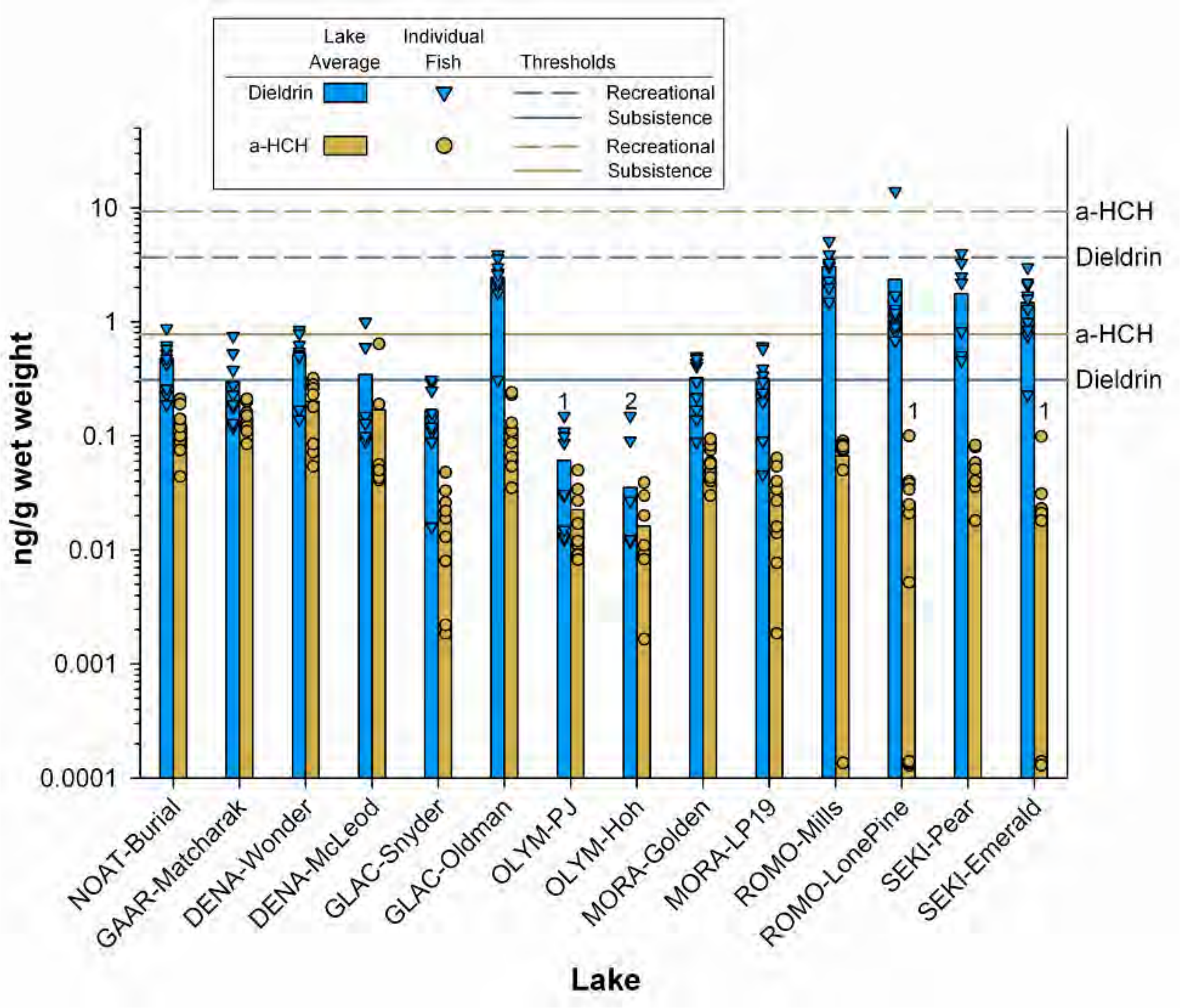


Figure 5-23. Concentrations of Historic-Use Pesticides for Dieldrin and a-HCH in Individual Fish (symbols) and Lake Average Fish (bars) Compared to Contaminant Health Thresholds for Cancer for Fish Consumption for Recreational and Subsistence Fishers (USEPA, 2000). Data are plotted on a log scale; below detection limit values are reported as ½ the EDL. Some fish from SEKI, ROMO, and GLAC exceed contaminant health thresholds for dieldrin for recreational fishing. The lake average concentration of fish from SEKI, ROMO, Golden Lake (MORA), Oldman Lake (GLAC), DENA, and NOAT, and some fish from GAAR and LP19 (MORA), exceed contaminant health thresholds for dieldrin for subsistence fishing. Exceedances imply that a lifetime consumption can increase the risk of developing cancer by more than 1 in 100,000. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. “1” indicates the analyte was detected in 50–70% of the samples; “2” indicates the analyte was detected in less than 50% of the samples.

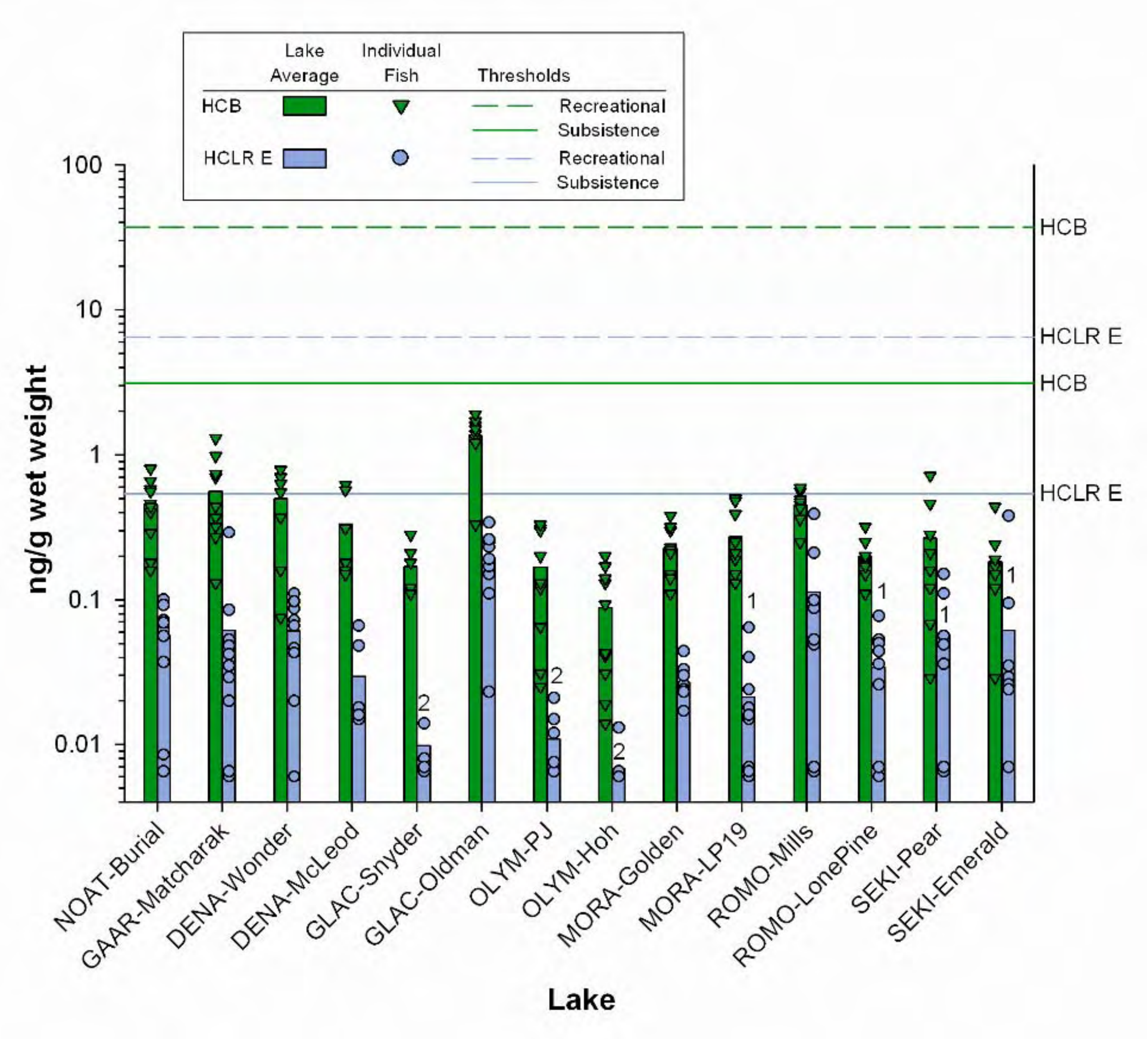


Figure 5-24. Concentrations of Historic-Use Pesticides for Hexachlorobenzene (HCB) and Heptachlor Epoxide (HCLR E) in Individual Fish (symbols) and Lake Average Fish (bars) Compared to Contaminant Health Thresholds for Cancer for Fish Consumption for Recreational and Subsistence Fishers (USEPA, 2000). Data are plotted on a log scale; below detection limit values are reported as ½ the EDL. Concentrations of all compounds were below contaminant health thresholds at all lakes. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. “1” indicates the analyte was detected in 50–70% of the samples; “2” indicates the analyte was detected in less than 50% of the samples.

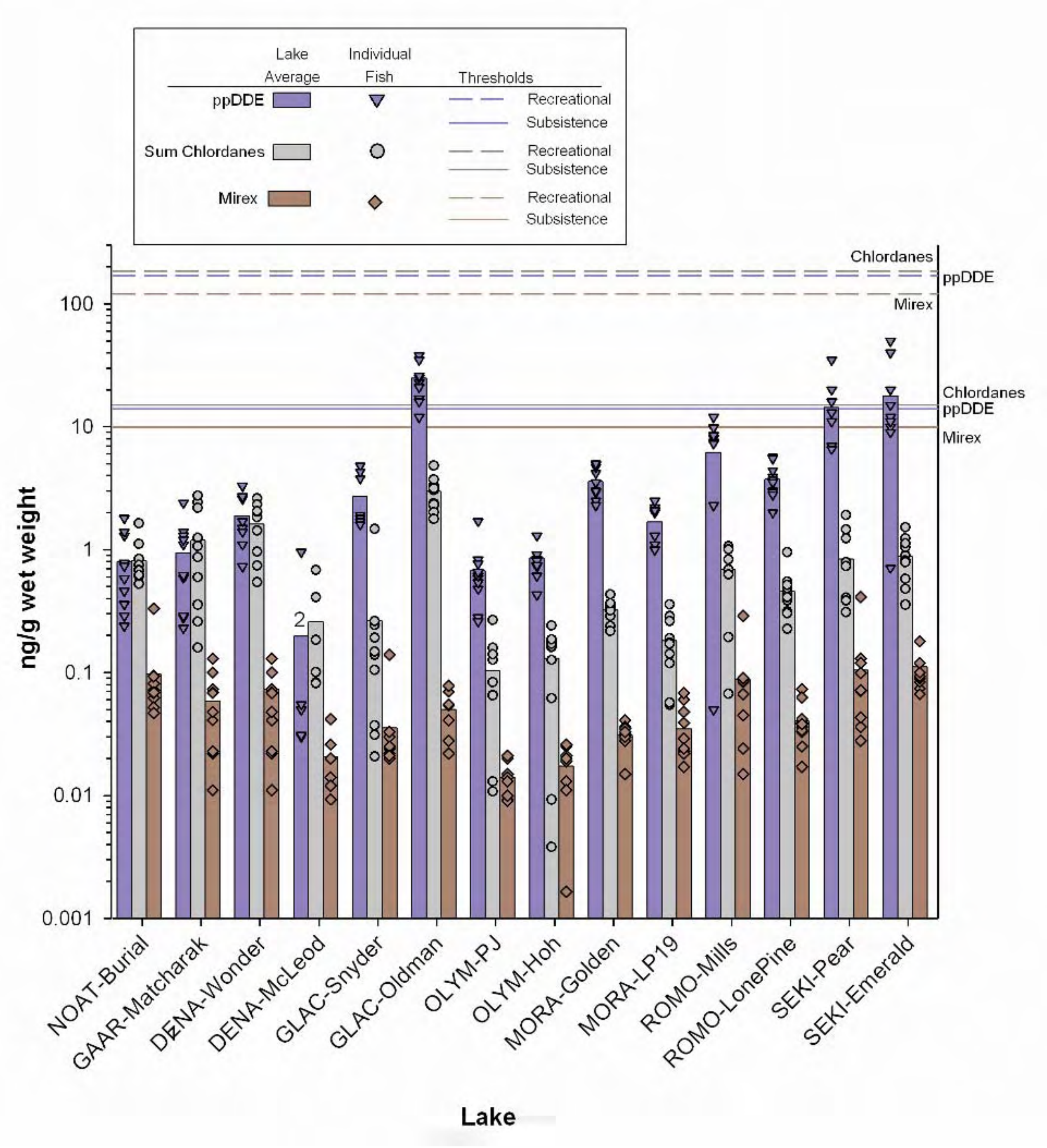


Figure 5-25. Concentrations of Historic-Use Pesticides (p,p′-DDE, chlordanes, mirex) in Individual Fish (symbols) and Lake Average Fish (bars) Compared to Contaminant Health Thresholds for Cancer for Fish Consumption for Recreational and Subsistence Fishers (USEPA, 2000). Data are plotted on a log scale; below detection limit values are reported as ½ the EDL. Concentrations of all compounds were below contaminant health thresholds for recreational fishers, but a lifetime consumption of fish from Pear and Emerald Lakes in SEKI and Oldman Lake in GLAC could increase cancer risk for subsistence fishers from p,p’-DDE. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. “1” indicates the analyte was detected in 50–70% of the samples; “2” indicates the analyte was detected in less than 50% of the samples.

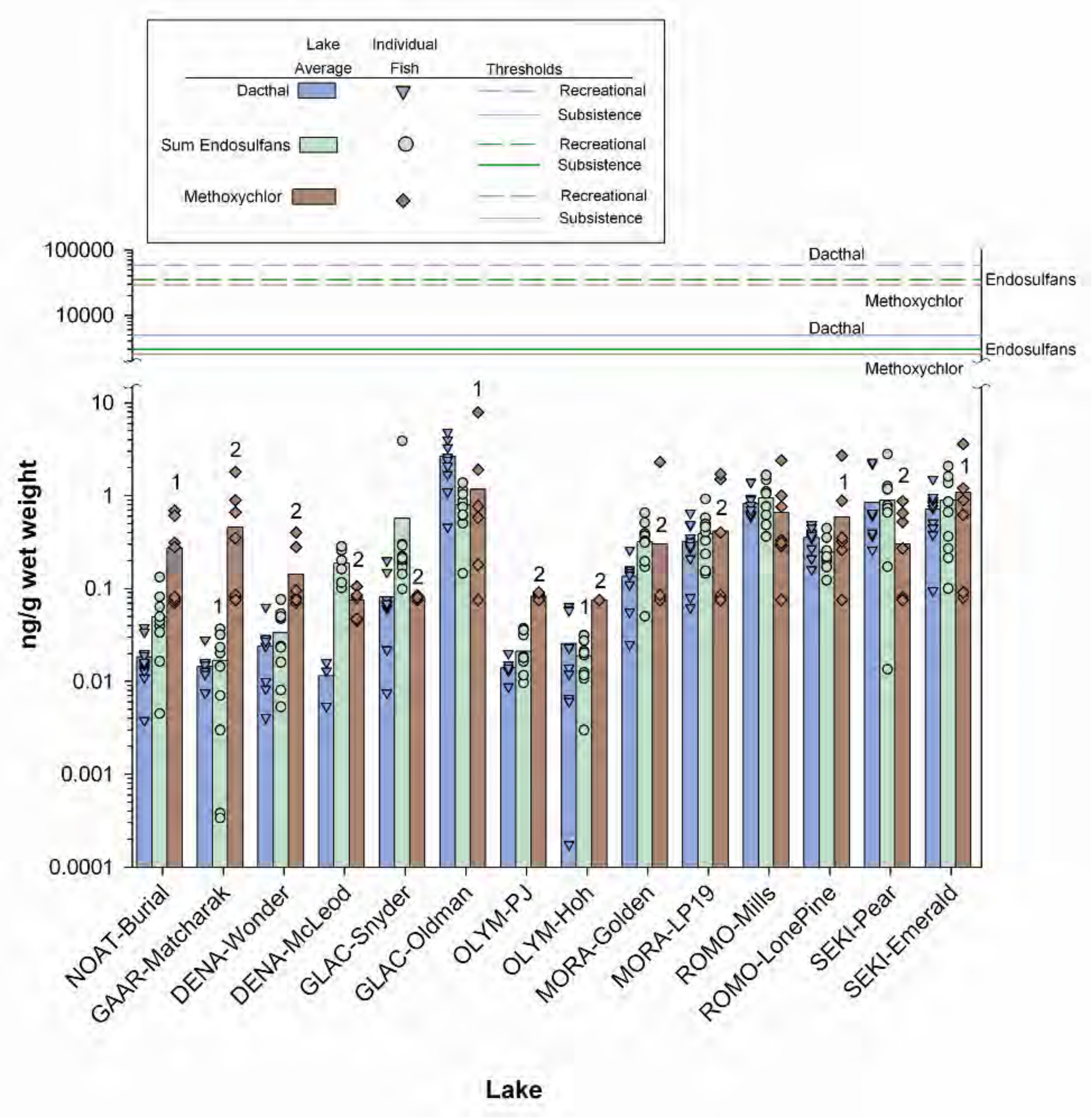


Figure 5-26. Concentrations of Current-Use (dacthal, endosulfans) and Historic-Use (methoxychlor) Pesticides in Individual Fish (symbols) and Lake Average Fish (bars) Compared to Contaminant Health Thresholds for Chronic Disease for Fish Consumption for Recreational and Subsistence Fishers (USEPA, 2000). Data are plotted on a log scale; below detection limit values are reported as ½ the EDL. Concentrations of all compounds were below contaminant health thresholds at all lakes. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. “1” indicates the analyte was detected in 50–70% of the samples; “2” indicates the analyte was detected in less than 50% of the samples.

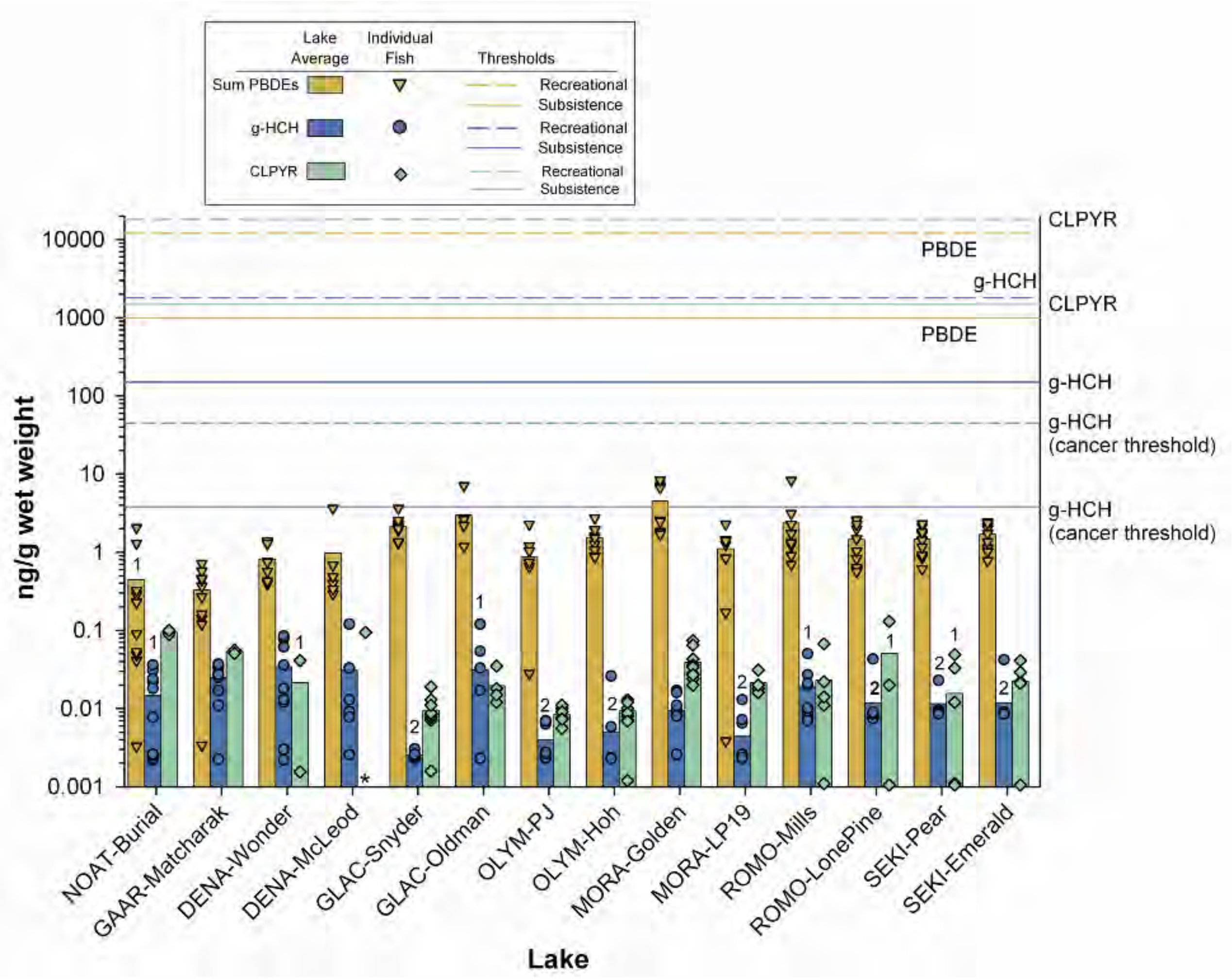


Figure 5-27. Concentrations of Current-Use Contaminants PBDEs, g-HCH, and Chlorpyrifos (CLPYR) in Individual Fish (symbols) and Lake Average Fish (bars) Compared to Contaminant Health Thresholds for Chronic Disease (and Cancer Thresholds for g-HCH) for Fish Consumption for Recreational and Subsistence Fishers (USEPA, 2000). Data are plotted on a log scale; below detection limit values are reported as ½ the EDL. Concentrations of all compounds were below contaminant health thresholds at all lakes. If no label is present at the top of a bar, the component was detected in at least 70% of the samples. “1” indicates the analyte was detected in 50–70% of the samples; “2” indicates the analyte was detected in less than 50% of the samples. * indicates results were available from only one sample from the site, and no average is presented.

The numbers of fish in each lake that exceeded these thresholds and the recreational fishing threshold for dieldrin are listed in Table 5-14. Although some individual fish (5) exceeded recreational fishing thresholds for dieldrin, the average fish contaminant concentration per lake did not exceed recreational fishing thresholds in any of the 14 lakes, but did exceed the subsistence fishing thresholds for dieldrin or p,p′-DDE in 9 of the 14 lakes. No other contaminant concentrations measured in fish from the core WACAP parks exceeded human contaminant health thresholds, and concentrations of the other target contaminants detected in fish were one to seven orders of magnitude below the adjusted recreational human contaminant health thresholds. PBDEs and the current-use pesticides dacthal, endosulfan, chlorpyrifos, and methoxychlor were at least three orders of magnitude below all contaminant health thresholds.

Table 5-14. Number of Fish Exceeding Human Cancer Thresholds

		Number of Fish out of 10 Sampled that Exceeded Threshold		
Population		Subsistence Fishing		Recreational Fishing
Contaminant		p,p′-DDE	Dieldrin	Dieldrin
Park	Lake			
NOAT	Burial	0	7	0
GAAR	Matcharak	0	3	0
DENA	Wonder	0	7	0
DENA	McLeod*	0	2	0
GLAC	Snyder	0	0	0
GLAC	Oldman	9	9	1
OLYM	PJ	0	0	0
OLYM	Hoh	0	0	0
MORA	Golden	0	5	0
MORA	LP19	0	4	0
ROMO	Mills	0	8	2
ROMO	LonePine	0	10	1
SEKI	Pear	3	10	1
SEKI	Emerald	4	9	0
	Cancer Threshold (ng/g wet weight)	14	0.31	3.7

* Number out of 6 total from lake

The EPA’s calculated contaminant health thresholds offer a uniform approach to evaluating human health risks from consumption of contaminated fish, but *individual* risk is probably higher or lower. Potential interactions or synergistic effects from the multiple contaminants present in fish could yield higher risks than those reported here. However, because most of the total risk is attributed to the contaminant dieldrin, cancer risks from additive interactions are not significantly different from exceedances of the dieldrin threshold. Also, the likelihood of these risks being realized is small, because (1) the lakes are remote, with small fish populations (which limit the people present and the frequency of fishing), (2) the risk scenario assumes lifetime consumption (which is probably rare), and (3) the acceptable risk values (1:100,000) add a safety factor.

Finally, salmonid consumption is associated with nutritional and health benefits, such as increased consumption of omega-3 fatty acids and reduced consumption of unhealthy fats. For some people, these benefits probably outweigh contaminant risk. Health risks from contaminants in fish can be reduced by removing the skin before cooking and by draining fats during cooking.

5.4.4 Potential Ecological Effects of SOC and Metal Contaminant Loads on Aquatic Systems in the Parks

Information generated from sampling allows hypotheses to be generated about the health and reproductive fitness of individual fish. We were also interested in making inferences regarding potential effects of contaminants on the fish populations and other components of the biotic communities of the lakes. We wanted to know if the presence of contaminants at levels with potential biological effects on the fish would affect the demographic structure of the fish populations. Furthermore, we conducted analyses to allow inferences about potential effects to bird and mammal populations that are dependent on these specific lakes for at least some part of their life cycle.

We obtained faunal lists for each of the respective lakes studied. These lists focused on birds and mammals known to use the lakes (see Table 5-13). For some lakes, the identity of species representing other taxa was available. For assessment of ecological risk of the vertebrate fauna of the parks to contaminant exposure, the use of population viability analyses would be desirable. However, quantitative data is lacking for such an assessment. There is no information on the abundance, age structure, birth or death rates, or predation rates. It is thus unfeasible for us to conduct any quantitatively-based risk assessment. Instead, we used a qualitative analysis (loop analysis) that is useful for allowing inference about systems such as these that are only partially specified.

We constructed generalized trophic webs for communities of the lakes sampled. Li and Li (1996) discuss how organisms can be classified into functional groups (guilds) and we followed their recommendations. Briefly, we assigned the biota into trophic guilds as follows: (1) mammals that eat fish, (2) birds that eat fish, (3) birds that eat invertebrates, (4) fish that eat invertebrates, (5) fish that eat fish, (6) predacious invertebrates, (7) herbivorous and detritivorous invertebrates, and (8) plant material and other detritus. Two different loop analyses were run. One was for lakes in parks in the conterminous United States that contain mainly one species of fish. Such systems are characterized by straight chain relationships between guilds. The second was for systems such as those in Alaska, and perhaps for Emerald Lake in Sequoia, where more than one fish species was present (Figure 5-28). Of course, piscivorous fish are also prey during early life stages. In addition, fish of two fish systems can shift between guilds 4 and 5 over time, as feeding ecology and abundance of various prey species change through time.

Considerable variation is likely, regarding the potential impact to the fish populations, because of the use of lakes by birds and mammals. That is, depending on whether predators were resident or transitory, potential impact to the fish population (and to the predators) could vary according to the relative predatory pressure on the population. In the case of resident keystone predators (birds and mammals), a top-down effect on fish would probably occur. At these lakes, birds and perhaps mammals use *central place foraging*. That is, these top fish predators would be resident over a substantial period of time and feed almost solely at this site, foraging for young as well as themselves. For such systems, predator guilds would be considered omnivorous. Although warm-blooded vertebrate species forage, such as the ouzel (*Cinclus mexicanus*), a bird

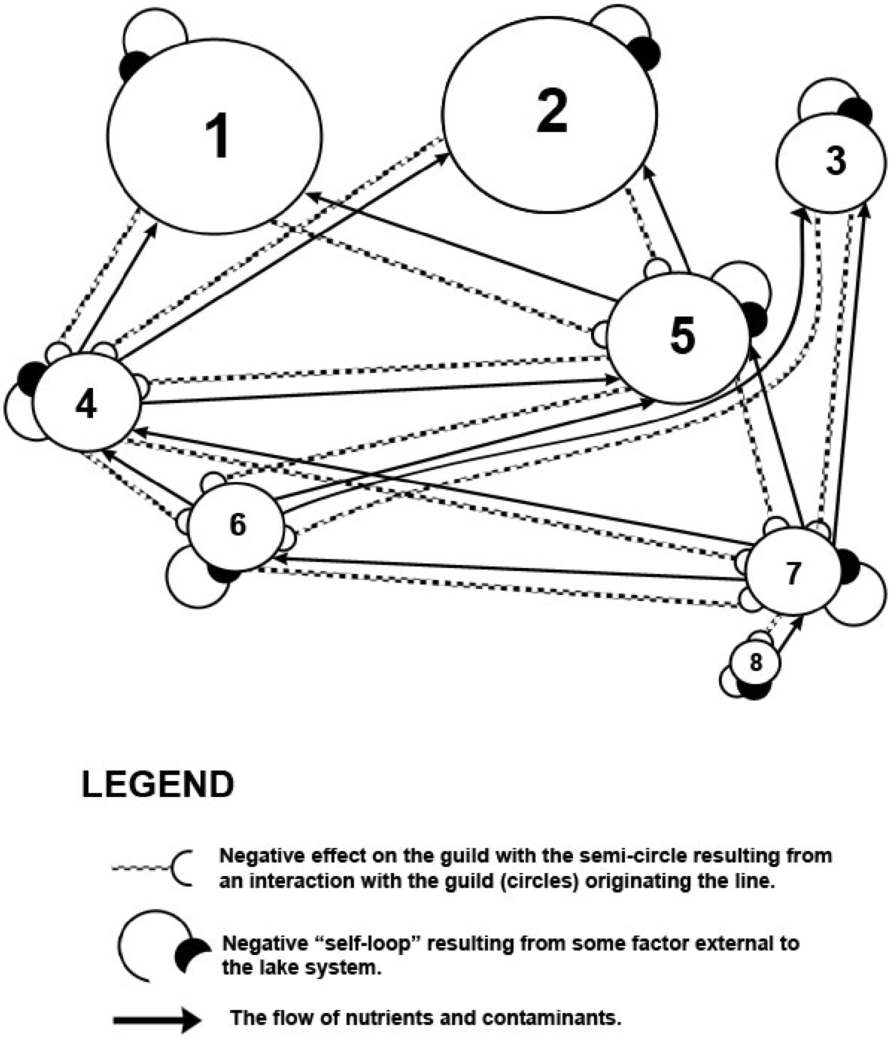


Figure 5-28. Trophic Model for Lakes with Two-Fish Guilds Representing Alaska Systems. Circle with numbers are guilds and 1= piscivorous mammal; 2 = piscivorous bird; 3 = insectivorous bird; 4 = insectivorous fish; 5 = piscivorous fish; 6 = invertebrate predator; 7 = invertebrate; and 8 = detritus. One-fish models would be similar, except that they would contain only one of the fish guilds. The self loops represent self-regulation, such as in the form of logistic growth, which accounts for intraspecific competition. The relative size of the circles indicates relative approximate position in the food web with larger circles indicating higher trophic level.

representative of a trophic guild that forages on aquatic invertebrates, we do not believe that the competition between members of this guild and fish would result in any population-level impact on the fish. This contention is based on their small biomass and the fact that the foraging habitat for this guild is relatively sparse in these lakes. Hence, there would be no top-down effect by this guild on the fishes, but there could be bioaccumulation and amplification of contaminants up the food chain from invertebrates into species such as ouzels. In the case of transitory top-order predators (perhaps only as a brief stopping place during migration), pressure on the fish would not be likely to affect the fish population. However, there could still be effects of toxicants via trophic transfer on these top-order predators, adding to concentrations accumulated elsewhere. Given that concentrations of certain endocrine disrupting contaminants found in fish in the WACAP lakes exceed tolerance thresholds for several species of predaceous birds and mammals (Figures 5-18 to 5-22), we also ran two other variations of the model. For non-omnivory systems, there would be no top-down control by the predators on the fish; for systems with omnivory, there would be population-level effects. In either case, the contaminants could have an effect on the warm blooded vertebrates foraging in the lakes.

5.4.4.1 Assumptions

We assumed that avian and mammalian predators at a lake function as though they are resident, foraging for themselves and for their progeny during the time that the aquatic system is free from ice. Any negative impacts on the fish predators are assumed to result from a reduced prey base as well as directly from contaminants. This predation pressure would have an impact on the biotic system of the lakes. We acknowledge that this is a significant assumption because we have no measurements on the impact of predators on the fish or the impact of contaminants on piscivorous biota. We are aware that mammals and birds, such as kingfishers and ouzels (the duck-like birds), and birds such as ospreys and eagles, probably forage beyond the confines of a sampled lake, but for this exercise, we assumed that the other foraging sites would have similar or greater (see Tables 5-1 and 5-2) concentrations of contaminants. Of course, birds are migratory and can be exposed to different contaminants when they are not resident at WACAP lakes, and we do not address the interactive effects of contaminant loading and unloading over the seasons for these species. Therefore, we used negative self loops in the model (Figure 5-28). In addition, birds and mammals export contaminants from the lake system.

We also did not consider the following in the analysis. Allochthonous matter, such as leaves and needles, which provides energy input into a lake system, is assumed to be accessed by higher trophic levels through the detritus; primary production in the lake is also subject to other inputs to the system. Thus negative self loops are also used for that guild. We also assume that allochthonous fish prey (e.g., terrestrial insects) are probably unimportant over the course of a year, compared with prey produced within the lake itself. We also ignored in the model the fact that constituents of aquatic organisms that are not removed from the lake will ultimately find their way into the detritus. Biomagnification of persistent organic pollutants through the food web, including aquatic ones, has been well documented (Kelly et al., 2007).

5.4.4.2 Loop Analysis

We used loop analysis (constructing signed diagraphs; see Figure 5-28) to analyze the trophic network of the lake systems. It resulted primarily in inferences about the flow of nutrients from which hypotheses about numbers of individuals could be made. Flow of contaminants through the system would be similar to that of nutrients. Hence, hypotheses can be generated about effects of contaminants on the various trophic guilds.

Loop analysis has been elaborated upon and validated in a series of recent publications (Hulot et al., 2000; Dambacher et al., 2002, 2003a, 2003b, 2005; Arkoosh et al., 2004; Zavaleta and Rossignol, 2004; Ramsey and Veltman, 2005). The computer programs are available in Dambacher et al. (2002), updated 2006, and at http://www.ent.orst.edu/loop/. We initiated the press (negative demographic effect of the contaminants) at the level of the fish in the system (Figure 5-28, Table 5-15a). For the two-fish system (Figure 5-28, Table 5-15b), separate presses were performed on each fish guild, but we interpret the results together as an intact system. The

Table 5-15a. Effects of a Negative Press Perturbation[1] on Fish in a One-Fish Guild Ecosystem.

Guild[2]	**No Omnivory**	
	Δ[3] in Life Expectancy [4]Press 4	**Δ in Abundance Press 4**
1	No effect	No effect
2	No effect	No effect
3	Increase	No effect
4	Increase	No effect
Guild[2]	**Omnivory**	
	Δ[3] in Life Expectancy [4]Press 4	**Δ in Abundance Press 4**
1	Increase	Decrease
2	Increase	Decrease
3	Increase	Decrease
4	Increase	Ambiguous

Table 5-15b. Effects of a Negative Press Perturbation[1] on Fish in a Two-Fish Guild Ecosystem.

Guild[2]	**No Omnivory**	
	Δ[3] in Life Expectancy [4]Press 4	**Δ in Abundance Press 4**
1	No effect	No effect
2	No effect	No effect
3	Increase	Decrease
4	Increase	Decrease
5	Increase	Ambiguous
Guild[2]	**Omnivory**	
	Δ[3] in Life Expectancy [4]Press 4	**Δ in Abundance Press 4**
1	Increase	Decrease
2	Increase	Decrease
3	Increase	Decrease
4	Increase	Ambiguous
	Increase	Ambiguous

[1] Press perturbation = decreased birth to fish resulting from contaminant induced fish death.
[2] See Figure 5-28 for key to guilds.
[3] Δ = change.
[4] The guild receiving a negative press perturbation.

modeling and interpretation of the results were performed by Drs. Phil Rossignol and Hiram Li and we acknowledge their contributions (Department of Fisheries and Wildlife and Oregon Cooperative Fish and Wildlife Research Unit, USGS, respectively, Oregon State University).

5.4.4.3 Loop Analysis Sensitivity

Two assessments were made to determine the sensitivity of the loop analysis model, one for stability and the other for predictability. The most complex community run by us in the loop analyses was used to test sensitivity.

5.4.4.3.1 Sensitivity of Stability

Sensitivity of stability is evaluated with simulations of the community matrix over a range of randomly selected interaction values, as explained on the Loop Analysis site: http://www.ent.orst.edu/loop/

The stability test is based on the signed digraph, in which the relationships between species are (+1, -1, 0). The qualitative stability offers no insight into the stable structure of quantitative domain of the system. For example, a signed digraph has an overall negative feedback with two negative loops (-2) and one positive loop (+1). However, if we have the measure of interaction strengths between species, the values of two negative loops could be -0.2 and -0.3, and the value of a positive loop could be 0.6. In this case, the strength of overall feedback would be 0.1 and then we would obtain a positive overall feedback.

In order to know the probability that the system is also stable in a quantitatively specified matrix, 5,000 quantitative matrices are constructed based on the unchanged sign structure of the system. Non-zero elements of each matrix are quantitatively specified with a pseudorandom number generator that assigns interaction strength but not a sign from a uniform distribution between 0.01 and 1.0. The stability of each quantitatively specified matrix is then examined in terms of Hurwitz criteria I and II.

- Hurwitz criterion I: Characteristic polynomial coefficients are all of the same sign.
- Hurwitz criterion II: Hurwitz determinants are all positive

The results of 5,000 simulations indicate that the system is very stable, particularly considering its fairly high connectivity:

- Pass Hurwitz criteria I and II: 4,305
- Pass Hurwitz criterion I, but not II: 50
- Pass Hurwitz criterion II, but not I: 0
- Not pass Hurwitz criteria I and II: 645

5.4.4.3.2. Sensitivity of Predictability

Sensitivity of predictions can be estimated from the weight of the predictions. These weights represent the likelihood that the prediction will be in the direction generated by the adjoint matrix. These weights correspond to simulation results, by the method discussed in Dambacher et al. (2003b). This matrix represents the probability, based on average proportion of correct sign, of a correct sign in a prediction (adjoint matrix) from simulations with uniformly distributed interaction strengths and interdependent trophic relationships:

0.88	0.75	0.66	0.82	0.55	0.57	0.63	0.63
0.75	0.88	0.66	0.82	0.55	0.57	0.63	0.63
0.69	0.69	0.85	0.50	0.73	0.64	0.77	0.77
0.50	0.50	0.50	0.95	0.95	0.50	0.50	0.50
0.80	0.80	0.71	0.75	0.95	0.57	0.66	0.66
0.70	0.70	0.83	0.77	0.55	0.90	0.57	0.57
0.50	0.50	0.50	0.83	0.83	0.87	0.85	0.85
0.50	0.50	0.50	0.83	0.83	0.87	0.85	0.83

5.4.4.4 Results

We assume that the primary impact of a toxin would be a negative press perturbation (i.e., a deleterious effect on fish). The mechanism would be reduced reproduction. Impact is assessed as changes in abundance and life expectancy (inverse of turnover). During our analysis, both systems tested appear to be stable, indicating that inferences can be drawn on the result of the press perturbation.

For the one-fish system, we can infer from the predicted results that, with little predation pressure from higher trophic levels, the abundance of fish would decrease. The results about abundance are ambiguous for single-fish systems where there is top-down control on the fish by predators, assuming that there would be fewer insectivorous birds, and those remaining would have a reduced life span. The populations of fish in both types of systems would have an older age structure, because of a decreased birth rate. Piscivorous mammals and birds are expected to live longer, but maintain fewer numbers (5-15a) in cases where they forage substantially on the contaminated fish. Invertebrate-eating birds would be expected to have a decreased abundance and an increase in the proportion of older individuals in the population.

The loop analysis infers that a press on fish in the two-fish system would lead to a response in piscivorous and invertebrate-eating birds and mammals similar to that of the one-fish system. There would probably be an increased life expectancy and reduced abundance of invertebrate-eating birds and those birds and mammals eating large numbers of contaminated fish. The birth rate would be expected to decrease in fish, with or without top-down control by predators, and the abundance of fish would probably decrease in predatory fish in systems without top-down control. Effects of a press on piscivorous fish in general and on invertebrate-eating fish in lakes with top-down control by avian or mammalian predators are ambiguous (Table 5-15b), because these fish, being more or less in the middle of the food chain, would be responsive to the contaminants directly, but also indirectly through the action of the contaminants on their predators.

For the analyses for scenarios that were complex and that included considerable interaction between various guilds (not just in a single straight chain food web), there was considerable ambiguity in the results. This is a logical result and stems from the fact that predators affect forage and the forage can be toxic to the predators. Therefore the system does not behave according to a simple predator-prey relationship. Paradoxical results were often found in these situations; for example, the presence of a predator could actually result in an increase in abundance of its prey because the contaminant in the prey would reduce the abundance of predators. We therefore thought it would be best to be conservative and not interpret these results (ambiguous cases in the tables). Results related to the age structures of the populations must also be interpreted with caution. The sign diagraph analyses show effects on birth rate. Therefore, in those cases where a decrease in birth rate was suggested, the interpretation would be that the age structure favored older individuals. So, there could be the same number, or even fewer, older individuals in that population, but proportionately there would be many fewer younger individuals than there were before the press. A population with proportionately older individuals does not *de facto* infer a population that is healthier than one with younger individuals.

For the cases in which the model results are ambiguous, one could rely on other information upon which to make an inference about contaminant effects. For example, in systems where the top predators use central place foraging, the toxicity tolerance information available (see Figures 5-18 to 5-22) would suggest the hypothesis that the abundance of those species would be negatively impacted.

5.4.4.5 Conclusion

Birds eating only invertebrates could be subjected to bioaccumulation and magnification of contaminants, and thus experience toxic effects. The ultimate risk to birds and mammals preying on fish, and especially species of fish that eat other fish, would be both the negative effects of a decreased prey base and the potential negative effects of bioaccumulation and magnification of contaminants.

The model runs allow the following inferences: Fish populations in lake communities with only one species of fish represented, hence with an absence of the omnivory loop, would be expected to experience a decrease in abundance and a decrease in life expectancy. These decreases could happen because of the potential negative effects of bioaccumulation and magnification of contaminants. Effects on abundance of fish in systems with more than one species present are ambiguous, but there would be fewer births and hence an older-aged population. Mammals and birds preying on these fish would experience double impacts (altered prey base and contaminants), leading to fewer births and a reduced abundance in systems without the omnivory loop. Birds eating only invertebrates could be subjected to bioaccumulation and magnification of contaminants and hence experience toxic effects.

We believe that piscivorous predators (birds, mammals, and fish) that forage on fish could be affected by contaminants. This is likely only if the predators forage on fish in the national parks with concentrations of contaminants that exceed tolerance levels for the birds and mammals. On a lake-by-lake and park-by-park basis, judgment regarding applicability of our conclusions would rest on knowledge unavailable to us regarding the period of time the birds and mammals were actually using those respective lakes.

5.5 Nitrogen Deposition Effects and Relationships

5.5.1 Ecological Effects of Enhanced Nitrogen Deposition in the Western United States

Nitrogen inputs to the United States from anthropogenic sources doubled between 1961 and 1997, mainly from inorganic N fertilizer use and emissions of nitrogen oxides from fossil fuels (Howarth et al., 2002; Burns, 2003). Chronic enhanced nitrogen deposition and excess available nitrogen can lead to a myriad of adverse ecological effects in forests in the western United States, such as eutrophication of water bodies, nitrate-induced toxic effects on aquatic biota, changes in plant community composition and aquatic communities through removal of N limitations on biotic activity, disruptions in nutrient cycling, decreased soil capacity for N retention, and increased emissions from soil of nitrogenous greenhouse gases (Fenn et al., 1998; Fenn et al., 2004). Current upward trends in population growth and energy use throughout the western United States suggest a need for continued monitoring of atmospheric deposition N and its ecological effects.

5.5.2 Evidence of Enhanced Nitrogen Deposition in Some Parks from Lichen N

The previous chapter explains that we found indication of enhanced N deposition to terrestrial ecosystems based on WACAP lichen N data at SEKI, GLAC, BIBE, and BAND. Lichens from these parks exceeded thresholds for background sites in the western United States; N in lichens from other parks was within expected ranges for clean sites. Elevated lichen nitrogen concentrations are associated with adverse changes to lichen community composition (Geiser and Neitlich, 2007; Jovan and McCune, 2005) and are an indicator that other N-sensitive ecosystem components could be affected.

Another measurement of nitrogen availability obtainable at most of the WACAP parks are ambient concentrations of fine particulate (<2.5 µm) ammonium nitrate and ammonium sulfate sampled by IMPROVE. The IMPROVE network was established by federal land management agencies to meet federal land manager responsibilities under the Clean Air Act to monitor visibility in Class I areas. Three days a week, synchronized nationally, 24-hour samples of particulate matter <2.5 µm diameter are collected onto a filter from a height of about 3 m (these fine particulates are associated with declines in visibility and adverse human health effects). The chemistry of the particulates is determined following national protocols at the University of California, Davis. Particulates composed of ammonium sulfate and ammonium nitrate are reported in µg m^{-3}. These data have value as indicators of nitrogen availability at the site, from agricultural as well as urban-industrial sources. IMPROVE data and trends analyses can be obtained from the IMPROVE website at http://www.coha.dri.edu/index.html.

Mean ambient atmospheric ammonium nitrate and ammonium sulfate concentrations (µg/m^3) reported from WACAP IMPROVE sites, 1999-2004, are displayed in Figure 5-29. SEKI has higher concentrations of both pollutants than all other parks except BIBE, which has the highest ammonium sulfate concentrations. Among the core parks, GLAC, ROMO, MORA, and OLYM are not different from each other and DENA is lowest (Tukey-Kramer multiple means comparisons, $\alpha = 0.05$). Only nitrate and sulfate concentrations are measured, as these anions are assumed to be balanced by ammonium. IMPROVE data can be further explored by examining trends over seasons and years and by comparing peaks during worst days instead of averages. The point of including the data here is to provide further evidence of enhanced nitrogen deposition at SEKI and BIBE. There is no IMPROVE monitor at KATM; data from the Tuxedni National Wildlife Refuge monitors were used in surrogate.

5.5.3 Correlations between Agricultural Chemicals and Measures of Agricultural Intensity, Atmospheric Pollutants that Contain Nitrogen, and Human Population

Correlations among mean annual ammonium nitrate concentrations in airborne fine particulates sampled by park IMPROVE monitors from 1998-2004, the agricultural intensity index, nitrogen concentrations in WACAP lichens and SOC concentrations in WACAP vegetation were calculated (Table 5-16). Agricultural intensity calculations are described by Hageman et al. (2006). See also Chapter 3 for more information about agricultural intensity, IMPROVE, and population density calculations.

Concentrations of the CUPs, chlordanes, dacthal, and endosulfans in lichens and in conifer needles, DDTs in conifer needles, and PAHs in lichens correlated well (Spearman’s Rho 0.62 to 0.85) with both agricultural intensity and concentrations of ammonium nitrate in fine particulates <2.5 µm diameter sampled by park IMPROVE monitors. Trifluralin in conifer needles was strongly correlated with IMPROVE ammonium nitrate.

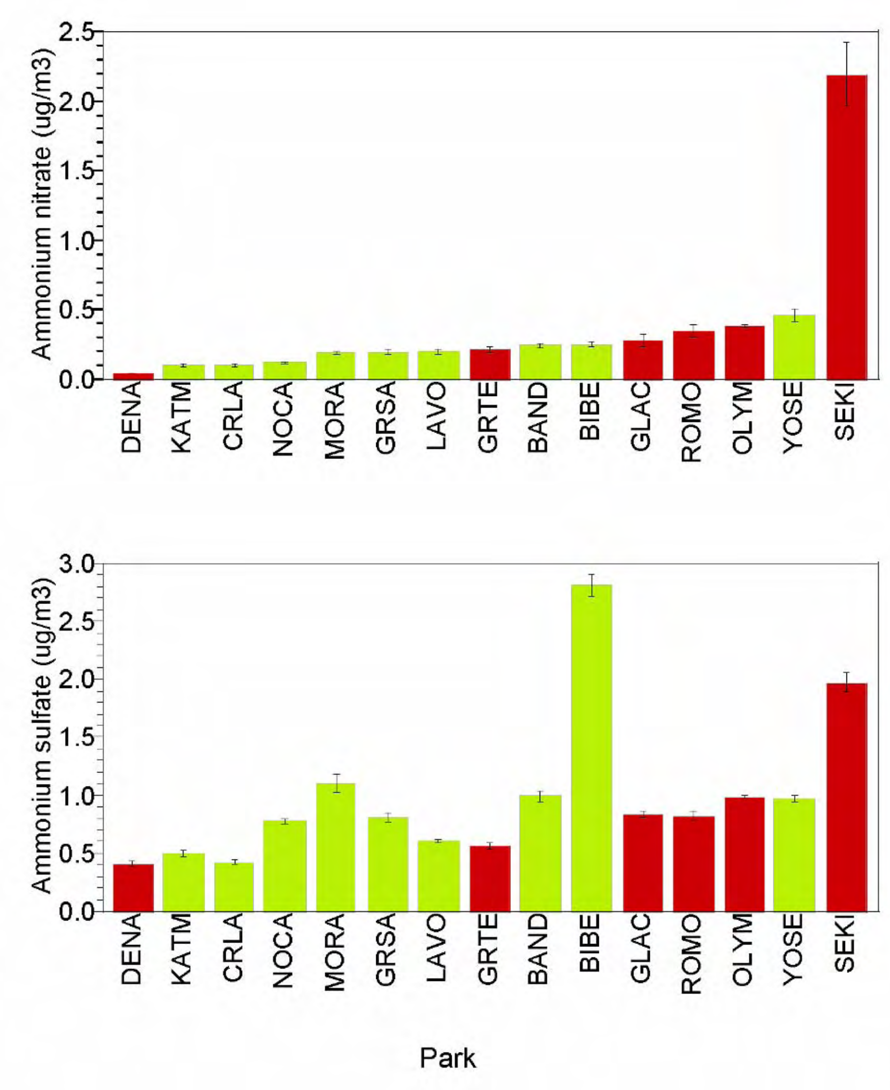


Figure 5-29. Mean Annual Concentrations (µg/m^3) of Ammonium Nitrate and Ammonium Sulfate in Ambient Fine Particulates (< 0.25 µm) Measured by IMPROVE at WACAP Parks, 1998-2004. Parks are sorted by increasing ammonium nitrate concentration. Red bars indicate core parks; green bars indicate secondary parks. Error bars indicate one standard error around the mean. SEKI has higher concentrations of both pollutants than all other parks except BIBE which has highest ammonium sulfate concentrations. Among the core parks GLAC, ROMO, MORA, and OLYM are not different from each other and DENA is lowest (Tukey-Kramer multiple means comparisons, α = 0.05).

Table 5-16. Rank Correlations among SOC Concentrations in Vegetation (pink), Agricultural Intensity, Mean 1998-2004 Ammonium Nitrate Concentrations in Fine Particulates Measured by IMPROVE (green), and Population Density (gray) for the 20 WACAP Parks. Bold-faced variables were highly significant in both lichen and conifer vegetation.

Conifer Variable	By Conifer Variable	Spearman Rho	Prob >|Rho|	Lichen Variable	By Lichen Variable	Spearman Rho	Prob >|Rho|
Agintensity	**Dacthal**	**0.873**	**<.0001**	**Agintensity**	**Dacthal**	**0.849**	**<.0001**
Agintensity	**Endosulfans**	**0.777**	**<.0001**	**Agintensity**	**Amm_NO$_3$ μg/m^3**	**0.787**	**<.0001**
Agintensity	**Amm_NO$_3$ μg/m^3**	**0.758**	**0.0002**	Agintensity	DDTs	0.779	0.0047
Agintensity	PAHs	0.745	0.0003	**Agintensity**	**Endosulfans**	**0.744**	**0.0002**
Agintensity	**Chlordanes**	**0.646**	**0.0038**	**Agintensity**	**Chlordanes**	**0.566**	**0.0116**
Amm_NO$_3$ μg/m^3	PAHs	0.655	0.0023	Amm_NO$_3$ μg/m^3	Triflualin	0.762	0.0280
Amm_NO$_3$ μg/m^3	**Endosulfans**	**0.644**	**0.0029**	Amm_NO$_3$ μg/m^3	DDTs	0.724	0.0117
Amm_NO$_3$ μg/m^3	**Dacthal**	**0.623**	**0.0058**	**Amm_NO$_3$ μg/m^3**	**Dacthal**	**0.700**	**0.0006**
				Amm_NO$_3$ μg/m^3	**Endosulfans**	**0.630**	**0.0029**
Pop. 150-km radius	**Pop. 75-km radius**	**0.900**	**<.0001**	Pop. 75-km radius	Dieldren	1.000	0
Pop. 75-km radius	**Amm_NO$_3$ μg/m^3**	**0.721**	**0.0005**	**Pop. 150-km radius**	**Pop. 75-km radius**	**0.914**	**<.0001**
Pop. 75-km radius	Endosulfans	0.698	0.0009	**Pop. 75-km radius**	**Amm_NO$_3$ μg/m^3**	**0.760**	**0.0001**
Pop. 75-km radius	PAHs	0.671	0.0016	**Pop. 150-km radius**	**Agintensity**	**0.677**	**0.0010**
Pop. 75-km radius	PCBs	0.664	0.0051				
Pop. 75-km radius	**Agintensity**	**0.629**	**0.0039**				
DDTs	**Chlorpyrifos**	**0.943**	**0.0048**	Chlordanes	Dieldrin	1.000	0
HCB	**a-HCH**	**0.874**	**<.0001**	Dacthal	Dieldrin	1.000	0
Endosulfans	**Chlordanes**	**0.864**	**<.0001**	DDTs	Dieldrin	1.000	0
a-HCH	Chlordanes	0.862	<.0001	PCBs	Dieldrin	1.000	0
PAHs	Chlordanes	0.847	<.0001	**Endosulfans**	**Dacthal**	**0.922**	**<.0001**
Endosulfans	**Dacthal**	**0.843**	**<.0001**	**Dacthal**	**Chlordanes**	**0.846**	**<.0001**
PAHs	A-HCH	0.828	<.0001	Dacthal	DDTs	0.818	0.0021
Endosulfans	**DDTs**	**0.821**	**0.0234**	PCBs	Chlordanes	0.798	<.0001
PCBs	DDTs	0.821	0.0234	a-HCH	g-HCH	0.795	<.0001
PAHs	Endosulfans	0.818	<.0001	**Endosulfans**	**Chlordanes**	**0.784**	**<.0001**
Endosulfans	A-HCH	0.807	<.0001	**HCB**	**a-HCH**	**0.773**	**<.0001**
HCB	Chlordanes	0.790	<.0001	**Endosulfans**	**DDTs**	**0.764**	**0.0062**
DDTs	**Chlordanes**	**0.786**	**0.0362**	PCBs	g-HCH	0.721	0.0007
PAHs	Dacthal	0.771	0.0002	PCBs	a-HCH	0.674	0.0016
PCBs	**Endosulfans**	**0.753**	**0.0008**	PCBs	Dacthal	0.663	0.002
Dacthal	**Chlordanes**	**0.738**	**0.0007**	PAHs	a-HCH	0.653	0.0018
PAHs	**HCH**	**0.735**	**0.0003**	PAHs	g-HCH	0.653	0.0025
Chlordanes	Chlorpyrifos	0.700	0.0037	**PCBs**	**Endosulfans**	**0.644**	**0.0029**
PCBs	Chlorpyrifos	0.685	0.0139	**PAHs**	**HCB**	**0.638**	**0.0025**
Endosulfans	HCB	0.672	0.0016				

Human population size within a 75-km radius of WACAP parks correlated most strongly with endosulfan, PAH, and PCB concentrations in conifers (Spearman's Rho 0.66 to 0.70) and with dieldrin concentrations in lichens (Spearman's Rho 1.00). Other radii tested (25, 150, 300) did not predict SOC concentrations as well. Human population size, agricultural intensity, and ammonium nitrate concentrations in ambient fine particulate were all strongly correlated with each other. In the west, the most productive agricultural areas and largest urban areas are often located in the same geographical and climatic zones.

Concentrations of endosulfans were strongly correlated with chlordanes, dacthal, DDTs, and PCBs in vegetation samples, regardless of vegetation type. Chlordanes were strongly correlated with dacthal and DDTs, and HCB was strongly correlated with a-HCH and PAHs in both vegetation types. Many other SOCs were strongly correlated with other SOCs in one vegetation type but not the other. Although correlations do not imply direct or causal relationships between variables, they can serve as indicators of each other. For example, high IMPROVE Amm_NO3 is a fairly good predictor of high dacthal, endosulfan, trifluralin, DDT, and PAH concentrations in conifer needles and/or lichens relative to cleanest sites.

5.6 The Influence of Environmental Factors on Fish Hg_{tot}

Observational and experimental studies show that total mercury (Hg_{tot}) in fish is strongly influenced by watershed and food web characteristics (Wiener et al., 2006), and that the interplay among these variables is complex and varies in unpredictable ways. Thus we are not able to predict Hg_{tot} in fish from an unknown lake, even when we have basic information such as basin characteristics, area of wetlands, TOC in the lake water, and the general structure of the food web. The best we can currently do is to suggest that the top predatory fish in any system are likely to have the highest $Hg_{tot.}$ There appears to be no strong relationship between Hg atmospheric deposition and Hg concentration in fish at the site level. When aggregated at a large scale (i.e., the state level), it has been demonstrated, with important caveats, that wet atmospheric deposition of mercury can account for about two-thirds of the methyl mercury (MeHg) in largemouth bass (*Micropterus salmoides*) (Hammerschmidt et al., 2006). The WACAP data clearly demonstrate this inability to anticipate Hg_{tot} in fish.

Figure 5-30 is a plot of the average fish Hg_{tot} concentration for each WACAP lake against lake water total phosphorus (P_{tot}). Two of the four lakes with the highest Hg_{tot} concentrations in target fish are Arctic lakes. The lake with the highest average Hg_{tot} is Burial Lake; this average value exceeds the USEPA criterion for human consumption. The other WACAP Arctic lake, Matcharak, is the fourth highest of all. These results are surprising for two reasons. First, the sedimentary records show that Hg_{tot} flux to the Alaska lakes in the last 50 years was only about one-fourth of the Hg_{tot} flux observed in WACAP lake sediments in the lower 48 states (see Section 4.3.5). Secondly, it is also true that the Arctic lake food webs tend to have fewer levels and are simpler than those in the lower 48 states; by conventional interpretation, this would lead to less biomagnification of Hg in fish. LP19 (MORA) and Hoh Lake (OLYM) are second and third highest, respectively, with respect to fish Hg_{tot}.

All WACAP lakes, except Burial Lake, are considered to be oligotrophic (water column $P_{tot} < 5$ µg/L); Burial Lake approaches being mesotrophic with water column $P_{tot} = 9$ µg/L (Wetzel, 1983). Since Burial Lake has at least double the concentrations of P_{tot} observed in any other WACAP lake, this could be an important factor contributing to the higher total Hg found in fish. However, several studies have indicated that increased algal primary production can reduce the uptake of MeHg in fresh waters as a result of dilution in greater planktonic biomass (Pickhardt et al., 2002). Only the methyl form of mercury can enter the food web and bioaccumulate. Lake trout (the target fish in both Arctic lakes) have been shown to rely heavily on snails derived from the benthic food web (Hershey et al., 1999). This was confirmed at the time of WACAP sampling in that the gross anatomical evaluation showed stomach contents of fish from the

Arctic lakes comprised mostly snails. Our evidence and the literature suggest that the Arctic food web in which the lake trout reside is quite short and simple: periphyton, snails, and lake trout.

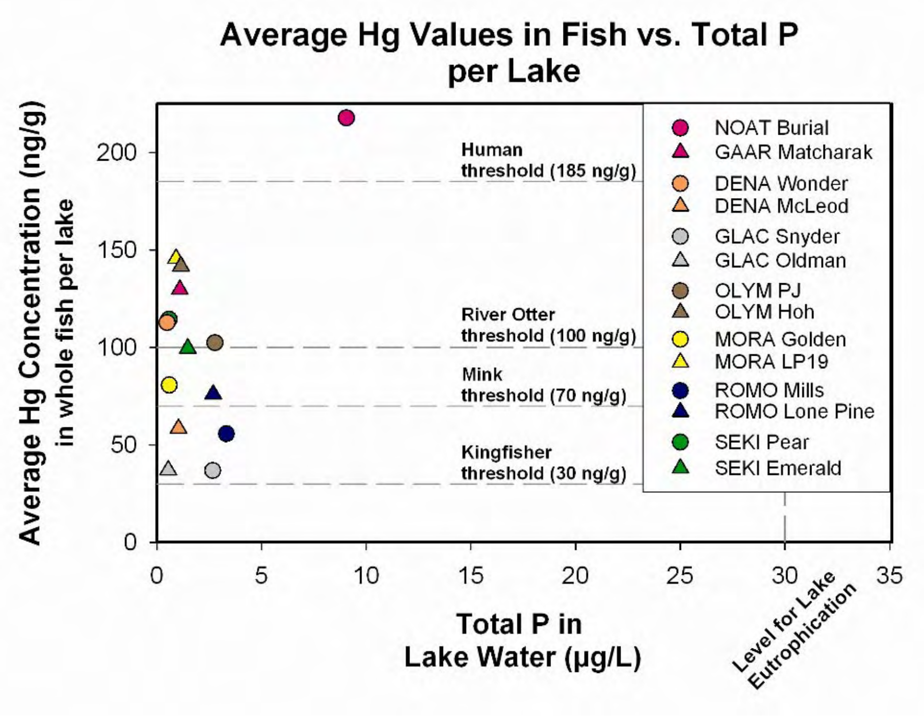


Figure 5-30. Average Total Mercury Values for Whole Fish Plotted Against Total Phosphorus (TP) in the Lake Water for All Lakes in the Core Parks. Notably, Burial Lake was mesotrophic with respect to TP and had the highest TP while also having the highest Hg_{tot}. All other lakes were oligotrophic. The human contaminant health threshold is 300 ng/g wet weight (USEPA, 2001), and is based on methyl-Hg in the fillet for a general population of adults with 70 kg body weight and 0.0175 kg fish intake per day. 95-100% of Hg in fish is methyl-Hg (Bloom, 1992), and 300 ng/g in the fillet is equivalent to 185 ng/g ww whole body methyl-Hg (Peterson et al., 2007). Contaminant health thresholds in piscivorous animals are based on 100% fish in the diet for whole body Hg_{tot} as determined by Lazorchak et al., (2003).

How might the high Hg_{tot} in Arctic fish be explained? One clue might be that the Arctic lakes had the highest DOC of all WACAP lakes (Burial = 3.3 mg/L; Matcharak = 4.7 mg/L). The range of DOC in the lakes in the lower 48 states was 0.65 – 2.25 mg/L (mean 1.3 mg/L). This suggests that there is a greater connection to sources of DOC, such as wetlands, sediment production littoral zones, and melting permafrost zones, than in other lakes. These locations are known and likely sites of mercury methylation (St. Louis et al., 1996) and DOC has been shown to be an important pathway for conveying methyl mercury from sites of methylation (i.e., anoxic, organic rich areas) to lakes. The high P content of the Burial Lake would stimulate periphytic algal growth on the lake sediment surface in the photic zone (depth ≤ ~ 10 m), providing the snail “grazers” with an abundant food source. It is probable that the combination of elevated P and DOC with the importance of the snail/ periphyton food web combined to provide a very efficient mechanism to transport MeHg into fish by using a short but efficient pathway. In other systems, lacking the snail/periphton linkage in an extensive photic zone, mercury reaching the sediment surface via “plankton rain” is typically lost to the accumulating sediment sink and little is conveyed back into the water column.

Another important function of DOC relating to MeHg in lakes and the bioaccumulation in fish is that DOC can attenuate light penetration and thereby decrease photodegradation of MeHg. This dynamic has been shown to be significant in an Arctic lake (Hammerschmidt et al., 2006) and would be likely to occur in Burial and Matcharak Lakes because of the fairly high DOC found there.

We determined that LP19 had the highest Hg flux (current vs. pre-industrial) ratio in lake sediments and that Hoh Lake had the lowest flux ratio of all WACAP lakes (Section 4.3.5), yet we observe that the mean Hg_{tot} in fish for these two lakes is almost identical. Clearly, there are factors other than mercury flux to the lakes, as indicated from the sediment record, responsible for Hg_{tot} concentrations in fish.

One of the best current tools available to scientists to examine the food web structure of an aquatic system and, therefore, to develop a quantitative understanding of the bioaccumulation of Hg_{tot}, is the application of stable isotope techniques (Kidd et al., 1995). Application of this technique to an exploratory observational research project such as WACAP was considered, but because we had no idea of the structure of the fish contaminant data, and of Hg concentrations in particular, it was not deemed to be cost effective. Application of this tool would be useful in deciphering causes behind the high concentrations of Hg_{tot} found in fish from selected WACAP lakes.

5.7 Summary

In this chapter we present an assessment of bioaccumulation in vegetation, fish, and moose; biological effects in fish; potential adverse ecological effects to piscivorous wildlife; and human health risks from atmospheric sources of anthropogenic semi-volatile organic compounds (SOCs), metals, and fixed nitrogen in national parks, preserves, monuments, and wildernesses of the western United States. The principal findings are itemized in the following subsections:

5.7.1 Bioaccumulation

- SOC concentrations were orders of magnitude higher in biota (fish, vegetation) and sediments compared to snow and air. Vegetation tended to accumulate more PAHs, CUPs, and HCHs, and fish tended to accumulate more PCBs and less volatile chlordanes, DDTs, and dieldrin.
- SOC burdens in conifer needles approximately tripled between first and second years.
- Western US coniferous forests have the capacity to accumulate annually in 2nd year needles amounts of pesticides that are comparable on a per ha basis to a significant fraction of regional pesticide application rates, providing an ecosystem service with un-examined ecological consequences. Forest productivity (annual needle biomass production), conifer species, proximity to sources, and application rates at the sources all appear to be important factors in needle concentrations.
- Fish lipid and age were the most reliable predictors of SOC concentrations.
- Whole-body mercury was age-dependent in all fish up to approximately 15 years of age. In lake trout older than 15, mercury was not age-dependent.

- Mean ammonium nitrate concentration in ambient fine particulates < 2.5 µm diameter, sampled at park IMPROVE monitors, was a fairly good predictor (Spearman's Rho correlation coefficient > 0.62) of dacthal, endosulfan, chlordane, trifluralin, DDTs, and PAH concentrations in vegetation.

5.7.2 Adverse Biological Effects Observed in Fish

- Most fish appeared normal during field necropsies. Lake trout from the Arctic had parasite infestations of varying severity but there was no evidence that this was related to contaminant concentrations.
- Kidney and spleen macrophage aggregates, a biomarker of tissue damage, varied considerably but between-site differences were not related to contaminant concentrations.
- Spleen macrophage aggregates were highly correlated with tissue mercury concentrations and age in brook, rainbow and cutthroat trout.
- Fish with both male and female characteristics (ova-testis) were found in ROMO and GLAC lakes. The incidence of intersex has significantly increased since the pre-organic pollutant era (pre-1930s).
- Elevated concentrations of vitellogenin, a female protein involved in egg production, were found in male fish from MORA, ROMO, and GLAC. At ROMO, vitellogenin appeared to be related to the concentration of several organochlorines. Small sample sizes limit the inferences that can be made and suggest that further sampling and analysis of SOC concentrations and vitellogenin might be warranted.

5.7.3 Potential Adverse Ecological Effects

- Mercury concentrations in fish exceeded contaminant health thresholds for some piscivorous mammals and birds in most parks (see Section 5.4.1 for caveats). Concentrations of the sum of the forms of DDT, DDD, and DDE in some fish in GLAC and SEKI exceeded contaminant health thresholds for piscivorous birds.
- Modeling of contaminant and nutrient transport through hypothetical food webs also suggests that contaminants may be adversely affecting life expectancy and abundance in piscivorous wildlife.
- IMPROVE fine particulate monitoring data and lichen nitrogen and sulfur concentrations in WACAP parks indicate that anthropogenic deposition of atmosphere nitrogen and sulfur-containing fertilizing and acidic compounds are enhanced in SEKI, GLAC, and BIBE. Elevated nutrient deposition is associated with adverse effects to sensitive species, community dynamics, and ecosystem processes.

5.7.4 Health Risks to Humans

- Over half (77 of 136) of the individual fish from 11 of the 14 WACAP lakes, carried concentrations exceeding subsistence fishing contaminant health thresholds for dieldrin and/or p,p′-DDE; thresholds were calculated using USEPA guidelines. Consuming fish exceeding a contaminant health threshold implies an increased risk (by 1 in 100,000) of developing cancer during a lifetime of frequent fish consumption.

- Concentrations of chlorpyrifos, dacthal, endosulfans, methoxychlor, mirex, HCB, a-HCH, g-HCH, chlordanes, heptachlor epoxide, and PBDEs, the other pesticides, and industrial compounds detected in >50% of fish, were 1-7 orders of magnitude lower than contaminant health thresholds for subsistence fishing.
- Risks from recreational fishing consumption were lower than risks from subsistence fishing, but concentrations of dieldrin in five individual fish from SEKI, ROMO, and GLAC exceeded contaminant health thresholds for recreational fishing.
- The average mercury concentration in fish from Burial Lake (NOAT) and in some individual fish from PJ and Hoh lakes (OLYM), LP19 (MORA), and Pear Lake (SEKI) exceeded the USEPA contaminant health thresholds for humans.
- SOC and metal concentrations in the three moose samples, all from DENA, were low and not of concern with regard to human health effects. The DENA moose were nutritionally deficient in copper, which might be of interest to DENA wildlife biologists.

CHAPTER 6

Recommendations and Conclusions

6.1 WACAP Recommendations to NPS

6.1.1 Introduction

These recommendations are related to the original five WACAP objectives and have been specifically requested by the NPS as a product of this project. They are based on the results of WACAP (as well as other relevant scientific literature, in some cases).

The WACAP objectives were to determine:

1. If contaminants are present in western national parks
2. Where contaminants are accumulating (geographically and by elevation)
3. Which contaminants pose a potential ecological threat
4. Which indicators appear to be the most useful to address contamination
5. What the sources were for contaminants measured at the national park sites

Recommendations stem from the question posed by NPS, “What did you learn in this project that could help guide or focus future work within the NPS on contaminants in western U.S. parks?”

6.1.2 Presence of Key Contaminants

- Dieldrin, DDT, chlordane, and mercury were found to be key compounds/elements that are atmospherically deposited within WACAP parks because they have a combination of higher concentrations and greater toxicity in the food web than other analytes.

  Therefore NPS could consider focusing on dieldrin, DDTs, chlordane, and mercury in future work when assessing highest risk to western park resources is desired. Since spectral analytical techniques for the semi-volatile organic compounds (SOCs) often result in identification of multiple compounds, the benefits of looking at additional compounds at minimal extra cost should be considered.

- Mercury concentrations in fish tissue routinely exceeded piscivorous animal thresholds, and in some parks, human contaminant health thresholds were also exceeded.

  Therefore, assessing mercury concentrations and impacts on fish could be considered a high priority for future analysis in parks. As evidence is emerging concerning the important role of selenium in binding with methyl mercury in organisms, and possibly reducing the toxic effects of mercury in the environment, future work on mercury should consider also measuring and evaluating selenium.

- Deposition of HUPs (historic-use pesticides) was shown to be decreasing fairly consistently, while deposition of CUPs (current-use pesticides) is increasing in many parks.

  Therefore, NPS could consider focusing on current-use pesticides and other current-use chemicals.

- Sediment records show that deposition of some current-use SOCs and PBDEs is increasing over time in some areas: McLeod Lake (DENA) shows increasing endosulfans; Matcharak Lake (GAAR) shows increasing PAHs; Oldman and Snyder lakes (GLAC) show increasing dacthal and endosulfans; PJ Lake (OLYM) shows increasing dacthal and endosulfans; LP19 and Golden Lake (MORA) show increasing endosulfans; Lone Pine Lake (ROMO) shows increasing endosulfans and Mills Lake (ROMO) shows increasing endosulfans and PBDEs.

  Because increased use and deposition of these SOCs has been documented, the deposition and potential health effects (on wildlife and humans) of these current-use pesticides could continue to be assessed over time, particularly in parks near agricultural sources (such as SEKI, ROMO, and GLAC). The most effective approach for tracking the changes in deposition in these compounds over time, and the thresholds for their impacts to human and wildlife health, would need to be determined.

6.1.3 Locations of Contaminant Accumulation

- Contaminants were found in all WACAP lakes; in some cases, the concentrations in fish were found to exceed important human and wildlife thresholds. It might be perceived that the two lakes per park that WACAP examined are somehow outliers and that they do not represent the total population of lakes within parks. From a strictly statistical perspective, these lakes are not representative of the population of lakes. However, the lakes were selected to provide “clean,” unambiguous signals of atmospherically deposited contaminants and in no way were they selected to provide the highest or lowest contaminant concentrations.

  Researchers conducting future work might choose to consider implementing a robust statistical sampling design for specific parks that would provide a quantitative estimate of the contaminant condition of all lakes in the population.

- SOC and nitrogen concentrations in WACAP parks were shown to be closely associated with proximity to regional sources (agricultural, point, and urban sources).

  Therefore NPS could consider monitoring SOC and nitrogen concentrations in areas closest to these source types, where identification of “hot spots” of contaminants is desired.

- Of the SOCs detected in air and vegetation throughout the 20 core and secondary WACAP parks, endosulfans and dacthal were the dominant current-use pesticides, and HCB and a-HCH were the dominant historic-use pesticides. In general, GLAC and SEKI, followed by YOSE and GRSA, had the highest concentrations of SOCs among the WACAP parks; air and vegetation concentrations of CUPs were lowest in Alaska parks; concentrations of HUPs did not differ among the parks. These findings imply risk to terrestrial ecosystems, but accumulation in aquatic ecosystems is unknown.

  Therefore monitoring of SOCs in vegetation and other indicators (snow, fish, sediment) might be fruitful in additional parks in California and the Rocky Mountains.

- GRSA contains very high concentrations in lichens (compared with most other parks) of dacthal, endosulfans, HCB, a-HCH, g-HCH, chlordanes, and DDT.

  Further investigation of the sources and extent of these contaminants in GRSA ecosystems might be desirable.

- Industrial and agricultural contaminants were abundant in ROMO ecosystems. Fish gonadal abnormalities (feminization of males and abnormalities in immature females) were observed in the park, and some of these fish had high contaminant burdens. The relationship between the two results is statistically significant, but complicated because of the small sample sizes.

  The NPS might wish to conduct future studies regarding causes of fish abnormalities, including evaluation of potential interactions of multiple contaminants.

- Pacific Coast parks contain a combination of high contaminant concentrations in needles and dense forest foliage.

Therefore, NPS might wish to assess whether this combination could result in high loading of contaminants to the ecosystem from canopy leachates and forest litter fall in these parks.

- High concentrations of some contaminants in a single snow sample in DENA (2,500-m elevation), along with greater precipitation amounts at higher elevations, suggests potential for greater contaminant loading and higher ecological effects at high elevations in this park.

  WACAP suggests further exploration of contaminants at elevational gradients in this park.

6.1.4 Ecological Threat From Contaminants

- Fish are a key indicator in parks because, as shown in this study and others, bioaccumulation of contaminants in their tissues puts them at risk for adverse effects, as well as the species that eat them (birds, wildlife, humans).

  Therefore, NPS might wish to give first priority in bioaccumulation studies to assessing contaminant concentrations in fish, to determine current risk to fish and consumers of fish, before investigating other food web indicators.

- Fish were chosen as the primary indicator of ecosystem health in WACAP. However, other studies have shown that each ecosystem food web varies in how it accumulates contaminants.

  Therefore, although fish are recommended as a key indicator for initial assessment of contaminant impacts, when fish contamination concentrations conflict with other measurements, fish concentrations might not reflect all parts of the food web. In these cases, assessing food web structure and ecosystem processing variables may help determine whether further bioaccumulation assessments might be needed in other indicators (e.g., song birds, insects, amphibians, mammals).

- Contaminant concentrations were generally correlated with fish age and lipid (in this and other studies), because fish tend to accumulate more contaminants in tissues as they eat and grow older.

  Therefore, determining the ages and lipid of fish assessed for contaminants in future studies could help provide comparability among data sets or aid in the understanding of variability among fish.

- Concentrations of mercury in fish were not always directly related to levels in atmospheric deposition and flux (e.g., in some Alaska sites, mercury deposition was low, but concentrations in fish were high). Bioaccumulation and biomagnification of mercury is controlled largely by methylation processes and food web structure.

Therefore future studies should consider these factors in study designs, when assessment of areas of highest risk is desired.

- Some lakes in GLAC and ROMO contain reproductively abnormal male fish, evidenced by the presence of eggs and sperm in the same fish, testicular abnormalities, elevated levels of female-specific protein in the blood, and elevated SOC concentrations in these fish.

  Further research in other lakes in these parks as well as other parks in the Rocky Mountains (GRTE, GRSA) could be conducted to assess the spatial extent of these conditions, associated fish SOC concentrations, and the potential impact on fish populations in these parks.

- There is strong inferential evidence that the intersex condition and female-specific protein (Vtg) found in some fish in the study can be explained by endocrine disruption related to contaminants.

  There is a chance that further investigation could find this contention to be wrong, but the "precautionary principle" argues for continuing to explore these potential linkages between fish condition and contaminants in western parks.

- Other studies have shown that fish accumulated greater amounts of some SOCs in livers than in fillets.

  Because NPS is concerned about effects of bioaccumulation on fish, birds, and wildlife, analysis of whole fish in parks (rather than fillets alone) is suggested to enable comparison of results with fish and wildlife toxicity thresholds. Conversions of concentrations from whole fish to fillet values can subsequently be made to estimate risk to humans.

- Willow bark was evaluated in this study to assess accumulation of contaminants in vegetation that could be browsed by animals. It was difficult, however, to identify the willow species in the field, and willow bark was more difficult to analyze for SOCs in the lab.

  Therefore willow bark is not currently recommended as a useful ecosystem indicator in NPS future studies.

- Select PBDE concentrations were fairly high in WACAP fish (higher than in Pacific Ocean salmon) and increasing in some sediments. In addition, human and wildlife contaminant health thresholds for select PBDEs have not yet been adopted, but are more accurate than the current threshold.

  Therefore in future studies, NPS might wish to measure select PDBEs in fish to determine if there is a temporal trend in concentrations or risk.

6.1.5 Sources of Contaminants

- This study identified several parks in which individual contaminants or suites of contaminants suggest current local or regional source contributions.

  NPS might wish to further investigate recent local source contributions of: (1) PAHs at GLAC, (2) current-use SOCs at ROMO, GLAC, and SEKI, and (3) PBDEs at ROMO and MORA.

- Sediment records showed steadily increasing mercury deposition over time at lakes in two parks (MORA and ROMO). Because these patterns differ from those at other western parks, the sources of mercury could be local rather than global.

  NPS could consider additional work to determine the extent to which local sources contribute to mercury deposition at these parks.

- Long-range, global (including trans-Pacific) SOC and mercury sources contribute a greater percentage of the total SOC deposition in OLYM, DENA, and NOAT than do regional North American sources.

  NPS might wish to continue monitoring the deposition of SOCs and mercury in these parks to better track the relative contribution of global sources over time.

6.1.6 Understanding Contaminant Processes in Ecosystems

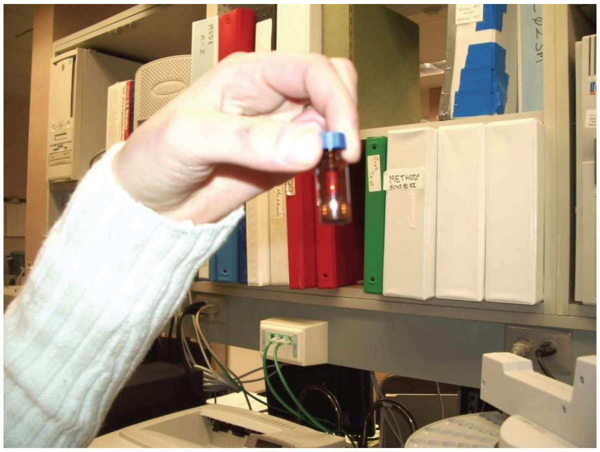
This project has helped to elucidate some of the questions that will have to be addressed in the future for a better understanding of how contaminants move into and through park ecosystems. Understanding these processes, mechanisms, and ecosystem interactions will be important in advancing contaminants research in the United States. However, because many of these types of questions are beyond the scope of the key WACAP objectives, they have not been developed as specific recommendations to NPS. However, several of the questions that have been identified by WACAP investigators are included here as potential areas of interest for future research:

- Which ecosystem variables are the best predictors of contaminants risk to lake catchments?
- How important are various deposition processes, including rain, snow, fog, rime ice, and dry deposition, in delivering contaminants to ecosystems?
- What is the fate (mass balance/budget) of SOCs in deposition? How much is re-volatilized to the atmospheric from vegetation, soil, or water? How much accumulates in terrestrial or aquatic ecosystems? How much is transported to downstream environments in stream flow?
- How can SOC concentrations be used to predict other contaminants?
- Can information about the half-lives of contaminants found in parks be used to predict future trends for increases or decreases in these ecosystems?
- What is the effect of interaction among multiple contaminants in ecosystems?
- What are the ecosystem variables in Alaska parks that result in higher bioaccumulation of mercury in fish there?
- What will be the synergistic impacts on bioaccumulation of contaminants with global change, regional land-use change, wildfire, and other regional-scale anthropogenic changes?

- What are the impacts of contaminants in parks on other parts of the food web not studied in the project (e.g., mink, piscivorous birds, amphibians)?
- What are the speciated components of mercury in the air, and what do the proportions of reactive gaseous mercury and particulate mercury tell us about regional mercury source contributions?
- How do the types and locations of vegetation selected for sampling influence contaminant uptake (e.g., vegetation under snowpack compared with vegetation exposed year round).
- What is the extent of the cold fractionation effect of SOCs in vegetation accumulating preferentially at high elevations in some parks?
- How should contaminants be tracked over time in parks where they have been identified as potentially increasing (in sediments, snow, air, vegetation, and fish)?
- What are thresholds of concern for the effects of bioaccumulation of emerging contaminants (e.g., PBDEs) on fish, wildlife, and humans?
- Over what timeframe do various contaminants degrade in sediments? Do concentrations of contaminants change over time once they have been deposited?

6.2 Conclusions

The transport, fate, and ecological effects of anthropogenic contaminants from atmospheric sources were assessed in air, water, snow, sediment, vegetation, and fish in eight core national parks in the western United States. In addition, air and vegetation were sampled in twelve secondary national parks, preserves, and national forests in the western United States to further enhance spatial interpretations of the data. Samples were analyzed for SOCs (CUPs and HUPs, industrial compounds, and PAH), mercury, and other metals. Relative to the WACAP objectives, major conclusions are as follows.



Out of more than 100 SOCs tested (excluding PBDEs in fish and sediments), 70 were found at detectable concentrations in air, snow, water, vegetation, sediment, and/or fish. Six contaminants of highest concern were identified for the eight core park ecosystems studied: mercury, dieldrin, DDT, PCBs, chlordane, and PAH. These contaminants are of highest concern because of (1) the high concentrations detected, (2) the bioaccumulation documented, and/or (3) their toxic or persistent characteristics in the environment. Other contaminants identified as potential concerns are PDBEs, endosulfans, dacthal, chlorpyrifos, HCB, a-HCH, and g-HCH, because they are (1) in current use, (2) are present at comparatively high concentrations in vegetation or fish, and/or (3) are increasing over time in sediment cores.

Contaminants were shown to accumulate geographically based on proximity to individual sources or source areas. Pesticide concentrations for both HUPs and CUPs were highest in parks and park watersheds closest to agricultural areas. Concentrations of industrial contaminants (PAHs and mercury) were sometimes elevated near parks where local/regional sources produce these contaminants. This finding is counter to the original working hypothesis that most of the contaminants found in western parks would originate from eastern Europe and Asia and travel across the Pacific to the western United States. There was evidence that this phenomenon does occur, but contaminant contributions from trans-Pacific sources of SOCs were small compared to other regional sources closer to the parks. Regarding mercury, in particular, deposition is composed of a complex mixture of local, regional, and global sources.

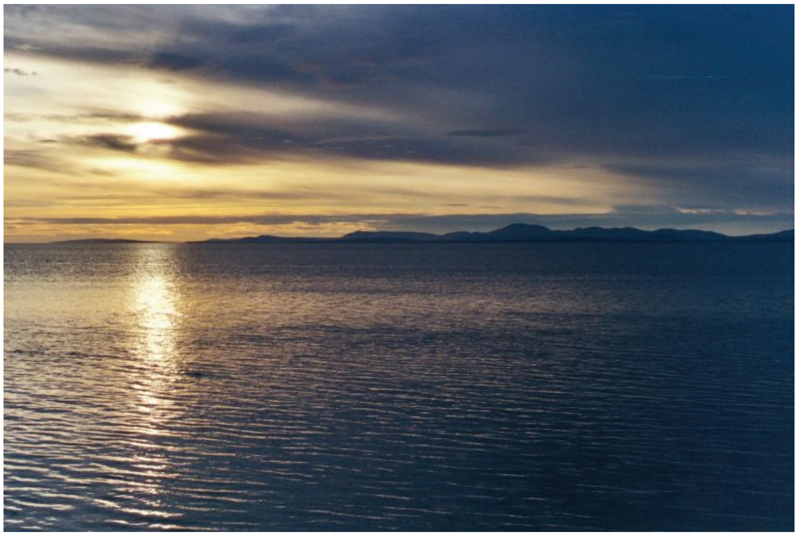
Contaminants were found to bioaccumulate in ecosystems (higher concentrations in older vegetation than in younger vegetation), and biomagnify at higher levels of the food web (concentrations in fish higher than those in air, snow, or water). Bioaccumulation and biomagnification of contaminants in ecosystems have been shown in other studies to occur elsewhere, but not at these regional scales in remote ecosystems in the western United States.

Among the contaminants found in western park ecosystems, mercury and dieldrin are likely to pose the greatest ecological threat. Mercury is a common component of coal. On a global scale, approximately two-thirds of the anthropogenic mercury emitted is from the combustion of fossil fuels. When mercury is deposited in the environment and biologically converted to its toxic form (methyl mercury), it can bioaccumulate readily in food chains and cause neurological and other detrimental effects in humans, fish, and other organisms. Although mercury deposition in Alaska parks was low, in-lake biological processes specific to the lakes in these parks contributed to concentrations in fish that exceeded contaminant health thresholds for humans and wildlife. The average mercury concentration in fish from Burial Lake (NOAT) exceeded the human contaminant health threshold. Average mercury concentrations in fish at GAAR and DENA (Wonder Lake) fell between the human and otter contaminant health thresholds, and mercury concentrations in all fish from the four Alaska lakes, except for one fish from McLeod Lake (DENA), were above the contaminant health thresholds for kingfisher (see Figure 5-18). Mercury concentration thresholds for risk to birds and wildlife were routinely exceeded at most lakes in most parks. Dieldrin is an acutely toxic insecticide, categorized as a carcinogen and a known endocrine-disrupting compound. It was banned from use in the United States in 1987 and in Canada in 1990. However, concentrations of dieldrin found in fish in some parks in this study were still high, and in some cases exceeded USEPA contaminant health thresholds for increased cancer risk to humans, but not the thresholds for risk to birds and wildlife. It is not currently known why concentrations remain high in parks near agricultural areas two decades after the product was banned, but dieldrin is known to be persistent in the environment.

The ecological indicators found to be most useful in interpreting contamination in this study were fish, sediments, conifer needles, and lichens. Fish were important as an indicator of bioaccumulation of contaminants and potential impacts to food webs. Sediments provided a historical context, documenting changes in contaminants over time, and retaining clues about contaminant sources through historical deposition of metals and SCPs (spheroidal carbonaceous particles). Second-year conifer needles proved to be an effective current measure of several types of contaminant concentrations over large spatial scales. Because their age is known and their biomass is large, conifer needles provided an ecologically relevant measure of yearly contaminant loading in vegetation. Lichens, with a higher capacity for SOC accumulation, and with occurrence in both forested and arctic-alpine ecosystems, indicate differences in SOC concentrations along elevational gradients and among sites within parks. However, lichens cannot be aged, and therefore, the period of time over which contaminants are accumulated in lichens is unknown, complicating their interpretation. Consistently sampling a single species and collecting samples above or below winter snow lines improves the sensitivity of vegetation indicators.

The sources of contaminants in western national parks vary by region. In Alaska, there are few local or regional sources of contaminants, and deposition of contaminants is influenced primarily by transport from other source regions. In general, deposition of CUPs and HUPs is most strongly influenced by proximity to agricultural and industrial areas. An aluminum smelter near GLAC contributes to high concentrations of PAHs in snowpack, sediment, and lichens at Snyder Lake.

The knowledge gained from this project should add considerably to the state of the science about contaminant transport, flux, and biological and ecological effects in remote ecosystems in the western United States. However, it also serves to raise many additional questions. Related work, if conducted in the future, might explore some of these areas, identifying the various temporal and spatial dimensions of contaminant pathways and defining and documenting the extent and magnitude of specific ecological effects.



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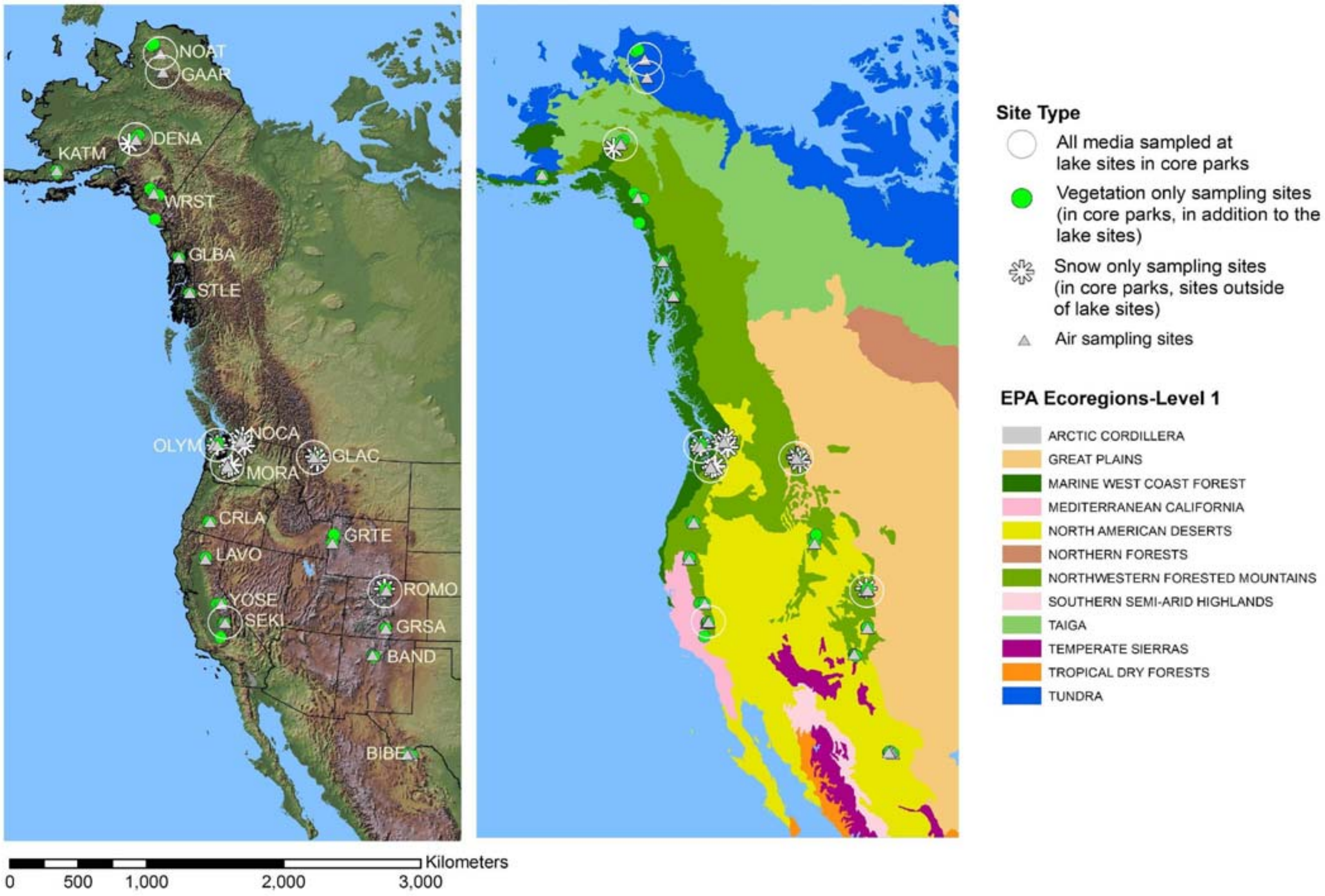

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