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

| | | | | | 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.**

| | | | | | Federal Regulatory Status 2007* | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Compound Name** | **Abbreviation** | **Chemical Class** | **Use/Source** | **First U.S. Usage** | **U.S.** | **Canada** | **China** | **Korea** | **Japan** |
| o,p'-DDT | op-DDT | Organochlorine | Insecticide | 1942 | B 1972 | B 1989 | 1983 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 |

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| | | | | | 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.

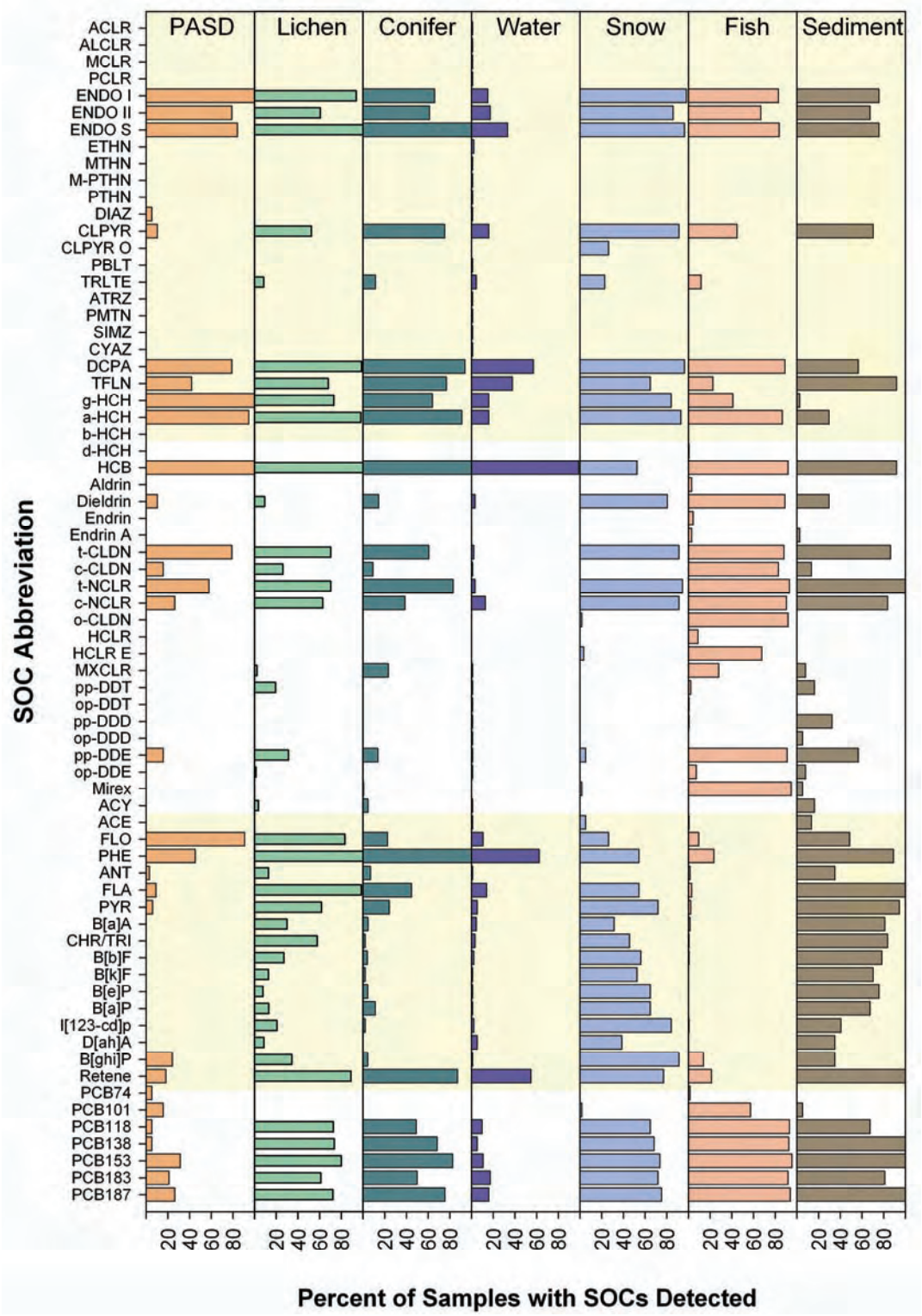



**Figure 3-1. Current Status of SOC Contamination in WACAP Parks.** The percent of all WACAP samples with SOC concentrations above the estimated detection limit is given for each medium. Only recent sediment samples from 1990 to present are included in the sediment column. PBDEs are not included because 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)** | |
| Nickel | Ni |
| Vanadium | V |
| **Petroleum Combustion** | |
| Arsenic | As |
| Barium | Ba |
| Beryllium | Be |
| Cadmium | Cd |
| Chromium | Cr |
| Copper | Cu |
| Lead | Pb |
| Manganese | Mn |
| Molybdenum | Mo |
| Nickel | Ni |
| Selenium | Se |
| Vanadium | V |
| Zinc | Zn |
| **Industrial (nonferrous metal production)** | |
| Cadmium | Cd |
| Chromium | Cr |
| Copper | Cu |
| Lead | Pb |
| Manganese | Mn |
| Vanadium | V |
| Zinc | Zn |
| **Agricultural** | |
| Arsenic | As |
| Mercury | Hg |
| Selenium | Se |
| Zinc | Zn |
| **Waste Incineration** | |
| Cadmium | Cd |
| Copper | Cu |
| Lead | Pb |
| Mercury | Hg |
| Zinc | Zn |

| | |
|---|---|
| **Automotive** | |
| Barium | Ba |
| Cadmium | Cd |
| Lead | Pb |
| Nickel | Ni |
| **Mineral (Earth's crust)** | |
| Aluminum | Al |
| Barium | Ba |
| Calcium | Ca |
| Cerium | Ce |
| Cesium | Cs |
| Holmium | Ho |
| Iron | Fe |
| Lanthanum | La |
| Lithium | Li |
| Magnesium | Mg |
| Manganese | Mn |
| Mercury | Hg |
| Neodymium | Nd |
| Praseodymium | Pr |
| Rhenium | Re |
| Rubidium | Rb |
| Samarium | Sm |
| Sodium | Na |
| Strontium | Sr |
| Tellurium | Te |
| Terbium | Tb |
| Thulium | Tm |
| Thulium | Tm |
| Tungsten | W |
| Uranium | U |
| Vanadium | V |
| Yttrium | Y |
| Ytterbium | Yb |
| Zirconium | Zr |
| **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.

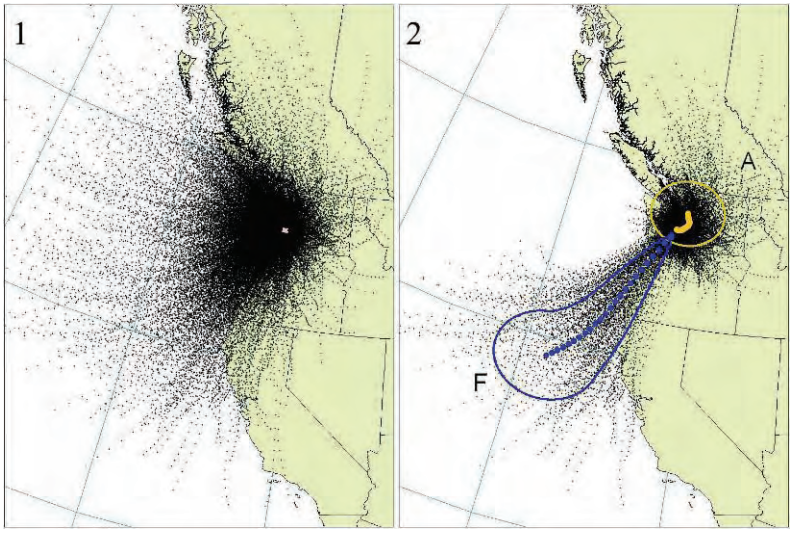



**Figure 3-2. All 2,922 One-Day Back-Trajectories for MORA.** The figure on the left (1) shows 2,922 individual one-day trajectories for MORA. The figure on the right (2) shows cluster means (dots), standard deviations (ellipsoid shapes), and member trajectories for clusters A and F.

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™ bags for organics aliquots were pre-rinsed with ethyl acetate, followed by a 1:1 mixture of hexane and acetone; Teflon™ 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™ 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™ 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™ 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™ 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™ 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™ 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 divinyl-benze 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$^{o}$ 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™ 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°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°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™ 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™ 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).

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

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.

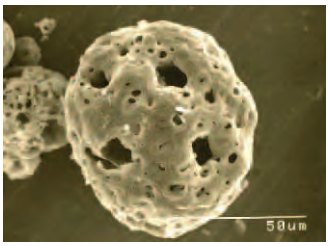



**Figure 3-4. Scanning Electron Micrograph of a Spheroidal Carbonaceous Particle (SCP).** Photo: Neil Rose.

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

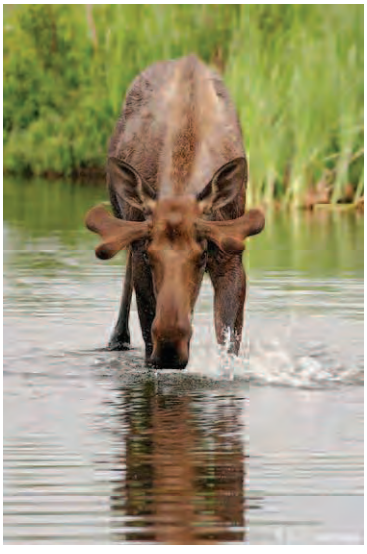
Total mercury was analyzed on a subsample of the whole body homogenate at the WRS Analytical Laboratory with a LECO® AMA254 Mercury Analyzer in accordance with EPA method 7473 (USEPA, 1998). The fish tissue homogenate samples were stored at –6° C, and were allowed to thaw before analysis. The freezing 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

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, sub-sampled, 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 ($^{o}$C), and minimum daily temperature ($^{o}$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 ($^{o}$C), and daily minimum temperature ($^{o}$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 ($^{o}$C), relative humidity (%), dew point temperature ($^{o}$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)
$\beta_0$ = the coefficient for the intercept
$\beta_{1i}$ = the coefficient for the *i*th Park
$\beta_2$ = 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)
$\beta_0$ = the coefficient for the intercept
$\beta_1$ = 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 ($\alpha$), then the probability of Type I error (incorrect rejection of the null hypothesis of equality of means) is guaranteed equal to $\alpha$ 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.