# Western Airborne Contaminants Assessment Project Research Plan

Lone Pine Lake,
Rocky Mountain National Park

*(M. Alisa Mast, USGS-Denver)*


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# WESTERN AIRBORNE CONTAMINANTS ASSESSMENT PROJECT

# RESEARCH PLAN

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# PURPOSE OF THE WACAP RESEARCH PLAN

This research plan is being produced to document the approach that will be followed by the WACAP researchers as they plan, implement, and interpret the WACAP. This plan has been reviewed by an international team of scientific experts (Seattle, December 2003), NPS staff, land managers, and policy makers and revised accordingly. This Final WACAP Research Plan will be published as an EPA Report and will be available to interested parties via a website.

The research plan is organized according to disciplinary (matrix) areas. After the introduction that discusses the rationale and general dimensions of the proposed work, each of the matrices to be sampled is discussed in considerable detail in separate, following sections. We view our approach as one that is interdisciplinary, integrated, and organized to develop an understanding of the problem we are addressing at multiple scales of time and space. We have explained in the individual sections how data from various components of the program will be used to assist in interpreting results across the program. One of the primary criteria for an integrated program is to conduct work in the same locations under a common objective. The WACAP program, as described in this research plan, is designed to meet this criterion.

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Finally, this research plan has been modified from the Draft version based on the Peer Review conducted in Seattle, Washington, December, 2002. We greatly appreciate the time and effort contributed by all peer reviewers: Colin Gray, Environment Canada, Vancouver; Joan Grimalt, Institute of Chemical and Environmental Research, Barcelona; Steve Kahl (chair), University of Maine, Orono; Kathy Tonnessen, National Park Service, Missoula, MT; and James Wiener, University of Wisconsin-La Crosse. Their comments were extremely useful and insightful; this document has been revised based on their comments and their help has resulted in a stronger, more coordinated and more fully explained WACAP program.

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## ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| AMAP | Arctic Monitoring and Assessment Program |
| ARD | Air Resources Division, National Park Service |
| ASE | accelerated solvent extraction |
| CIC | constant input concentration |
| CPO | Cheeka Peak Observatory, Neah Bay, WA |
| CRS | constant rate of supply |
| DENA | Denali National Park |
| DOC | dissolved organic carbon |
| ECNI | electron capture negative ionization |
| EI | electron impact |
| ELISA | enzyme-linked immunosorbant assay |
| EMAP-SW | Environmental Monitoring and Assessment Program- Surface Water |
| EMERGE | European Mountain lake Ecosystems: Regionalisation, diagnostics & socio-economic Evaluation |
| EROD | 7-ethoxyresorufin-O-deethylase |
| GAAR | Gates of the Arctic National Park and Preserve |
| GC | gas chromatograph |
| GC/MS | gas chromatographic mass spectrometry |
| GLAC | Glacier National Park |
| GPC | gel permeation chromatography |
| GPS | global positioning system |
| HCB | hexachlorobenzene |
| HCH | hexachlorocyclohexanes |
| HM | heavy metals |
| ICP-AES | inductively coupled plasma- atomic emission spectrometry |
| ICP-MS | inductively coupled plasma mass spectrometry |
| IMPROVE | Interagency Monitoring of Protected Visual Environments |
| MA | macrophage aggregate |
| MORA | Mount Rainier National Park |

| | |
|---|---|
| MS | mass spectrometry |
| NADP | National Atmospheric Deposition Program |
| NCI | negative chemical ionization |
| NF | National Forest |
| NHEERL | National Health and Environmental Effects Research Laboratory, USEPA |
| NMHC | non-methane hydrocarbons |
| NOAT | Noatak National Preserve |
| NPS | National Park Service |
| OLYM | Olympic National Park |
| OSU | Oregon State University |
| PAH | polycyclic aromatic hydrocarbon |
| PAN | peroxyacetyl nitrate |
| PBDE | polybrominated diphenyl ethers |
| PCB | polychlorinated biphenyls |
| PIs | principal investigators |
| PNW | Pacific Northwest |
| POPs | persistent organic pollutants |
| QA | quality assurance |
| QAPP | Quality Assurance Project Plan |
| QC | quality control |
| RIA | radioimmunoassay |
| RMS | Rocky Mountain Snowpack |
| ROMO | Rocky Mountain National Park |
| SCPs | Spheroidal Carbonaceous Particles |
| SEKI | Sequoia/Kings Canyon National Park |
| SOCs | semi-volatile organic compounds |
| SWE | snow water equivalence |
| UMN | University of Minnesota |
| UMNRAL | University of Minnesota Research Analytical Laboratory |
| USDA | United States Dept. of Agriculture |
| USEPA | United States Environmental Protection Agency |

| | |
|---|---|
| USGS | United States Geological Survey |
| USGS-BRD | United States Geological Survey- Biological Resource Division |
| VOC | volatile organic compound |
| WACAP | Western Airborne Contaminants Assessment Program |
| WBC | white blood cells |
| WED | Western Ecology Division, NHEERL, USEPA, Corvallis, OR |
| WRS | Willamette Research Station (Corvallis EPA Analytical Laboratory) |

# 1.0 INTRODUCTION

*Dixon Landers*

Atmospheric contaminant transport has been recognized as a potential threat to aquatic and terrestrial ecosystems for many decades. However, it was not until the 1970's and 1980's that the potential for significant regional scale ecological impacts of long range transport of contaminants, particularly the acidic precursors of acidic deposition, was recognized (Likens et al., 1979) and later documented across multiple special scales (Linthurst et al., 1986). In this case, the combustion byproducts $SO_2$ and $NO_x$ were demonstrated to be transported thousands of kilometers in the atmosphere where they were deposited via precipitation on sensitive ecosystems that lacked sufficient buffering capacity to neutralize the acid (Galloway and Cowling, 1978). In addition, metals were recognized as another class of contaminants associated with the combustion of fossil fuels that could also be transported great distances in the atmosphere (Galloway et al., 1982) .

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

Recent studies have pointed out the atmospheric linkage between air masses traversing Eurasia and arriving in North America (Welch et al., 1991; Wania and Mackay, 1996; Jaffe et al., 1999). While few studies have measured persistent and bioaccumulating toxics in these air masses, model output suggests that they should contain a variety of contaminants (Perry et al., 1999; Koziol and Pudykiewicz, 2001). Many of the tracers used by air monitors to identify trans-Pacific air masses (i.e. CO, aerosols, $O_3$) are directly related to human activities and combustion sources. However, from an ecological perspective, it is either very complicated or impossible to track these short lived and/or highly reactive tracers through ecosystem compartments.

At present there is ample evidence of regional as well as long-range threats of atmospheric contamination to remote ecosystems to the Western United States, but there is scant evidence from any published source that this threat is realized. One of the major problems is that the atmospheric scientists who have identified the long-range transport across the Pacific Ocean from Eurasia have little information regarding the

deposition of inorganic and organic contaminants in these air masses. One of the few and most convincing publications regarding this issue describes the concentration of POPs in snow sampled in the Canadian Rocky Mountains during the Spring of 1995 and 1996 (Blais et al., 1998). The data in this publication suggests that there is good evidence that high elevation ecosystems are at risk with respect to POPs for two primary reasons: 1) long-range transport of contaminants are possibly being deposited with the annual snow pack and 2) global fractionation of the lighter POPs results in migrations of these and other compounds to the higher (i.e. colder) alpine areas (Wania and Mackay, 1996). Fortuitously, snow was also sampled (Landers, unpublished data) in the Sierra (California) at two different elevations in Spring 1994 using identical methods and analyzed by the same laboratory used by Blais. There is a remarkable fit to the elevational gradients identified by Blais (Figure 1.1) for three of the four contaminants, suggesting that the phenomena described by Blais et al. operate over large spatial and temporal scales and that there is some consistency from year to year. Cold fractionation also appears to function at latitudinal as well as elevational gradients, putting northern ecosystems are risk. A recent publication documents the cold-trapping of POPs by vegetation in mountains in Western Canada (Davidson et al., 2003a).

Certainly there is sufficient evidence to consider the acquisition of additional information with which to evaluate the risk to high elevation ecosystems. These bits and pieces of data derived from various disciplines, published and reported independently, generated considerable concern regarding the risk to western ecosystems, prompting the USEPA to convene the First International Conference on Trans-Pacific Transport of Atmospheric contaminants in Seattle, Washington, in July 2000. This meeting was attended by over 100 experts representing areas of energy, emissions, atmospheric sciences, marine sciences, biological sciences, biogeochemistry, and international environmental policy. This workshop culminated in a consensus statement that was published in *Science* (Wilkening et al., 2000). Three of the conclusions from this conference most pertinent to this undertaking are worth noting here:

- **The nature, magnitude and spatial distribution of effects of airborne chemicals transported in the Pacific region, including changes in variability, are largely unknown.**
- **The chemistry of the troposphere above the Pacific Ocean and of the ocean itself, and contaminant concentrations in terrestrial and aquatic ecosystems, could be significantly impacted due to long-range transport.**
- **Some airborne chemicals, especially organochlorines and mercury, have the potential to enter foodwebs and biomagnify thereby increasing the toxicological risk to top predators, including humans.**

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

At this point, the National Park Service Air Resources Division (Denver, Colorado) became interested in this issue and the risk that might be posed to the many

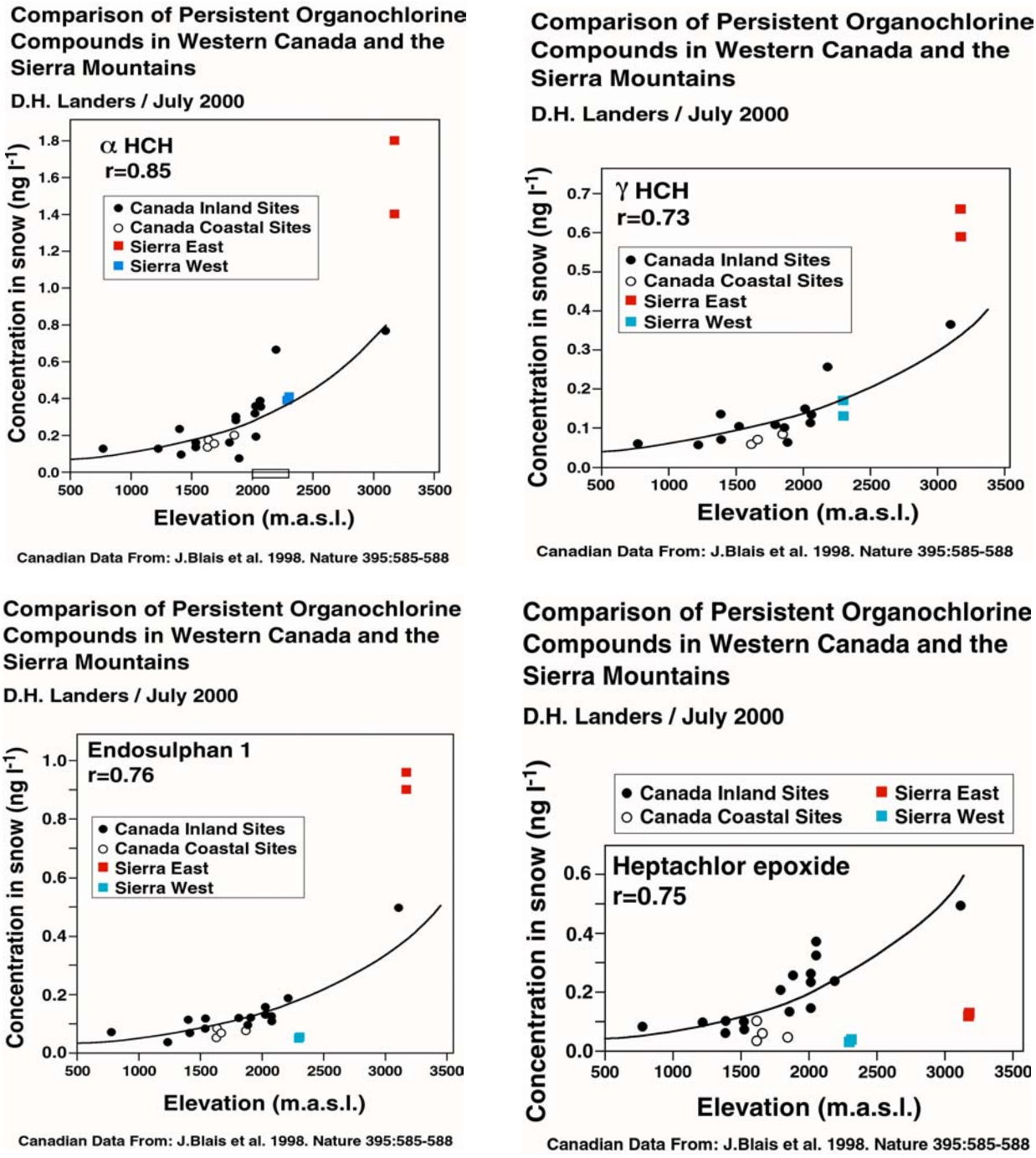



**Figure 1.1 Unpublished data from D. Landers (USEPA) collected in Spring 1994 in the Sierra Nevada (CA) at two different elevations plotted over Blais et al. (1998) data collected in the Canadian Rockies during spring 1995 and 1996. Very similar concentration gradients are observed for three of the four compounds. Only gamma HCH and endosulphan are currently used in the US and Canada. Alpha HCH and heptachlor epoxide may be due to long-range transport.**

National Parks in the Western United States from airborne contaminants. This interest is derived from the legal mandate described in the Organic Act which created the NPS. This federal legislation required protection of the National Parks for perpetuity "…unimpaired for the enjoyment of future generations." The Clean Air Act augmented this responsibility in 1977 by defining specific goals, objectives and mechanisms for protecting air quality related values in major parks and preventing "significant deterioration" of air quality. Not only are the National Parks widely distributed but also many of them possess considerable elevation ranges, possibly predisposing these higher elevation locations to become long term sinks for some classes of contaminants due to their cold alpine climates. Moreover, high latitude National Parks in Alaska and the Arctic are also at risk to become sinks for air pollution given their cold climates and the polluted air masses to which they are exposed.

The Air Resources Division convened two workshops attended by experts in the field in 2001 to evaluate the risk and then to assist in the design of an assessment program that would evaluate the risk posed to the Western National Parks from airborne contaminants. The second workshop developed a draft objective to aid in moving the process forward and a general consensus was reached regarding the objective and approach that should be taken by the NPS to develop information to achieve the objective. Since virtually nothing was known about the contaminant concentrations in any of the parks, an inventory of baseline contaminant conditions across various components of the ecosystem was selected as the approach to be taken. Over the next several months and in communication with a broad range of NPS personnel, the goal of the Western Airborne Contaminant Assessment Program (WACAP) was finalized.

**Goal: TO ASSESS THE DEPOSITION OF AIRBORNE CONTAMINANTS IN WESTERN NATIONAL PARKS, PROVIDING REGIONAL AND LOCAL INFORMATION ON EXPOSURE, ACCUMULATION, IMPACTS, AND PROBABLE SOURCES.**

## *Approach*

The general approach to be followed by the WACAP was largely agreed upon during the July 2001 Seattle workshop convened by the NPS-ARD. During this workshop several conceptual approaches were presented to and discussed with the assembled group of scientists, resource managers and administrators. The consensus of this group was that a spatially diverse, interdisciplinary effort that utilized a mixture of ecological indicators (e.g. sediments, biota, snow, etc.) to assess impacts of metals, POPs and current-use chemicals was desired. "Impacts" in this sense refers to evidence of accumulation in the food web – particularly in animals – and does not go so far as to attempt to establish "effects" such as reproductive or lethal responses. Dr. Dixon Landers assumed the responsibility of refining the design and assembling a group of scientists (principal investigators) with expertise in the required disciplines. Over the next several months these concepts were formed into a design that was, in

turn, presented and discussed among a broad range of NPS personnel resulting in a variety of changes and improvements to the design. As various experts joined the WACAP scientific team at the invitation of ARD, further definition and refinement of specific disciplinary approaches were made. Figure 1.2 is a conceptual diagram of the approach to be used by the WACAP.

In addition, the following specific objectives were identified:

**WACAP Objectives:**

1) **Determine if contaminants are present in Western National Parks.**

2) **If present, determine where contaminants are accumulating (geographically and by elevation).**

3) **If present, determine which contaminants pose a potential ecological threat.**

4) **Determine which indicators appear to be the most useful to address contamination.**

5) **If present, determine the source of the air masses most likely to have transported contaminants to the National Park sites.**

**Park Selection**

One of the most difficult issues addressed was to identify which National Parks should be included in the spatial design. The number of parks that could be included was fixed at six by the estimated budget available for the effort assuming that each park would have two sites. The decision on which parks would be included was made based on the physical locations and characteristics of the parks rather than any other criteria. It was an iterative process to identify indicators of interest, identify the number of sites in each park, set criteria for the attributes of sites within parks, and do this with an eye toward the overall spatial design and budget realities.

It was clear from the outset that a strong spatial design containing enough sites to provide ample statistical power for hypothesis testing was outside the budget and scope of this program. Moreover, given the absolute lack of information of any kind regarding the impacts of airborne contaminants on the systems of interest, it would probably be unwarranted and premature to pursue such a design, even if funding was available. Rather, it was decided that the first question that needed to be answered across large-scale spatial gradients appropriate to the Western National Parks was “is there a problem with respect to airborne contaminants in the Parks?” It was decided that if this policy question could be answered in a rigorous way by WACAP, then future work, if warranted, could be designed to deal with more detailed secondary questions

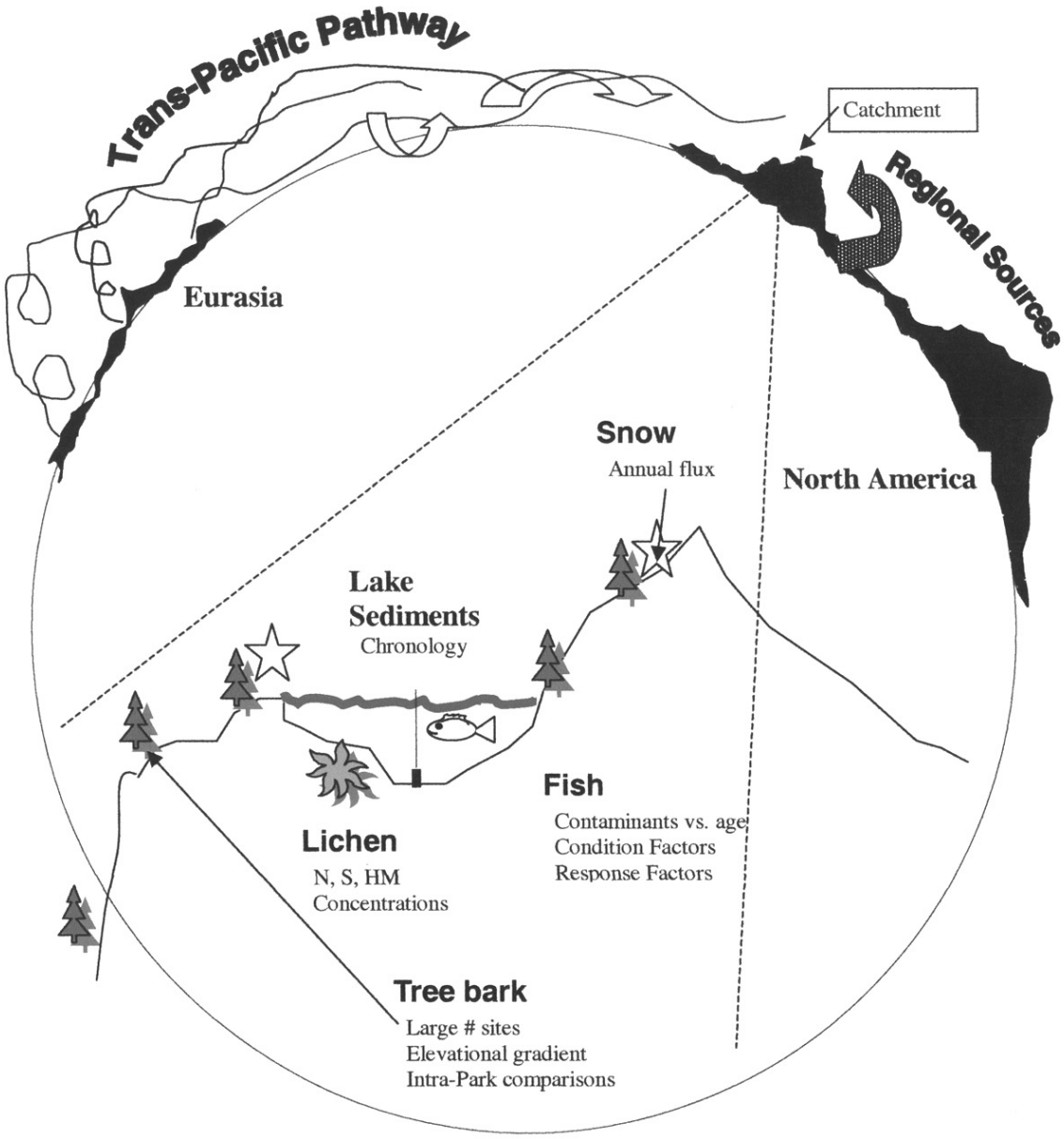



**Figure 1.2 WACAP Conceptual Diagram of Airborne Contaminant Assessment Approach**

such as resolving the various temporal and spatial dimensions of contaminant pathways and defining the suite of ecological effects.

Since trans-Pacific air masses moving generally from West to East impact the West coast of the North American mainland and these air masses are known to impact the US from Alaska to California (Bailey et al., 2000; Husar et al., 2001), we decided to select a series of National Parks from arctic Alaska to California. We wanted to identify

a series of Western National Parks along a North-South latitudinal gradient that could be impacted by air masses moving across the Pacific Ocean. Recognizing, however, that air masses originating in North America are also of potential interest. We also wanted to include some Parks in the "interior" of the Western U.S. that could also be impacted by trans-Pacific air masses but which may also have more of an opportunity to intercept regional air masses. We initially selected four West "Coast" Parks (Noatak, Denali, Olympic, and Sequoia) and two interior Parks (Glacier and Rocky Mountain). Figure 1.3 shows the latitude and elevation ranges for a group of Western National Parks. The Parks with the red bars are those selected for WACAP. Mt. Rainier was added quite recently when additional funds became available. This addition will assist WACAP in identifying risk in the complex Puget Sound area surrounding Seattle. In addition, one of the lakes we selected in the eastern portion of Noatak, actually was found to reside in the adjacent Gates of the Arctic National Park. Therefore, WACAP sites are now selected in eight different National Parks in the Western United States.

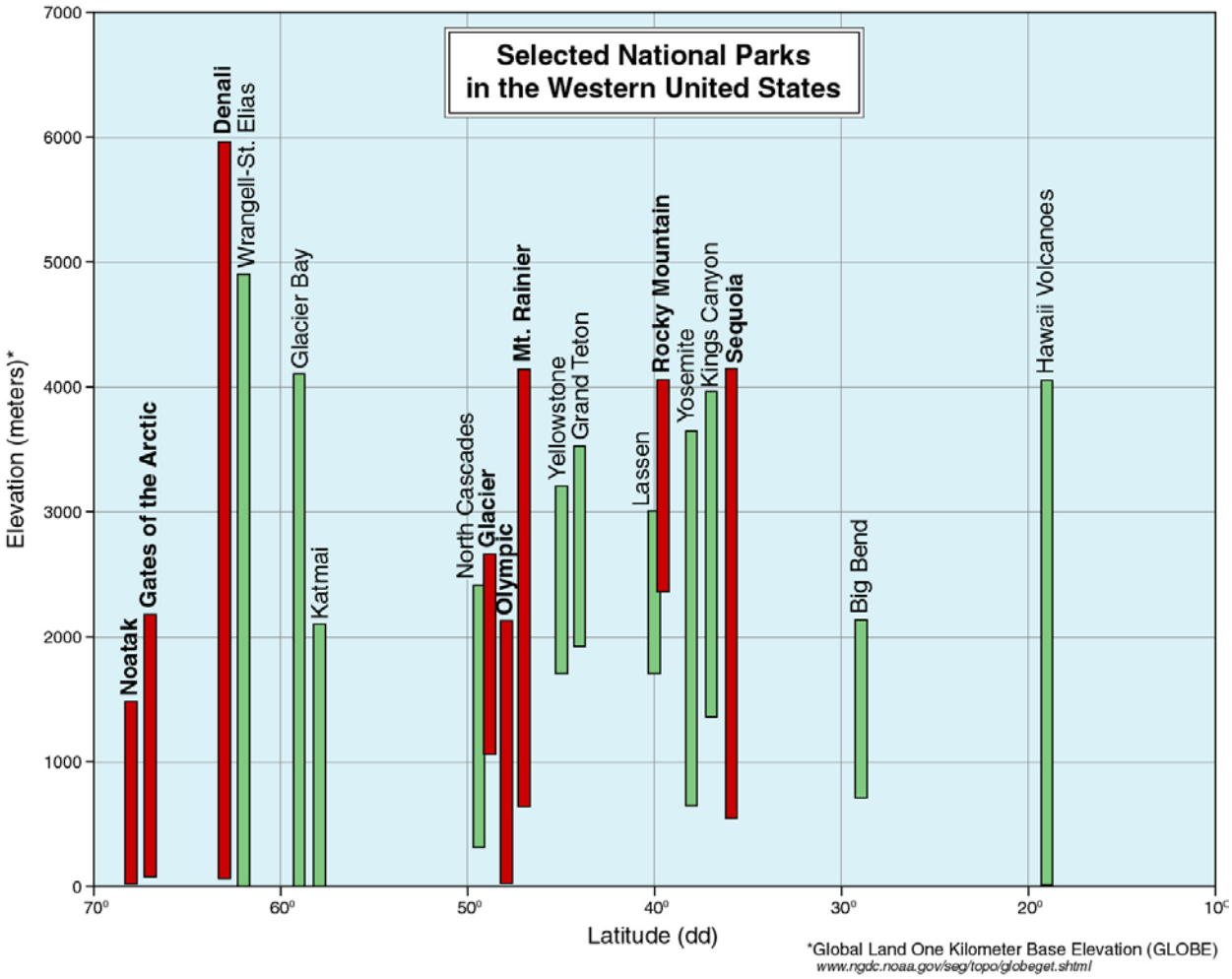
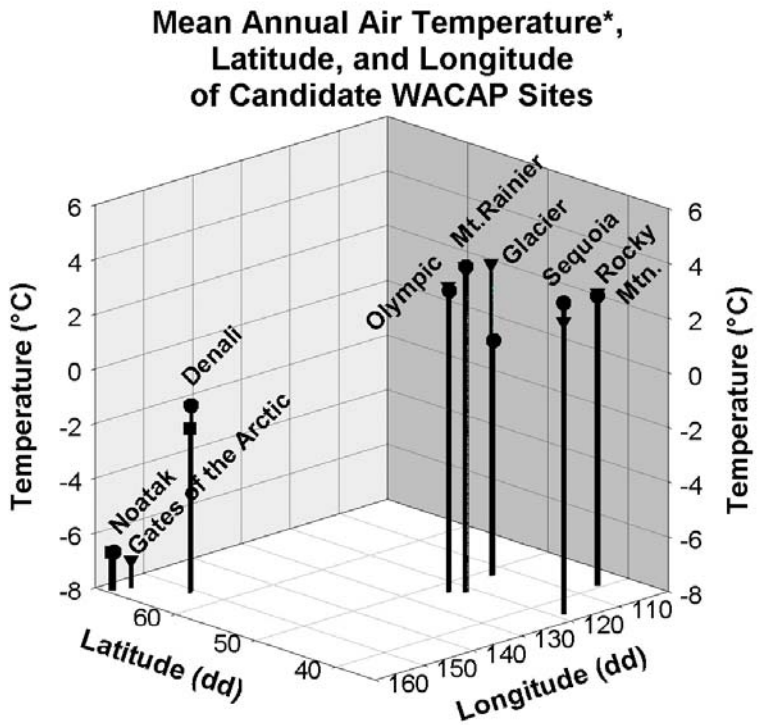



**Figure 1.3 Selected National Parks in the Western US plotted by latitude and showing their minimum and maximum elevations. Parks shown in red bars are those selected for inclusion as core sites for the WACAP.**

The selection of the core set of National Parks provides a group of eight Parks ranging over 30 degrees of latitude with two pairs of parks (one coastal and one interior) rather closely linked at about the same latitude (Olympic and Glacier; Sequoia and Rocky Mountain). This spatial arrangement along with the location of other Western National Parks is shown in Figure 1.4.

The dominant factor influencing the deposition and accumulation of SOCs in the ecosystem is temperature. This influence is especially true for those contaminants that demonstrate cold fractionation. Figure 1.5 depicts the estimated mean annual air temperature at each of the WACAP sites in the eight National Parks. It is useful to note the general agreement in temperature for all of the sites in the conterminous US and that the four sites in Alaska, although lower in elevation, are significantly colder.

**Figure 1.4 Spatial relationships among WACAP selected (i.e. core) National Parks (in red) and other Western National Parks**




*Temperature data was estimated from the nearest and most representative locations with long-term meteorological data. In some cases a small correction was made to account for the difference in altitude between the meteorological and lake site. (D. Jaffe, Univ. of Washington-Bothel)

**Figure 1.5 Relationships among latitude, longitude and mean annual temperature in the eight National Parks and 14 sites to be sampled in WACAP**

## Site Selection

Within each of the core National Parks (with the exception of Noatak and Gates of the Arctic in which only one catchment was selected) we selected two catchments (i.e. sites) that met the following pre-established criteria:

- **Small catchment typical of the types of catchments found in the park in question (elevation, soils, vegetation, aspect, etc.)**
- **Catchment contains a lake (≥ 5 m deep; larger than ~0.8 hectares in surface area)**
- **Lake should contain reproducing fish population (preferably salmonids)**

- **No anadromous fish reach the lake**
- **Lake should be without major inlets or outlets, or glaciers in the catchment**
- **Lake bathymetry is acceptable for sediment core analysis**
- **Safe access is possible by available means in late spring and summer**
- **Gill netting of fish is acceptable**
- **Catchments are located within the seasonally persistent, non-melting snowpack development for the Park**
- **Both catchments located in the same general quadrant within the Park**

There is large variability among candidate catchments within and among parks. Given the large geographic scale of WACAP, several major ecological regions were included in the final selection. We were initially interested in selecting sites within each park that differed by 1000 m or more in elevation in order to examine elevational gradients and their influence on contaminants. We learned that sites with this elevational difference simply do not exist once we began examining catchments meeting our criteria. We also sought to choose catchments that were generally in the same air-shed, whether or not they differed significantly in elevation. Therefore, candidate sites were discussed with Dr. Jaffe (WACAP atmospheric science PI) prior to final selection to ensure that atmospheric transport issues would likely not be problematic. The two exceptions to this strategy are in Rocky Mountain NP and Glacier NP where the selected lakes are at almost the same elevation but on opposite sides of the continental divide. The sites in Glacier NP also differ by about 426 m.

In our final selections of catchments in each Park, the catchments selected represent “elevation duplicates” in the sense that they are located at approximately the same elevation. Table 1.1 summarizes the attributes of the selected catchments/lakes for each core Park. Appendix A contains maps with the locations of the candidate sites in each Park, and Appendix B contains bathymetric maps prepared for two candidate sites in Rocky Mountain NP.

## Indicators and Contaminants

There are a wide variety of possible indicators that could be used to provide information regarding the degree to which airborne contaminants have become entrained in National Park ecosystems. Similarly, there is a large selection of contaminants that could be measured. One of the early WACAP design tasks was to winnow the expansive list of possible indicators as well as contaminants down to a manageable and affordable number. In doing this, we frequently referred back to the goal of WACAP to insure that indicators that we selected fulfilled, collectively, broad and in some cases, multiple, purposes. Moreover, a secondary concern was to select indicators that would compare to other similar ongoing and historic studies (e.g., the EMERGE or European Mountain Lake Ecosystems: Regionalisation Diagnostics &

**Table 1.1 Lake catchments Selected for the WACAP as of March 2003**

| Park | Lake Name | Elevation (m) | Fish Species | Latitude (dec.) | Longitude (dec.) |
|---|---|---|---|---|---|
| Noatak | Burial | 427 | lake trout | 68.43 | 159.18 |
| Gates of the Arctic | Matcharak | 488 | lake trout | 67.75 | 156.21 |
| Denali | Wonder | 610 | lake trout, burbot, arctic char, arctic grayling | 63.48 | 150.88 |
| Denali | McLeod | 609 | unknown | 63.38 | 151.07 |
| Denali | Foraker | 732 | unknown | 63.22 | 151.60 |
| Glacier | Oldman | 2026 | cutthroat trout | 48.50 | 113.46 |
| Glacier | Synder | 1600 | westslope cutthroat trout | 48.62 | 113.79 |
| Olympic | PJ Lake | 1433 | brook trout | 47.95 | 123.42 |
| Olympic | Hoh Lake | 1384 | brook trout | 47.90 | 123.79 |
| Mt. Rainier | Unnamed LP19 | 1372 | rainbow trout | 46.82 | 121.89 |
| Mt. Rainier | Golden | 1372 | rainbow trout | 46.89 | 121.90 |
| Rocky Mt. | Mills | 3030 | rainbow trout | 40.29 | 105.64 |
| Rocky Mt. | Lone Pine | 3024 | brook trout | 40.22 | 105.73 |
| Sequoia | Emerald | 2800 | brook trout | 36.58 | 118.67 |
| Sequoia | Pear | 2904 | brook trout | 36.60 | 118.67 |

Socio-Economic Evaluation Program, see Section 6.0) regarding contaminant impacts in remote alpine and arctic locations. Table 1.2 contains the list of the indicators selected for WACAP and additional information regarding the purpose and approach relating to each one. In each of the following sections devoted to a particular matrix or indicator, additional information is provided regarding the rationale for selection of various types of analyses, technical approaches and explanations regarding how the resulting data will be analyzed and interpreted. There is only a brief section that deals with moose meat (Section 3.4- Subsistence Food Analysis) as this analysis of the

**Table 1.2 Indicators to be used in the WACAP**

| Indicator/Matrix | Frequency | Purpose | Approach |
|---|---|---|---|
| **SNOW** | Annually; 8 Parks (14 sites, plus up to 7 additional elevational transects at snow-only sites in Rocky Mountain NP) | Measure of direct atmospheric contaminant loading and in many cases, ~90% of the annual precipitation | Volumetric "clean" field methods using pre-washed Teflon containers at maximum late Winter/early Spring snowpack development-organic and metals analysis |
| **WATER** | Once per site* | Standard EMAP water sample | System characterization – standard water quality variables |
| | Once per site* | Filtered ~50L water sample collected *in situ* | Hydrophilic "current-use" chemicals and SOCs |
| **LAKE SEDIMENT** | Once per site* | Historic trends (~150 y) of contaminant loading to catchments | Collect sediment cores thru the ice in late spring or summer -Motorized access if possible. Summer collection were required. Date cores and analyze for most SOCs, metals + totHg |
| **FISH** | Once per site* | Direct measure of food web impacts, bioaccumulation and link to the terrestrial component; will look at health and condition | "standard salmonid" fish of up to 5 different age classes linked to the ecosystem<br>Analyze for most SOCs, metals + totHg, and health and condition indices |
| **LICHEN** | Once per site* | Direct measure of food web impacts and bioaccumulation; used to evaluate N, S and heavy metal impacts; | Collected using clean techniques and attempt to use similar species in as many Parks as possible |
| **WILLOW BARK** | Collected Once – FY 2004 or 2005 | Measure of ecosystem exposure, large "n" for statistical comparisons within and among sites, parks and elevations | Bark contains lipids, and thus the ability to accumulate lipophylic SOCs. Collect samples at ~5 elevations within as many parks (e.g. 20) as possible. Analyzed for SOCs. Number of samples ~100 |
| **SUBSISTENCE NATIVE FOOD** | Alaska Only; collected as available from native hunters | Direct measure of food sources (moose) used by native people | Samples provided to specific Parks by native hunters. Analyzed for SOCS and metals. About 20 samples total. |

*2 Parks (4 sites) during the first two years, and 3 Parks (6 sites) during the third year

human component/pathway of the foodweb is being done as a service rather than to meet a specific research objective.

There are three classes of contaminants in which we are especially interested: heavy metals, POPs and current-use chemicals. POPs (persistent organic pollutants) are a sub-set of SOCs (semi-volatile organic compounds) which comprise the broader classification of organic chemicals of interest which includes POPs and current-use chemicals. The primary difference in the more narrowly defined POPs is that they are more persistent in the environment. They are also more widely recognized as a group because of the international attention that they have gained. Heavy metals and SOCs are of interest because they are emitted into the atmosphere by human actions, can be transported in the atmosphere, and have toxic effects on biota. Many of these contaminants can also persist and bioaccumulate in ecosystems. There is scant information available about current-use chemicals. However, many of these compounds are toxic, and can be transported by the atmosphere but are less persistent than POPs. Table 1.3 lists, explicitly, those analytes we will measure under each of these general headings. Again, choices had to be made that maximized our ability to determine the presence of the most likely contaminants while avoiding those that were extremely expensive to analyze. More detailed discussions regarding analytical approaches, detection limits and sample preparation are provided in subsequent sections of the research plan.

**Table 1.3 Contaminants selected for inclusion in WACAP**

| Heavy metals (total values) | POPs (9 of 12 United Nations Environmental Program POPs) | Current-Use Chemicals |
|---|---|---|
| Cadmium<br>Copper<br>Lead<br>Mercury<br>Nickel<br>Vanadium<br>Zinc | Hexachlorobenzene (HCB)*<br>Hexachlorocyclohexanes (HCH, including Lindane)*<br>Chlordanes<br>Nonachlors<br>Heptachlors<br>DDTs/DDEs*<br>Aldrin<br>Dieldrin<br>Endrins<br>Mirex<br>PCBs*<br>PAHs*<br>*Link to EMERGE (see Section 6.0)<br><br>Note: Toxaphene, and polychlorinated dibenzo-*p*-dioxins and furans are not included but we will attempt to analyze some fish samples for toxaphene | Triazine Herbicides (Atrazine, etc.) and degradation products<br>Organophosphorus Pesticides (chlorpyrifos, diazinon, malathion, etc.) and degradation products<br>Dacthal (DCPA)<br>Trifluralin<br>Chlorothalonil<br>Chloroacetanilide Herbicides (Metolachlor, Acetochlor, etc.)<br>Thiocarbamate Herbicides (EPTC (Eptam), Pebulate)<br>Endosulfans<br>Polybrominated diphenyl ethers (pending funding) |

The relationships among WACAP indicators and the broader contaminant pathways, sources, sinks and ecosystem components are depicted in Figure 1.6. This is not an all-inclusive diagram. It includes key WACAP components and some of the components and contaminant pathways that will not be studied. The diagram should assist the unfamiliar reader with some of the complexity that WACAP will be examining and the ecological position and interrelationships among key areas of investigation.

## *Timeline and Implementation*

WACAP is planned as a five-year program commencing in fiscal year (October 1 to September 30) 2002 and continuing through fiscal year 2006. Year one is a pilot year that has been devoted to design, organization, PI funding, and methods development for the program. Some methods development will continue into the first half of fiscal year 2003. Fieldwork and associated laboratory work will be conducted during fiscal years 2003, 2004 and 2005. The last year, 2006, will be devoted to finalizing and publishing a master database, completing a synthesis report for the National Park Service that addresses in considerable detail the objective and primary questions that the NPS is interesting in answering (c.f. end of this section), and continuing to publish results in the peer literature. Table 1.4 depicts the sequencing and timing of field collections to be acquired as part of WACAP.

## *Data Management, Interpretation and Reporting*

Data management will occur at several levels. At the analytical laboratory level sample data will be summarized along with all QA/QC results at the batch level. This data management activity will be guided by the QAPP (Quality Assurance Project Plan). Batches of data will be combined for each matrix/indicator and forwarded to the appropriate PIs. Copies of these data will be maintained by the analytical laboratories and a copy will be sent to the WACAP coordination group at EPA (Corvallis). The coordination group will confirm laboratory QA/QC procedures and will work with each laboratory group to verify and validate the data on a batch-by-batch basis. Their overall objective is to incorporate these data, along with meta data derived from a variety of sources (i.e. reconnaissance, field work, PIs, laboratories, park resources) into a working, integrated database. This database will be completed annually and the annual databases combined into a final master database of the WACAP data during the final year of the program. This final database is intended as a final repository for the work conducted in the WACAP program and will contain all data and associated QA/QC information. This final database will be published as a peer reviewed EPA report and made available to the public. It will also be stored permanently in NPS and USEPA searchable data archival systems.

We envision four levels of reporting for the WACAP data: Individual PI generated professional papers (journal articles, dissertations, theses), synthesis journal articles

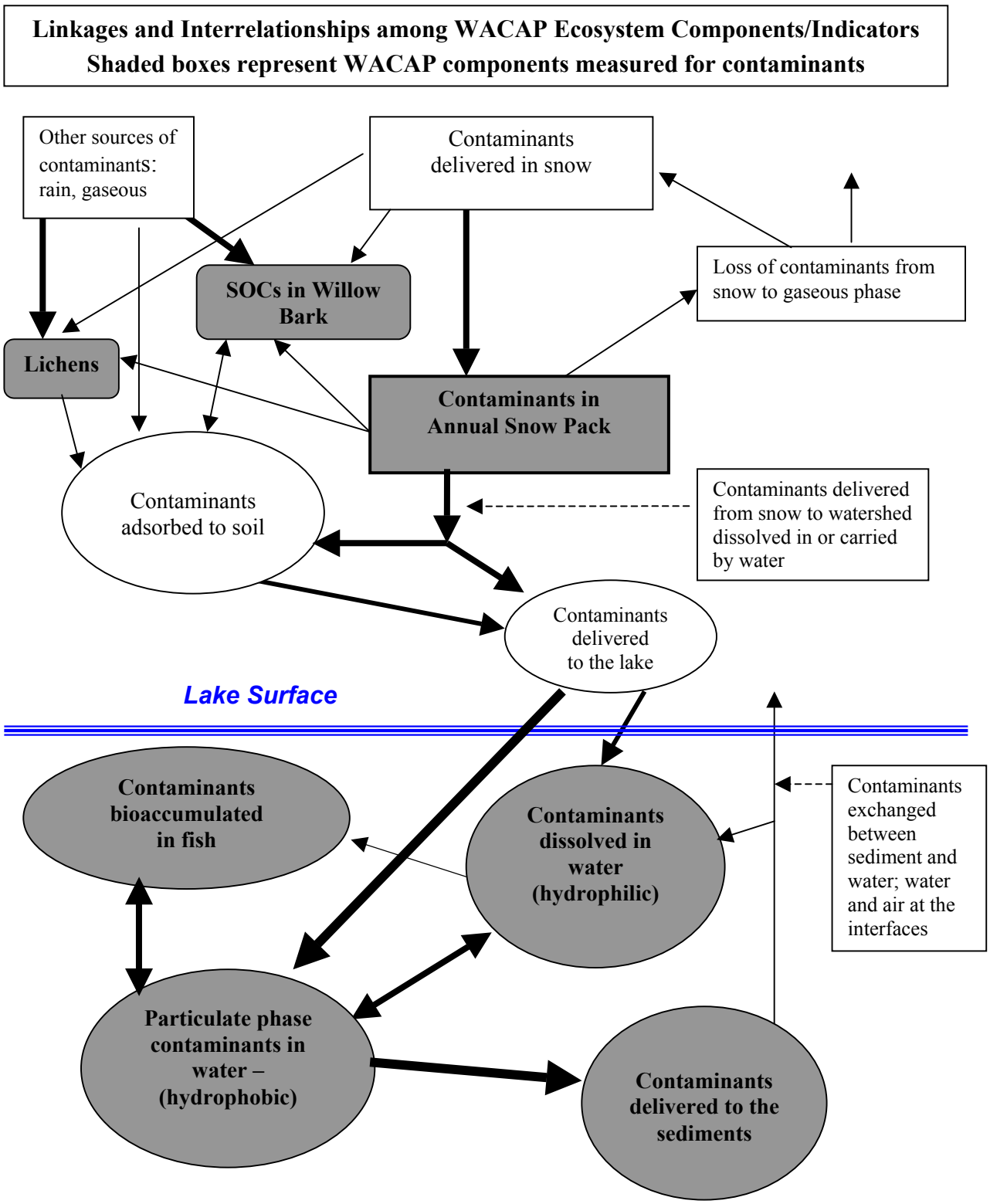



**Figure 1.6 Linkages among major WACAP matrices, ecosystem components, contaminant pools and pathways. Shaded components will be investigated as part of WACAP.**

**Table 1.4 WACAP Timeline and Site Sampling Strategy**

| Year | Activity | |
|---|---|---|
| Year 1 (2002): | Design, organization, funding mechanisms, methods development, written Research Plan, Peer Review | |
| | ***Annual Snow Sampling*** | ***Intensive Study Year (fish, water, sediment, lichens, willow bark, moose)*** |
| Year 2 (2003): | All 8 Parks (14 sites) | Sequoia, Rocky Mountain (4 sites) |
| Year 3 (2004): | All 8 Parks (14 sites) | Noatak, Gates of the Arctic, Denali (4 sites) |
| Year 4 (2005): | All 8 Parks (14 sites) | Olympic, Mt. Rainier, Glacier (6 sites) |
| Year 5 (2006): | Data synthesis, final NPS report, final database, publications | |

prepared by various combinations of PIs, annual information summaries prepared as NPS brochures, and a final report. In addition, PIs will be active in their disciplinary societies by making oral presentations at annual national and international meetings.

## *Coordination within WACAP*

The WACAP scientists are an experienced group who have committed to work in the context of an interdisciplinary, integrated program. Table 1.5 lists the WACAP Science Team. Coordination of such an effort is not a trivial task as it involves multiple laboratories, complex logistics and a need for a common vision. The common vision is largely set forth in this research plan which has been a group effort beginning with an all-PI meeting in Corvallis, OR, in June 2002. At that time the WACAP PIs agreed to the strategy and approaches documented in this research plan and to attending two coordination meetings annually to plan work, discuss results and make interim decisions necessary to conduct a successful program.

Logistic coordination for WACAP is complex in that each National Park is somewhat different than the others, operates independently with regard to administration, internal regulations (i.e. sampling permits, allowable means of access,

## Table 1.5 WACAP Science Team

| Name and Affiliation | Contributed Sections | Email |
|---|---|---|
| **Tamara Blett**<br>NPS-Air Resources Division<br>12795 W. Alameda Parkway<br>Lakewood, CO 80228 | Section 1.0 (Introduction) | Tamara_Blett@nps.gov |
| **Donald H. Campbell***<br>**George P. Ingersoll**<br>**M. Alisa Mast**<br>U.S. Geological Survey, MS 415 Denver Federal Center, Denver, CO 80225 | Section 2.0 (Contaminants in Snow) | dhcampbe@usgs.gov |
| **Marilyn Morrison Erway**<br>Dynamac Corp.<br>c/o U.S.EPA, NHEERL<br>Western Ecology Division<br>200 SW 35th St., Corvallis, OR 97333 | Section 4.1 (Water Quality Information)<br>Section 9.0 (Database)<br>Section 10.0 (Quality Assurance) | Erway.Marilyn@epa.gov |
| **Linda Geiser***<br>USDA-FS, PNW Region Air Resource Management Program, P.O. Box 1148<br>Corvallis, OR 97339<br><br>**Peter Neitlich**, NPS,<br>Forest Inventory and Analysis Program | Section 3.2 (Lichens) | lgeiser@fs.fed.us |
| **Daniel Jaffe***<br>University of WA-Bothell, 18115 Campus Way NE, Bothell, WA 98011<br><br>**Lyatt Jaeglé**<br>Dept. of Atm.Sciences, U. of Washington<br>Seattle, WA | Section 8.0 (Atmospheric Analysis) | djaffe@u.washington.edu |
| **Michael Kent**<br>Dept. of Microbiology<br>Oregon State Univ., Corvallis, OR 97331<br><br>**Carl Schreck**<br>Oregon Cooperative Fish and Wildlife Research Unit, USGS-BRD, 104 Nash Hall<br>Oregon State Univ., Corvallis, OR 97331 | Section 3.1 (Fish) | Michael.Kent@orst.edu<br><br>Carl.Schreck@orst.edu |
| **Dixon Landers**<br>U.S. EPA, NHEERL, Western Ecology Division<br>200 SW 35th Street<br>Corvallis, OR 97333 | Section 1.0 (Introduction)<br>Section 5.0 (Sediment) | Landers.Dixon@epa.gov |
| **Staci Simonich**<br>Dept. of Env. and Molecular Toxicology<br>Dept. of Chemistry<br>1141 Ag and Life Sciences<br>Oregon State Univ., Corvallis, OR 97331 | Section 3.3 (Willow Bark)<br>Section 3.4 (Subsistence Food Analysis)<br>Section 4.2 (In Situ Large Volume Water Sampler)<br>Section 6.0 (Organic Analysis)<br>Section 7.0 (Heavy Metals Analysis) | staci.simonich@orst.edu |
| **Howard E. Taylor**<br>U. S. Geological Survey<br>3215 Marine St., Suite E-127<br>Boulder, CO 80303 | Section 7.0 (Heavy Metals, elemental analysis and interpretation) | hetaylor@usgs.gov |

* lead PI

etc.), and has a unique set of resource managers and specialists with which WACAP must effectively coordinate. WACAP has established a logistics coordinator, Marilyn Erway (Dynamac, Inc.), located at EPA (Corvallis) who has the responsibility of working with the individual Parks and each PI to effectively accommodate WACAP needs while achieving a smooth and satisfactory interface with park personnel and procedures. This system was implemented during summer 2002 when several different PIs visited many of the Parks for various reconnaissance purposes during the pilot year.

## *External Coordination*

It is imperative that WACAP objectives, approaches and findings are coordinated and communicated with other related programs in North America and elsewhere in the world. At the outset of WACAP, we are interested in this coordination to ensure that our approaches are linked via indicators and analytes with other programs so that comparisons can be appropriately made. Later, as we interpret our own data it would be invaluable for us to discuss findings and interpretations with other researchers in North America and elsewhere to maximize the value of the information we will develop. Such coordination should serve to advance scientific knowledge and understanding at a much larger scale than any one group could accomplish independently.

We have already begun this effort in the summer of 2002 by discussing our ideas for WACAP with Canadian researchers involved with similar work in British Columbia. This objective was further advanced when Dr. Landers presented the WACAP program to a mix of Canadian scientists and managers for Parks Canada at a meeting (Ecological and Earth Sciences in Mountain Areas) in Banff, Alberta, in September 2002. Similarly, WACAP researchers are keenly aware of the European EMERGE Program that involves multiple countries and a variety of researchers. We desire to continue our interaction with this group by formal and informal means.

In this regard, we have already established the foundation for official collaboration with Dr. Neil Rose, a member of the EMERGE scientific team with expertise in spheroidal carbonaceous particles (SCPs) as indicators of toxic pollutants in remote lakes (Rose et al., 1994; Rose et al., 1996). Dr. Rose plans to analyze sediment samples from WACAP for SCPs and will assist with sediment sampling in 2004. He is currently seeking funding in England to support this work. Finally, Drs. Simonich and Landers convened a scientific session at the Salt Lake City meeting of the Society of Environmental Toxicology and Chemistry (SETAC) in November 2002 on the topic of Atmospheric Fate Processes (long title: Atmospheric Transport and Deposition of Pollutants to Western North America). This session highlighted presentations by WACAP scientists and other well-known researchers from throughout North America. We intend to maintain and increase our interactions in the future with other researchers in a variety of disciplines and research programs related to the WACAP in order to maximize our understanding of the complex contaminant issues with which we are dealing.

## *WACAP Direction and Funding*

The WACAP is administered and funded primarily by the Air Resources Division of the National Park Service, directed by Ms. Christine Shaver, in Denver, Colorado. Funding is derived from a variety of sources within the ARD and the NPS that vary among funding cycles. In this context, interagency agreements between the NPS and the United States Geological Survey (USGS) and the United States Environmental Protection Agency (USEPA) supplement funding with in-kind services provided by these other federal agencies. In addition, several PIs have sought and received funding from a variety of sources external to the NPS to supplement funding that they receive from the ARD/NPS. These funds have been targeted to support graduate students, provide research equipment and to provide supplemental technical support. The USGS has contributed additional funding for the snow contaminants work. The success of the WACAP depends upon continued funding from the NPS and its collaborators at sufficient annual levels to support the core WACAP efforts described in this research plan. Figure 1.7 depicts the organizational structure of WACAP.

The Technical Director of WACAP is Dr. Landers who is a Senior Research Environmental Scientist with the USEPA, National Health and Environmental Effects Research Laboratory, Western Ecology Division in Corvallis, Oregon. He works closely with Ms. Tamara Blett, Resource Specialist with ARD to administer the program and determine overall technical direction. Future technical decisions for WACAP will be made after discussions among the various WACAP PIs in order to maximize activities in support of the WACAP objective and in recognition of available funding.

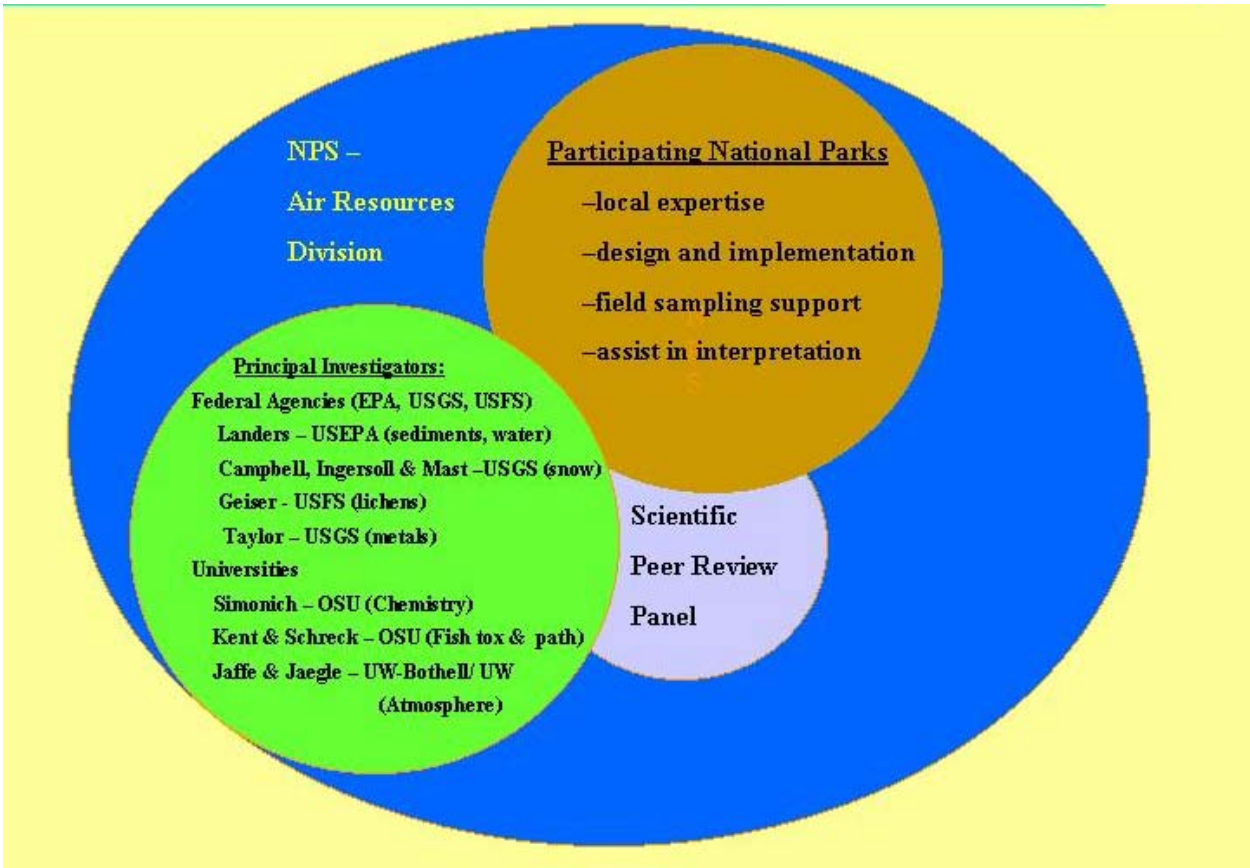



**Figure 1.7 Relationships among WACAP, the participating Federal Agencies, other cooperating institutions, and participating personnel**

# 2.0 CONTAMINANTS IN SNOW

*Donald Campbell*
*George Ingersoll*
*M. Alisa Mast*

## *Introduction*

Snowfall provides 50 to 90 percent of annual precipitation in high altitude and high latitude areas of the Western United States. In many of these areas, seasonal snowpacks that accumulate during the fall, winter, and spring contain an integrated record of chemicals deposited during the snow-covered season. One method for sampling these accumulated chemicals is collection of a full-depth column of the snowpack near the time of maximum snow accumulation, but before melt begins (Ingersoll et al., 2002) . This single sample provides a cost-efficient method for determining 50-90% of annual atmospheric deposition inputs to these types of ecosystems.

Over the past decade, the U.S.Geological Survey (USGS) has used this technique to establish the most extensive monitoring network of its kind in the U.S.: the Rocky Mountain Snowpack (RMS) Chemistry Synoptic. The network includes more than 50 sampling sites along the Continental Divide from New Mexico to Montana that have been sampled each year since 1993. Snowpack samples are analyzed for major ions, nutrients, trace elements, mercury, dissolved organic carbon (DOC), isotopes of sulfur and nitrogen, and organic contaminants.

Techniques have been developed using robust tracers to separate and quantify local and regional sources of atmospheric deposition of airborne pollutants (Mast et al., 2001b; Turk et al., 2001; Campbell et al., 2002; Clow et al., 2002). These data can be used for estimation of background levels of atmospheric deposition, identification of elevated chemical concentrations at specific locations, and detection of temporal trends in atmospheric deposition. Isotopic tracers of nitrogen and sulfur also have been used to aid in distinguishing between local and regional sources of atmospheric pollutants. Because the network provides data on atmospheric deposition at a relatively fine spatial resolution, with documented quality assurance and consistent methodology, the data have been used in policy and regulatory decisions regarding air-quality-related values in federally protected Class 1 National Parks and National Forest Wilderness Areas. This expertise in using snowpack sampling to determine atmospheric deposition is now being applied to toxic compounds as well. Total mercury was added to the suite of constituents analyzed in 2002. A NPS-USGS Partnership project is also examining current-use pesticides and POPs at a subset of sites in Rocky Mountain and Glacier National Parks.

A major unknown in estimating atmospheric deposition of mercury and organic pollutants is the stability of these compounds in the snowpack. Inorganic pollutants are generally quite stable in the snowpack throughout winter months. Semi-volatile

compounds such as mercury and organic pollutants are more likely to exchange between the snowpack and the atmosphere or soil. Because the snowpack sample is collected just before contaminants enter the ecosystem during melt, it may provide a more ecologically relevant measurement of winter deposition than precipitation samples that are collected on a more frequent basis. However, if contaminants in vapor phase exchange between the snowpack and the soil, snow samples may not accurately represent winter deposition. Processes that affect snowpack concentrations of volatile contaminants are poorly understood and likely vary depending on climate and ecosystem characteristics. Snowpack sampling provides a cost-efficient approach to evaluate spatial variability in atmospheric deposition of semi-volatile contaminants, and ongoing research by WACAP investigators and others will provide better understanding of how well snowpack samples represent total atmospheric deposition to high-elevation and high-latitude ecosystems.

**Mercury in Deposition**

The Mercury Deposition Network (MDN) (Figure 2.1) provides a consistent nationwide dataset for mercury in wetfall, but there are few sites located in remote locations at high elevation or latitude. In fact, the only site at high elevation and similar to deposition-sensitive sites in parks is Buffalo Pass, Colorado (3234 m), about 100 km west of Rocky Mountain National Park. Annual mercury deposition at Buffalo Pass is comparable in magnitude to sites in the upper Midwestern U.S. where fish consumption advisories for mercury are common. The volume-weighted mean concentration of mercury at the Buffalo Pass MDN site was 7.9 ng/L in 2000, with the highest concentrations occurring during summer weeks. The snowpack concentration of mercury at Buffalo Pass was 4.2 ng/L in 2002. Whether mercury deposition at Buffalo Pass is typical of high-elevation sites in the Western U.S. is unknown. In the 2002 RMS samples, total mercury concentrations at most sites ranged from 2 to 10 ng/L. For comparison, mercury concentrations in glacial ice core sections collected in Wyoming had total mercury concentrations of 10-15 ng/L during recent years (Schuster et al., 2002). Total mercury concentrations in snow collected on the north slope of Alaska ranged from 1 to 7 ng/L (Snyder-Conn et al., 1997).

Separation of the particulate and dissolved fractions of mercury on a subset of the RMS samples indicated that most of the mercury in the snowpack is associated with particulates, and whole-water mercury concentrations were positively correlated with particulate organic carbon concentrations. Fluxes of mercury between the snowpack and the atmosphere may help to explain the difference between measurements of mercury in wet deposition and measurements in the spring snowpack. In the arctic, large fluxes of mercury from the atmosphere to the snowpack during and after polar sunrise are well-documented (Barrie and Platt, 1997; Schroeder et al., 1998); however, recent studies indicate that subsequent fluxes from the snowpack back to the atmosphere may lessen the net effect of atmospheric mercury depletion events in polar regions (Steffen et al., 2002). Similarly, in temperate regions photoreduction of mercury and flux of gaseous mercury from the snowpack to the atmosphere may substantially

reduce net deposition of mercury (Lalonde et al., 2002). Because fluxes of mercury from the snowpack to the atmosphere are dependent on photoreduction of mercury in the snowpack, concentrations of snowpack mercury may be spatially heterogenous on relatively small scales, as slope and aspect strongly affect incident solar radiation in mountain terrain. These processes are likely to affect other atmospheric deposition of other semivolatile contaminants such as organic compounds as well.

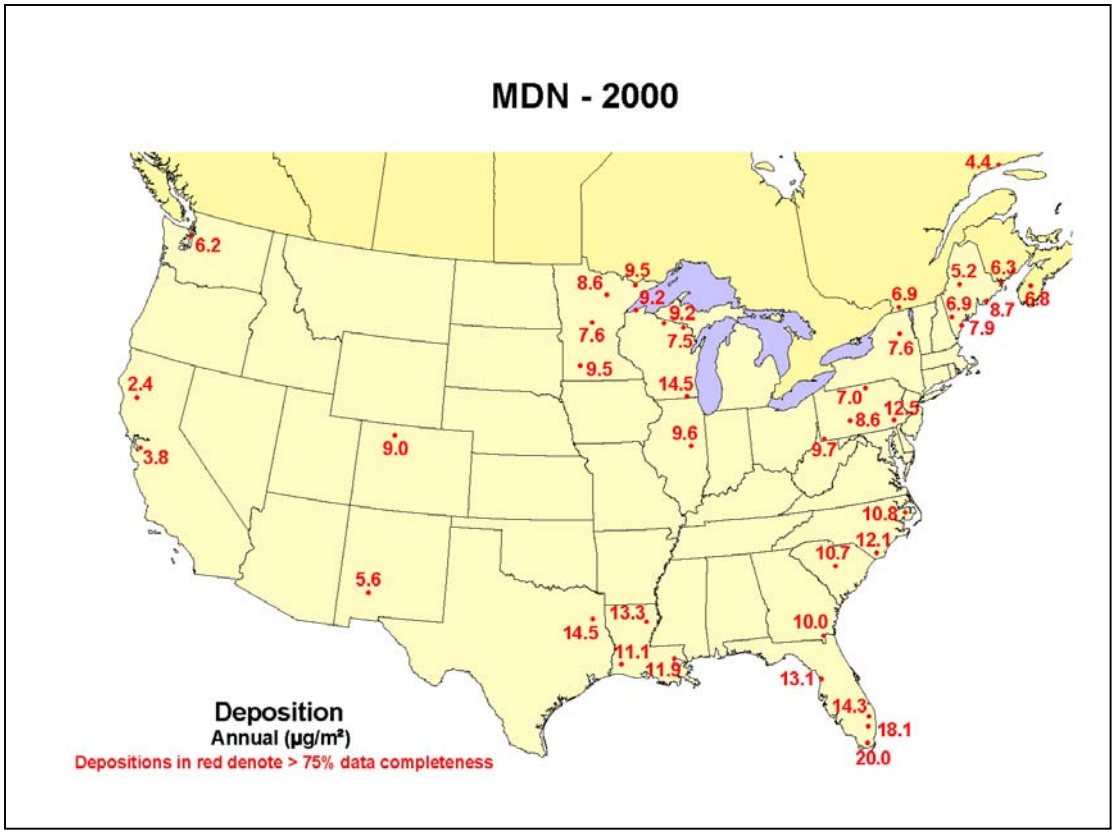



**Figure 2.1 Mercury Deposition Network**

## Organic Compounds in Deposition

One major category of organic pollutants is semivolatile organochlorine compounds, which includes PCB's, and insecticides such as HCH, DDT, aldrin, and toxaphene (Majewski and Capel, 1995). Although usage of most of these compounds ceased in the United States in the 1970's or 1980's, they are still detected in the environment because of their resistance to natural degradation processes and because some are used in other parts of the world (Majewski and Capel, 1995). Several factors including climate warming, increased UV, temperature-dependent volatility, and greater

accumulation in cold regions appear to be enhancing the movement of organochlorine pollutants from warm regions to high altitudes and latitudes (Schindler, 1999). Organochlorine compounds recently were detected in high-elevation snowpacks in British Columbia and Alberta, Canada (Blais et al., 1998), where concentrations were found to increase with increasing elevation. This pattern is likely caused by the effects of global fractionation, a process which causes semivolatile organic compounds used at warmer temperate latitudes to accumulate at cooler northern latitudes (Simonich and Hites, 1995a; Blais et al., 1998). Similar results have been reported in the Sierra Nevada where concentrations of POPs in snow appeared to increase with increasing elevation (Landers et al., 2000, also see Section 1.0, Figure 1.1). Based on these results, it has been suggested that high-elevation ecosystems in temperate mountains, such as the Rocky Mountains, Cascades, and Sierra Nevada, may be particularly susceptible to organochlorine accumulation because they have low annual air temperatures, relatively high rates of precipitation, and are close to agricultural and urban contaminant sources. Other studies reported elevated concentrations of a class of less volatile (and more toxic) organochlorine compounds in precipitation, lake sediment, and fish tissue in mountainous areas of Europe (Grimalt and Berdie, 2000; Carrera et al., 2002). The authors hypothesized that low annual air temperature at high elevations was causing selective accumulation of organic pollutants in these temperate mountain areas.

Although the widespread occurrence of organochlorine compounds in the environment has been documented, much less is known about the occurrence and persistence of current-use pesticides, particularly in areas believed to be relatively unaffected by anthropogenic pollutants. Organophosphorate insecticides, which account for about 65 percent of pesticide usage in the United States, are not as environmentally persistent as the organochlorine compounds (Majewski and Capel, 1995) and thus, may not be as easily accumulated in high-elevation ecosystems. Other important classes of current-use pesticides include triazine and acetanilide herbicides, which account for about 50 percent of total herbicide usage in the U.S. (Majewski and Capel, 1995). Several of these compounds, such as atrazine and alachlor, have been detected in rain throughout the U.S., including one high-elevation site in Rocky Mountain National Park (Goolsby et al., 1995). In another study, current-use pesticides were detected in rain and snow samples collected in Sequoia National Park (McConnell et al., 1998). In the Sequoia study, atmospheric transport of pesticides from the Central Valley of California, an area with intense pesticide-use, was implicated as the most likely source of the pesticides.

## *Objectives*

Snowpack sampling will address the following overarching objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**

**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**

Snow water equivalent and snowpack concentrations of various contaminants will provide an index of current levels of deposition of those contaminants and will provide a snapshot of spatial variability in winter deposition to cold ecosystems in national parks of the Western United States, and will be the primary way in which spatial variability of contaminant deposition will be evaluated and quantified. Winter deposition of mercury and organic contaminants may be greater in high elevation and high latitude snowpacks than in those at lower elevations and latitudes. Patterns of contaminant deposition will be used to infer processes of atmospheric transport, atmospheric deposition, transformations in the snowpack, and loading to the ecosystem.

**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

Contaminant deposition in the snowpack should be related to contaminant levels in air, lake water, lake sediments, and biotic matrices, thereby linking ecosystem impacts to airborne contaminant pathways and the history of contaminant loading to the catchment.

**WACAP Obj. 5) If present, determine the source of the air masses most likely to have transported contaminants to the National Park sites.**

Contaminant signals (including ratios of individual contaminants) from local sources should be distinguishable from those that that can be attributed to long-distance transport (e.g. trans-Pacific air masses). Local contaminant source signals should be highest where atmospheric modeling indicates contaminant emissions in air-mass source areas.

## *Approach*

Snow will be sampled at two sites in each park during each year of the study. These sites will be located in or near the watersheds of the lakes selected for water, sediment, and biological sampling. Additional snow samples will be collected to evaluate environmental factors affecting deposition of contaminants to snow. These would be collected opportunistically rather than in every park every year. Elevational transects will be sampled when the seasonal snowpack extends over a wide range of elevation with accessible sites. Multiple snowpits within a single watershed will be sampled to evaluate the effects of snow temperature, solar radiation, and organic matter content in the snowpack on contaminant accumulation.

Snow samples will be collected by USGS with assistance from the NPS and other WACAP partners. Access to the sites will be by helicopter, snowmobile, skiing, snowshoeing, hiking, pack animals, or a combination of these techniques. Two sub-samples will be collected from each snowpit: one inorganic sample for analysis of major

ions, nutrients, dissolved organic carbon, trace metals, mercury, and particulate matter; and one organic sample for analysis of organic contaminants (Figure 2.2).

### Site Selection

Because no construction of permanent structures is necessary for sampling seasonal snowpacks, locations may be selected in the most optimal locations without permanently affecting wild areas in National Parks. The only disturbance at sampling sites is the digging of a small snowpit, which is backfilled after sample collection. Wind and snowfall events usually restore smooth, untracked snowscapes soon after sampling visits. Sampling locations are selected that are free from avalanche activity and reasonably accessible to sampling crews.

Samples are collected in small clearings or open areas on cooler, north-facing slopes. Snow cover should be uniform and free of human effects or other disturbances such as excessive tree litter or animal activity. The snow profile is inspected for visible contaminants. Scoured or drifted snowscapes are avoided because such areas may not be representative of the cumulative seasonal snowpack from all snowfall events. Sites are located at least 200 m away from potential local sources of contamination such as roadways, snowmobile trails, or aircraft landing zones.

During some years, the maritime climate in some of the parks may cause midwinter snowmelt or rain-on-snow events that wash accumulated contaminants out of the snowpack at lower-elevation sites. The potential for wash-out will be evaluated before each year's sampling by examining meteorologic and snowpack data from nearby sites, and consulting local experts such as NPS backcountry rangers and snow hydrologists at the Natural Resources Conservation Service (NRCS). Safety of field crews will also be a consideration, especially with respect to avalanche, snow, weather, and trail conditions. When necessary, alternate sites for snow sampling will be chosen. Ideally, these sites would be near the lake watersheds, and on the same side of major mountain ranges, but at higher elevations where snow is likely to be colder. It is expected that snowpack at the alternate sites will adequately represent deposition to WACAP watersheds, but that will be evaluated by sampling both the alternate and watershed sites in years when the intact seasonal snowpack extends over a wide elevation range.

When possible, snow-sampling sites are located near snow-telemetry (SnoTel) instrument sites operated by Natural Resources Conservation Service for daily measurement of snow-water equivalence (SWE) throughout the Western United States. SnoTel sites also report other meteorological information useful in choosing sampling locations for the study, including depths, total annual snowfall accumulations, air temperature, and total precipitation (Western Regional Climate Center, 2001).

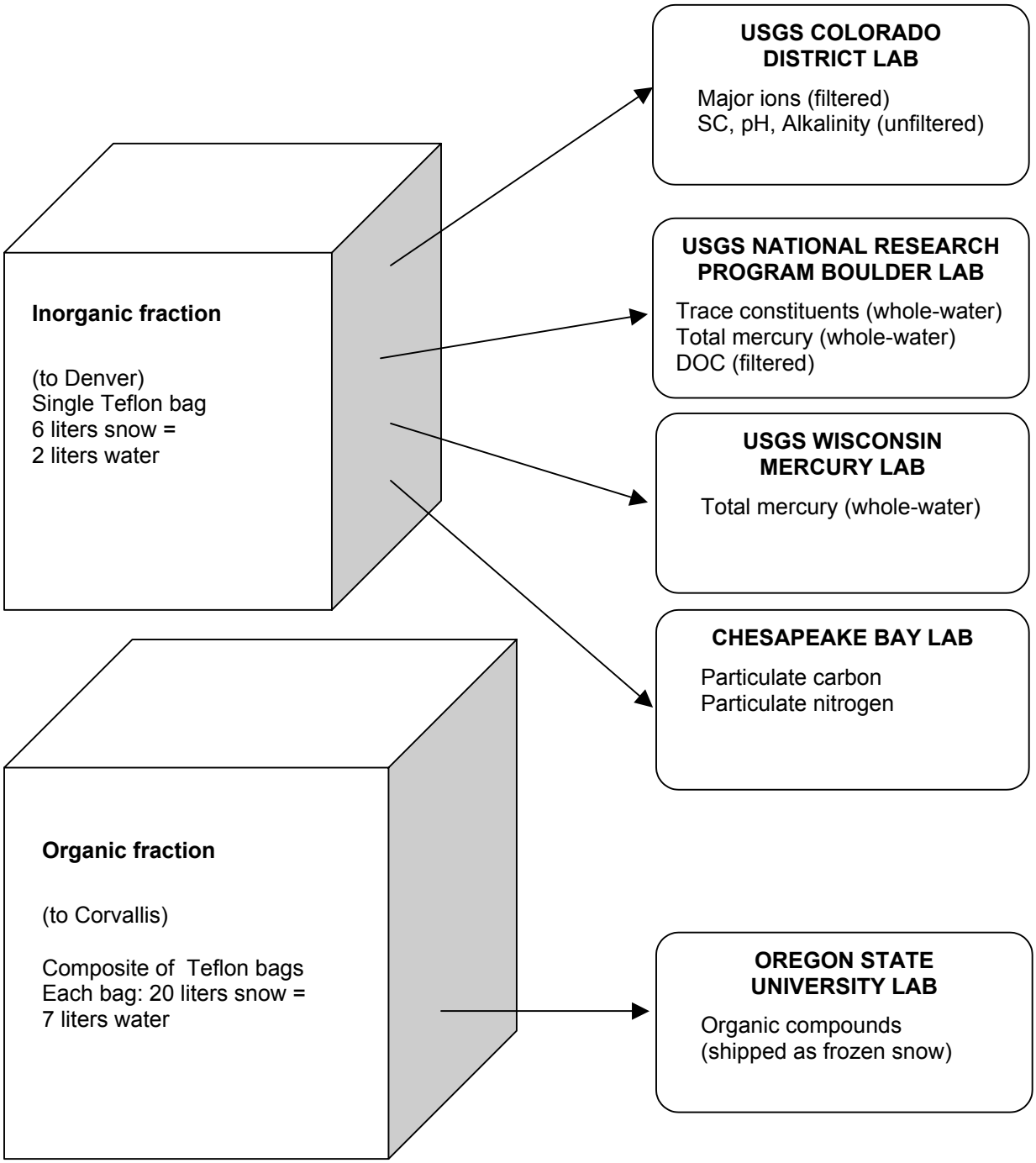



**Figure 2.2 Snow sample flow diagram**

## Timing of Sample Collection

Sampling is done near the time of annual maximum snow accumulation but before the onset of spring snowmelt. Timing of maximum accumulation at the sampling site is determined by averaging maximum SWE values over 30 years from nearby SnoTel sites at similar elevations. Sampling dates are scheduled 2 or 3 weeks before the average maximum date in order to ensure that samples are collected prior to episodes of early snowmelt. Waiting to capture additional snowfall from a few end-of-season storms is not worth risking loss of part of the seasonal pack to snowmelt. Obtaining snow samples before melt begins is crucial to preserving the chemical record of the snowpack because the liquid water flowing downward through the snowpack in early stages of snowmelt tends to be more concentrated compared to snowmelt occurring later in the melting process.

## Sample Vessel Preparation

Each sample for inorganic analyses will be collected in an 8-liter Teflon bag that will contain approximately 6 liters of snow, yielding about 2 liters of meltwater. Sample bags will be prerinsed three times with de-ionized water, placed in polyethylene bags, and frozen until use.

Each sample for organic analyses will consist of six 24"x24" Teflon bags to contain approximately 150 liters of snow, yielding about 50 liters of meltwater. The bags will be pre-cleaned according the protocols developed for pesticide sampling for the USGS NAWQA program (Sandstrom, 1995). All bags are washed in warm soapy water (liquinox) then rinsed several times with tap water to remove all soap, followed by three rinses with de-ionized water. The washed bags are then rinsed with hexane: acetone to remove non-polar compounds and ethyl acetate to remove polar compounds. Each Teflon bag is air dried, folded, double-bagged in clean zip-lock polyethylene bags, and stored in a chemical-free freezer.

## Methods of Sample Collection

Snowpits are prepared with a smooth, freshly cut, shaded face extending from the surface of the snow to the ground (Figure 2.3). Prior to sampling, snow temperature is measured at 10- or 20-centimeter (cm) intervals to ensure that the snowpack is below freezing.

Snow-crystal size, type, and hardness of all homogeneous layers are recorded to document snow metamorphism through the winter. Observations of ice layers, evidence of melt, saturated wet snow, and soil moisture beneath the snowpack are recorded. Snow density is measured at 10-20 cm intervals in order to calculate snow water equivalent.

**Figure 2.3 Snowpit physical profile and sampling for organic compounds**

During sampling, a vertical column of snow is cut from the pit face and placed in the Teflon bag. The vertical column integrates snow that accumulated throughout the season. Snow samples are collected carefully to prevent contamination. The top 5 and bottom 10 cm of snow from the pit face are excluded from the sample to reduce the possibility for contamination. Powder-free vinyl gloves are worn, and clean shovels and scoops are used during sampling. Pre-cleaned polycarbonate shovels and scoops are used for inorganic samples; pre-cleaned aluminum and/or stainless steel shovels and scoops are used for organic samples.

The snow columns are cut and sealed in Teflon bags, which are placed in clean polyethylene bags for protection. Teflon bags containing organic samples are separated from the polypropylene by an additional wrapping of aluminum foil. Samples are frozen on dry ice to prevent chemical reactivity during transport and shipping.

The sample for inorganic analyses is shipped to Denver where it is stored at –10°C until processed by USGS. The sample for organic analyses is shipped frozen from field sites to Oregon State University for storage, processing, and analysis.

### Analytical Methods for Major Ions and Nutrients

Snow samples for inorganic analyses are melted in the Teflon collection bags and processed within 12 hours of being removed from the freezer. Major cation

concentrations [calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), sodium ($Na^{+}$), and potassium ($K^{+}$)] are determined on filtered (0.45 μm), acidified aliquots using inductively coupled plasma spectroscopy. Ammonium ($NH_4^{+}$), nitrate ($NO_3^{-}$), chloride ($Cl^{-}$), and sulfate ($SO_4^{2-}$) concentrations are determined within 2 weeks of melting on filtered (0.45 μm) chilled aliquots by ion chromatography. Detection limits are better than 0.5 μeq/L for all major ions. Specific conductance, pH, and alkalinity are determined on unfiltered, chilled aliquots: specific conductance is measured with a platinum electrode; pH is measured with a combination glass electrode designed for low-ionic strength waters; and alkalinity is determined by automatic titration and Gran calculation. Dissolved organic carbon (DOC) concentrations are determined on a filtered, chilled sample using infrared detection with a detection limit of 0.5 mg/L.

### Analytical Methods for WACAP Trace Metals

Total mercury is analyzed on whole-water samples (unfiltered) by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry in the USGS Wisconsin District Mercury Lab (Olson and DeWild, 1999). The detection limit is 0.04 ng/L. Laboratory splits are analyzed at the USGS National Research Program Laboratory in Boulder, Colorado, with a detection limit of 0.4 ng/L.

Trace constituents are analyzed on acidified whole-water samples (unfiltered) by Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) at USGS research labs in Boulder Colorado. Trace constituents and limits of detection for each element analyzed during 2001 are listed in Table 2.1.

## *Quality Assurance/Quality Control*

### Field

Quality assurance and quality control procedures for USGS snow chemistry samples are well established with annual regional surveys dating back to 1993. A detailed description of sampling protocols is contained in each field kit, and experienced personnel lead each site visit. Information regarding snowpack physical characteristics is recorded on prepared data sheets. All original data sheets are carried as personal baggage during transit and photo copied and kept in separate locations as soon as facilities permit.

Approximately 10% of the total number of samples will be field processing blanks and field replicates. Field blanks are collected to detect possible contamination from collection methods, laboratory processing, DI rinse water, filtering apparatus, and Teflon collection bags. Field replicates are also useful for this purpose, but also reflect natural variability in snow chemistry and precision of analytical techniques as well as contamination.

**Laboratory**

Detailed laboratory QA/QC procedures will be part of the final WACAP QAPP that is planned for completion in June 2003. Quality control at the USGS Colorado District lab involves systematically analyzing blanks, an internal reference sample, USGS standard reference water samples, and certified nutrient standards from High Purity Standards, Inc. Blind audit samples from Environment Canada are analyzed

**Table 2.1 Trace metals and detection limits for snow sample analyses at the USGS National Research Program Laboratory, Boulder, CO**

| Analyte | Units | Detection Limit | Analyte | Units | Detection Limit |
|---|---|---|---|---|---|
| Al | µg/L | < 0.2 | Nd | µg/L | < 0.0006 |
| As | µg/L | < 0.02 | Ni | µg/L | < 0.02 |
| B | µg/L | < 3 | Pb | µg/L | < 0.004 |
| Ba | µg/L | <0.005 | Pr | µg/L | < 0.0003 |
| Be | µg/L | < 0.005 | Rb | µg/L | < 0.0006 |
| Bi | µg/L | < 0.0009 | Re | µg/L | < 0.0002 |
| Cd | µg/L | < 0.002 | Sb | µg/L | < 0.001 |
| Ce | µg/L | < 0.0002 | Se | µg/L | < 0.05 |
| Co | µg/L | < 0.002 | Sm | µg/L | < 0.0002 |
| Cr | µg/L | < 0.2 | Sr | µg/L | < 0.03 |
| Cs | µg/L | < 0.009 | Tb | µg/L | < 0.0001 |
| Cu | µg/L | < 0.04 | Te | µg/L | < 0.005 |
| Dy | µg/L | < 0.0004 | Th | µg/L | < 0.0004 |
| Er | µg/L | < 0.0002 | Ti | µg/L | < 0.001 |
| Eu | µg/L | < 0.0002 | Tm | µg/L | < 0.0001 |
| Gd | µg/L | < 0.0002 | U | µg/L | < 0.0004 |
| Ho | µg/L | < 0.0001 | V | µg/L | < 0.07 |
| La | µg/L | < 0.0002 | Y | µg/L | < 0.0002 |
| Li | µg/L | < 0.008 | Yb | µg/L | < 0.0002 |
| Lu | µg/L | < 0.0001 | Zn | µg/L | < 0.04 |
| Mn | µg/L | < 0.01 | Zr | µg/L | < 0.0008 |
| Mo | µg/L | < 0.03 | | | |

twice per year. Approximately 40 percent of sample batch run time for the analytical instrumentation is dedicated to analyzing blanks, duplicates, reference samples, and standards. Calibration verifications are made with standards at the beginning and end of each batch of sample analyses on the ion chromatograph.

Ionic charge balance is calculated as the sum of cations (hydrogen ion, calcium, magnesium, sodium, potassium, and ammonium) minus the sum of anions (alkalinity, chloride, nitrate, and sulfate) divided by the total cations and anions in solution. Alkalinities are predominantly negative for snow samples; only positive values for alkalinity are included with the sum of anions in charge-balance calculations. Analytical results and charge balance values are examined and outliers for the snow sample database and rerun are performed as necessary.

# 3.0 CONTAMINANTS IN THE FOODWEB

## *3.1 Fish*

*Michael Kent*
*Carl Schreck*

### Introduction

This task within the overall project will focus on assessing the impacts of airborne contaminants on fish. We are using contaminants in fish tissues, and associated pathological and physiological changes to elucidate bioaccumulation of contaminants in the food web and their effects. Fish were chosen as they are immersed in the aquatic environment, and thus would be in intimate contact with the putative contaminants. Moreover, they are keystone species in lakes of all Western National Parks where they occur, and as top aquatic predators are very likely to bioaccumulate contaminants. In addition, these bioaccumulated compounds may also be trophically transferred to birds of prey (e.g., osprey), and potentially humans that forage within the parks. An ancillary contribution of this task will be the description of health and reproductive parameters and indices of fishes of our National Parks; such information is heretofore nonexistent for any species of fish in the wild in mountain lakes.

Links between contaminants in sediments, bioaccumulation in fish and resulting pathological changes in fish have been demonstrated in many impacted watersheds (Myers and Fournie, 2002). One of the best examples is in flatfishes from polluted areas of Puget Sound, where liver lesions (e.g., cancers) are associated with contaminants in tissues and sediments (Krahn et al., 1986; Myers et al., 1990; Stein et al., 1990). A similar situation occurs in other polluted sites along the Pacific coast (Myers et al., 1994) and other areas such as the Exxon Valdez oil spill (Marty et al., 1999) and the North Sea (Dethlefsen et al., 1987). Similar phenomena have been observed in freshwater systems. Baumann (1998) linked liver lesions with sediment contaminants in bullhead catfish in the Black River, Ohio. Whereas histological changes have often been the end point for these studies, macroscopic changes (i.e., visible to the naked eye) are also correlated with exposure to pollution (Fournie and Summers, 1996).

Anthropogenic contamination of aquatic environments is well documented to be linked to pathological and physiological changes in fishes (see review by Kime, 1998). The histological and hematological evaluations will be used as indicators of exposure to contaminants. They will also provide an indicator of the general health status of the fish. Physiological data will provide an indicator of the general level of distress that the fish are under at the precise time of capture. Fish serve as excellent “biomarkers” of the disruptive effect of contaminants on normal function of physiological systems, particularly those associated with reproduction but also those associated with general health and disease resistance. These biomarkers denote not only organismic responses to contaminants but also indicate the likelihood of population-level consequences as well (Rose et al., 1999). In addition, data suggesting reproductive

and developmental (and general health) effects of contaminants can be used in ecological risk assessment (Clark et al., 1999).

Histological Endpoints

Whole-organism, necropsy based indicators of fish health can be useful indicators of environmental degradation (Geode and Barton, 1990). However, histology provides more detailed and accurate assessments. It is particularly useful as an indicator of chronic or previous exposure to a toxicopathic insult. The target organs in this study are gills, liver, kidney, and spleen. Gills are intimately exposed to the external environment and are particularly sensitive to acute and chronic toxicant exposure. A wide variety of insults, including changes such as low pH, heavy metals, increased ammonia, detergents, and organic agents have been reported to damage gills. Sublethal (usually chronic) exposure results in diffuse, hyperplasia of the gill epithelium (see reviews by Hinton, 1993), while acute, lethal exposure often causes diffuse necrosis of the epithelium.

Many studies have documented liver damage in fishes from polluted waters (e.g., Myers et al., 1987; Hinton, 1993). Preneoplastic lesions, neoplasms, and hepatic megalocytosis are examples of chronic changes often found in fish exposed to contaminants. Two reasons that the liver is often a primary target organ is that it can metabolize many contaminants (e.g., pro-carcinogens) into more toxic forms, and nutrients (along with toxicants) derived from gastrointestinal absorption are stored in hepatocytes.

The kidney in fish serves two main functions – excretory and hematopoiesis. Therefore, it is critical to the survival of fish and may accumulate certain toxicants. Histological damage in the kidney renal portion associated with toxicant exposure includes damage to the renal tubules. Toxicants that target blood cells may cause depletion or necrosis of hematopoietic tissue in the renal interstitium, and accumulation of blood breakdown pigments in this region. Contaminants also cause a variety of abnormalities in peripheral blood. For example, Hose (1987) observed increased micronuclei in red blood cells in marine fish to be related to exposure to chlorinated hydrocarbons and PAH metabolites.

Gonadal tissue may be particularly sensitive to aquatic contamination because of its role in gametogenesis (McNabb et al., 1999). Quality and quantity of gametes of either sex are at risk when adult fishes are exposed to contaminants. It is also possible that sex determination and/or differentiation are interfered with by anthropogenic chemicals during early development. There can be direct action on ovarian or testicular cells, or contaminants can affect fish reproduction via endocrine disruption (Kime, 1998).

In addition to general histological evaluations, a key focus of this work will be directed toward pigmented macrophage aggregate (MA) analysis. For many years certain researchers have promoted the use of quantitative analysis of MA's in the spleen and kidney as a tool to access previous exposure to contaminants (Wolke, 1992). Increase in the MA's have been demonstrated in fish exposed to oil or other specific compounds in laboratory studies. More recently, Fournie (2001) showed a

convincing correlation between MA size in the spleens of several fish species and exposure to contaminants (Figure 3.1.1). This was a field study involving the analysis of about 1,000 fish from several stations throughout the Gulf of Mexico. MA's increase with age under normal conditions, but they increase much more rapidly in fish exposed to contaminants. Most important for the present study is that approach has been used by the EMERGE program, in which significant increases in MA's were observed in salmonids from contaminant impacted mountain lakes in Europe.

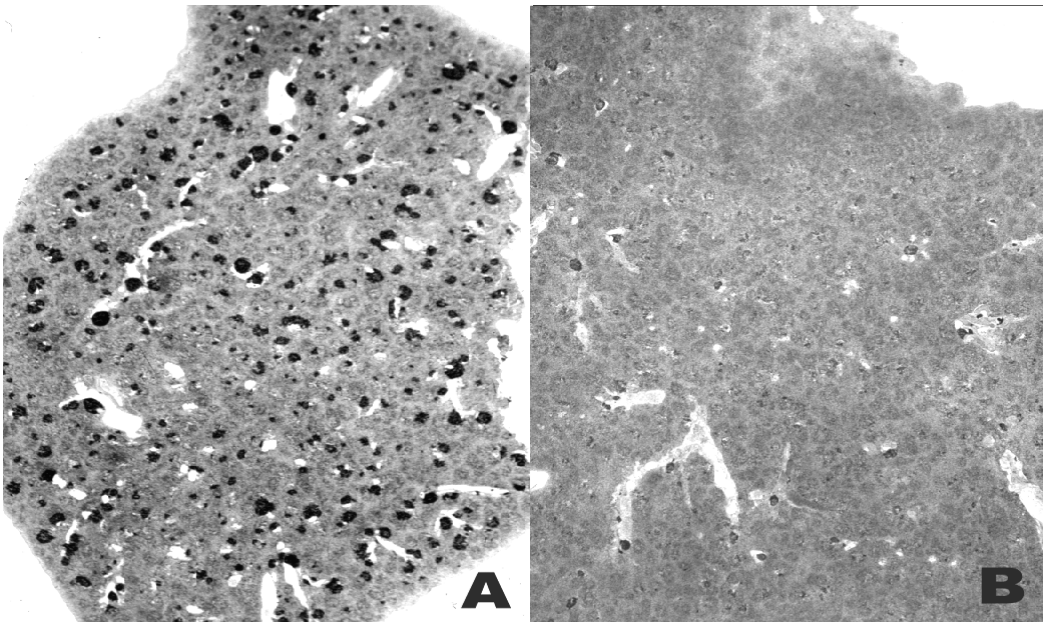



**Figure 3.1.1 Pigmented macrophage aggregates in the spleens of hardhead catfish *Arius felis.* A from heavily contaminated site, and B from a reference site.**

Physiological Endpoints

Indicators of stress in fish can be of value for assessing the health of the aquatic environment. Physiological assessment of performance traits such as osmoregulation and bioenergetics can be of value in assessing health (Wedemeyer et al., 1990). Measurement of the above physiological indicators as well as those associated with the primary and secondary stress response (Wedemeyer et al., 1990) are of use for determining the effects of any collection technique that may be necessary to capture the study animals. Reproductive biomarkers that can be used in ecological risk assessment of fishes include concentrations of sex hormones and vitellogenin (egg yolk precursor); the maturational cycle of these have been characterized for salmoniform fishes of both sexes (McNabb et al., 1999). Certain compounds (e.g., heavy metals) can disrupt normal reproductive development or cycling while other compounds can mimic

reproductive-controlling factors (e.g., estrogen mimics) and hence cause abnormal sexual differentiation or premature development. Fishes employ microsomal P450 enzyme systems, for example 7-ethoxyresorufin-O-deethylase (EROD), to cope with many exogenous chemicals by transforming and/or clearing them form the body. Measurement of the activities of enzymes involved in this process can be of value in determining if a fish has been exposed to a contaminant (Burke and Meyer, 1974; Prough et al., 1978).

**Objectives**

Fish sampling will address the following objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**
**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**

The objective of the fish sampling component of WACAP is to determine if airborne contaminants impact fish health in high mountain lakes and to link contaminants in fish tissue to other ecosystem components. Two major approaches will be used: 1) chemical analysis of tissues and 2) evaluation of pathological and physiological changes in fish. Baseline data will be collected on fish health and condition parameters in fish from high mountain lakes, including “pristine” systems.

**WACAP Obj. 3) If present, determine which contaminants pose a potential ecological threat.**
**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

We will assess fish as bioaccumulators of contaminants in the seven parks, and correlate fish health and condition parameters and contaminant concentrations with environmental contaminants in other ecosystem components (snow, sediment, water). Correlations of fish health and condition parameters will be provided for specific pollutants and the specific lakes selected for the study. In addition, we hope to determine the importance of terrestrial versus aquatic nutrients contributing to fish production, and use this information to establish the route(s) whereby contaminants move into fish tissues. Patterns of contaminant loading in individual catchments will be used to infer processes of atmospheric transport and catchment deposition.

**Methods**

Our target sample will include several age classes with at least 3 fish from each age class and both sexes from a single species (see below). As spatial distribution of fish is not random, we recommend collecting at least 30 fish/lake if feasible. We will concentrate the sampling to capture both juveniles and adults if possible. Juveniles would be of value in ascertaining the potential for precocious maturation due to contaminants; sampling of adults at the onset of the spawning season could produce data directed at determining if endocrine disruption is present. We will age fish by either scales or otoliths (ear bones which have rings useful for aging).

Trophic level will be assessed by stomach analyses. The trophic web of most alpine lake systems is driven by allochthonous inputs. Detection of contaminants through the food chain using stable isotopes will be attempted in those cases where contaminants are found.

Assuming that the question is whether the fish trophic web is of terrestrial or aquatic origin, that to be certain one would need to collect algae (sestonic and benthic), aquatic or terrestrial invertebrates. Terrestrial signatures for carbon $\delta^{13}C$ are rather predictable and perhaps literature values could be used to denote terrestrial sources. Aquatic carbon isotope values are dependant upon inorganic carbon availability and therefore can change from lake to lake. The terrestrial signatures for these have been rather well worked out, and literature values could be used to help strengthen the conclusions relative to inputs from terrestrial sources. Nitrogen isotope values ($\delta^{15}N$) can also vary between lakes and therefore conclusions that inputs are aquatic would be less robust. However, $\delta^{15}N$ can inform us of the trophic chain in the lakes, thereby helping interpret the $\delta^{13}C$ values.

Stable isotopes will be measured to provide information on the origin of the components of the trophic web contributing to fish production in the lakes. We hope to be able to ascertain the importance of terrestrial versus aquatic nutrients contributing to fish production. Such information will be of use in establishing the route(s) whereby contaminants may find their way into fish tissues. Such an approach has been used successfully in the past to track trophic relationships in food webs of lakes (Campbell et al., 1997; Pinnegar and Polunin, 1999; Vander Zanden et al., 1999; Vander Zanden et al., 2000; Dufour and Gerdeaux, 2001; Grey, 2001; Johnson et al., 2002; Vander Zanden and Vadeboncoeur, 2002) and the transfer of contaminants through the food chain (Kiriluk et al., 1995; Schindler et al., 1995; Kiriluk et al., 1996; Garcia and Carignan, 2000; Fisk et al., 2001).

The same fish will be used for both chemistry and pathology/physiology for the following reasons: 1) this strategy will allow us to correlate chemical burdens directly with health changes on individual fish; 2) this strategy will likely reduce the overall number of fish collected at each lake, which is very important at lakes with sparse populations; and 3) examination of the same fish for pathology and chemistry is consistent with the EMERGE program in Europe.

We will, therefore, save pieces of individual organs from fish for pathology/physiology studies, and save the remaining carcass for chemical analysis.

Pathology/physiology will require about 10% of the blood, 50% of the kidney, the entire spleen (at least for smaller fish), and about 25% of the liver. For other organs (e.g., gills, skin, muscle, gastrointestinal tract) only 10-20% of these organs are needed. We will calculate the overall % of total weight removed from the fish due to these pathology procedures. The remaining carcass will saved following procedures recommended by Dr. Simonich to avoid chemical contaminations in the field. When possible, additional fish will be collected and saved whole as additional samples for chemistry. Fecundity estimates will be performed only on females with maturing eggs. Eggs will either be counted directly in the field or when Dr. Simonich processes carcasses for chemistry. Therefore, eggs will available for chemistry.

Salmoniform fishes will be the targets of our sampling. We will always sample fish of the same species (we anticipate that these will be salmonids) from an individual lake. In addition, when ever feasible, we will sample fish of the same species from the different lakes and from different parks. Fish will be sampled each year of the study from at least one lake in one of the parks to provide information on possible inter-annual effects. The park selected for this sampling will be based on accessibility of the lakes. Lakes in the other parks will only be sampled once. Sampling will be accomplished by gill net and/or rod and reel.

Dr. J. Fournie (US EPA, Gulf Ecology Division, Gulf Breeze, FL) will process samples from Year 1 for histology and assist Dr. Kent with MA subjective and objective evaluations. MA analysis will be conducted by preserving tissues, processing for routine histology, and staining sections with hematoxylin and eosin. Three sections will be prepared from the liver, kidney and spleen separated by 50 µm increments. Tissues will be examined at Dr. Fournie's or Kent's laboratory with compound microscopes and images recorded using SPOT digital imaging system (available at both labs). After subjective evaluations (Fournie et al., 2001), macrophage aggregate parameters will be measured by using a true color (HSI Imaging) particle analysis package (MicroComp Integrated Image Analysis System).

Each fish will be analyzed as follows (see Figure 3.1.2):

1. **Condition Factors (Weight/Length).** Provides a general indicator for health.

2. **Aging.** Scales and otoliths will be collected for aging. Based on our previous studies of salmonid from mountain lakes, we should be able to determine age from scales. Otoliths will be evaluated if needed, but this requires more labor.

3. **Hematology.** The following data will be collected from blood samples, obtained by caudal vein puncture:

    - Hematocrits
    - Leucocrits – this provides a crude white blood cell count. High WBC's (leucocytosis) indicates an infectious disease is present.
    - Plasma

Collection of Fish →→→

External Examination →→→

1. Condition Factors
2. Scales for Aging
3. Blood
    a. hematocrit
    b. leucocrit
    c. cortisol & glucose
    d. blood smears
    e. plasma for physiology
4. Remaining carcass for contaminant analysis

Internal Examination

1. Goede Index
2. Otoliths for Aging
3. Organs for Histology
    a. gills
    b. liver
    c. kidney
    d. spleen/kidney for MA analysis
4. Organs for Chemistry
5. Gonads for Fecundity
6. Stomach for Food Contents
7. Tissues for Stable Isotopes

**Figure 3.1.2 Collection and Analysis of Fish Samples**

- Stress parameters – cortisol (RIA, modified from Redding et al., 1984) and glucose (colorimetric, modified from Wedemeyer and Yasutake, 1977). These data are useful as indicators of acute stress – i.e., an indication of the immediate health status of the fish when it is euthanized.
- Reproductive parameters – sex hormones (Estradiol, testosterone, 11-ketotestosterone, and 17α-dihydroxy-20β-dihydroxyprogesterone) will be assayed by RIA (Fitzpatrick et al., 1987) and vitellogenin will be measured by ELISA (Heppell and Sullivan, 1999).
- Blood smears – Used for WBC differentials to compliment leucocrits. Smears will also be examined for potential morphological anomalies in the blood cells.

4. **Goede Index for general health.** Provides a macroscopic evaluation of external and internal changes for general health (Geode and Barton, 1990).
5. **Gonads.** Gonads are examined for sex determination. Also, egg number and size will be evaluated (and correlated with age) as parameters for fecundity.
6. **Histology.** Provides a general evaluation of pathological changes and MA analysis; organs are preserved in 10% neutral buffered formalin. Organs to examine: gills, kidney, liver, spleen.
7. **Liver.** EROD activity will be determined in a small sub-sample of liver to help suggest the presence of a contaminant in the fish as described by Foster et al. (2001) and papers cited therein.
8. **Chemical Analysis.** The remaining carcass and blood will be collected for chemical analysis of contaminants.
9. **Stomachs.** Stomachs will be saved for feed analysis; i.e., food selection may influence pathways of bioaccumulation.
10. **Stable Isotopes.** We will collect tissue from fish for stable isotope analysis as well as from potential aquatic and terrestrial basal and prey sources. Terrestrial invertebrates will be collected by sweep nets, and algae and invertebrates will be collected from the lakes with plankton nets and dip nets. Samples will be analyzed for $\delta^{13}C$ and $\delta^{15}N$ by a commercial laboratory such as at the University of Georgia.

## Quality Assurance/Quality Control

Field

Quality assurance and quality control with regard to fish analyses are important issues. Fieldwork will follow established protocols involving fish capture, necropsy procedures and sample collections throughout the entire analytical processes. Information regarding fish species, age, sex, general health condition (Geode Index) will be recorded on prepared data sheets at the time of necropsy along with details of collection site. In addition, a digital image of unusual macroscopic changes will be

made. Labels will be permanently fixed to all containers of fish tissues filled out in permanent marker. All original data sheets will be carried as personal baggage during transit and photocopied and kept in separate locations as soon as facilities permit.

Laboratory

Detailed laboratory QA/QC procedures will be part of the final WACAP QAPP that is planned for completion in June 2003. Laboratory-reared salmonids will serve as control fish for histological evaluations and comparisons with age, sex, etc. related changes. These fish are control rainbow trout from the OSU's Marine and Fishwater Biomedical Institute. Fish are reared on a defined "toxicant free" diet as they are used in chemical carcinogenous studies.

**Research team**

The fish studies will be lead by Drs. Michael L. Kent (Dept. Microbiology, OSU) and Carl Schreck (USGS-BRD). Dr. Jack Fournie (US EPA, Gulf Breeze, Florida) is an international expert in fish histopathology, especially pertaining to lesions associated with contaminants, and he will consult with Dr. Kent on histological interpretations. A post-doctoral fellow will be employed to collect samples in the field and conduct laboratory analysis under the guidance of Drs. Schreck, Kent and Fournie.

## *3.2 Lichens*

*Linda Geiser*

### Introduction

The use of lichens as indicators of a wide variety of air contaminants is a well-established field of lichenology (e.g., see the "Air Pollution and Lichens" series chronicled in the journal *The Lichenologist*, or search the lichenological literature at http://www.toyen.uio.no/botanisk/bot-mus/lav/sok_rll.htm ). A wide variety of measurements and techniques have been used to detect the presence and relative amounts of pollutants, trends and changes in pollutants over time, map affected areas, and assess adverse effects. The two most commonly used techniques are chemical analysis of lichen tissue to test for accumulated pollutants, and analysis of lichen communities as a measure of biological effects. Reviews of the literature and methods regarding air quality assessment using lichens include Nimis et al. (2002), Garty (2001), Stolte et al. (1993), Nash (1989), and Nash and Wirth (1988). Articles specific to POPs assessment include Calamari et al. (1991), Morosini et al. (1993), Muir (1993), Jensen (1997), and AMAP (1997).

Lichens were first used as indicators of sulfur dioxide pollution in Great Britain during the last half of the 19$^{th}$ century when high sulfur coal was widely used for home heating and cooking. $SO_2$ gas causes declines in sensitive species. Since then, lichens have been widely used to monitor sulfur- and nitrogen-containing pollutants, metals, other trace and crustal elements, radioisotopes, and organic contaminants. Lichens have been used to study air pollution chemistry in national parks and forests of the United States for 18 years (Table 3.2.1). Baseline concentrations and trends for multiple elements in lichen tissue have been reported for numerous parks and forests, including Olympic NP (Rhoades, 1999), Sequoia-Kings Canyon NP (Wetmore, 1986) and Denali NP (Crock et al., 1992). Data and draft thresholds for enhanced levels of elements for 10 regional lichens of Alaska and the Pacific Northwest are available from the USFS Air Program ( http://www.nacse.org/lichenair). In 2001, an interagency/academic workgroup was formed to produce and share lichen-monitoring information for use in decision-making processes by federal air managers (http://ocid.nacse.org/research/airlichen/workgroup). Geiser and Reynolds (2002) summarized current efforts to use lichens to monitor air quality on federal lands in the United States.

**Table 3.2.1 Summary of NPS and USFS Lichen Elemental Analysis Programs**

| Item | National Park Service | US Forest Service |
|---|---|---|
| Number of Parks or Forests | 28 | 38 |
| Number of Localities | 335 | 2206 |
| Number of Species | 55 | 78 |
| Number of Collections | 2159 | 4970 |
| Number of Years | 18 | 15 |

Chemical analysis of contaminant levels in lichen tissue will provide a present-day assessment of metals, sulfur, and nitrogen levels in the parks. This information will make it possible to evaluate whether metals, sulfur or nitrogen should be considered a concomitant stress in analyses of other matrices. We anticipate that lichen analysis can corroborate some contaminant signals or combinations (i.e. ratios) of signals from sediment data that will enable us to link impacts in some catchments to trans-Pacific air masses if such impacts exist.

The techniques that will be used to determine contaminant accumulation in lichen tissue require several critical pieces of information about the watersheds. First, we need to know what species occur in quantities sufficient for tissue collection at all watersheds, and second, we need to select a limited number of target species with overlapping distributions so that as many of the same species as possible can be used at all Parks. Both pieces of information can be established by visiting all the watersheds before the first sampling season begins. There are several widely accepted techniques for analyzing element concentrations in lichens. Of these, ICP-AES or ICP-MS has been used with greatest success by researchers in national parks and forests during the past 18 years. It is used most reliably when lichen reference materials are used to analyze laboratory accuracy and precision, and when large field samples, representative of the population mean of the target sites, are collected.

Since air pollution composition, climate, elevation, and proximity/exposure to emissions sources differ among the watersheds, contaminant content is expected to vary somewhat among watersheds. The key factors controlling lichen contaminant content include lichen species, topographic exposure, frequency and duration of precipitation events, temperature ranges, presence or absence of winter snow cover, substrate pH and surface texture, location on the substrate, deposition rates, and pollution chemistry. To some extent, these environmental influences do moderate the amount of contaminants to which lichens and other organisms are exposed, how much they accumulate, and how much they are affected by them. For example, sensitive lichen communities in a rainy climate can tolerate more pollution than sensitive lichens in an already stressful, dry climate. On the other hand, standardized elemental analysis work in national forests of the Pacific Northwest and Alaska Region have shown that tissue concentrations of elements in lichens from clean sites are quite similar and significantly lower than element concentrations in lichens collected from urban, industrial and agricultural environments (e.g. Table 3.2.2). This difference between urban and forest sites occurs despite the fact that the forests span a wide range of altitudes, climatic extremes, and experience large differences in rainfall, humidity, and temperatures, from the temperate coastal rainforests to dry, cold, continental forests.

To maximize data comparability across parks, maximize the pollution signal, and minimize differences in other environmental variables, we will use the same or overlapping species at all parks, collect one epiphytic lichen and one terricolous lichen at each watershed, note substrate type and try to collect from similar substrates across watersheds. The sulfur, nitrogen and metals data we obtain will be compared to other data for the same lichen species from known clean or polluted sites within the same regions and broader areas. Within a watershed, our objective will be to identify average values for contaminants within the lichen population. To do this we will collect many

**Table 3.2.2 Mean concentrations of tissue nitrogen (% dw) in 938 samples of the epiphytic lichen, *Platismatia glauca*, from national forests of the Oregon and Washington Cascades, the Columbia River Gorge National Scenic Area, and rural and urban areas of the Willamette Valley and Puget Trough, 1993-2000.**

| Area | Location | # Samples | Mean | Std Dev | Std Err | Tukey Pairs |
|---|---|---|---|---|---|---|
| Umpqua NF | West Cascades, S OR | 115 | 0.35 | 0.08 | 0.01 | a |
| Willamette NF | West Cascades, C OR | 226 | 0.39 | 0.08 | 0.01 | a |
| Gifford-Pinchot NF | West Cascades, S WA | 159 | 0.41 | 0.09 | 0.01 | a, b |
| Deschutes NF | East Cascades, C OR | 23 | 0.42 | 0.07 | 0.02 | a, b |
| Mt. Hood NF | West Cascades, N OR | 203 | 0.46 | 0.12 | 0.01 | b |
| Columbia River Gorge NSA | OR/WA boundary | 94 | 0.73 | 0.19 | 0.02 | c |
| Willamette Valley/Puget Trough | W OR and WA, rural | 86 | 0.77 | 0.27 | 0.03 | c |
| Urban Areas | W OR and WA, cities | 32 | 0.98 | 0.22 | 0.04 | d |

individuals from the range of exposures and microhabitats in the watershed, and collect several field duplicates of each species.

### Objectives

Lichen sampling will address the following objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**
**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**

The objective of the lichen sampling component of WACAP is to determine concentrations of nitrogen, sulfur, arsenic, cadmium, chromium, lead, mercury, nickel, zinc and other metals in lichens in the 14 WACAP watersheds. We will compare the concentration levels of respective contaminants in the target watersheds.

**WACAP Obj. 3) If present, determine which contaminants pose a potential ecological threat.**
**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

Our objective will be to identify average values for contaminants within the lichen population of each watershed, and then assess whether these values are higher than those at known clean sites, and assess the ecological implications of the findings. We expect to estimate the degree of loading of nitrogen and sulfur to the target watersheds by comparisons with “local” monitoring stations. Except for Mt. Rainier and Sequoia, these levels are expected to be within natural, historic ranges, and unlikely to impact

sensitive species. We also plan to compare results from the WACAP parks to other sites in the Western US and Canada, primarily on federally managed lands, and to places in Europe and Asia that have been studied using the same species. Findings will be integrated with other indicator matrices, for example to calculate bioconcentration factors, and indicate potential synergistic stresses from metals, and sulfur and nitrogen containing pollutants.

**Objective 5) If present, determine the source of the air masses most likely to have transported contaminants to the National Park sites.**

We plan to compare background levels of the sulfur- and nitrogen-containing criteria pollutants and toxic metals to determine if sources appear to be regional or not.

## Approach

Minimally, six lichen samples will be obtained from each target watershed in August of the year in which the catchment in that park is studied intensively (c.f. Table 1.4). Lichens will be collected from trees and other woody substrates (Figure 3.2.1) or possibly from the ground (Figure 3.2.2) into Kapak bags (Figure 3.2.3). No other special equipment is required except unpowdered latex gloves to wear while collecting samples, lab tape to seal the bags air-tight after collection, and permanent markers to label the bags. Samples will be collected during day light hours (sufficient light is needed to distinguish species), in equal amounts from at least eight different locations in the watershed. Our target is to collect approximately 20 grams dry weight of one lichen species per sample. Each sample should contain a large number of individuals representing the various aspects and exposures in the watershed between ground level and arms reach. We will not climb trees or perform other hazardous acts to collect lichen samples. Samples should be in good condition. Epiphytes will be collected directly from tree branches, boles or from shrub stems, and only above ground portions of terricolous species are to be collected. Three replicate samples of two lichen species, six total, will be obtained per watershed. At 14 watersheds, this sums to 84 samples/year.

Part of the FY2002 objective is to visit the target watersheds and assess which lichens are present in sufficient quantities for tissue collection and then to select the species to be used at all Parks. *Hypogymnia physodes* and *Parmelia sulcata* are our preferred target species. They are widely used for tissue analysis around the world and plentiful data exists regarding enhanced and “clean site” ranges for these species (Bennett, 2001). Other potential target species known from all or most of the Parks are *Bryoria fuscescens, Cetraria islandica, Cladina rangiferina, Flavocetraria cucullata, F. nivalis, Parmelia saxatilis, Peltigera aphthosa, P. canina, P. leucophlebia, Platismatia glauca* and *Umbilicaria hyperborea* (Figure 3.2.4). Target species selection is most limited by Sequoia NP which lacks nearly all the arctic-alpine lichens common to the other Parks.

**Figure 3.2.1 Examining epiphytic lichens in the Willamette Valley of Oregon**

**Figure 3.2.2 Collecting terricolous lichens for metals analysis; Alpine site, Chugach NF, southcentral AK.**

**Figure 3.2.3 Sealing and labeling Kapak bags containing lichen samples for chemical analysis**

**Figure 3.2.4 Potential WACAP target lichen species for sulfur, nitrogen, and metals analysis**
Photographs, except *C. islandica* and *F. cucullata*, courtesy of S. Sharnoff

We do not anticipate eliminating any species from the target watershed through over-collection. The total amount needed of any single species from any single watershed will be 60 grams (2.1 ounces) over 3 years. No rare species will be collected; only species that are abundant in the target watershed will be used. Furthermore, all of the potential target species are considered abundant and widespread in Western North America.

Damp samples will be kept cool, then air dried in the field within 48 hours and repackaged. To air dry samples, lichens will be transferred to cleaned mesh bags and suspended from a clothesline at the field location (Figure 3.2.5). Surface debris, bark, and damaged parts of the lichen thalli, will be removed by hand. Air-dried samples for S, N and metals analysis will be repackaged and delivered to Linda Geiser's office in Corvallis and stored at room temperature until they are mailed to UMN Research Analytical Laboratory for further drying, grinding, and nitrogen and sulfur analysis (Figure 3.2.6). Aliquots of dried, ground lichens from each site will be shipped to the USGS Boulder Laboratory for trace metals analysis, and to the WRS Analytical Laboratory in Corvallis for mercury analysis.

**Figure 3.2.5 Lichen samples air-drying on-site in nylon mesh bags**
Kamchatka Oblast.

Laboratory methods for sulfur, nitrogen, and metals analysis will follow established methods and involve standard analytical instrumentation and techniques. See the University of Minnesota Research Analytical Laboratory (UMNRAL) website, http://ral.coafes.umn.edu/plant.htm, for more detailed descriptions of the following sample analysis procedures:

- The lichen sample is ground to a powder consistency in a stainless steel Wiley mill (#20 mesh sieve) then oven dried at 65 $^{o}$C to constant weight. Sample aliquots for separate analyses of sulfur, nitrogen, metals, and mercury are then weighed.

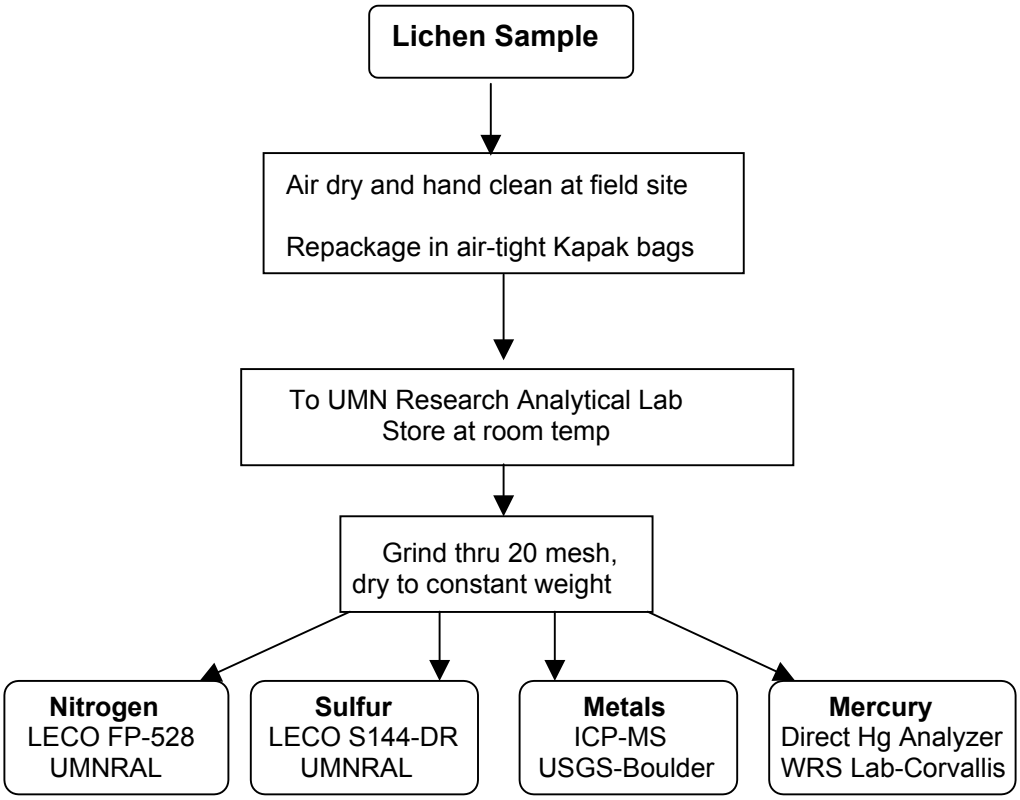



**Figure 3.2.6 Lichen sample flow diagram**

- **Nitrogen** is determined by a LECO FP-528 Nitrogen Analyzer. The N analyzer combusts a 200 mg sample, converts the resulting $NO_x$ to $N_2$, scrubs other combustion products, then measures total N using a thermal conductivity cell.
- **Sulfur** is determined spectrophotometrically using a LECO S144-DR Sulfur Determinator. This instrument combusts a 150 mg sample then measures evolved sulfur dioxide by infrared absorption. Both sulfur and nitrogen are reported as % dry weight.
- **Metals (cadmium, copper, lead, nickel, vanadium, zinc and others listed in Table 2.1)** are determined by Inductively Coupled Plasma- Mass Spectrometry (ICP-MS) at the USGS laboratory in Boulder, CO. Freeze-dried tissue samples are totally digested in a closed-vessel microwave oven procedure, using high purity nitric acid. After digestion, samples are diluted to volume with 1% high-purity nitric acid.

- **Mercury** is determined with a Milestone DMA-80 using a direct analysis method at the WRS Analytical Laboratory at EPA-Corvallis.

## Quality Assurance/Quality Control

Field

Quality assurance and quality control with regard to lichen analyses are important issues. The lichen indicator methodology would follow protocols already in use by the respective air divisions of the US Forest Service and National Park Service and will draw from baseline and thresholds lichen tissue data established by the USFS Air Program (http://www.fs.fed.us/r6/aq/lichen) and the Midwest National Parks Project (http://www.ies.wisc.edu/brd). In 2002, the WACAP lichen indicator was also supported by the natural resources program at Denali National Park and the Western Arctic Parks ecology program. Lichens will be collected in sufficient quantities to ensure the desired on-site repeatability. A pilot study to test the repeatability of using various sized sampling areas and sample weights was conducted at Denali NP during summer 2002 in collaboration with the natural resources program at Denali NP. Samples collected by Alexander Mikulin and Denali NP personnel Andrea Blakesley and James Walton are presently being cleaned in preparation for laboratory analysis. Results will be used to help define data quality objectives, sampling size and sampling area before the first sampling season. Sampling area and sample volume should be adequate to evaluate each target watershed. Triplicate samples will be used to evaluate repeatability of estimates for each analyte and element within a watershed.

A limited number of species will be collected, and ideally the same species will be collected at all sites. At the minimum, we hope that each species collected will occur in at least 5 parks so that the comparisons across parks can be made. Lichen tissue samples would be collected using gloves and packed into clean, airtight, inert containers. They would be air-dried in the field as soon thereafter as possible, stored in airtight containers at room temperature and analyzed within 1 year.

Collection locations will be determined using GPS and stored as electronic waypoints in addition to being recorded in field notebooks and on topographic maps. Information regarding substrate, substrate location, sample condition, sample moisture status, drying history, and cleaning will be recorded on prepared data sheets. In addition, a digital image of each collection site (habitat) will be made. Vouchers of samples from each watershed will be collected (Figure 3.2.7) labeled and stored in the lichen herbarium at the Siuslaw SO. Kapak bags will be labeled with site number, date, lichen species, substrates, moisture status, collectors name, and field weight. All original data sheets will be carried as personal baggage during transit and photo copied and kept in separate locations as soon as facilities permit.

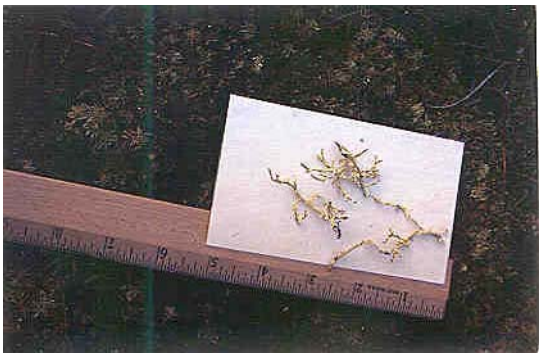


**Figure 3.2.7 Example of a voucher collection of the arctic-alpine, terricolous lichen, *Flavocetraria cucullata*, a potential WACAP target species.**

Laboratory

Three laboratories will analyze lichen samples collected from WACAP watersheds:

- University of Minnesota Research Analytical Laboratory (UMNRAL) will analyze nitrogen and sulfur in addition to drying and grinding the lichen samples.
- USGS National Research Program Laboratory in Boulder, CO will analyze metals (except for mercury)
- WRS Analytical Laboratory at EPA-Corvallis will analyze mercury

Laboratory QA will include analysis of replicates, blanks, and a lichen standard reference material such as IAEA-336 ( available from Analytical Quality Control Services, Agency's Laboratories, Seibersdorf , Austria). This information will allow us to assess laboratory accuracy and repeatability, necessary for establishing significant differences between sample groups and accurately assessing accumulation of contaminants in lichens.

## *3.3 Willow Bark*

*Staci Simonich*

### Introduction

It is clear from research over the past decade that natural vegetation is an important sink for semi-volatile organic compounds (SOCs) (Simonich and Hites, 1994b; Simonich and Hites, 1994a; Simonich and Hites, 1995a; Wagrowski and Hites, 1997; McLachlan and Horstmann, 1998; Ockenden et al., 1998; Wagrowski and Hites, 1998; Wania and McLachlan, 2001; Davidson et al., 2003b). Although there is some debate over the magnitude of this sink (Simonich and Hites, 1994a; Wagrowski and Hites, 1997), natural vegetation is now included in multi-media environmental models and is recognized for it's ability to decrease the atmospheric life-times and the long-range transport potential of lipophilic SOCs by efficiently trapping and transferring these compounds to soils (McLachlan and Horstmann, 1998; Wania and McLachlan, 2001).

Natural vegetation is an important sink for these compounds because roughly 80% of the earth's land area is covered with vegetation and this vegetation generally has 6-14 times more surface area than the land it is growing on (Simonich and Hites, 1994b). In addition, most natural vegetation exposed to air is covered in a wax or lipid layer that prevents excessive evapo-transpiration during times of drought (Simonich and Hites, 1994b). Research indicates that the main pathway for plant uptake of lipophilic SOCs, with log octanol-air partition coefficients of 9 – 10 (Wania and McLachlan, 2001), is via the atmosphere (Simonich and Hites, 1995b). However, at sites with contaminated soil, there is potential for hydrophilic SOCs to be taken up during evapo-transpiration (Simonich and Hites, 1995b). Finally, there is some indication that the uptake of lipophilic SOCs from the atmosphere is dependent on plant species (Ockenden et al., 1998) and lipid content (Simonich and Hites, 1994b; Simonich and Hites, 1995b).

Vegetation is recognized as a good qualitative indicator of atmospheric contamination of lipophilic SOCs and can be used to assess regional and even global variation in atmospheric contamination levels. Several studies have used tree bark to assess regional and global atmospheric contamination levels of polycyclic aromatic hydrocarbons (Simonich and Hites, 1994a), organochlorine pesticides (Simonich and Hites, 1995a; Simonich and Hites, 1997) and polychlorinated dibenzo-*p*-dioxins and furans (Wagrowski and Hites, 2000). Tree bark was used for these studies because it is present globally and has a relatively high surface area and lipid content (Simonich and Hites, 1995b). In addition, tree bark remains on most trees for several years and integrates the atmospheric concentration of lipophilic SOCs over this time period (Simonich and Hites, 1995b).

Willow bark (*Salix*) has been chosen as a matrix in this study because it is present throughout the selected Parks, grows at relatively high elevations, and is part of the terrestrial food-web within the Parks. In addition, it is easy to collect and will be available for collection throughout the year. Because the soil at the park sampling sites will not be contaminated by agriculture or industrial activity and many of our analytes of

interest (see Section 6.0) are lipophilic, the main pathway for contamination of willow bark will be from the atmosphere. The degree of accumulation will be dependent on the octanol-air partition coefficient of the analyte and its concentration in the atmosphere.

If willow bark is found to be a poor accumulator of SOCs, conifer needles will be used instead. Conifer trees are unlikely to be as prevalent at high elevations as willow trees, however conifer needles have been used as qualitative indicators of atmospheric SOC contamination in high elevation ecosystems (Davidson et al., 2003a).

## Objectives

Willow bark sampling will address the following objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**
**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**

The objective of the willow bark component of WACAP is to understand patterns of SOC contamination along elevational gradients, within each park, along latitudinal gradients, and in relation to proximity to regional sources, by comparing concentrations among different parks. Approximately 20 parks (including the 8 WACAP parks) will participate, with willow bark collected from up to five different elevation sites within each park in FY 2004.

**WACAP Obj. 3) If present, determine which contaminants pose a potential ecological threat.**
**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

Willow bark will be used as a qualitative indicator of atmospheric and terrestrial ecosystem contamination of SOCs. Relationships between total lipids and concentrations of SOCs, along with stem age, elevation, latitude and longitude will be explored. We also hope to determine how closely National Parks not included in the core WACAP sites compare with regard to contaminant uptake in vegetation.

## Approach

Because willow bark is ubiquitous throughout the parks, it will be possible to collect samples from multiple sites within a given park and among parks. Willow bark has the distinct advantage in that it is easy to collect and carry out of a park, but the disadvantage of not being present at the highest elevations within some parks. By including willow bark as a matrix in this study, we propose that additional parks, not

originally included in this study, may choose to participate in the study by collecting willow bark samples.

Willow bark stems will be collected in ~30 cm pieces using nitrile gloves and a clean pair of garden snips. Five 30 cm pieces will be snipped from a given willow tree and samples will be collected from at least three different willow groups within a site. The willow bark stems will be placed in a Teflon or polyethylene bag, stored cold or frozen, and shipped next-day to the analytical laboratory for analysis. Samples will be stored frozen and sealed at the laboratory until analysis.

Analytical method development is underway, using field samples collected during the summer 2002 from Desperation and Burial Lakes in Noatak National Preserve and Matcharak Lake in Gates of the Arctic National Park. Additional samples were collected from an elevational transect in Banff National Park (Alberta, Canada). The willow bark stems will be aged by counting the growth rings and lipid content will be measured in all samples. Willow bark will be analyzed for the SOCs listed in Table 6.1. See Section 6.0 for details on the analytical method development for measuring SOCs in willow bark.

### Quality Assurance/Quality Control

Multiple samples will be collected and analyzed for SOCs within a given site. From these data, we will be able to calculate the variation in willow bark SOC concentration within each site and determine if any concentration differences measured between sites are statistically relevant. Field blank and laboratory blank experiments will also be conducted (see Section 6).

## *3.4 Subsistence Food Analysis*

*Staci Simonich*

### Introduction

Subsistence food and its quality with respect to contaminants has been of great concern to the State of Alaska as well as the native communities which continue to use a wide variety of subsistence foods in their diets (Chary, 2000; USDI et al., 2000). WACAP is taking an interdisciplinary, ecosystem approach to evaluate and assess contaminants in ecosystems at risk for contaminants and we believe that including subsistence foods is a good way to make the connection to the human component of the ecosystem. This effort is not directly related to the overall goal and objectives of WACAP but it will provide an important link to the human subsistence component of the Alaskan foodweb.

### Approach

We plan to work with our NPS contacts to provide moose meat samples from individual moose killed by subsistence food hunters in Alaska and possibly Montana (Glacier National Park). Although sampling details may vary, we will need information on the location of the kill (elevation, latitude and longitude) and an approximate age of the animal. If possible, close proximity to WACAP sampling sites would be preferred and we would like samples from as many different parks as possible. The meat sample should be a single tissue sample that would be eaten by subsistence hunters (i.e. rump roast) of sufficient size (i.e. 5 lbs.) so that interior sub-samples can be taken by the analytical laboratory. Sample collectors should be careful not to contaminate the meat sample by human hands or unclean implements. Samples will be labeled and frozen solid at the park and sent to the analytical laboratory in Corvallis by overnight courier.

### Quality Assurance/Quality Control

Multiple samples will be sub-sampled and analyzed for metals and organic contaminants from each meat sample. From these data, we will be able to calculate the variation in contaminant concentration in moose meat within each sample and among sampling sites. Extraction, field blank and laboratory blank experiments will also be conducted (see Section 6.0 and Section 7.0).

# 4.0 SURFACE WATER ANALYSIS

## *4.1 Water quality information*

*Marilyn Morrison Erway*

### Introduction

Water quality data about the lakes in the WACAP catchments will provide basic information that will be used to characterize these ecological systems. We will follow water chemistry protocols from the Environmental Monitoring and Assessment Program's Surface Water (EMAP-SW) group. The EMAP program is planned and implemented by the U.S. EPA in cooperation with other federal and state organizations with the goal to monitor and assess the condition of the Nation's ecological resources and to contribute to decisions on environmental protection and management (Chaloud and Peck, 1994). The goal of EMAP-SW is to characterize the ecological condition of inland surface waters, and the water chemistry component contributes data that can be used to determine acid-base status, water clarity, primary productivity, chemical stressors, and nutrient status. WACAP will be collecting data from multiple indicators in the catchments, and it will be helpful to know basic ecological information, such as trophic status, as we interpret and relate data amongst multiple sources.

### Objective

The objective of the water quality component of WACAP is 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. Lake characteristics will be used to help interpret information from other ecosystem indicators, such as sediments and fish.

### Approach

We will follow the EMAP-SW sampling protocols for the water chemistry indicator by collecting a bulk water chemistry sample, and by measuring *in situ* variables such as specific conductance, dissolved oxygen, temperature, and transparency. These measurements will be collected at the same time as the fish sampling, during summer or early fall. The water chemistry sample will be collected at a depth of 1.5 m, from the deepest area of the lake, with a 2-L Kemmerer sampler, and stored in a 4-L cubitainer. Syringe samples will be collected from a port in the Kemmerer for closed system analyses of pH and dissolved inorganic carbon. A portion of the sample will be filtered with a hand pump through a glass fiber filter for chlorophyll analyses. The EMAP-SW analytes and their detection limits are listed in Table 4.1.

## Table 4.1 EMAP-SW analytes, methods, and detection limits

| Analyte | Method[1] | Detection Limit[2] |
|---|---|---|
| Specific Conductance | EPA 120.6; US EPA (1987) | NA |
| Temperature | YSI Model 6920 Datasonde | NA |
| Dissolved Oxygen | YSI Model 6920 Datasonde | NA |
| Turbidity | YSI Model 6920 Datasonde | 0.1 NTU |
| Secchi Disk Transparency | US EPA (1987) | |
| pH (syringe, closed system) | US EPA (1987) | NA |
| Acid Neutralizing Capacity (ANC) | EPA 310.1 (modified), US EPA (1987) | NA |
| Chlorophyll a | APHA (1989) | 1 µg/L |
| Total Suspended Solids (Residue) | EPA 160.2; APHA (1989) | 0.1 mg/L |
| True Color | APHA (1989), EPA 100.2 (modified), US EPA (1987) | NA |
| Dissolved Organic Carbon (DOC) | EPA 415.2, US EPA (1987) | 0.1 mg/L |
| Dissolved Inorganic Carbon (DIC), (syringe, closed system) | US EPA (1987) | 0.1 mg/L |
| Ammonium | Lachat 10-107-06-3-D | 2 µg/L |
| Nitrate + Nitrite Nitrogen | EPA 353.2 | 1 µg/L |
| Silica (SiO2) | EPA 370.1 (modified), U.S. EPA (1987) | 5 µg/L |
| Total Nitrogen | EPA 353.2 (modified), US EPA (1987) | 10 µg/L |
| Total Phosphorus | EPA 365.1 (modified), US EPA (1987) | 2 µg/L |
| Chloride | EPA 300.6; US EPA (1987) | 0.03 mg/L |
| Nitrate | EPA 300.6; US EPA (1987) | 0.03 mg/L |
| Sulfate | EPA 300.6; US EPA (1987) | 0.05 mg/L |
| Calcium | EPA 215.1; US EPA (1987) | 0.02 mg/L |
| Sodium | EPA 273.1; US EPA (1987) | 0.02 mg/L |
| Potassium | EPA 258.1; US EPA (1987) | 0.04 mg/L |
| Magnesium | EPA 242.1; US EPA (1987) | 0.01 mg/L |
| Zinc | EPA 289.1; US EPA (1987) | 0.005 mg/L |
| Selenium | EPA 270.2; US EPA (1987) | 0.002 mg/L |

[1] American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater. Seventeenth Edition. American Public Health Association, Washington, D.C.

U.S. EPA. 1983. Methods for Chemical Analysis of Water and Wastes. Environmental Monitoring and Support Laboratory. EPA/600/4-79/020, U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati.

U.S. EPA. 1987. Handbook of Methods for Acid Deposition Studies: Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026. U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C.

[2] The method detection limit is determined as a one-sided 99% confidence interval from repeated measurements of a low-level standard across several calibration curves.

## Sample Stream and Analyses

The cubitainer, syringes, and filter will be stored on ice in a cooler, and shipped via overnight FedEx as soon as possible after collection to the WRS Analytical Laboratory. The water samples will be collected on the last day of the fish sampling work to minimize the holding times. The water chemistry analytes have holding times that indicate the maximum length of time between sample collection and analyses that should be allowed and still maintain the integrity of the analyte. The holding times range from 48 hours to 6 months. WACAP lake sites are in remote areas, and we anticipate that it will take at least one day to get a water sample to a FedEx shipping location.

The bulk cubitainer sample is split into aliquots at the WRS Analytical Laboratory, following the sample preparation and preservation protocols for each analyte. Figure 4.1 shows the sample aliquots prepared from the bulk sample, with holding times and preservation methods. The chlorophyll filters are stored in the freezer.

## Quality Assurance/Quality Control

The EMAP-SW sample will be collected during the site visits for fish sampling. Two Parks will be visited the first two summers, and three Parks will be visited in the third summer. Each summer one field duplicate will be collected. Even though there will only be three or four samples each summer from WACAP, once the samples are received at the WRS Analytical Laboratory, they will be in regular EMAP-SW sample batches, which follow a regular schedule for analytical duplicates and filter blanks.

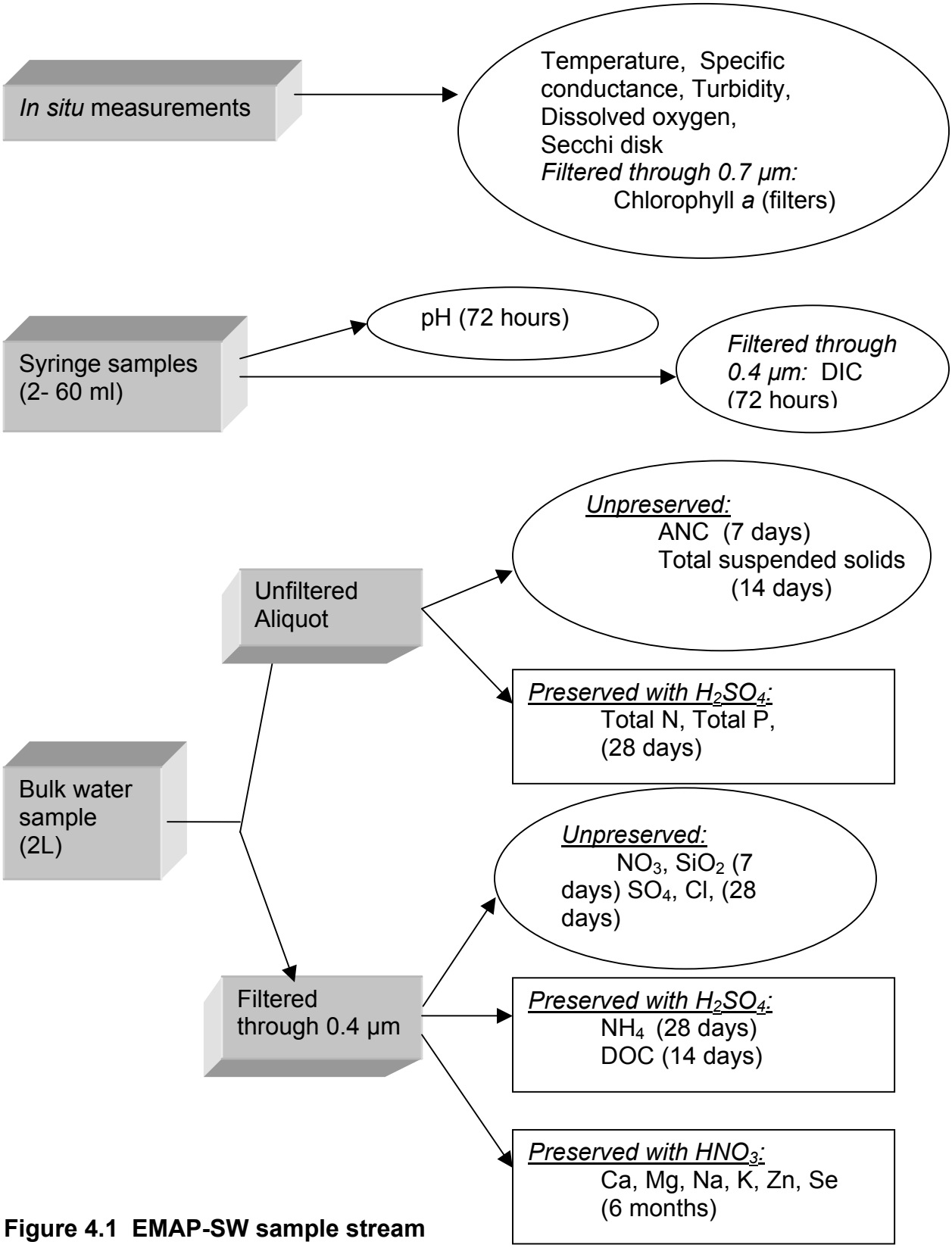



**Figure 4.1 EMAP-SW sample stream**

## *4.2* In Situ *Large Volume Water Sampler*

*Staci Simonich*

### Introduction

We have chosen to include the measurement of semi-volatile organic compounds (SOCs) in lake water because it is a direct link to the atmosphere during snow- and ice-free periods of the year. The current-use pesticides that are included as target analytes may only be detectable in the ecosystem during periods of use (Spring – Fall) and these use periods may not overlap with the period of snowfall and snow sample collection. Although some of the current-use pesticides may not bioaccumulate in fish (and may not be detectable in fish tissue) they may have other adverse affects on aquatic ecosystems. For these reasons, we believe it is important to measure SOCs in lake water at the WACAP sites during late Summer or early Fall.

There are many challenges associated with measuring SOCs in high elevation lake water. For example, the hydrophobic SOCs listed in Table 6.1 of Section 6.0, including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polybrominated diphenyl ethers and organochlorine pesticides, are relatively insoluble in water and sorb to organic particulates in lakes. In contrast, the current-use pesticides listed in Table 6.1, including the triazine herbicides and organophosphorus pesticides, are relatively soluble in water and may sorb only moderately to organic particulate in lakes. In addition, the fate of an SOC in a lake will be highly dependent on whether it is sorbed to particulate (sediment burial) or dissolved in the water column (uptake by aquatic organisms, degradation, or outflow from the lake). Because of the wide range of SOCs we plan to study in WACAP, we must be able to collect and measure both the dissolved and particle sorbed SOCs in the lakes.

In addition, it is likely that the concentration of SOCs within some WACAP lakes will be very low, on the order of parts-per-trillion or less. Even though the analytical techniques we will use in WACAP are very sensitive, we must collect and extract large volumes (50 L) of lake water in order to have acceptable detection limits for the analytical method. Multiple samples will be collected from each lake, which would make it very difficult and costly to transport 200 L or more of lake water out of the sampling site and ship it to the analytical laboratory for processing. In order to collect multiple large volume samples of lake water without the difficulty of transporting the water, we will filter and extract the lake water *in situ* using a micro processor controlled, battery operated, submersible pump (Infiltrex 100) made by Axys Environmental Systems Ltd. (Sidney, B. C., Canada). This system has been previously used by Grimalt and co-workers in European high elevation lakes and by Canadian scientists (Vilanova et al., 2001a; Vilanova et al., 2001b; Vilanova et al., 2001c). The lake water is pumped into the system and is first filtered through a 1 µm, 142 mm diameter filter to trap particulate and then passed through a column packed with sorbant (such as XAD-2 resin) to extract the SOCs from the water. After passing through the system, the extracted water is discharged back into the lake. The filter and sorbant are returned to the laboratory and extracted and analyzed for the SOCs listed in Table 6.1 of Section 6.0.

Because of the wide range of SOCs being studied in the WACAP project, we have been conducting exploratory research to determine the best sorbant for extracting the SOCs listed in Table 6.1 from lake water, using this system. XAD-2 resin has been used to extract hydrophobic SOCs from water but it is not efficient at trapping more water soluble SOCs from water, such as the triazine herbicides and organophosphorus pesticides (Vilanova et al., 2001a; Vilanova et al., 2001b; Vilanova et al., 2001c). We have been exploring the use of hydrophobicly and hydrophilicly modified divinylbenzene sorbants in this system, with good success (see Section 6). We have been conducting recovery and breakthrough experiments in the laboratory using a variety of sorbants and flow rates. In addition, we have conducted some preliminary field validation work at Waldo Lake (Oregon), at the crest of the Cascade Range and one of the most dilute lakes in North America, to refine the use of this system. Additional laboratory validation is underway and an additional field test is planned for Spring 2003. Preliminary results suggest that we will be able to quantitatively measure the SOCs targeted in WACAP in 50 L of lake water.

## Objectives

Lake water sampling will address the following objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**
**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**
**WACAP Obj. 3) If present, determine which contaminants pose a potential ecological threat.**
**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

The objective of the lake water sampling for SOCs is to determine the presence and concentration of SOCs (especially current-use pesticides) in lake water in the WACAP watersheds during late summer and fall. Relationships between lake water SOC concentration, elevation, latitude and longitude will also be explored.

## Approach

Water will be sampled *in situ* from all WACAP lakes at the same time that fish are sampled during the ice-free summer season on the schedule of 4 sites per year (6 sites during the third year). Final procedures were developed during late 2002 and early 2003 and field-tested prior to adoption by WACAP investigators. We will filter and extract 50 L of water per sample *in situ* and are investigating the use of various sorbants, including XAD-2 resin and the modified divinylbenzene sorbants that will be used to extract snow samples (see Section 6). Lake water will be filtered to remove

suspended particulate matter and the filter removed from the system, along with the sorbant column, and extracted and analyzed. Each 50 L sample is expected to take 4-6 hours to collect and extract with the Infiltrex System.

Duplicate samples will be taken (i.e. two separate system runs with a new filter and sorbant column) from both the epilimnion and hypolimnion of lakes that are thermally stratified by a temperature differential equal to or greater than 4° C. The strength of temperature stratification will be determined with a portable field themistor. The sampler will be deployed in the middle of each stratified lake layer. In the case that the lake is not stratified, duplicate samples will only be collected from the middle of the water column. All sampling will be performed over the deepest portion of the lake.

Filters and sorbant columns will be prepared in the laboratory and appropriately sealed to prevent contamination during transport to the field sites. At the field site, new filters and sorbant columns will be installed and the submersible pump will be programmed for the attributes desired for the run (i.e. start time, flow rate, ending criteria, etc.) using hand-held, programmable, portable, battery operated computers. When the run is finished, the sampling parameters will be verified and recorded using the computer. The filter and the sorbant columns will be removed from the pump, labeled, sealed to prevent contamination and stored in coolers under refrigeration for transport to the analytical laboratory.

In the laboratory, the filters and sorbant columns will be extracted and analyzed for the SOCs listed in Table 6.1 of Section 6.0. The filters and sorbants will be extracted using Accelerated Solvent Extraction (See Section 6).

**Quality Assurance/Quality Control**

Standard laboratory procedures will be followed for QA/QC involving development of standard curves, duplicate and blank analysis. The specific frequency and numbers of these QA samples will be determined during the final phases of the methods development.

Lake water field blanks will consist of bringing extra sorbant packed columns and filters into the field, installing the column and filter into the Infiltrex System, deploying the system without collecting a water sample, and removing the column in the same way that it is done for a real sample. The sorbant column and filter will be returned to the laboratory, extracted, and analyzed and used as a field blank.

# 5.0 SEDIMENT

*Dixon Landers*

## *Introduction*

The use of lake sediments as chronological repositories of a wide variety of ecological information is well developed in the field of limnology (e.g., see the Journal of Paleolimnology, and Last and Smol, 2001). A wide variety of information and techniques have been used to reconstruct long-term temporal trends preserved in lake sediments. Indicators that are used for these reconstructions are chemical, physical, and biological, depending upon the questions being asked.

Contaminants related to human activities generally became widespread coincident with or soon after the industrial revolution during the last quarter of the 19$^{th}$ century. Sediment chronology of contaminant deposition in each of the 14 WACAP catchments will provide a long-term glimpse of contaminant flux to each catchment. This information will make it possible to evaluate contaminant results from the analyses of other matrices in the context of pre- and post-industrial contamination loading. We anticipate that some contaminant signals or combinations (i.e. ratios) of signals will enable us to link impacts in some catchments to trans-Pacific air masses if such impacts exist.

The techniques that will be used to determine contaminant flux in sediment cores require two critical pieces of information about the cores. First, we need to know that the stratigraphy of the core is intact (i.e., the layers of sediment were deposited in chronological order and have not been disturbed) and second, we need to know the sedimentation rate (i.e. flux or rate of transfer of particulate material to the sediment surface). Both pieces of information can be established by accurate determination of the date of sediment layers within the core. The most widely accepted dating technique used to develop chronologies for lake sediments deposited over the last 200 years is one involving the natural radioactive isotope of lead, $^{210}$Pb (half-life of 22.3 y). This method has been used very reliably where the sedimentation rates are relatively constant and the sediment stratigraphy is unambiguous. $^{210}$Pb occurs naturally as one of the products of the $^{238}$U decay series (Appleby, 2001).

Since each lake catchment and lake basin is different, the sedimentation rate is expected to vary considerably among lakes. The key factors controlling sediment flux include land use practices, land cover, climate, topography, geology, basin configuration and lake productivity. Sedimentation rates among lakes in different settings may easily range from 2 cm to 0.02 cm/yr. Therefore, since a cm of sediment might equal from one-half to 50 years of time, it is important to date lake sediments in some rigorous way to understand the sediment flux regime for any given lake. We expect that for the alpine lakes we are studying that generally have small catchments, low productivity, and minimal catchment disturbance, one cm of sediment will represent from 30 to 100 years. Therefore, a 50 cm deep sediment core would represent from 1500 to 5000 years. The last 200 years of contaminant flux would then be found in the top 7 to 2 cm of the sediment core.

## *Objectives*

The sediment sampling component will address the following objectives of the WACAP program described in Section 1.0:

**WACAP Obj. 1) Determine if contaminants are present in Western National Parks.**
**WACAP Obj. 2) If present, determine where contaminants are accumulating (geographically and by elevation).**
**WACAP Obj. 4) Determine which indicators appear to be the most useful to address contamination.**

The objective of the sediment work is to develop decennial to century trends in contaminant (SOCs and metals) flux to the 14 WACAP catchments by dating and analyzing sediment cores from each lake. The sediment analysis and interpretation will be the primary way in which longer term trends will be evaluated and quantified for each catchment. Patterns of contaminant loading in individual catchments will be used to infer processes of atmospheric transport and catchment deposition.

## *Approach*

Sediment cores will be obtained from each lake during the year in which the catchment in that park is studied intensively (c.f. Table 1.4). Our preference would be to core all lakes in the late winter to early spring, prior to ice out, when ice is still at maximum thickness (Figure 5.1). This provides a stable platform for coring and if aircraft access can be used makes for efficient sampling. In some cases we will need to pack in a floating platform in order to core the lakes in the summer ice-free season where aircraft access is not permitted and accessing the site in spring by skiing with significant amounts of equipment is not feasible. Up to three sediment cores will be obtained from each lake using a Uwitec gravity corer with an 86 mm internal diameter. Our target is to obtain cores between 25 and 50 cm in depth. A winch fitted with a depth counter and stainless steel aircraft cable will be used to deploy the coring device (Figure 5.2).

The Uwitec coring device uses external weights added to the device to control the depth of penetration into the sediment. The amount of weight required is determined by trial and error at each lake.

The coring device can be configured for use in three retrieval modes. The core can be held by the surface tension with the side of the core tube and by a “flapper” device on the top of the core that seals the tube when it is retrieved through the water column. There are also two closing devices that can be fitted to the distal end of the corer. One is an elastic ball closure and the other is a hydraulically operated tube closure. These can be used if the sediments are of a *dy* consistency (unconsolidated gelatenous sediments) that does not adhere well to the sediment core tubes.

**Figure 5.1 Drilling a 10 inch diameter hole in the ice is accomplished using a gasoline powered auger. Ice is usually from 1 to 2 meters deep at high elevation and or high latitude lakes.**

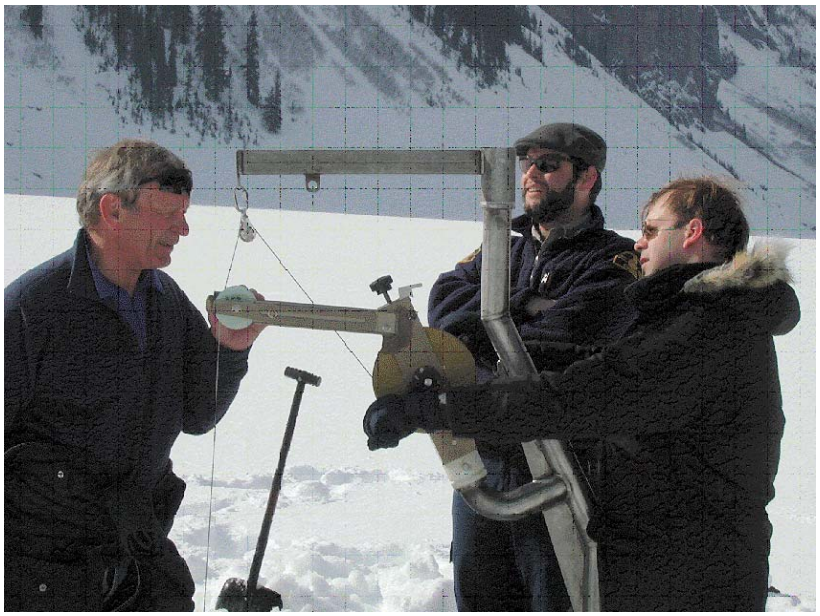


**Figure 5.2 Portable winch used to deploy the coring device and retrieve it slowly through the water column.**

Intact cores will be examined to determine that the surface layer is intact and that the core was taken in a vertical plane. Figure 5.3 shows how the surface of an acceptable core appears, complete with undisturbed invertebrate tubes. If acceptable, they will be capped and put in a rack for transport to a location where core sectioning will be accomplished. Sectioning involves extruding and precisely slicing the core in 0.5 cm or 1.0 cm increments with stainless steel implements. We intend to slice the first 10 cm of the core in 0.5 cm increments and the remainder of the core at 1 cm increments. Each increment will be stored in a pre-cleaned glass jar with a cleaned aluminum foil cap liner and stored in the dark under refrigeration until processing.

Sediment cores were obtained from Cottage Grove Reservoir in Oregon in August 2002, sectioned, and delivered to the analytical laboratory so that analytical methods development can be performed. We anticipate that we will have sufficient material in the surficial 0.5 cm increments of our target lakes to detect analytes of interest at a reasonable detection limit (approximately 1 ng/g wet weight). The anticipated detection limits will be provided in our final QAPP (Quality Assurance Project Plan). In some cases it may be necessary to combine two or more sediment strata in order to detect analytes of interest.

Core increments will be processed sequentially, only proceeding to the chemical analysis phase after it has been determined that the sediment core can be dated and interpreted unambiguously. Therefore, slices of each core will be homogenized and sub-sampled so that they can be dated using $^{210}$Pb, $^{137}$Cs and $^{241}$Am activity (non-destructively by counting gamma ray emissions) (Appleby et al., 1986; Appleby et al., 1991). If the dating sequence is acceptable as determined by adequate fit of the Constant Rate of Supply (CRS) (Robbins, 1978) or Constant Initial Concentration (CIC) model, we will proceed with other physical and chemical analyses (i.e. dry mass (%water), and total organic carbon). Figure 5.4 shows the sediment sample flow diagram and the analyses that will be performed in sequence.

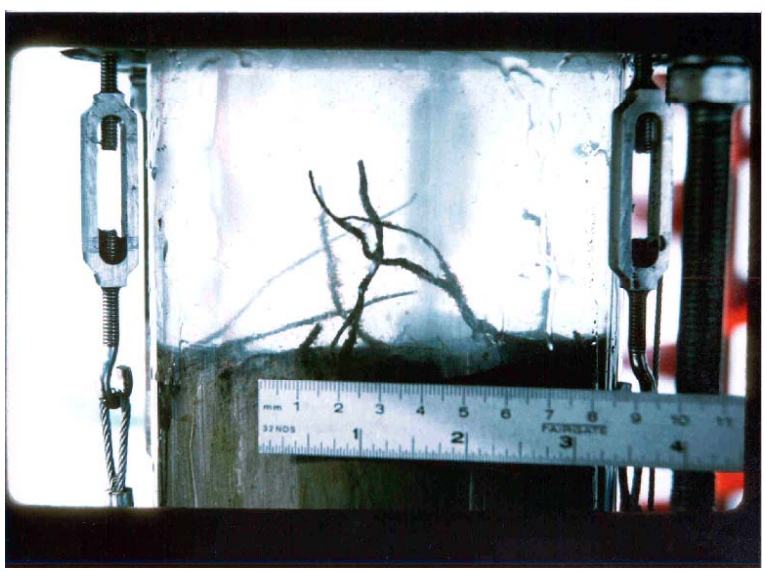


**Figure 5.3 The surface of a good sediment core, as seen through this Plexiglas 13 cm. diameter core tube, is undisturbed and perpendicular to the walls of the tube, often showing invertebrate tubes and light flocculent surface material.**

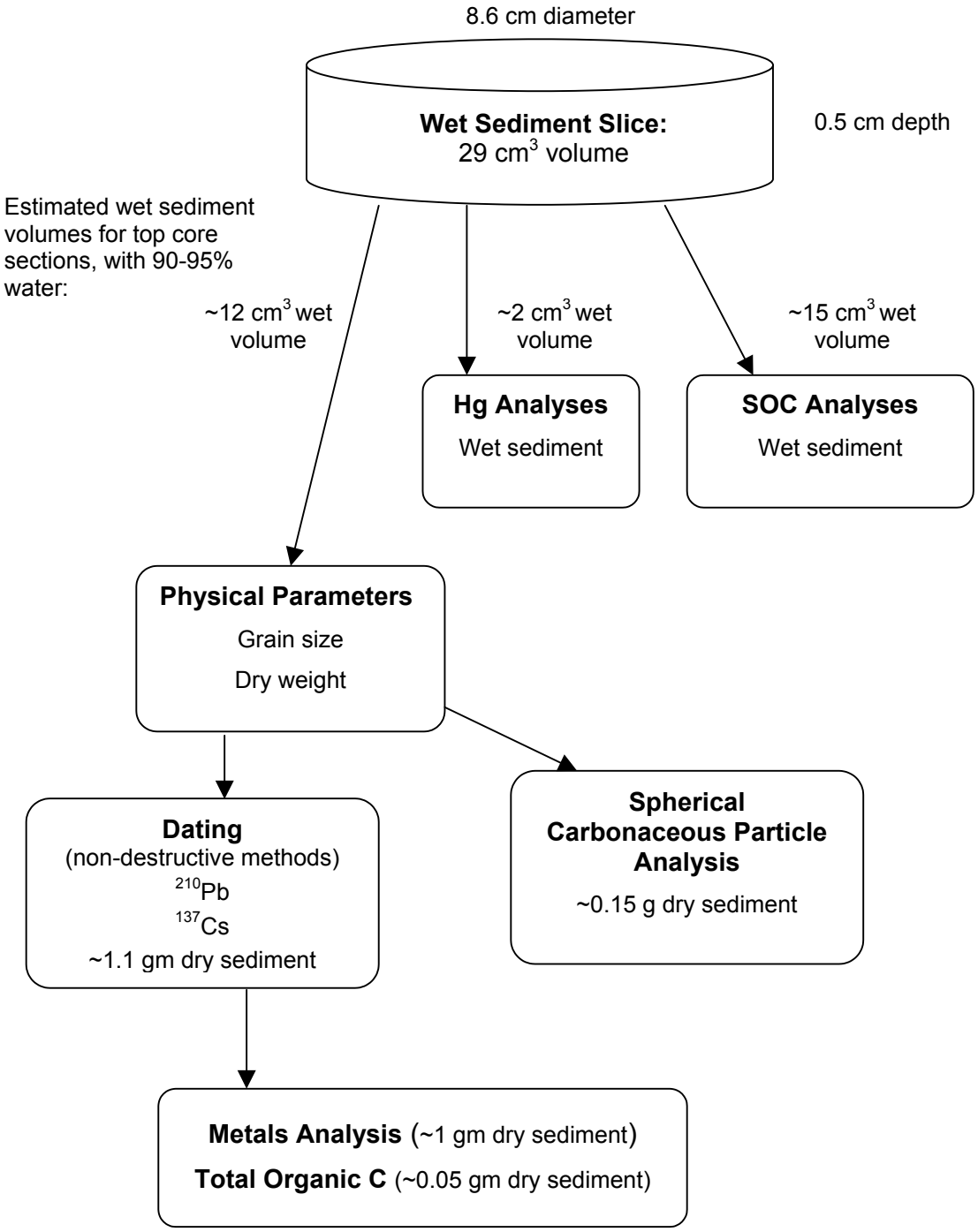



**Figure 5.4 Sediment sample flow diagram**

## *Quality Assurance/Quality Control*

### Field

Quality assurance and quality control with regard to sediment analyses and reconstruction of sediment chronologies of contaminants are important issues. Field work will follow established protocols involving core handling and sectioning to ensure that proper identification of the coring site and section depth are carried through the entire analytical processes. Each section container of each core will be labeled with the unique alphanumeric identifier for each core, and the section depth.

The coring locations in each lake will be selected before visiting the lake by examining bathymetric maps of the lakes to be sampled. Cores will be taken from deep water (i.e. profundal) sites that have a relatively uniform depth and are located distant from steep sided features that could contribute catastrophic or irregular sedimentation rates due to slumping or sediment focusing. Site locations will be determined using GPS and stored as electronic waypoints in addition to being recorded in field notebooks.

Information regarding core length, color and physical appearance with depth will be recorded on prepared data sheets prior to sectioning along with the details of the coring site. In addition, a digital image of each core surface and vertical condition will be made through the Plexiglas core tube. Labels will be permanently fixed to all containers of sliced sediment and filled out in permanent marker. All original data sheets will be carried as personal baggage during transit and photo copied and kept in separate locations as soon as facilities permit.

### Laboratory

Detailed laboratory QA/QC procedures will be part of the final WACAP QAPP that is planned for completion in June 2003. We intend to use a contract laboratory to date the sediment cores. At this time the laboratory has not been selected but several reasonable options exist. We shall stipulate in the request for assistance that the laboratory provide a full Quality Assurance Project Plan detailing the approach that will be followed in dating and interpreting the quality of the stratigraphy of the sediment cores. The QAPP will include not only the instrument calibration techniques, background radiation interference and all analytical steps and decision criteria but also the approach taken to determine the fit of the CRS or CIC models. Close interaction with the dating laboratory will be necessary in order to proceed judiciously with additional contaminant analysis after the core has been successfully dated.

# 6.0 ORGANIC ANALYSIS AND INTERPRETATION

*Staci Simonich*

## *Introduction*

This section describes the analytical approach for semi-volatile organic compounds (SOCs) and is, therefore, integral to achieving success in the entire WACAP project and directly or indirectly contributes to all project objectives. European and Canadian researchers have been very active in studying the atmospheric deposition of SOCs to high elevation ecosystems. Previous work of Grimalt and co-workers has focused on the measurement of SOCs in snow, lake water, fish, sediment, and wet and dry atmospheric deposition samples from high elevation ecosystems in the Alps, Pyrenees, and Caledonian mountain ranges in Europe (Carrera et al., 2001; Grimalt et al., 2001; Vilanova et al., 2001a; Vilanova et al., 2001b; Vilanova et al., 2001c; Carrera et al., 2002). This work indicates that SOCs, including those that are Persistent Organic Pollutants (POPs), undergo atmospheric deposition to high elevation ecosystems, accumulate in sediment and fish, and some undergo preferential deposition to high elevation ecosystems due to the global fractionation effect (Calamari et al., 1991; Wania and Mackay, 1993; Simonich and Hites, 1995a). Grimalt and co-workers are responsible for the "regionalisation of lake micropollutant distribution" portion of the European Mountain lake Ecosystems: Regionalisation, diagnostics & socio-economic Evaluation (EMERGE) program. This work includes the measurement of hexachlorobenzene (HCB), hexachlorocyclohexanes (HCH - $\alpha$ and $\delta$-isomers), DDTs (p,p'-DDE and p,p'-DDT), polychlorinated biphenyls (PCB congeners 28+31, 52, 101+84, 118+149, 153, 138+163+160, and 180), and polycyclic aromatic hydrocarbons (63 parent, methyl and sulfur derivative PAHs) in fish, sediment, soil, lake water, and atmospheric deposition samples from lake districts throughout Europe. The goals of this work are to understand and model transport of SOCs throughout the lake systems and to understand the regional variability of SOC distribution.

The majority of Canadian research on the atmospheric deposition of SOCs to high elevation ecosystems has taken place in the Canadian Rockies, including Banff National Park in Alberta (Blais et al., 1998; Donald et al., 1999; Donald et al., 2000; Blais et al., 2001). These studies confirm the potential for preferential atmospheric deposition of SOCs to high elevation ecosystems and that melting snow and glaciers have the potential to supply significant concentrations of persistent SOCs to high elevation freshwater ecosystems. These studies also suggest that temperate zone mountain ranges, with significant levels of annual participation and close proximity to regional pollution sources, may be particularly susceptible to contamination. In general, the Canadian research has focused on the measurement of HCB, PCBs, HCHs, and organochlorine pesticides (such as endosulfans, chlordanes, dieldrin, and DDT) in glaciers, snow, lake water, and rain (Blais et al., 1998; Donald et al., 1999; Donald et al., 2000; Blais et al., 2001). More recently, Shaw and co-workers (Environment Canada) have studied the atmospheric deposition of chlorobornanes, PCBs, and

organochlorine pesticides (including toxaphene) in snow and accumulation in fish in Southwest British Columbia.

In comparison, far less work has been done in the U.S. to study the atmospheric deposition of SOCs to high elevation ecosystems. Research by McConnell, Seiber, and co-workers during the mid 1990's in the Sierra Nevada Mountain Range (including Sequoia National Park) on the atmospheric deposition of organochlorine and current-use pesticides clearly indicates that regional sources, such as emissions from agricultural sources in California's Central Valley, may contribute to contamination of high elevation ecosystems (McConnell et al., 1998; LeNoir et al., 1999; Sparling et al., 2001). Some organochlorine compounds were measured in lake sediment from Denali National Park in 1991 (Gubala et al., 1995). More recently, the USGS collected and analyzed snowpack samples from Rocky Mountain National Park for organochlorine and current-use pesticides and detected low concentrations of endosulfan I, HCH, and some current-use pesticides (Mast et al., 2001a). Finally, the USEPA (Las Vegas) has started a research project to study the deposition of current-use agricultural pesticides in the Sierra Nevadas and the potential effects of these pesticides on amphibian populations.

The likely sources of SOCs deposited to high elevation ecosystems in Western National Parks include industrial, combustion, and agricultural sources from North America and Eurasia. In separate but related research, the PI responsible for the organic (SOC) analysis for this project is collecting air samples to study the atmospheric transport of SOCs from Eurasia to the West Coast of the U.S. These air samples are collected from a remote site on the Olympic Peninsula of Washington (within 200 miles from Olympic National Park) and there are plans to establish a free tropospheric site in Southern Oregon for sampling SOCs and other compounds indicative of trans-Pacific transport. The SOCs measured in this NPS project are the same SOCs that are measured in the air samples collected by the PI's laboratory. The PI recently received a National Science Foundation CAREER award to fund this research for 5 years.

## *Approach – Analytical Method Development, Validation, and Use*

### Selection of SOCs

Significant consideration has gone into the selection of target SOCs for the project. We have attempted to select analytes that would overlap with the previous studies cited in the Introduction of this section as well as to overlap, in part, with current work in the field, including the EMERGE Project, the Environment Canada study in British Columbia, and current measurements by the USGS in Rocky Mountain National Park. We have also tried to include analytes and techniques of "emerging" interest. Given the limited budget for the project, it is not possible to overlap completely with all of the SOCs measured in previous and current studies in the field. The target SOCs for this project are given in Table 6.1. We hope to use these SOCs as molecular markers to estimate combustion, agricultural, and industrial source contributions from Eurasia

**Table 6.1 Target SOC Analytes**

| |
|---|
| **Polycyclic Aromatic Hydrocarbons (PAHs)** |
| Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene |
| **Polychlorinated Biphenyls (PCBs)** |
| PCB 6 (2,3'-Dichlorobiphenyl), PCB 8 (2,4'-Dichlorobiphenyl), PCB 28 (2,4,4'-Trichlorobiphenyl), PCB 31 (2,4',5-Trichlorobiphenyl), PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl) |
| **Organochlorine Pesticides and Degradation Products** |
| o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Hexachlorocyclohexanes (HCH) - $\alpha$*, $\beta$, $\gamma$-(lindane), and $\delta$, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlorepoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorthalonil, Mirex |
| **Other Pesticides and Degradation Products (including organophosphorus pesticides and triazine herbicides)** |
| Chlorpyrifos and oxon, Diazinon and oxon, Demeton S, Ethion, Malathion*, Parathion and Parathion - methyl, Phorate, Disulfoton, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Triallate, Pebulate, EPTC, Carbofuran, Carbaryl, Trifluralin, Propachlor, Atrazine and degradation products, Metribuzin, Simazine, Cyanazine |
| **Exploratory Research** |
| Chiral analysis (* denotes chiral compound in table) and Polybrominated diphenyl ether flame retardants |

and North America. In addition, by determining the enantiomer ratios of chiral SOCs, we hope to distinguish between 'new' and 'historical' emissions, as well as to track microbial degradation through the high elevation ecosystems. The inclusion of these compounds in WACAP will allow us to address WACAP Objectives 1-5 (see Introduction – Section 1.0).

Polycyclic aromatic hydrocarbons (PAHs) have been chosen as target SOCs because they overlap (in part) with the EMERGE program and they are the only SOCs included in the target analyte list that are produced by combustion sources. To date, the majority of air measurements of trans-Pacific transport have been for combustion derived pollutants such as CO, $NO_x$, and $O_3$ and PAH measurements will help link this study to these atmospheric measurements. In addition, it is possible that the PAH distribution in snow could be used to distinguish between fossil fuel and biomass combustion source emissions.

Because PAHs are produced from combustion sources, it is possible that if helicopters are used to access sampling sites, matrices that are exposed to the atmosphere (snow, lake water, and willow bark) may be contaminated due to helicopter

emissions. If a helicopter is used, we will attempt to land it far enough away from the sampling sites to minimize potential contamination.

Selected polychlorinated biphenyl (PCB) congeners have been chosen as target analytes (see Table 6.1). These PCBs represent a significant fraction of the potential PCB toxic equivalent present in the ecosystem. The presence of PCBs will be indicative of emissions from industrial and urban North American and Eurasian sources. These congeners overlap, in large part, with the EMERGE project and current and previous work by Canadian researchers. We have chosen to analyze for two ecologically relevant congeners within each chlorination level (dichloro– to heptachlorobiphenyls). By analyzing for PCBs with a wide range of chlorination levels, we will likely see evidence of global fractionation as a function of vapor pressure, within a single class of compounds (Blais et al., 1998). A limited number of fish samples will be analyzed for a larger number of PCB congeners using high resolution mass spectrometry at a contract lab facility.

The target analyte list also includes persistent organochlorine pesticides such as DDT, hexchlorocyclohexanes, chlordanes, endosulfans, dieldrin, and hexachlorobenzene and some of their degradation products. These pesticides are included as target analytes to estimate emissions from Eurasia and North American agricultural sources. In general, these same organochlorine compounds have been measured in the majority of the previous and current studies in the field of atmospheric deposition to high elevation ecosystems. It is possible that the detection of certain organochlorine pesticides (like DDT) will serve as tracers for current use of these pesticides in Eurasia.

Finally, we have chosen some of the North American current-use pesticides, including organophosphorus, triazine and carbamate pesticides, as target analytes because they may serve as tracers for North American air emissions and may be transported and deposited to high elevations during periods of use (Spring-Fall). Because these compounds are not as persistent in the atmosphere or in environmental matrices as many of the other target compounds, we have included some of their degradation products as target analytes. It is possible that the parent pesticide volatilizes into the atmosphere, undergoes atmospheric transport and degradation, and the atmospheric degradation product, not the parent pesticide, is deposited to high elevation ecosystems. We believe the study of current-use pesticides in high elevation ecosystems will be challenging, but their inclusion is fairly novel and may help us understand the potential impact of current-use pesticides on these ecosystems. Many of the current-use pesticides we have chosen to study are the same pesticides included in the USGS and USEPA (Las Vegas) studies.

The goal of the analytical method development for the project is to be able to quantitatively measure all of the target analytes in Table 6.1 in all park matrices. However, if it becomes impossible to quantitatively measure a few of the target analytes because of poor analyte recovery these analytes may be dropped from the target analyte list. This may occur for some of the triazine or organophosphorus pesticides because they may degrade during analysis.

The target analytes listed in Table 6.1 will be used for the basis of the project. In addition, chiral analysis and polybrominated diphenyl ether flame retardants will be evaluated by the PI's laboratory as exploratory research. The addition of these exploratory research areas to the project has great potential to add significantly more to our understanding of which current-use SOCs are being deposited to high elevation ecosystems and why.

Many of the target SOCs exist as chiral compounds (noted by a * in Table 6.1). Chiral SOCs emitted from new or biologically unmodified sources exist as racemic mixtures, while chiral SOCs emitted from historical or biologically modified sources (such as soils, bodies of water, or sediments) exist as nonracemic mixtures (Bidleman and Falconer, 1999). It is possible that the enantiomer ratio of chiral SOCs in snow, and the corresponding air trajectories, could be used to distinguish between new and historical Eurasian and North American emissions. Chiral measurements could also be used to estimate the degree of biodegradation within the park watersheds (Falconer et al., 1995) and to study biomagnification within the park ecosystem (Wiberg et al., 2000).

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in a wide range of consumer products, including cabinets and circuit boards for personal computers and televisions, building materials, seat cushions, carpets, and textiles (Darnerud et al., 2001). The characteristics which make PBDEs excellent flame retardants, including a high degree of bromination, high thermal stability, and low cost, have resulted in large volume releases to the environment, especially since the early 1970s (Darnerud et al., 2001). Unlike many other known persistent organic pollutants, such as PCBs, PBDEs are currently being produced and used in developed countries. The concentration of PBDEs in mother's milk from North American women is 40 times greater than the levels measured in women from Sweden and the levels appear to be doubling every 2-5 years in North Americans (Betts, 2002). PBDEs have been detected in the Arctic and, if use trends continue, PBDEs will surpass PCBs as the most prevalent organohalogen compound in the Arctic ecosystem by 2050 (Ikonomou et al., 2002). The research to date indicates that PBDEs undergo long-range atmospheric transport and deposition to cold regions.

We have chosen not to include toxaphene (an organochlorine pesticide) and polychlorinated dibenzo-*p*-dioxins and furans as target analytes. Instead, we believe that the analysis of PBDEs and current-use pesticides will, because of their wide range of physical chemical properties and current use in North America, better enhance our understanding of which current-use SOCs are deposited to high elevation ecosystems. A limited number of fish samples will be analyzed for toxaphene using high resolution mass spectrometry at a contract lab facility.

## Analysis of SOCs

All extracts will be analyzed for the SOCs listed in Table 6.1 by gas chromatographic mass spectrometry (GC/MS) with both electron impact (EI) ionization and negative chemical ionization (NCI – also known as Electron Capture Negative Ionization ECNI), using two Agilent 6890 GC/5973 MS systems located in the PI's

laboratory. One system will be operated EI mode, while the other instrument will be operated in NCI mode, with $CH_4$ as the reagent gas. A GC/MS/MS instrument is also available, if needed, and is located in the same building as the PI's laboratory.

Some of the target analytes will be measured in the EI mode, while other analytes will be measured in the NCI mode in order to optimize instrument sensitivity. Instrumental limits of detection for the target analytes range from 10 to 100 pg/μL for EI and 0.1 to 100 pg/μL for NCI. A 30 m J&W DB-5MS GC column will be used for the chromatographic separation in either MS ionization mode. Stable isotope labeled analogs of some of the SOCs listed in Table 6.1 will be used as surrogates (added to samples prior to extraction and used to calculate the analyte concentration in samples) and internal standards (added to extracts just prior to analysis to calculate surrogate compound recoveries). Table 6.2 lists the target analytes and stable isotope labeled surrogates and internal standards that will be measured using EI or NCI modes.

**Sample Extraction and Extract Purification**

Because of the wide range of environmental matrices being studied in the project, we have prioritized analytical method development based on the number of samples to be analyzed within a given matrix and the storage compatibility of the matrix. Based on these factors, we have established the following prioritization for analytical method development: 1) snow (requires a lot of storage space) and lake water (extractions to be done in-field using the Infiltrex System with no storage), 2) whole fish (large number of samples to be collected and analyzed), 3) willow bark (potentially large number of samples but relatively easy to store), 4) sediment (two cores per year and relatively easy to store sections), and 5) subsistence foods other than fish (relatively small number of samples and easy to store).

**Snow**

Historically, there has been a wide range in the volume of melted snow extracted and in the extraction methods used. Extracted snow volumes (melted) range from 1-6 L (McConnell et al., 1998; Carrera et al., 2001; Mast et al., 2001a; Carrera et al., 2002) to 20 - 65 L (Blais et al., 1998; Franz and Eisenreich, 1998; Donald et al., 1999) and extraction techniques include the use of sorbant extraction using $C_{18}$ (McConnell et al., 1998; Mast et al., 2001a; Carrera et al., 2002) and XAD-2 (Franz and Eisenreich, 1998) resins and the use of a Goulden liquid-liquid extractor (Blais et al., 1998; Donald et al., 1999). Some researchers have chosen to filter the melted snow water and extract the particulate and dissolved phases separately in an attempt to understand the relative importance of gas and particle scavenging by snow (Franz and Eisenreich, 1998; Carrera et al., 2001; Mast et al., 2001a; Carrera et al., 2002). However, Wania and co-workers have shown that this process assumes that repartitioning does not occur during and after melting of the snow but in actuality, this equilibration takes place on the order of seconds. As a result, filtering of melted snow and measurement of dissolved and

**Table 6.2 MS ionization technique used for SOC analytes and stable isotope labeled analogs**

| Electron Impact Ionization | Negative Chemical Ionization |
|---|---|
| PAHs: Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Retene, Benz[a]anthracene, Chrysene, Triphenylene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[e]pyrene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene<br><br>Pesticides and degradation products: o,p'-DDT*, p,p'-DDT, o,p'-DDD*, p,p'-DDD, o,p'-DDE, p,p'-DDE, Diazinon and oxon, Disulfoton, Demeton S, Ethion, Malathion*, Parathion and Methyl - Parathion, Phorate, Metolachlor*, Methoxychlor, Acetochlor*, Alachlor, Prometon, Triallate, Pebulate, EPTC, Carbofuran, Carbaryl, Propachlor, Atrazine and degradation products, Simazine, Cyanazine<br><br>Surrogates: $d_{10}$-Fluorene, $d_{10}$-Phenanthrene, $d_{10}$-Pyrene, $d_{12}$-Triphenylene, $d_{12}$-Benzo[a]pyrene, $d_{12}$-Benzo[ghi]perylene, $d_{14}$-EPTC, $d_{10}$-Phorate, $d_5$-Atrazine, $d_{10}$-Diazinon, $d_7$-Malathion, $d_{10}$-Parathion, $d_8$-p,p'-DDE, $d_8$-p,p'-DDT, $d_6$-Methyl Parathion, $d_{13}$-Alachlor, $d_{11}$-Acetochlor<br><br>Internal Standards: $d_{10}$-Acenaphthene, $d_{10}$-Fluoranthene, $d_{12}$-Benzo[k]fluoranthene | PCBs: PCB 6 (2,3'-Dichlorobiphenyl), PCB 8 (2,4'-Dichlorobiphenyl), PCB 28 (2,4,4'-Trichlorobiphenyl), PCB 31 (2,4',5-Trichlorobiphenyl), PCB 52 (2,2',5,5'-Tetrachlorobiphenyl), PCB 74 (2,4,4',5-Tetrachlorobiphenyl), PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), PCB 118 (2,3',4,4',5-Pentachlorobiphenyl), PCB 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), PCB 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), PCB 183* (2,2',3,4,4',5',6-Heptachlorobiphenyl), and PCB 187 (2,2',3,4',5,5',6-Heptachlorobiphenyl)<br><br>Pesticides and degradation products: Hexachlorocyclohexanes (HCH) - $\alpha$*, $\beta$, $\gamma$-(lindane), and $\delta$, Chlordanes – cis*, trans*, oxy*, Nonachlor – cis, trans, Heptachlor*, Heptachlorepoxide*, Endosulfans - I, II, and sulfate, Dieldrin, Aldrin, Endrin, Endrin Aldehyde, Hexachlorobenzene, Dacthal, Chlorthalonil, Chlorpyrifos and oxon, Trifluralin, Metribuzin, Mirex<br><br>Surrogates: $^{13}C_{12}$ PCB 9 (2,5 –Dichloro-biphenyl), $^{13}C_{12}$ PCB 101 (2,2',4,5,5'-Pentachlorobiphenyl), $^{13}C_{12}$ PCB 180 (2,2', 3,4,4',5,5'-Heptachlorobiphenyl), $d_{10}$ - Chlorpyrifos, $d_{14}$-Trifluralin, $^{13}C_6$-HCB, $d_6$-$\gamma$-HCH, $d_4$-Endosulfan I<br><br>Internal Standards: $d_6$ - $\alpha$ - HCH, $d_6$ – PCB 77 (3,3',4,4'-Tetrachlorobiphenyl) |

sorbed fractions may not be a true measure of the partitioning in frozen snow (Wania et al., 1999).

The goal of the analytical method used to extract snow samples is to quantitatively extract 50 L of melted snow, using sorbant extraction. See Section 2.0 for details on the collection of snow samples. For the reasons mentioned above, and because we are interested in the total deposition to the ecosystem and reducing analysis costs, we will extract the particulate and dissolved phases together for a bulk deposition measurement. A bulk deposition measurement of snow has routinely been used by Canadian researchers (Blais et al., 1998; Donald et al., 1999). Because the target analytes have a wide range of polarities, it is unlikely that a single sorbant resin

will extract all of the target analytes quantitatively. There is evidence that $C_{18}$ and XAD-2 resins do not efficiently trap polar analytes, like the organophosphorus pesticides and the triazine herbicides and their degradation products, from water efficiently (Sandstrom et al., 2001).

Based on the PI's previous experience with extraction disks (Simonich et al., 2000; Simonich et al., 2002), we have been investigating the use of a hydrophilicly modified and a hydrophobicly modified divinylbenzene Speedisk sorbant for the extraction of the target analytes listed in Table 6.1 from water. In the PI's experience, the Speedisk technology is superior to 3M's Empore technology because a graded pre-filter allows for extraction of water samples with moderate to high suspended solids, with improved flow rates. Our initial investigations have found that the combination of these new phases results in quantitative recovery of all of our analytes from 1 L of water and is superior to $C_{18}$ (Empore and Speedisk technologies) and XAD-2 sorbants for our analyte list. Excess water is removed from the extracts with sodium sulfate and the extract purified using silica-gel chromatography. This same method has been modified and validated for the extraction of 50 L water samples.

**Lake Water**

The Infiltrex Pumping System (Axys, Vancouver, B.C.) that will be used for *in situ* extraction of lake water samples has traditionally been used with XAD-2 resin (see Section 4.2). Because XAD-2 is not an ideal resin for all of our analytes and because we would like to make a direct comparison to the concentration of SOCs in the snow samples, the goal of the analytical method used to extract lake water samples is to quantitatively extract 50 L using the same sorbant that is used to extract the snow samples. The second field validation of this system will take place in Spring 2003.

In the case of lake water, the concentration of SOCs in the particulate and dissolved phases will be determined separately. These data have ecological relevance because they will give us information about the bioavailable fraction of SOCs in the water column. The Infiltrex System contains a filter for trapping suspended particulate, followed by an extraction column packed with sorbants for trapping dissolved analytes (see Section 4.2). The filters and sorbant will be extracted using an Accelerated Solvent Extraction (ASE) System in the PI's laboratory and the extract analyzed for the target analytes.

ASE is a relatively new extraction technique used for extracting SOCs from solid environmental matrices such as fish, sediment, and vegetation. This technology replaces traditional Soxhlet extraction and uses much smaller volumes of organic solvents, at subcritical, elevated temperatures and pressures, and significantly less time than historical extraction techniques. A Dionex ASE 300 system is located in the PI's laboratory and the PI has experience with the use of this instrument for the extraction of SOC from solid environmental matrices (Simonich et al., 2000). The ASE System will also be used to extract the analytes off of the sorbants that are used in the extraction column and sodium sulfate will be used to remove excess water from the extracts. The PI's laboratory has developed a method for extracting atmospheric particulate from

glass fiber filters using the ASE system and this method will be modified for the extraction of lake particulates from filters.

**Whole Fish**

Organochlorine compounds (Berdie and Grimalt, 1988; Bjorklund et al., 2001), PAHs (Wang et al., 1999; Vives and Grimalt, 2002), and some current-use pesticides (Santerre et al., 2000) have been previously measured in fish. See Section 3.1 for details on fish collection. Whole fish samples will be cut into pieces and mixed with dry ice in a 1:1 ratio. The frozen fish sample will be homogenized in a Waring stainless steel blender and subsampled for extraction using ASE.

Dichloromethane and ethyl acetate are solvents that are likely to be used for the ASE extraction of fish samples. Sodium sulfate will be used to remove water from the matrix. Because the co-extracted fish lipids will interfere with the GC/MS analysis, lipids will be removed during the ASE extraction procedure by packing sulfuric acid-impregnated silica in the bottom of the ASE cell as a fat retainer (Bjorklund et al., 2001) or by treating the ASE fish extracts with 9 M or 18 M sulfuric acid prior to analysis (Berdie and Grimalt, 1988; Wang et al., 1999). If the target analytes are degraded during either of these procedures, gel permeation chromatography (GPC) will be used to remove lipids from the extracts prior to analysis (Lazar, 1992). If needed, further extract purification will include silica or alumina column chromatography. The percent moisture and lipid content of the fish samples will be measured. If funding is available and the analytical method developed for whole fish is applicable, we will analyze specific fish organs (liver) and blood for SOCs.

**Willow Bark**

The PI has previous experience with the extraction and analysis of SOCs in tree bark and other forms of vegetation (Simonich and Hites, 1994b; Simonich and Hites, 1994a; Simonich and Hites, 1995a; Simonich and Hites, 1995b). See Section 3.3 for information on the collection of willow bark.

Analytical methods are currently being developed using field samples collected during the summer 2002 from the Noatak National Reserve sites of Desperation and Burial Lake and the Gates of the Arctic site at Matcharak Lake. Additional samples were collected from an elevational transect in Banff National Park (Alberta, Canada). The bark will be removed by dissecting it away from the stems using clean techniques and solvent washed implements (i.e. forceps, scalpel). The bark will be extracted using ASE, with a solvent system similar to the one used for the fish samples. ASE has been previously used to extract SOCs from vegetation samples (Wenzel et al., 1998). The extracts will be purified using silica or alumina column chromatography prior to analysis. The percent moisture and lipid content of the willow bark samples will be measured. If the decision is made to measure conifer needles instead of willow bark, it is likely that the analytical methods that are developed for willow bark will also apply to conifer needles.

### Sediment

Sediment cores will be sectioned in the field and stored frozen in glass jars (see Section 5.0). The sections will be thawed, mixed with sodium sulfate and extracted using ASE. ASE has been previously used to extract SOCs from sediment and soil (Zhu et al., 2000; Martens et al., 2002). Extract purification will include silica or alumina column chromatography. The percent moisture of the sediment samples will be measured.

### Subsistence Foods other than Fish

There is interest in having moose samples, especially from the Alaskan Parks, analyzed for SOCs (see Section 3.4). We expect that the analytical method developed for determining the SOC concentration in fish will also be applicable to the moose samples. The percent moisture and lipid content of the moose samples will be measured.

## *Quality Assurance/Quality Control*

### Analytical Method Validation

Analytical method validation will include data on the percent recovery of the target analytes from the various matrices, the limit of detection and limit of quantitation, reproducibility, and typical laboratory blank concentrations. Studies are also underway to determine the stability of analytical standards. Stable isotope labeled internal standards will be used with all samples to track the recovery of the stable isotope labeled surrogates.

### Laboratory

Throughout sample analysis, experiments will be conducted to determine if there is laboratory contamination of the samples. Laboratory blank experiments will consist of the extraction of 50 L of purified water from the laboratory to simulate snow and lake water extraction, and in the case of fish, vegetation, sediment, and moose, laboratory blank experiments will consist of all reagents and steps used to measure SOCs in these samples, without the actual matrix.

### Field

Field blanks, in the case of lake water, will consist of bringing extra sorbant packed extraction columns into the field, installing the column into the Infiltrex System, and removing the column in the same way that it is done for a real sample. The extraction column will be returned to the laboratory, extracted, and analyzed and used as a field blank. See Section 2.0 for details on the preparation of a field blank for snow samples. For fish, vegetation, sediment, and moose, field blanks will consist of the

storage container being taken into the field and returned to the laboratory and extracted and analyzed. See Section 10.0 for a discussion of field blanks.

## *Research Team*

Personnel in the PI's laboratory associated with this project include:

Glenn Wilson: Faculty Research Assistant, 1.0 FTE, B.S. Chemistry; Glenn has 20 years experience in GC/MS and analytical method development. He is involved in analytical method development and validation and will also participate in field sampling and sample processing.

David Schmedding: Faculty Research Assistant, 0.60 FTE, B.S. Biology; Dave has 30 years experience in field sampling, environmental chemistry, and analytical method development. He will participate in field sampling and logistics, as well as in analytical method development and validation and sample processing.

Sascha Usenko: OSU Ph.D. student in Department of Chemistry; Sascha's Ph.D. thesis will focus on the application of chiral separations to the environmental chemistry of chiral SOCs in the ecosystems and identification of source emissions. He will also participate in field sampling.

Luke Ackerman: OSU Ph.D. student in Department of Chemistry; Luke's Ph.D. thesis will focus on the measurement of PBDEs in park ecosystems. He will be involved in analytical method development, sample processing, and field sampling.

Eli Moore: OSU undergraduate student in Department of Chemistry and Bioresources Research; Eli's undergraduate research thesis will focus on the measurement of SOCs in park vegetation.

Judy Wang: OSU Ph.D. student in Department of Chemistry; Judy's Ph.D. thesis will focus on the measurement of SOCs in sediment cores and their use in reconstructing historical atmospheric deposition to park ecosystems.

# 7.0 METAL AND ELEMENTAL ANALYSIS AND INTERPRETATION

*Staci Simonich*
*Howard Taylor*

## *Introduction*

This section describes the analytical approach for metal and elemental analysis and is, therefore, integral to achieving success in the entire WACAP project and directly or indirectly contributes to all project objectives. As with semi-volatile organic compounds (SOCs), little is known about the atmospheric deposition of metals to high elevation ecosystems in National Parks. This lack of information is due, in part, to the complexity of distinguishing between natural and anthropogenic sources of metals within an ecosystem. Also, data suggests that metal concentrations decrease rapidly and approach background concentrations in moss and lichens within 150-200 km of point sources and that only a limited number of heavy metals and elements may undergo atmospheric long-range transport (Reimann et al., 1997; Perry et al., 1999). These metals include Hg, Zn, Cu, Pb, Cd, Ni, and V (Reimann et al., 1997; Perry et al., 1999).

A wide array of metals and elements have been selected by scientists to study in remote high elevation and high latitude ecosystems throughout the world. For example, Hg, Pb, Zn, Al, Cd, Tl, Co, Cr, Mo, Sb, Cu, Li, B, Ti, V, Mn, Fe, Pd, Ag, Sn, Ba, Pt, Au, Bi, and U, have been measured in high elevation snow and ice cores throughout the world (Cheam et al., 1998; Van de Velde et al., 1999; Van de Velde et al., 2000; Veysseyre et al., 2001; Schuster et al., 2002). However, only Pb, Cd, and Hg were studied in the Canadian Northern Contaminants Program (Braune et al., 1999; MacDonald et al., 2000). More recently, Shaw and co-workers (Environment Canada) have measured the concentration of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, K, Se, Si, Ag, Na, Sr, S, Sn, Ti, V, and Zn in snow and in fish collected from British Columbia. The European Mountain lake Ecosystems: Regionalisation, diaGnostics & socio-economic Evaluation (EMERGE) program includes the measurement of Cd, Pb, Cu, Co, Zn, Fe, Cr, Mn, Al, Ti, As, Se, and Hg in snow, lake water, soil, and sediment samples. Finally, the USGS collected and analyzed snowpack samples from Rocky Mountain National Park for Hg, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Re, Sb, Se, Sm, Sr, Tb, Te, Th, Tl, Tm, U, V, Y, Yb, Zn, and Zr in 2001 (see Section 2.0). While WACAP is most interested in those metals that undergo atmospheric long-range transport (paragraph 1, above), we are fortunate that the same USGS analytical group, headed by Dr. Howard E. Taylor, that conducts the ICP-MS analysis for snow will also conduct analyses on other WACAP matrices. The total Hg analyses will be performed by the EPA-Corvallis laboratory. In this way, WACAP will be able to examine the seven metals of most interest while screening for a large suite of other elements that may provide useful information, especially in comparison to other programs interested in remote, high elevation contaminant impacts.

Although there will be some uncertainty in distinguishing between natural and anthropogenic sources, it is important to focus on those metals that are known to undergo atmospheric long-range transport in WACAP because we have a unique opportunity to link WACAP metals measurements to the measurement of the same metals in atmospheric particulate collected within some of the Parks through the Interagency Monitoring of Protected Visual Environments (IMPROVE) particulate monitoring network (http://vista.cira.colostate.edu/improve/Overview/Overview.htm). IMPROVE is a cooperative program that includes the National Park Service, the Fish and Wildlife Service, the Forest Service, the Bureau of Land Management, and the Environmental Protection Agency and was established in 1985 for protection of visibility in 156 National Parks and wilderness areas. An IMPROVE monitoring site is located in, or near, each of the National Parks included in WACAP. The particulate monitoring portion of the IMPROVE program measures the fine ($PM_{2.5}$) and $PM_{10}$ particle mass, optical absorption, and concentration of organic and elemental carbon, nitrate, and major and trace elements, with samples collected every third day. For the concentration of elements on the particles, Na through Mn are measured by Proton Induced X-ray Emission (PIXE) and Fe through Pb are measured by X-ray Fluorescence (XRF). The linking of WACAP metals measurements in snow and lichens to the corresponding IMPROVE data patterns will be very valuable in helping to distinguish between natural presence due to local geologic sources within an ecosystem and atmospheric transport from long-range and regional sources.

## *Approach – Sample Collection, Preparation and Analysis*

### Sample Collection

It is imperative that all samples collected for metals analysis not come into contact with metal objects such as shovels, containers or utensils. All matrices collected for metals analysis will be collected and stored in metal-free environments and transported back to the laboratory for preservation.

### Sample Preparation and Analysis

Snow and lichen samples will be prepared for metals analysis as described in Sections 2.0 and 3.2. The remaining matrices will be prepared for Hg analysis at the USEPA's Willamette Research Station (WRS) Analytical Laboratory, and other metal analyses at the USGS National Research Program Laboratory. Solid samples, including sediment, fish, lichen, and moose tissue, will be digested with a mixture of mineral acids in a closed-system microwave digestion oven prior to analysis.

Total mercury analysis will be conducted on sediment, fish, lichen, and moose at WRS using a Direct Hg Analyzer (EPA Method 7473). The remaining elements, including Zn, Cu, Pb, Cd, Ni, and V, will be measured by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) at the USGS Laboratory.

## *Quality Assurance/Quality Control*

Quality assurance procedures followed at the USGS National Research Program Laboratory in Boulder and the WRS Analytical Laboratory in Corvallis include the use of blanks to detect contamination, replicate samples to measure precision, and standard reference materials to determine accuracy. Blanks for fish, sediment, lichen, and moose samples will consist of all reagents and steps used to measure metals in these samples, without the actual matrix. Field blanks will consist of the storage container being transported into the field and returned to the laboratory and extracted and analyzed for the metals of interest. Detailed laboratory QA/QC procedures will be part of the final WACAP QAPP that is planned for completion in June 2003.

# 8.0 ATMOSPHERIC ANALYSIS

*Daniel Jaffe*
*Lyatt Jaeglé*

## *Introduction*

The fifth WACAP objective states:

***If present, determine the source of the air masses most likely to have transported contaminants to the National Park sites.***

This objective requires that we consider atmospheric transport processes in relationship to the WACAP chemical measurements. Because of strong westerly flow in the middle latitudes, we anticipate that long-range transport from distant sources will be important in explaining the WACAP results, but we do not exclude consideration of contributions from other sources.

### Background on Trans-Pacific Transport of Pollutants

The East Asian region is one of the largest and most rapidly developing regions on the planet (e.g. Galloway et al., 1995; Elliot et al., 1997; Streets and Waldhoff, 2000). From the mid-1970s to the 1990's the emissions of both NOx and $SO_2$ from the East Asian region increased at an average rate of ~4% per year and now exceed the emissions from other developed regions such as North America and Europe (Akimoto and Narita, 1994). A number of researchers have documented episodic transport of pollutants into the central North Pacific (Duce et al., 1980; Prospero and Savoie, 1989; Jaffe et al., 1997; Talbot et al., 1997)

There is now no question that pollutants from the Eurasian continent can be transported to North America (Jaffe et al., 1997; Husar et al., 2001; Jaffe et al., 2001; Kotchenruther et al., 2001; McKendry et al., 2001; Jaffe et al., 2002; Price et al., 2002; Thulasiraman et al., 2002). We have detected transport of industrial pollutants, mineral dust and emissions from biomass burning in Siberia. These can be transported to the Western U.S. in as little as 6 days.

Table 8.1 shows a summary of 6 Trans-Pacific episodes that we have observed (Jaffe et al., 2002) and Figure 8.1 shows the isentropic back-trajectory for one of these episodes, which depicts the transport pathway of the polluted air mass. These episodes probably occur most frequently during spring, and during other seasons as well. The transport is episodic, relying on rapid zonal flow between the Aleutian low and Pacific high synoptic systems. To date, we have shown that CO, $O_3$, nitrogen oxides, sulfur oxides, aerosols and non-methane hydrocarbons (NMHC) can be transported from Asia. Recent (preliminary) results indicate that Hg can also be transported from Asia. However, at present very little is known about the deposition of these pollutants.

While generally, the pollutant concentrations observed are low, below levels that would raise concern about immediate impacts, in 2 of these 6 cases, concentrations

**Table 8.1 Some Episodes of Trans-Pacific Pollution Transport**

| Date/Location | Elevated species | Outstanding features | Reference |
|---|---|---|---|
| 4/28/93: several sites in the Western U.S. (simultaneously) | Aerosol sulfate, nitrate, metals, soot | Substantial enhancements in many species observed simultaneously at Crater Lake, Mt. Rainer and Mt. Lassen | Jaffe et al., 2002 |
| 3/29/97; Cheeka Peak Observatory (CPO) | CO, PAN, VOCs, and aerosols | No $O_3$ enhancement | Jaffe et al., 1999 |
| 4/21/98; CPO | CO, PAN, $O_3$, aerosols | Probably due to transport of biomass burning emissions from Siberia | Jaffe et al., 2001 |
| 4/28/98; CPO and other locations | Mineral aerosol, trace metals | Elevated PM-10 levels at numerous sites on the west coast (e.g. 73 ug/m3 in Seattle) | Anderson et al., 1999; Husar et al., 2001 |
| 4/9/99; PHOBEA aircraft observations | Aerosol scattering, absorption, $O_3$, PAN, CO and VOCs | Enhancements in PAN, CO, VOCs and $O_3$ in layers between 10,000-18,000 feet off the coast of Washington. $O_3$ mixing ratio reached 85 ppbv. (back-trajectories originate near Southern Japan/East China.) | Kotchenruther et al, 2001 |
| 4/14/01 | Aerosol scattering, CO, NMHCs | Large enhancements in aerosol scattering and CO. Probably a mixed dust/pollution episode. Trajectories and GEOS-CHEM model indicate transport from East Asian sources | Jaffe et al., 2002; Price et al., 2002; Thulasiraman et al., 2002 |

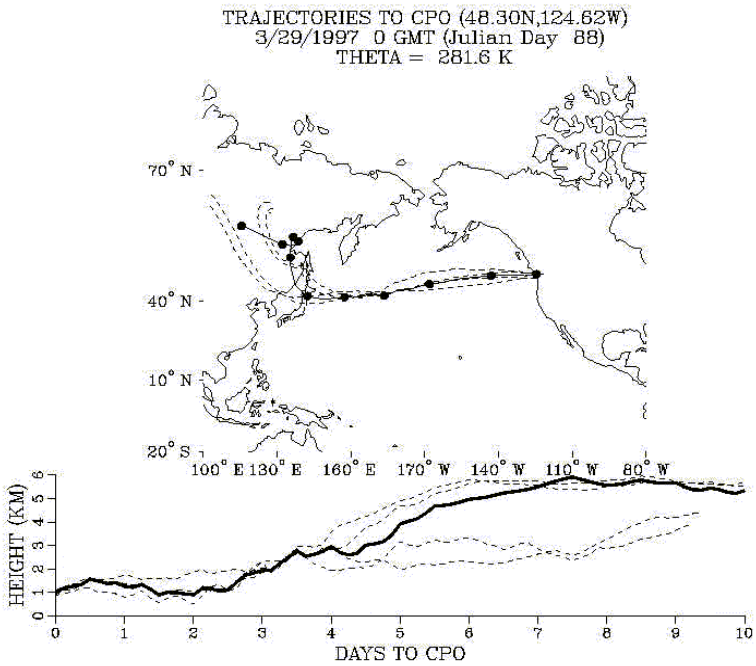
were significantly elevated, and not far from U.S. air quality standards. This includes the well documented Asian dust event of April 1998 (Husar et al., 2001) and the high $O_3$, CO, PAN, NMHC and aerosol event we identified in the 3-6 km region during April 1999. This later event had $O_3$ mixing ratios of up to 85 ppbv (Kotchenruther et al., 2001).

Despite this large amount of data on gaseous pollutants, such as CO and other species, we have almost no information on traditional contaminants, such as persistent organic pollutants (POPs) and heavy metals (Hg and others). Undoubtedly these contaminants must get transported with the other pollutants, but to date we have very little information on these. There is some important information from Canadian studies, which suggest that various Asian POPs do get transported and deposited (Blais et al., 1998; Bailey et al., 2000). However, no direct measurements have identified atmospheric transport of these compounds.

We utilize a variety of tools to identify long-range transport. This includes local meteorological data, isentropic back-trajectories, the chemical composition, satellite data and global models, such as GEOS-CHEM (Bey et al., 2001). No one tool is sufficient by itself. We look for a consistent pattern using as many of these as possible for a given situation. For example isentropic trajectories by themselves can be quite misleading. We have identified many cases of trans-Pacific transport using trajectories (e.g. see Figure 8.1), but we can also show cases with similar trajectories, but no

pollution transport. The reason for this difference is likely the complexities of the atmospheric boundary layer, which is poorly characterized by the large-scale meteorological data. However, using climatological distribution of trajectories, it is possible to derive broad patterns of the atmospheric transport in a given region (e.g. Jaffe et al., 1997; Mahura et al., 1999).

GEOS-CHEM is a global three-dimensional model of tropospheric chemistry driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS) of the NASA/Goddard Data Assimilation Office (DAO). The assimilated meteorological data are available continuously from 1985 through the present, with a horizontal resolution of 2°×2.5° (1°×1° starting in 2000), and 48-70 layers (Schubert et al., 1993). The model is being developed at Harvard and used by a number of groups around the world (http://www-as.harvard.edu/chemistry/trop/geos/geos_home.html).




00 UT

| DAY | KM | hPa | C |
|---|---|---|---|
| 0 | 1.0 | 905 | 0 |
| 1 | 1.3 | 872 | −2 |
| 2 | 0.9 | 916 | 1 |
| 3 | 1.9 | 795 | −9 |
| 4 | 3.0 | 685 | −20 |
| 5 | 3.9 | 600 | −29 |
| 6 | 5.0 | 510 | −40 |
| 7 | 5.5 | 472 | −45 |
| 8 | 5.6 | 465 | −46 |
| 9 | 5.7 | 458 | −47 |
| 10 | 5.3 | 486 | −43 |

**Figure 8.1 Isentropic back-trajectory showing the air mass transport associated with an Asian pollution episode, which was identified in data from the Cheeka Peak Observatory (CPO) on March 29th, 1997. See Table 8.1 for more information on this episode (Jaffe et al., 1999; 2002).**

Bey et al. (2001) has presented a global evaluation of the model and the GEOS-CHEM model has also been extensively used to study ozone and its precursors over a number of regions, including the Asian Pacific Rim (Liu et al., 2001), the western and tropical Pacific (Bey et al., 2001) the United States (Palmer et al., 2001; Fiore et al., 2002), and the Atlantic (Li et al., 2002). We have used this model to analyze observations at the Cheeka Peak Observatory (CPO) site for 1997, 1998, 2001 and 2002. The model captures not only background levels of CO, $NO_x$, ozone, PAN, and radon but also the timing and duration of episodic enhancements occurring during long-range transport events (Jaeglé et al., manuscript in preparation, 2002). The relative contributions of different source regions can be determined by "tagging" anthropogenic tracers according to emission regions. This approach is illustrated in Figure 8.2, showing the respective contributions of North American, Asian and European fossil fuel emissions to surface CO levels over the United States during March-April 1997.

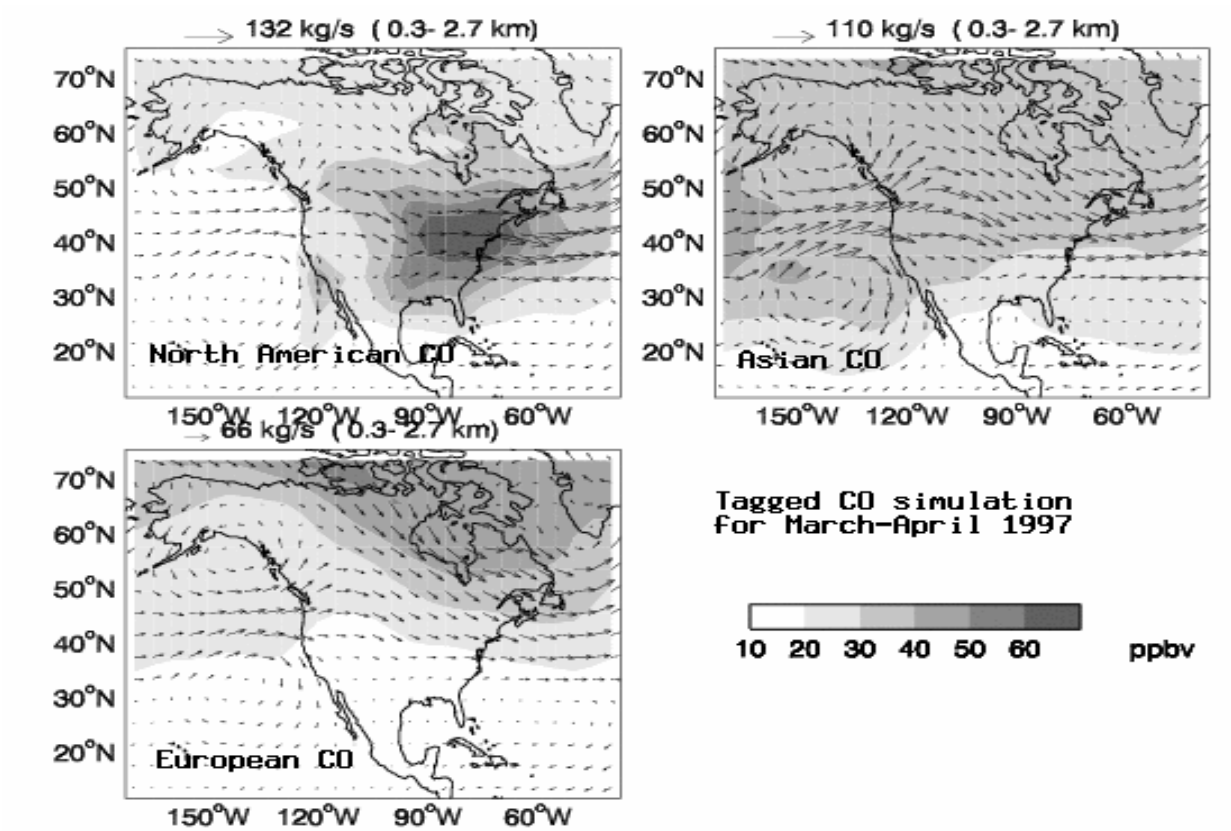



**Figure 8.2 Simulated concentrations of "tagged" CO from the surface to 2.7 km altitude for March-April 1997. The three panels represent the respective contributions of anthropogenic North American, Asian and European fossil fuel emissions to the CO levels over the United States. Arrows show the flux of the respective tracers**.

Integrating our understanding of the atmospheric processes into the WACAP program is not trivial. In particular, one of the key challenges will be reconciling the different time-scales involved. Atmospheric processes and transport occur on timescales of hours to days. The persistence of Asian pollution over the Western U.S. is typically a day or two. In contrast, ice and lake accumulation of contaminants and/or the bio-accumulation of contaminants operate on much longer time scales. Over the course of one year, a given watershed will be potentially affected by atmospheric transport from many different sources. Some key questions, which must be considered to meet WACAP objective #5 are:

1. How do we reconcile deposition and bio-accumulation processes, which occur on long time scales, with episodic atmospheric transport, which may have a persistence of just 1 or 2 days?
2. Can we identify long-range transport of POPs, which require several days for atmospheric sample collection, with an atmospheric variability (persistence) of just 1 or 2 days?
3. How do we locate sampling sites to optimize our understanding of the atmospheric deposition processes? For example, some sites will likely have enhanced contaminant deposition, while other sites may “under-sample” the deposition. This discrepancy could result from a variety of factors including precipitation effects and/or orographic effects.
4. How do we interpret the atmospheric flows and deposition in mountainous terrain, where the atmospheric flow can be quite complex?
5. How do we isolate contaminants that come from long-range transport as opposed to U.S. sources?

While addressing these questions will be quite challenging, we believe that the atmospheric component will be key to interpreting WACAP data. Therefore, as part of the interdisciplinary NPS WACAP we will conduct detailed atmospheric transport studies at the WACAP National Park sites.

## *Specific objectives for atmospheric component of WACAP*

To meet the WACAP source objective #5, we will combine atmospheric transport models with WACAP chemical data to understand the sources. Specifically we will:

1. Develop a climatology of transport patterns for each WACAP National Park. This will be done by season and using both near-surface heights, as well as elevated heights to examine the source of air at the surface and heights from where precipitation is forming.
2. Using the patterns for each site, establish the precipitation regime for each pattern. In other words, quantify the precipitation received for each site resulting from each transport pattern.

3. During the actual sampling year of each location, we will calculate trajectory distributions and compare with the climatological patterns. We will also use the actual sample year trajectories to quantify the transport for the days when precipitation actually fell at that site.
4. Utilize the global GEOS-CHEM transport model to simulate the atmospheric transport and deposition in a Eularian framework for the 14 sites. By tagging source regions, we will determine the origin of the air masses arriving at the sites as a function of season.

## *Approach/Specific Tasks*

The following tasks will be carried out during the first year of WACAP:

1. Calculate a set of atmospheric back trajectories for the WACAP Parks based on a climatological database of at least 5 years. For each location we will calculate a full set of trajectories at two heights, one at a near surface elevation and the second set at an elevation chosen to characterize the transport at the height of precipitating clouds.
2. The trajectories will be clustered to identify the primary transport pathways for each season. Clustering will be performed using a disjoint cluster method on the basis of Euclidean distances, as we have done previously, both in the Arctic and Pacific regions (e.g. Jaffe et al., 1997; Mahura et al., 1999; Baklanov et al., 2001). As an example of our previous work on clustering, Figure 8.3 shows a set of isentropic back-trajectories for 1991 for Nome, Alaska. This work was part of a project to quantify the likelihood of atmospheric transport to Alaska from the Bilibino nuclear plant, 1300 km west of Nome in eastern Russia. By clustering the trajectories, we identified 6 atmospheric transport patterns. The mean cluster back-trajectories are shown in Figure 8.4. The cluster numbers are arbitrary, but the % values correspond to the percentage of time that transport reflects this particular cluster. We will conduct a similar analysis for the WACAP sites.
3. Utilize the global GEOS-CHEM transport model to simulate the atmospheric transport and deposition in a Eularian framework for the same 14 sites. Based on our recent work using observations from CPO and vertical profiles from the west coast, we know that the GEOS-CHEM model does an excellent job of simulating the long-range transport of pollutants from both Asia and Europe to the U.S. west coast (Jaeglé et al., manuscript in preparation, 2002). Using meteorology for the year 2001, we will provide hourly time series of CO, ozone, dry and wet deposition at those 14 sites. In addition we will determine the origin of CO with a tagged simulation and quantify the relative influence of Europe, Asia and North America for the air arriving at these sites (as shown in Figure 8.2).

During subsequent years of WACAP we will continue with the following tasks:

1. We will utilize the 5 year set of trajectories to characterize the precipitation for each transport pattern. This will be done by identifying the closest, most

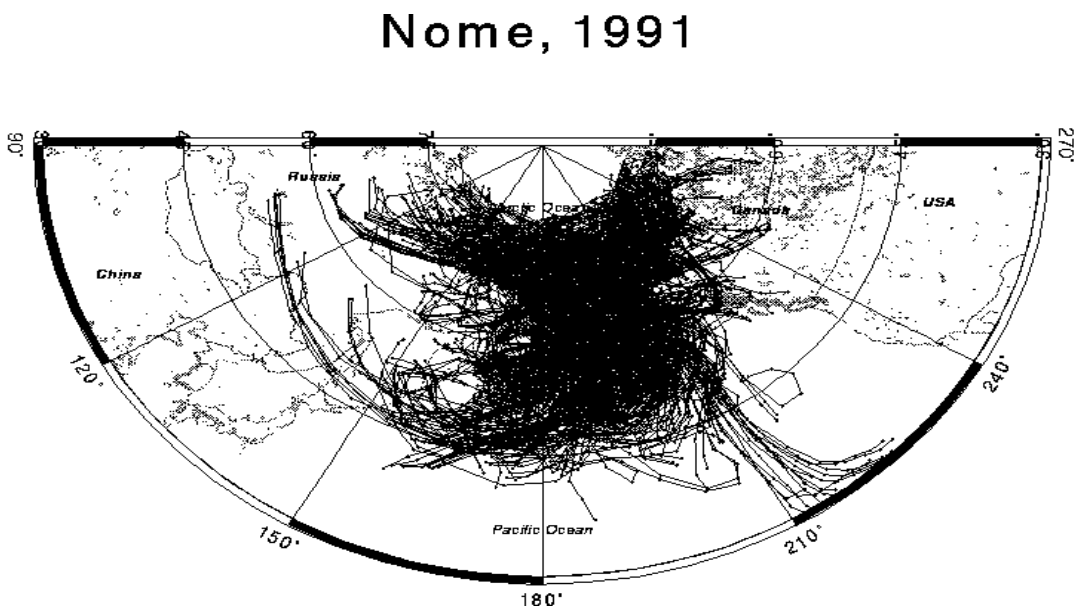



**Figure 8.3 Isentropic back-trajectories for every day in 1991 for Nome Alaska. These were calculated two times each day (O and 12 GMT).**

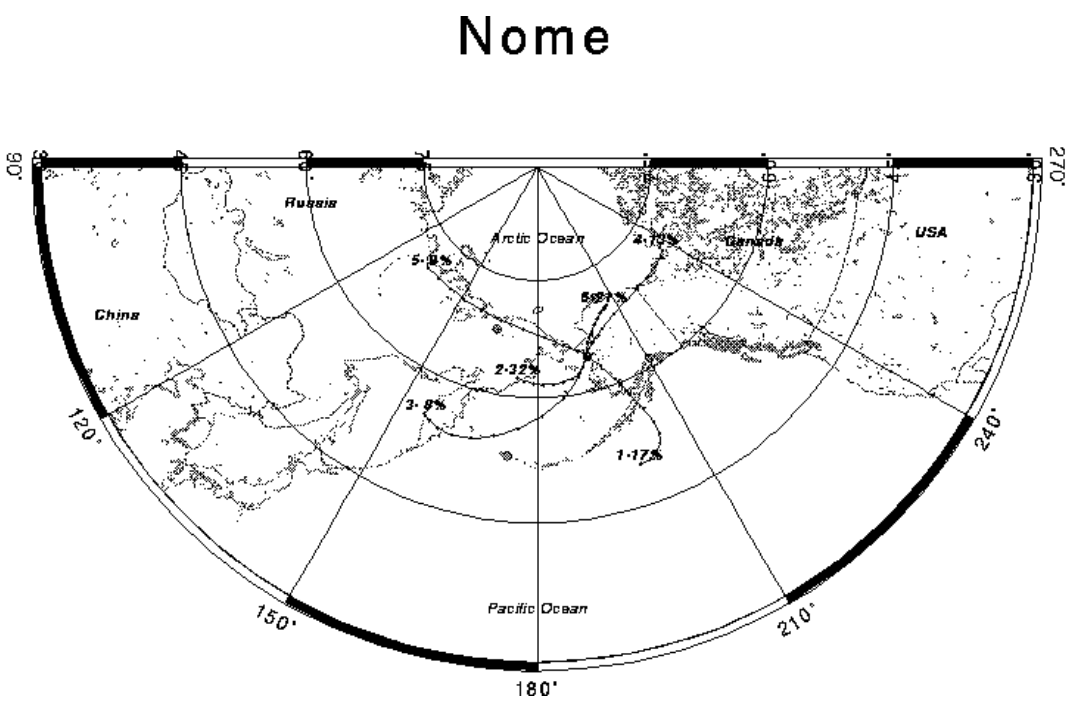



**Figure 8.4 5-day Back trajectory clusters based on 5 years of trajectory data for Nome Alaska**

representative meteorological site with long term precipitation records and matching to the transport pattern (cluster). Summing up the annual precipitation for each cluster will give us more information on the transport associated with highest precipitation periods.

2. During the years when each specific site is sampled, we will calculate trajectories for the precipitation/sampling period (fall through summer). These trajectories can then be compared with the climatological patterns already developed to determine how closely the specific sampling year reflects “normal” transport patterns. This will be important to ascertain that the snow samples taken are representative of climatological conditions. We will also evaluate the transport on the actual days with precipitation.
3. We will conduct global simulations of tagged-CO tracers with the GEOS-CHEM model for the sampling years and will quantify the origin of the air masses arriving at the sampling sites. We will also work towards the implementation of a mercury chemistry module in the GEOS-CHEM model, to help quantify the sources of atmospheric Hg, and the role of deposition at each site; and
4. Most importantly, we will integrate the atmospheric component into the full suite of chemical observations. To do this, we will compare the evidence from chemical data with the transport patterns to ascertain the degree of contamination and the sources.

# 9.0 DATABASE DESIGN AND DEVELOPMENT

*Marilyn Morrison Erway*

## *Software*

WACAP data will be reported in Microsoft Excel, and will be developed into a Microsoft Access database. Excel is used by most laboratories, and can be imported into many statistical software programs. Excel files will be structured similar to database files so they can be easily imported into Access, with columns becoming fields, and rows becoming records. Each sample type (e.g., snow, fish, water, sediment, lichen, bark) will have a separate Excel file.

## *Approach*

WACAP will have 14 sites, and some Parks will have additional snow sampling sites. Each site will have snow analyses each year, and then will have data from one year from the different matrices, such as fish, water, sediment, lichen, bark, and for the Alaska Parks, subsistence foods. Each sample matrix will also have multiple analyses (organic compounds, mercury, etc.) performed by different laboratories. There will also be field observations and ancillary data (e.g., bathymetric maps) that will be kept for reference. We will want the data in a format that we can:

- combine all data from the same matrix into one file
- sort the data by site
- sort the data by matrix
- trace to laboratory QA data
- refer to analytical methods

WACAP sites will be consistent from year to year, so a SITEID code will be used that will easily identify all samples from a site. The SITEID will be a four letter combined park and lake name acronym so the ID will be easily confirmed by field personnel, e.g., the SITEID for Emerald Lake in Sequoia National Park would be SEEM. Additional snow sampling sites, or sites not in the catchment, will be identified by number, e.g., SE3. Sample numbers will be assigned based on matrix type, in increments of 1000. Figure 9.1 lists the sample series by matrices. Each sample can be assigned a SITEID and SAMPLENO at collection that will follow the sample through all analyses.

Data for each analyte will be stored in three fields that will include the concentration, the analysis date, and the laboratory code. A numerical code will be assigned to identify each laboratory. QA and method information can then be linked based on the analysis date and laboratory. Table 9.1 provides an example of the site IDs for the candidate sites, with sample numbers assigned for the first year's snow samples.

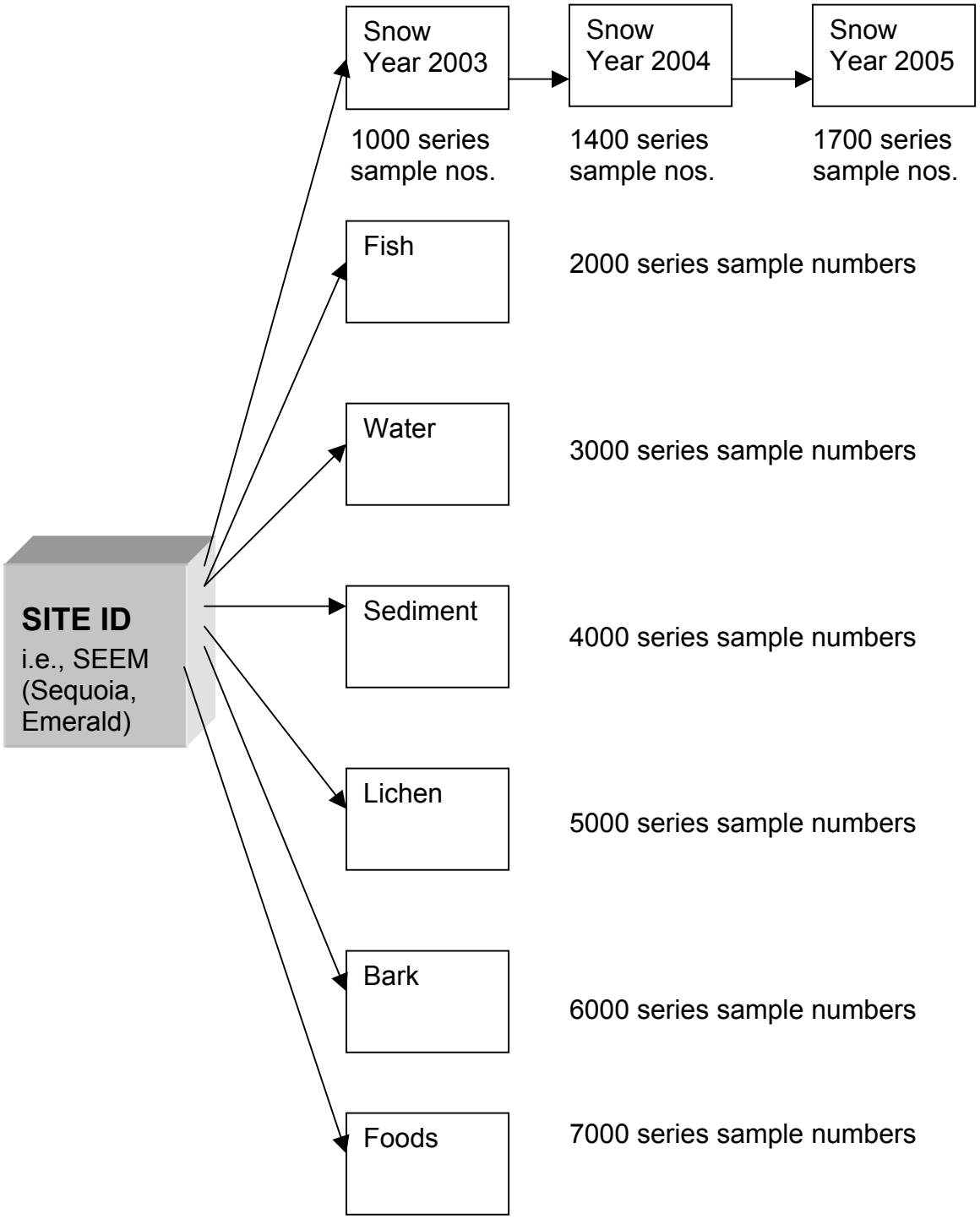



**Figure 9.1 Example of sample numbers for one site**

**Table 9.1 Example of spreadsheet site IDs and sample numbers for snow samples**

| SITE ID | SAMPLENO | MATRIX | SAMPLETYPE | SAMPLEDATE |
|---|---|---|---|---|
| DEMC | 1001 | snow | R | |
| DEWO | 1002 | snow | R | |
| DE3 | 1003 | snow | R | |
| DE4 | 1004 | snow | R | |
| GAMA | 1005 | snow | R | |
| GLOL | 1006 | snow | R | |
| GLSY | 1007 | snow | R | |
| MT1 | 1008 | snow | R | |
| MT2 | 1009 | snow | R | |
| MT3 | 1010 | snow | R | |
| NODE | 1011 | snow | R | |
| NODE | 1012 | snow | FLDUP | |
| OLBO | 1013 | snow | R | |
| OLHO | 1014 | snow | R | |
| ROLO | 1015 | snow | R | |
| ROMI | 1016 | snow | R | |
| RO3 | 1017 | snow | R | |
| RO3 | 1018 | snow | FLDUP | |
| SEEM | 1019 | snow | R | |
| SEPE | 1020 | snow | R | |

## *Data Management*

Samples will be tracked via computer database and spreadsheets and backed-up with printed forms whenever major sample or data transfers occur. Data from field activities will be entered into a permanent database as annotated Excel spreadsheets with hard copy remaining in field notebooks residing with each principal investigator.

Analytical results with appropriate batch calibration, precision, and performance evaluation along with any other QA/QC information will be compiled into complete data files at each laboratory. Where possible, data files from the analytical laboratories will be merged electronically to construct databases for each sample type. All data entered into the permanent database will be visually checked, line by line to eliminate any errors in transcription.

Data from each year will be verified and validated at each laboratory, then sent to the PI for that ecosystem indicator and to the data management group in Corvallis. Excel files will be combined into an Access database.

## *Distribution*

The final database will be in Access, with linked tables containing data for each site and all the ecosystem indicators, and available on CD. Documentation on the CD will include analytical methods, QA plans, and field notes. The data will also be available as Excel files. Our intention is to compile the database with enough information so that the data will be useful in the future.

# 10.0 QUALITY ASSURANCE AND QUALITY CONTROL

*Marilyn Morrison Erway*

## *Introduction*

A coordinated effort to develop and implement a system for quality assurance (QA) is necessary for a project like WACAP that is conducted by an interdisciplinary team of researchers over a period of time. Quality assurance is the "system of activities whose purpose is to provide to the producer or user of a product or a service the assurance that it meets defined standards of quality with a stated level of confidence" (Taylor, 1987). The objective of the quality assurance component of WACAP is to ensure that the data collected for all components of WACAP will be of sufficient quality to meet the project's objective "to assess the deposition of airborne contaminants in Western National Parks, providing regional and local information on exposure, accumulation, impacts and probable sources."

It is important to include planning for QA during the research planning process. A Quality Assurance Project Plan will be prepared for WACAP after the Research Plan is finalized. The QA Project Plan will describe the objectives for data quality that will be required to meet the project objectives, and then will describe the procedures that will be used to evaluate data quality. This document is a USEPA requirement and will be reviewed and approved by the USEPA Quality Assurance Officer. It will be published as an EPA document and will guide all analytical work conducted on all matrices sampled by the WACAP.

WACAP has some difficult QA issues to work with. The total number of sites is relatively small (14), and spread over a wide geographic area that will probably require multiple sampling teams. Most of the sites are very remote, so it will be important to maintain sample integrity during transport and storage. Sampling will occur over a three-year time period, with only one indicator (snow) being sampled annually, so there will be both site-to-site comparability issues as well as year-to-year comparability issues for the same site.

## *Approach*

WACAP will follow a standard QA approach of establishing QA objectives, then specifying how data quality will be controlled and assessed. This approach will include:

- Selecting methods and sample processing procedures with detection limits low enough to detect the contaminants and measure other metrics of interest;
- Establishing sampling protocols that will be consistent and standardized at all sites each year and among all sampling participants;
- Selecting shipping, storage, and processing methods to maintain sample integrity until analysis and minimize contamination;

- Establishing quality control (QC) procedures to monitor performance and calibration of measurement systems and provide rapid feedback so corrective actions can be taken before affecting data quality;
- Establishing methods to assess data quality, e.g., collection of duplicates to estimate precision and analysis of performance evaluation samples to estimate accuracy;
- Preparing a database with procedures to verify and validate data and document data quality.

WACAP involves sampling a wide range of ecosystem indicators, including snow, fish, lake sediment, water, lichen, tree bark, and in Alaska, subsistence native foods. Each ecosystem indicator has a lead researcher who will be responsible for developing a detailed QA section in the QA Project Plan for that indicator. Each section will include QA objectives, and protocols for sample collection, sample custody (shipping, storage, holding times), sample processing, and sample analysis. Quality control procedures will be specified, as well as data quality evaluation procedures including collection of field duplicates. We will have to make critical choices to maximize the use of project resources and establish in advance the information needed to evaluate data quality.

Quality assurance uses both quality assessment and quality control (QC). Quality assessment evaluates data quality as samples are being measured with performance evaluation samples, while QC is used to control the analytical processes before and during sample analysis to minimize data loss through out-of-control analytical systems. WACAP will be using both, but because of the high costs of collecting samples, QC will be important so corrective actions can be initiated and data loss minimized.

QA objectives are established based on the data quality required to meet project objectives. For example, data collected for WACAP will be used to report information about ecosystem indicators, and will not be used to detect trends in contaminants. Objectives are described and measured by indicators of data quality, with the most common being precision and accuracy. These indicators and the samples used to measure them are described below:

- Precision is the “degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions” (Taylor, 1987). Precision indicates variability, and is estimated in terms of the standard deviation of duplicates or replicates. It can be estimated at different points in the sampling process, e.g., in the field during sample collection by collecting field duplicates, in the laboratory during sample processing, and in the laboratory during analysis.
- Accuracy indicates the degree of agreement between a measured and true value of a reference sample, and is estimated in terms of difference from the reference value. Accuracy is usually assessed during sample analysis.
- Bias is a systematic error in the measurement process, and can be caused by any number of factors, such as contamination, calibration errors, temperature

effects, or extraction inefficiencies (Taylor, 1987). Bias is controlled by using procedures in the field and laboratory that will control and reduce these effects, e.g., QC calibration checks, monitoring storage temperatures, extraction spikes.

- Method detection limit is the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero (Glaser et al., 1981). Detection limits are assessed at the analytical level, and are an important characteristic of the measurement process, especially when comparing data from different time periods.
- Contamination is the influence of non-sample sources of the analytes of interest. Contamination can occur at multiple points during the sampling process, e.g., from containers, handling, and storage. The lower the concentration levels of the analytes of interest, the more critical it becomes to prevent contamination. Blanks at various points in the sampling process are used to measure contamination.
- Percent recovery is a measure of the efficiency of the extraction procedure. Recovery is assessed with the use of analytical spikes during the extraction procedure.
- Completeness is the amount of valid data actually obtained that is required to achieve the project objectives. For example, if only one year of snow sampling data is collected from a site instead of three years, will we still be able to meet the project objective of using snow as a measure of direct atmospheric loading?
- Representativeness is the degree to which data truly represent a characteristic of a population or environmental condition.
- Comparability is the degree of confidence with which two or more datasets may be compared. Datasets with similar precision, accuracy, and detection limits and little bias will be comparable.

Data comparability both within WACAP and outside WACAP will be an important issue to consider when deciding how much information about data quality will be needed. Data from most of the ecosystem indicators will be collected one time at each site, so we will want the data to be comparable among the sites over the three-year time period, i.e., we will want to compare information from each site, even though the information may not have been collected in the same year. This information will be used to describe spatial patterns in contaminants, so we want to be sure that any differences are true differences in ecosystem indicators, and not due to differences in collection or data analysis from year to year. Estimating variability each year will give some idea of the normal variability in these ecosystem indicators. Variability in data analysis can be controlled and evaluated within the laboratory, but variability in ecosystem indicators, field conditions, and collection processes will need to be estimated by collecting field duplicates. Field duplicates add extra samples at every step, so careful consideration needs to be given to how many we need.

### Collection of field duplicates

Each ecosystem indicator has a unique set of circumstances that will affect the number of duplicates to collect. Collection of field duplicates for snow sampling will be difficult because of the large volume of snow required, and the time required to collect snow at some of the remotes sites will make it very difficult to collect a second sample. Snow is also the only ecosystem indicator that will be sampled every year for three years. An estimate of within-year variability from field duplicates at each site would be helpful when comparing data from year-to-year, but the effort and analysis cost involved in collecting field duplicates at each site may be prohibitive. We plan to collect field duplicates at extra sites in Rocky Mountain National Park from more accessible sites to estimate within-year variability. When feasible, we will collect field duplicates from other sites (ideally at least once from each park during the three-year collection period). See Table 10.1 for a list of the proposed numbers of snow samples and field duplicates.

Collection of field duplicates for other ecosystem indicators will follow a similar pattern, except for sediment. Duplicate sediment cores will be collected, but not analyzed unless there are problems with the stratigraphy in the primary core. Sediment sections from the primary core will be dated using Pb-210 and Cs-137 before any other analyses. The dating profile will determine if the layers of sediment in the core were deposited in chronological order, and if so, the core will be considered good and other analyses will proceed. Duplicate cores are not necessary because each core will have approximately 20 sections, and we will be looking for changes in concentration through the chronology represented by the sections.

### Field Blanks

Collection of field blanks for SOC analyses is critical for determination of contamination, yet very difficult to do with remote field sites and with samples that require large volumes DI water. Ideally, organic-free DI water would be brought to each field site and treated the same as a sample. However, that would require 50 to 60 L of water be transported to the field site, then transported back, and shipped to the laboratory. We are considering alternatives, including adding DI water to the sampling container or extraction column at an easily accessible park location, but we also have to be sure we are not creating opportunities for additional contamination. Another alternative would be to bring extra sample containers or extraction columns to the field, handled in the same manner as if a sample were added, exposed to ambient air, then transported back to the laboratory along with the regular samples. The advantage to this method is that it would be possible to have field blanks associated with each field site.

**Table 10.1 Snow Sampling Sites and Field Duplicates**

| Park | Site | Elevation (meters) | Number of snow sites | Number of snow samples (3 yr.) | Number of field duplicates (3 yr.) |
|---|---|---|---|---|---|
| Sequoia | Emerald | 2800 | 2 | 6 | 1 |
| | Pear | 2904 | | | |
| Rocky Mtn. | Mills | 3030 | 3 | 9 | 3 |
| | Lone Pine | 3024 | | | |
| | Extra | TBD* | | | |
| Glacier | Oldman | 2026 | 2 | 6 | 1 |
| | Synder | 1600 | | | |
| Olympic | PJ Lake | 1433 | 2 | 6 | 1 |
| | Hoh Lake | 1384 | | | |
| Mt. Rainier | Golden | 1372 | 2 | 6 | 1 |
| | Puyallup | 1372 | | | |
| Denali | Wonder | 610 | 2 | 6 | 1 |
| | Foraker | 732 | | | |
| Noatak | Desperation | 427 | 2 | 6 | 1 |
| Gates of the Arctic | Matcharak | 488 | | | |
| | | Totals: | 15 | 45 | 9 |

*To be determined

**Performance Evaluation**

Another data comparability issue involves the comparability of data from different laboratories participating in WACAP, and comparing WACAP data with data from other projects. Within WACAP, we have made an effort to have all analyses for each parameter analyzed at the same analytical facility. However, up to six different laboratories will be analyzing WACAP samples, and even though the samples may be from different sample types (water, fish, lichens, etc.) we still want the analytical results to be comparable (see Table 10.2). For example, mercury data from fish, sediment,

water, and snow will be used to describe the impact of mercury to a catchment. All participating laboratories will participate in external performance evaluation program for analytes when they are available, e.g., major ions, metals, and mercury. Programs for organic compounds are not presently available, so round robin exchanges with other laboratories will be planned. Certified standard reference material will also be used when available.

**Table 10.2 WACAP Laboratories By Analyte Group And Ecosystem Indicator**

| Ecosystem Indicator | Organic Compounds | Mercury | Metals | Major ions/ nutrients |
|---|---|---|---|---|
| Snow | OSU | USGS Wisconsin Lab | USGS Boulder Lab | USGS Colorado District Lab & USGS Boulder Lab |
| Fish | OSU | WRS | USGS Boulder Lab | — |
| Water | OSU | — | — | WRS |
| Sediment | OSU | WRS | USGS Boulder Lab | — |
| Lichens | — | WRS | USGS Boulder Lab | UMNRAL |
| Willow Bark | OSU | — | — | — |
| Moose | OSU | WRS | USGS Boulder Lab | — |

WACAP Laboratories:

OSU: Oregon State University, Department of Environmental and Molecular Toxicology, Corvallis, OR
USGS: United States Geological Survey,
WRS: Willamette Research Station Analytical Laboratory, U.S. EPA, Corvallis, OR
UMNRAL: University of Minnesota Research Analytical Laboratory, Department of Soil, Water, and Climate, St. Paul, MN

**Laboratory Quality Control**

Quality control samples and practices in each laboratory will provide immediate feedback on analytical processes as well as contamination sources in the laboratory. Calibration QC samples will be analyzed at regular intervals to ensure instrument calibrations do not drift. Blanks will be included in sample processing steps and

laboratory deionized water systems will be routinely monitored to detect contamination. Low concentration detection limit samples will be used to monitor instrument detection limits where applicable. Temperatures of freezers, refrigerators, and coolers will be monitored on a daily basis where possible. Each laboratory will describe their specific QC samples in the QA Plan.

## *Database Development*

Each laboratory will be responsible for data verification and validation before releasing data. In addition, each laboratory will be responsible for providing results from performance evaluation samples, analytical precision and accuracy, instrument detection limits, and blank analyses. QA data will be summarized for each sample type from each catchment, and will include precision, both from field duplicates and analytical duplicates, accuracy, method detection limit, percent recoveries, and a summary of blank analyses. Samples that do not meet the QA objectives will be noted. QA data summaries will be reported annually.

# 11.0 REFERENCES

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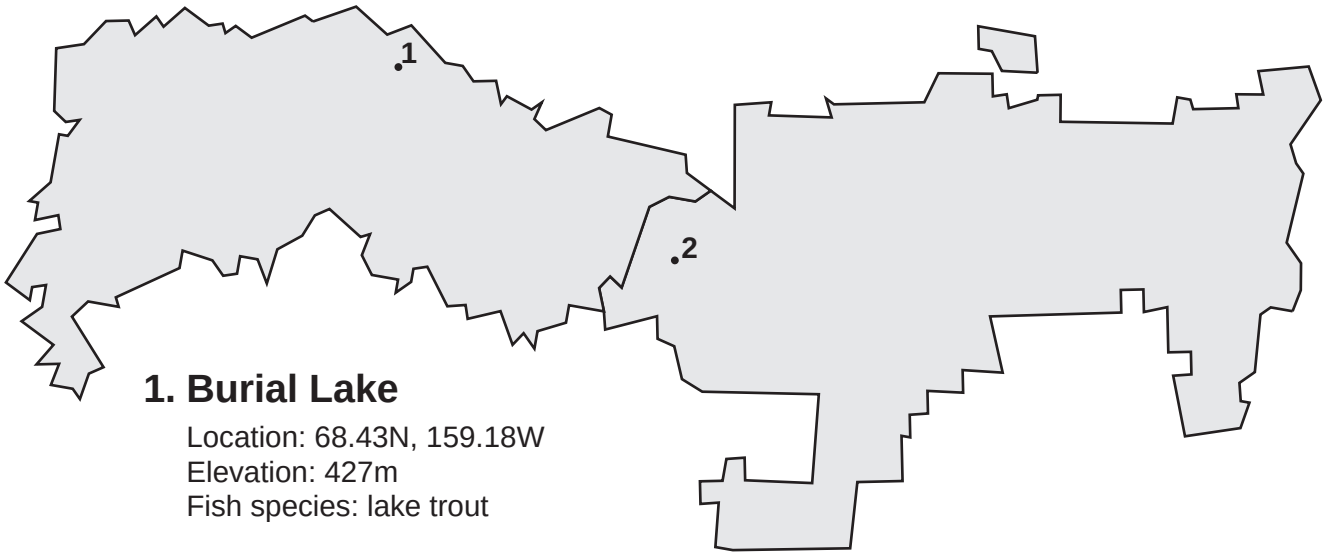
# APPENDIX A: CANDIDATE SITE MAPS AND BATHYMETRIC MAPS

Noatak National Preserve and Gates of the Arctic National Park and Preserve ..... A-2
Burial Lake ..... A-3
Matcharak Lake ..... A-4
Denali National Park ..... A-5
Wonder Lake ..... A-6
McLeod Lake ..... A-7
Foraker Lake ..... A-8
Olympic National Park ..... A-9
PJ Lake (bathymetry scheduled for collection in Summer 2003)
Hoh Lake ..... A-10
Mt. Rainier National Park ..... A-11
Golden Lake ..... A-12
Unnamed LP19 ..... A-13
Glacier National Park ..... A-14
Synder Lake (bathymetry scheduled for collection in Summer 2003)
Oldman Lake (bathymetry scheduled for collection in Summer 2003)
Rocky Mountain National Park ..... A-15
Mills Lake ..... A-16
Lone Pine Lake ..... A-17
Sequoia National Park ..... A-18
Pear Lake ..... A-19
Emerald Lake ..... A-20

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




## 1. Burial Lake

Location: 68.43N, 159.18W
Elevation: 427m
Fish species: lake trout

## 2. Matcharak Lake

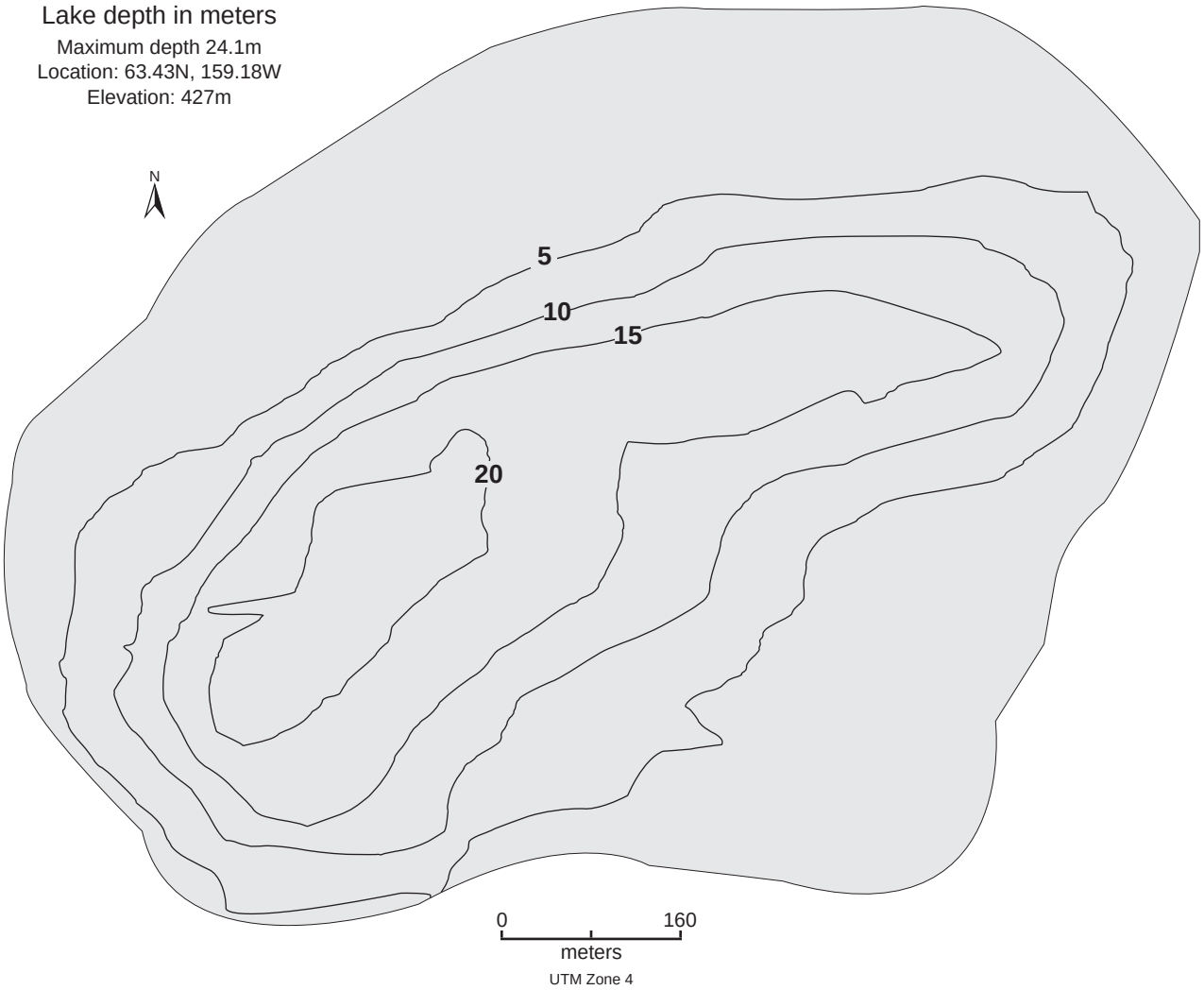
Location: 67.75N, 156.21W
Elevation: 488m
Fish species: arctic char

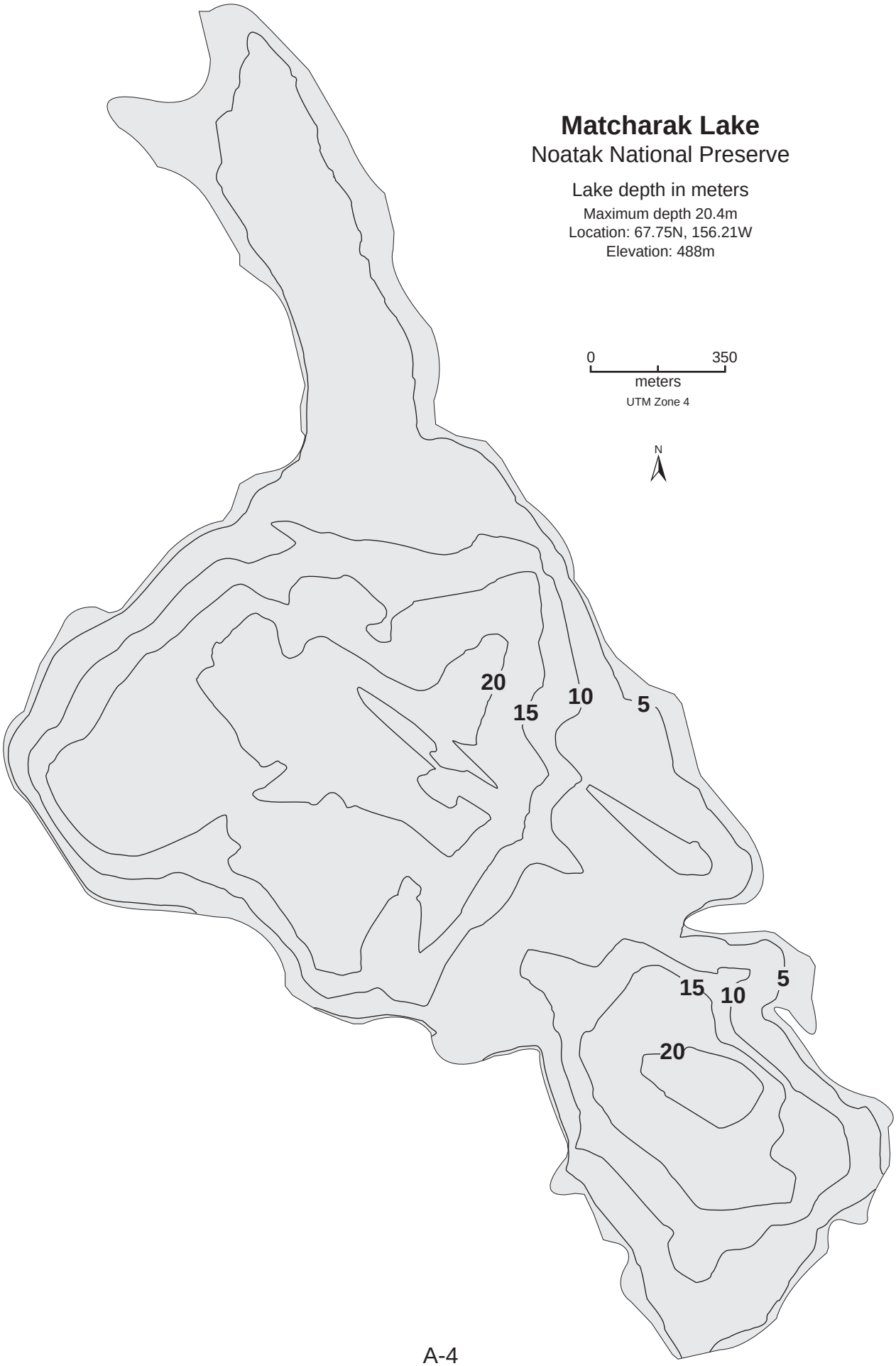
# Burial Lake

Noatak National Preserve

Lake depth in meters

Maximum depth 24.1m
Location: 63.43N, 159.18W
Elevation: 427m




Matcharak Lake
Noatak National Preserve
Lake depth in meters
Maximum depth 20.4m
Location: 67.75N, 156.21W
Elevation: 488m
0
350
meters
UTM Zone 4
N
20
15
10
5
15
10
5
20

# Denali National Park

## 1. Wonder Lake

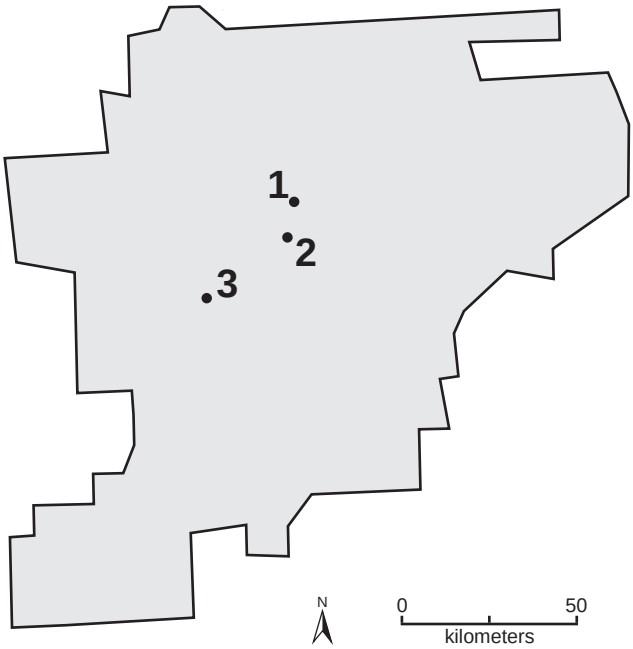
Location: 63.48N, 150.88W
Elevation: 610m
Fish species: lake trout, arctic grayling, burbot, arctic char

## 2. McLeod Lake

Location: 63.38N, 151.07W
Elevation: 609m
Fish species: Unknown

## 3. Foraker Lake

Location: 63.22N, 151.60W
Elevation: 732m
Fish species: Unknown



# Wonder Lake

Denali National Park

Lake depth in meters

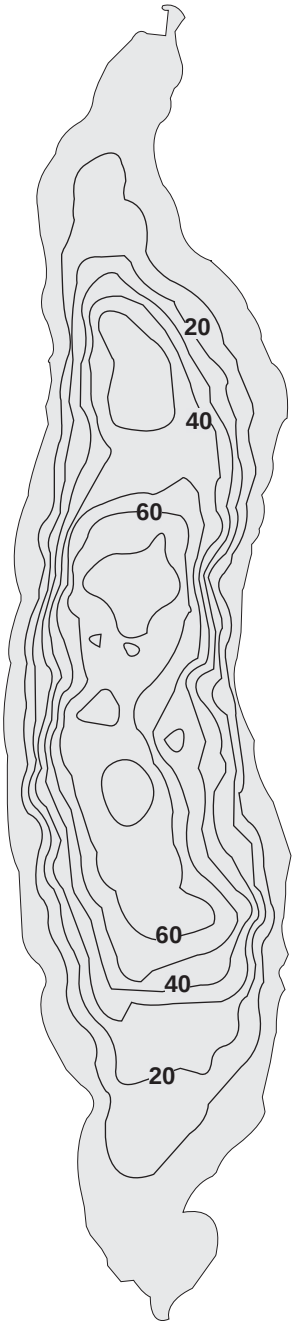
Location: 63.48N, 150.88W

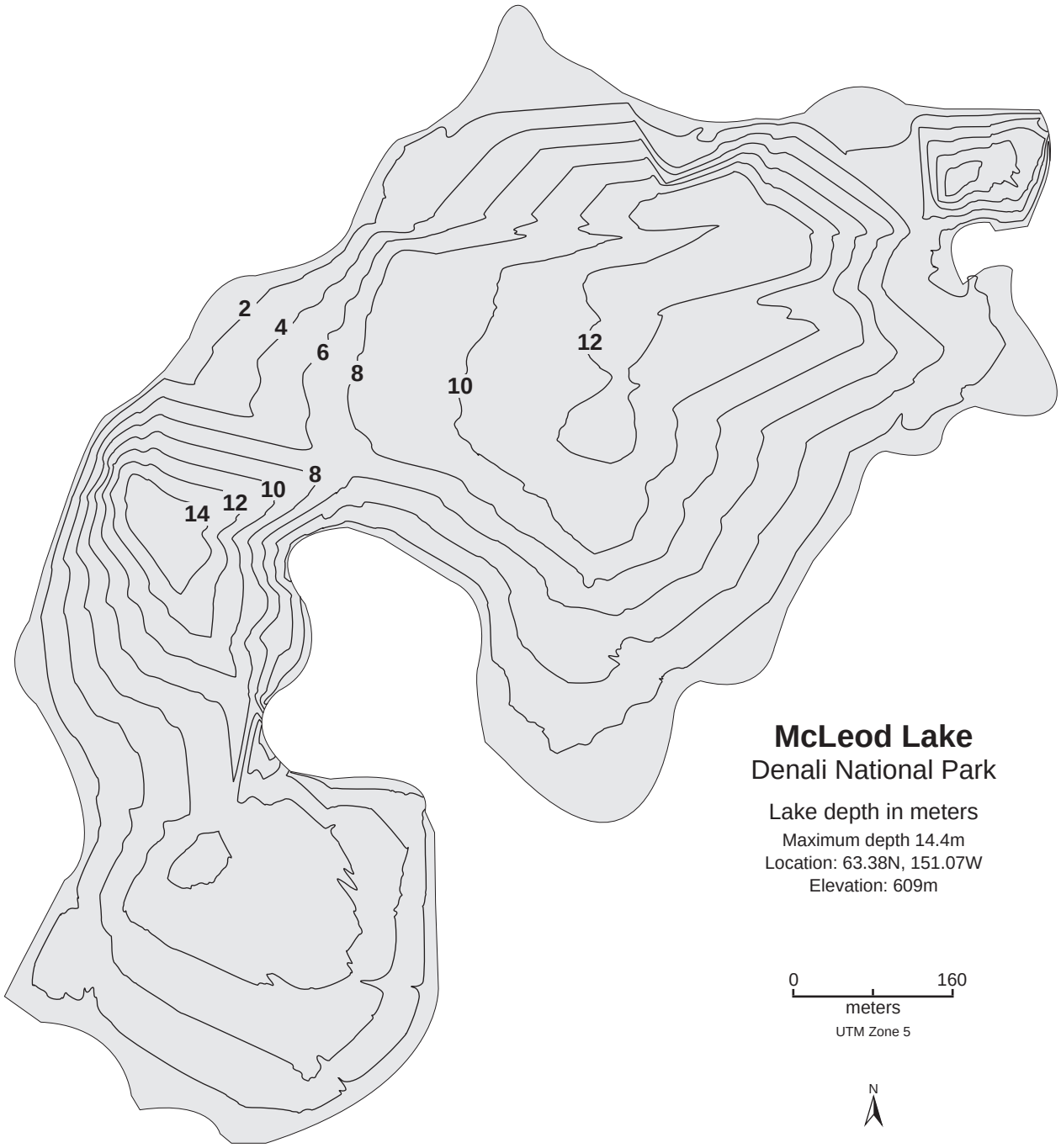
Elevation: 610m

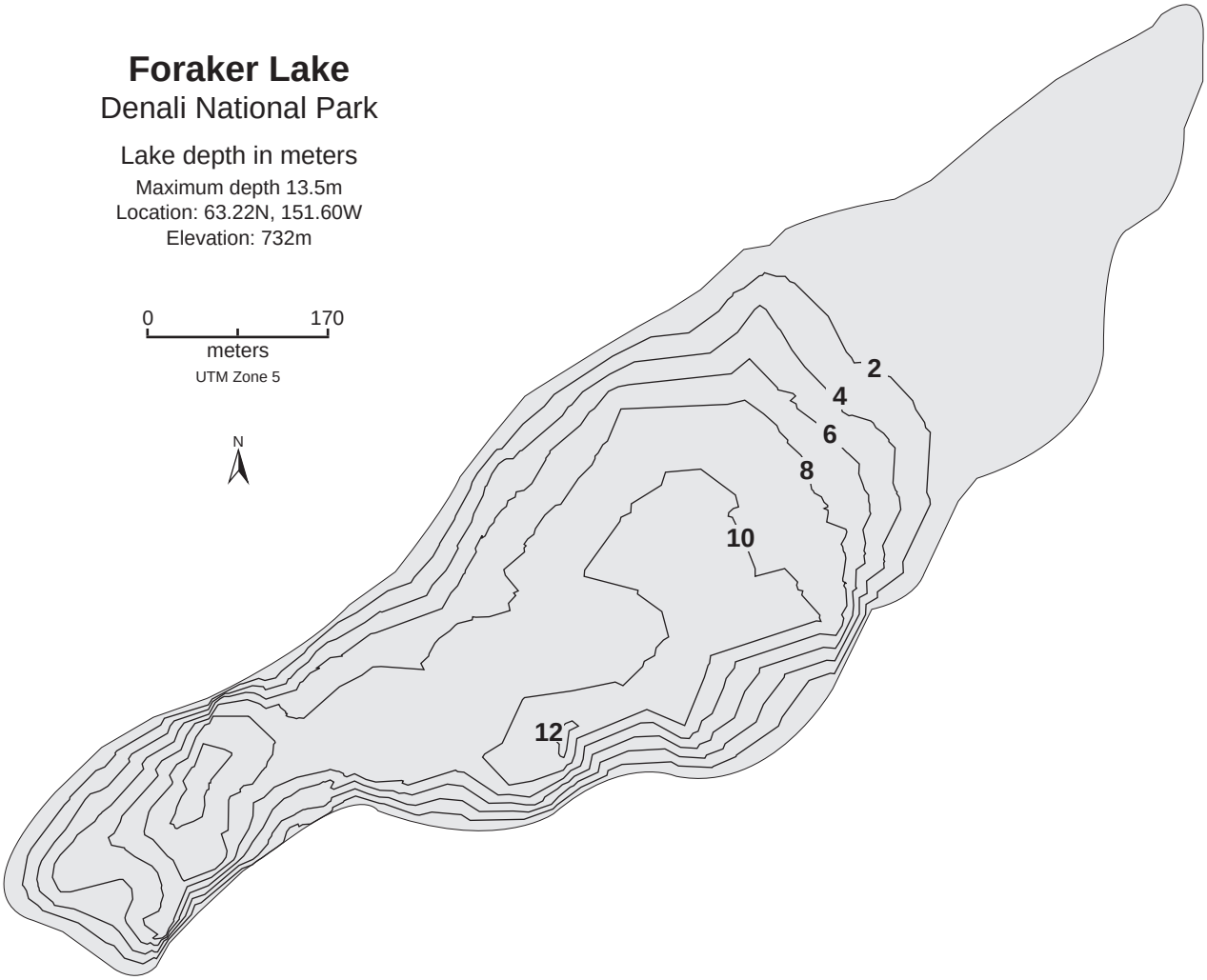
0 670

meters

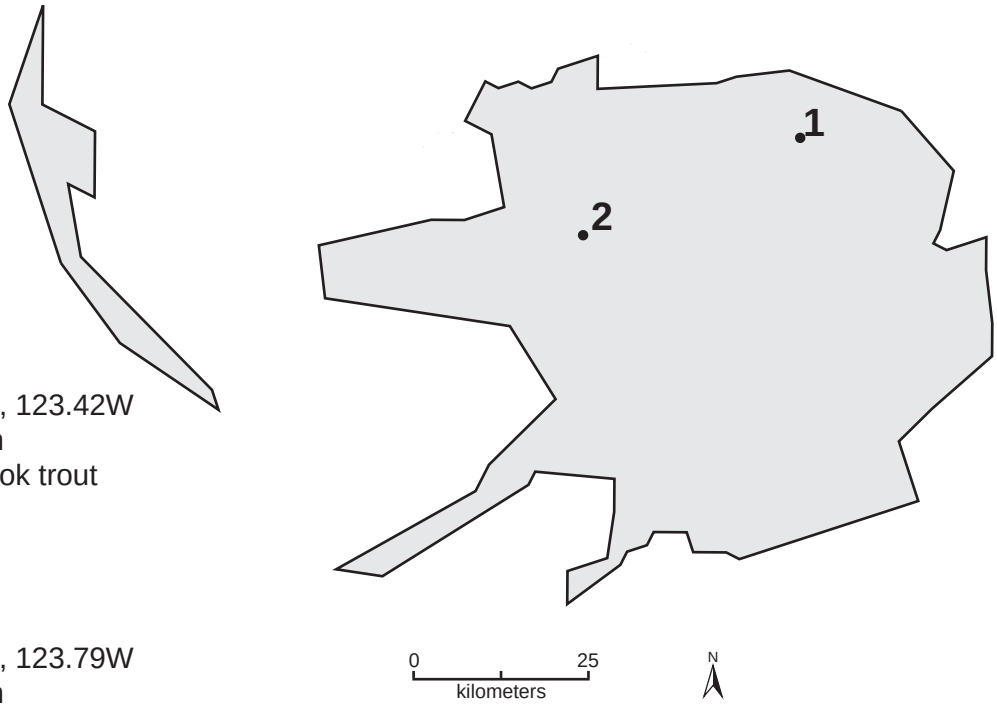
N




2
4
6
8
10
12
8
10
12
14
McLeod Lake
Denali National Park
Lake depth in meters
Maximum depth 14.4m
Location: 63.38N, 151.07W
Elevation: 609m
0
160
meters
UTM Zone 5
N


Foraker Lake
Denali National Park
Lake depth in meters
Maximum depth 13.5m
Location: 63.22N, 151.60W
Elevation: 732m
0
170
meters
UTM Zone 5
N
2
4
6
8
10
12

# Olympic National Park

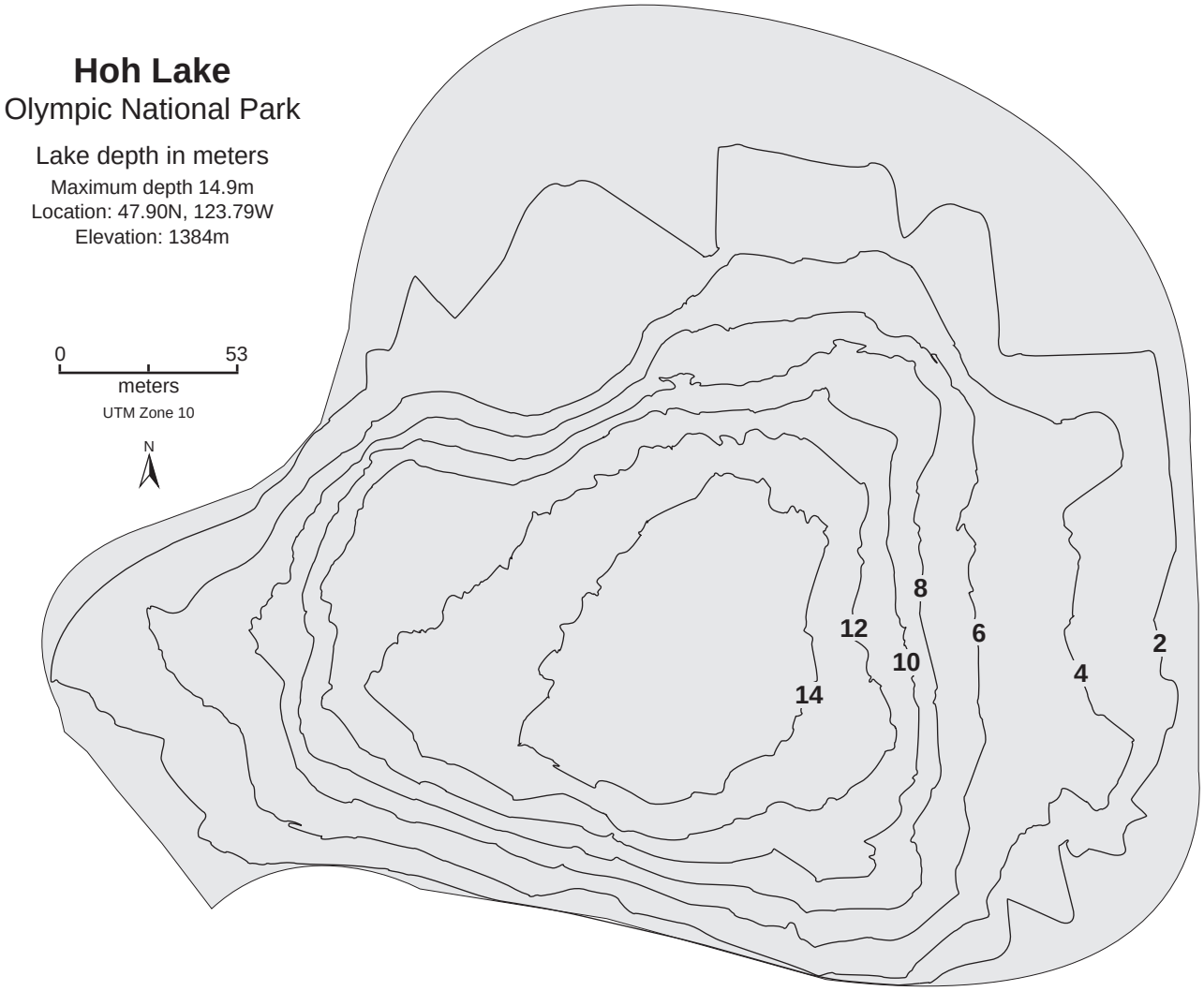



## 1. PJ Lake

Location: 47.95N, 123.42W
Elevation: 1433m
Fish species: brook trout

## 2. Hoh Lake

Location: 47.90N, 123.79W
Elevation: 1384m
Fish species: brook trout


Hoh Lake
Olympic National Park
Lake depth in meters
Maximum depth 14.9m
Location: 47.90N, 123.79W
Elevation: 1384m
0
53
meters
UTM Zone 10
N
2
4
6
8
10
12
14

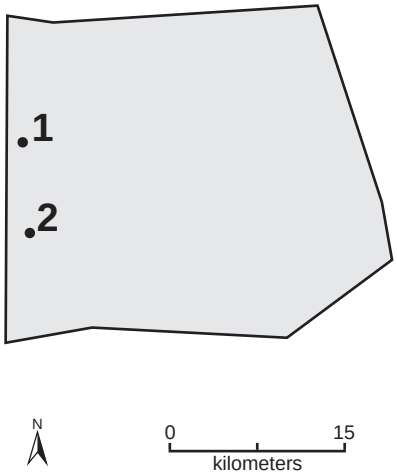
# Mt. Rainier National Park

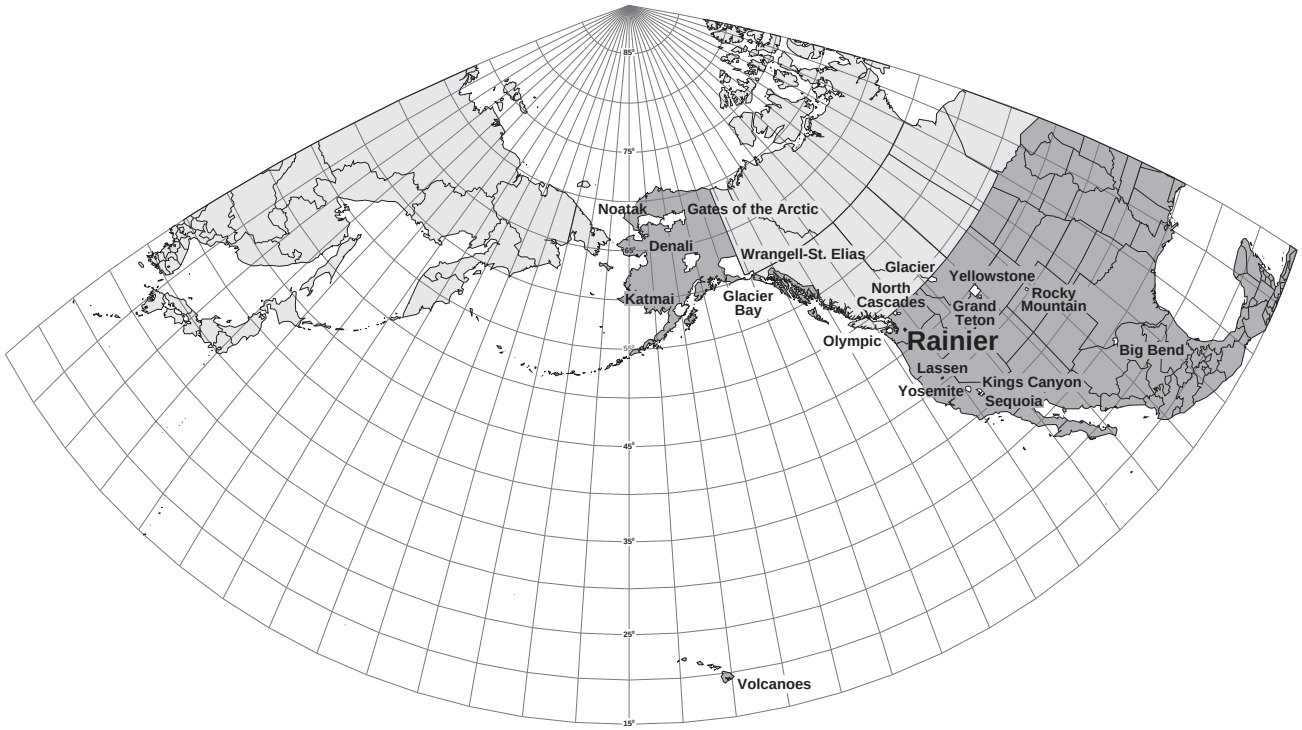
## 1. Golden Lake

Location: 46.89N, 121.90W
Elevation: 1372m
Fish species: rainbow trout

## 2. Unnamed LP19

Location: 46.82N, 121.89W
Elevation: 1372m
Fish species: rainbow trout



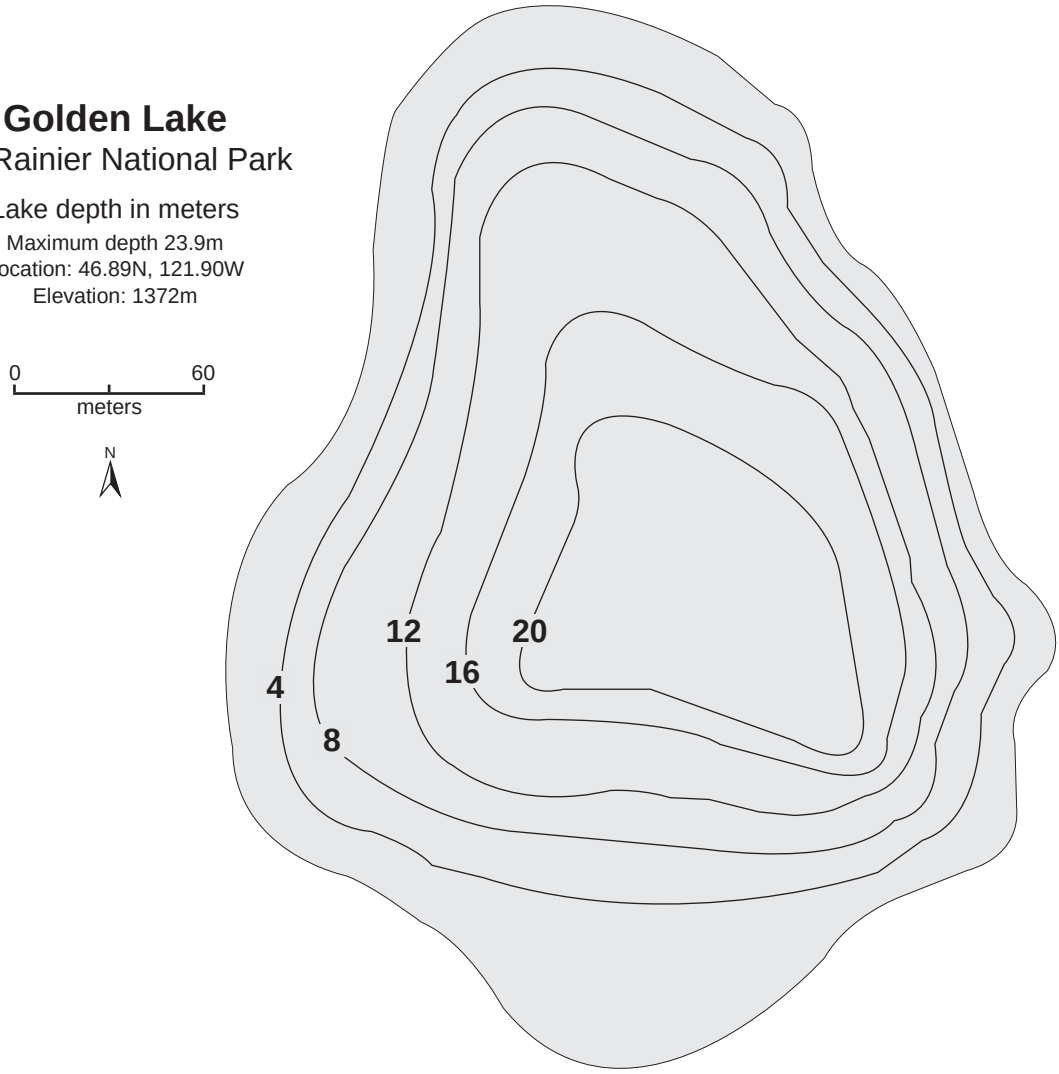



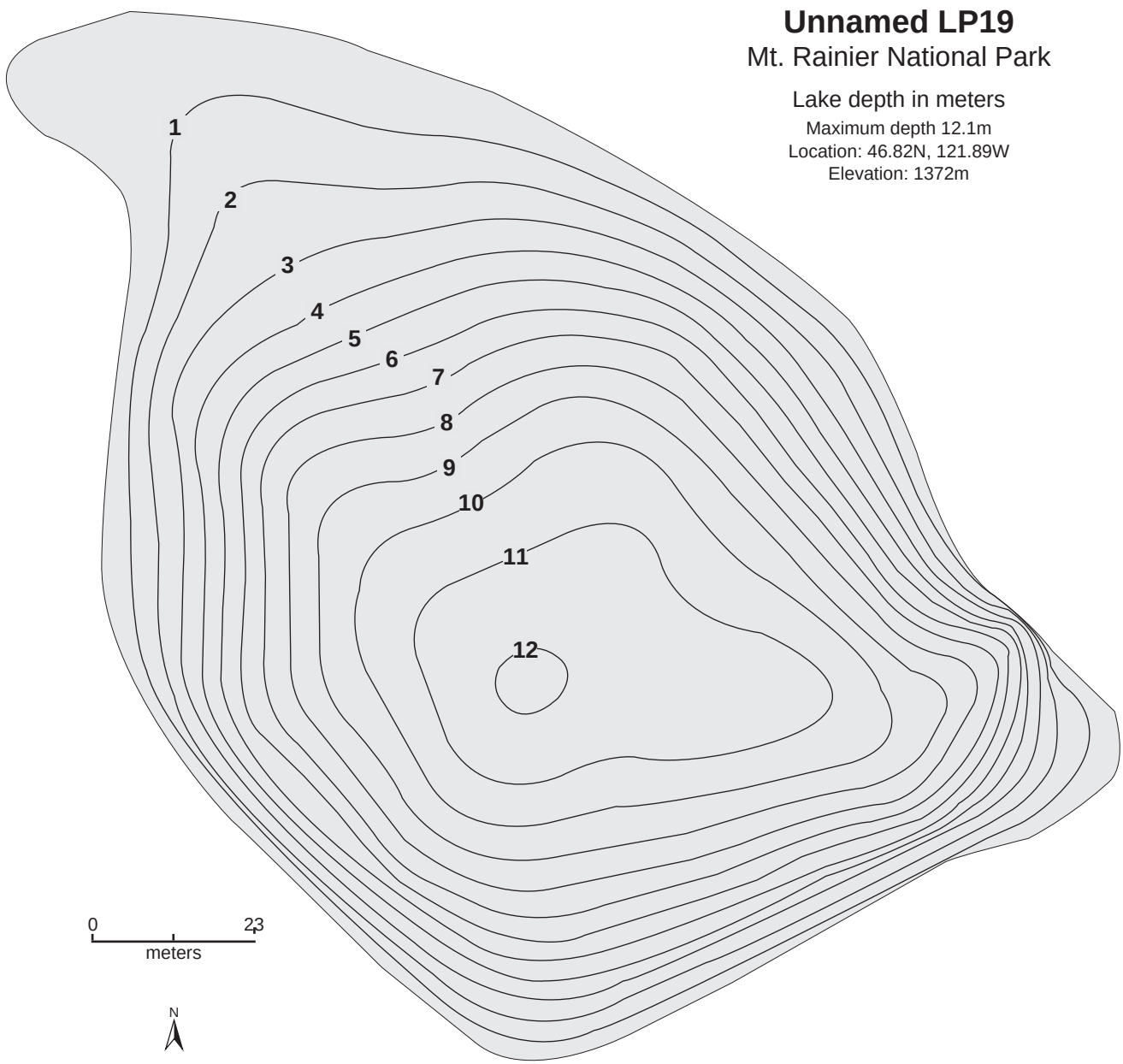
# Golden Lake

Mt. Rainier National Park

Lake depth in meters

Maximum depth 23.9m
Location: 46.89N, 121.90W
Elevation: 1372m




Unnamed LP19
Mt. Rainier National Park
Lake depth in meters
Maximum depth 12.1m
Location: 46.82N, 121.89W
Elevation: 1372m
1
2
3
4
5
6
7
8
9
10
11
12
0
23
meters
N

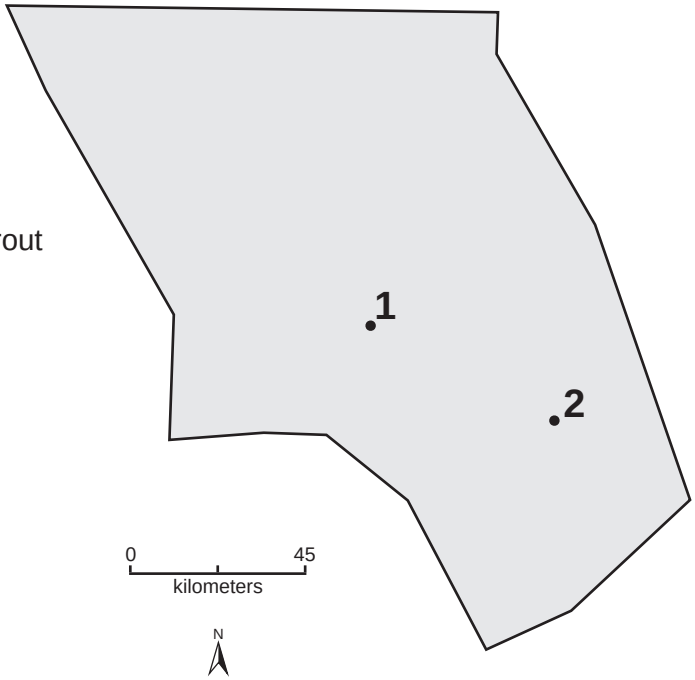
# Glacier National Park

## 1. Synder Lake

Location: 48.62N, 113.79W
Elevation: 1600m
Fish species: westslope cutthroat trout

## 2. Oldman Lake

Location: 48.50N, 113.46W
Elevation: 2026m
Fish species: cutthroat trout



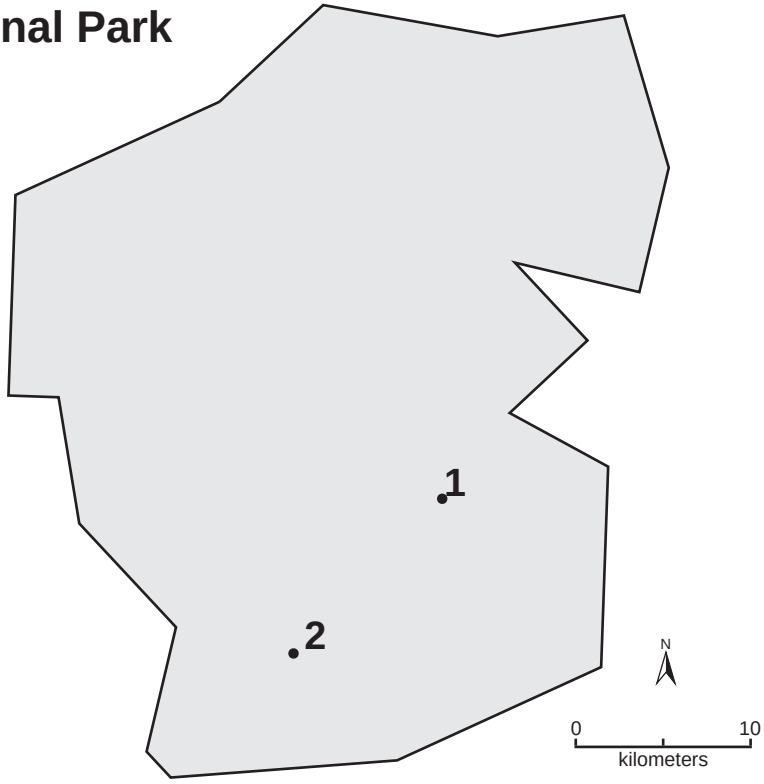
# Rocky Mountain National Park

## 1. Mills Lake

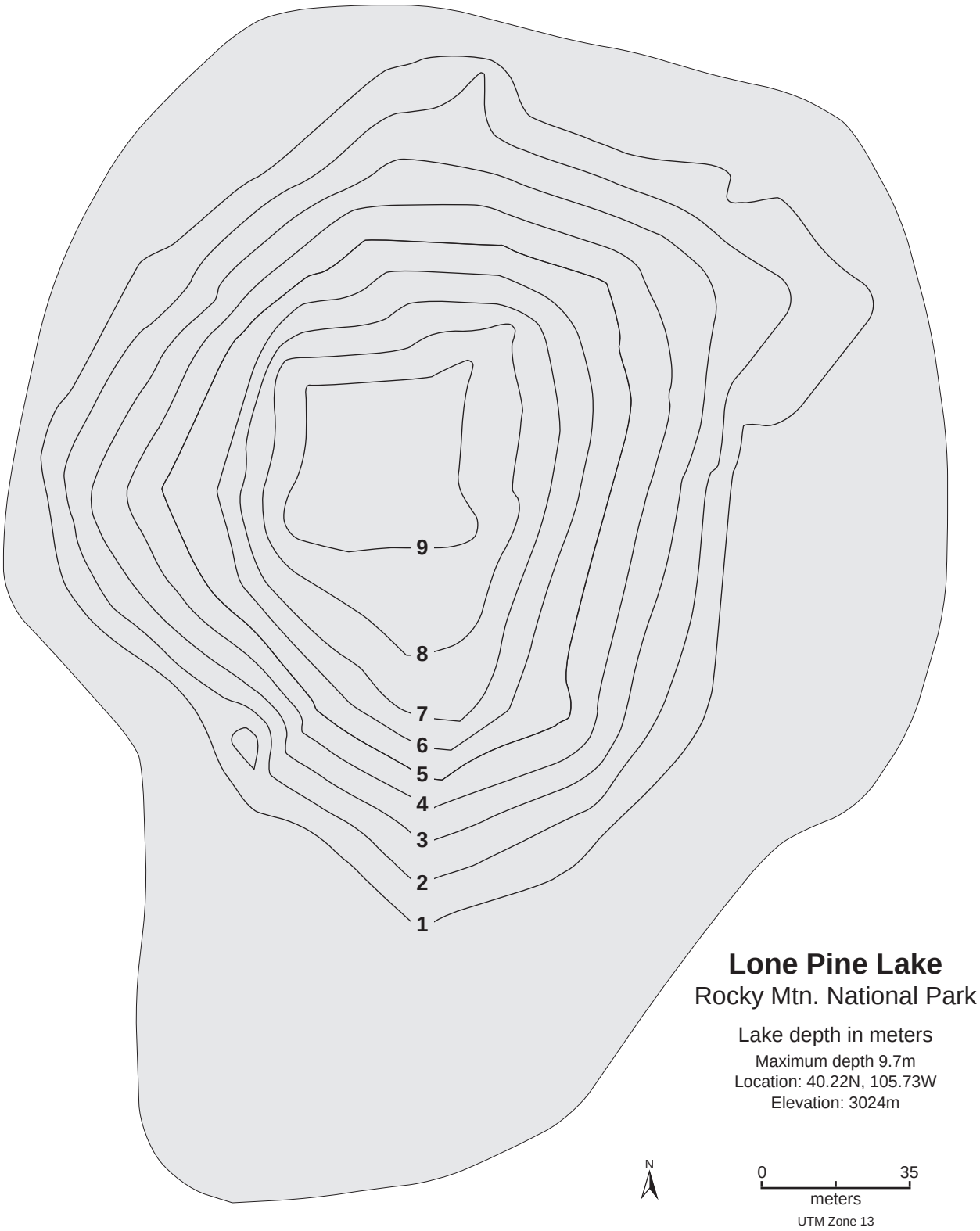
Location: 40.29N, 105.64W
Elevation: 3030m
Fish species: rainbow trout

## 2. Lone Pine Lake

Location: 40.22N, 105.73W
Elevation: 3024m
Fish species: brook trout



Mills Lake
Rocky Mtn. National Park
Lake depth in meters
Maximum depth 9.0m
Location: 40.29N, 105.64W
Elevation: 3030m
0
35
meters
UTM Zone 13
N
1
2
3
4
5
6
7
8




**Lone Pine Lake**

Rocky Mtn. National Park

Lake depth in meters

Maximum depth 9.7m
Location: 40.22N, 105.73W
Elevation: 3024m

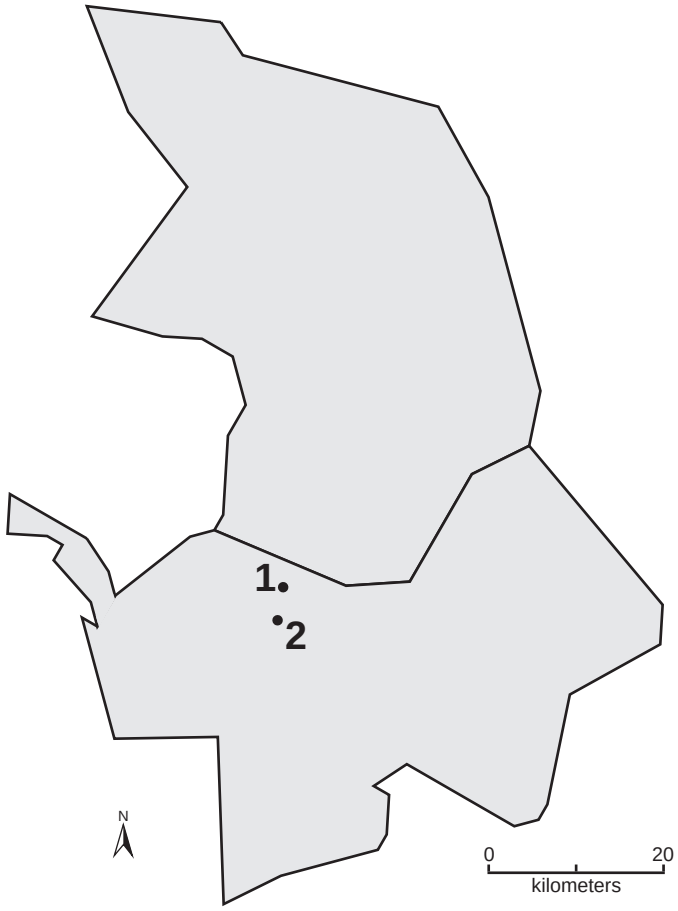
# Sequoia National Park

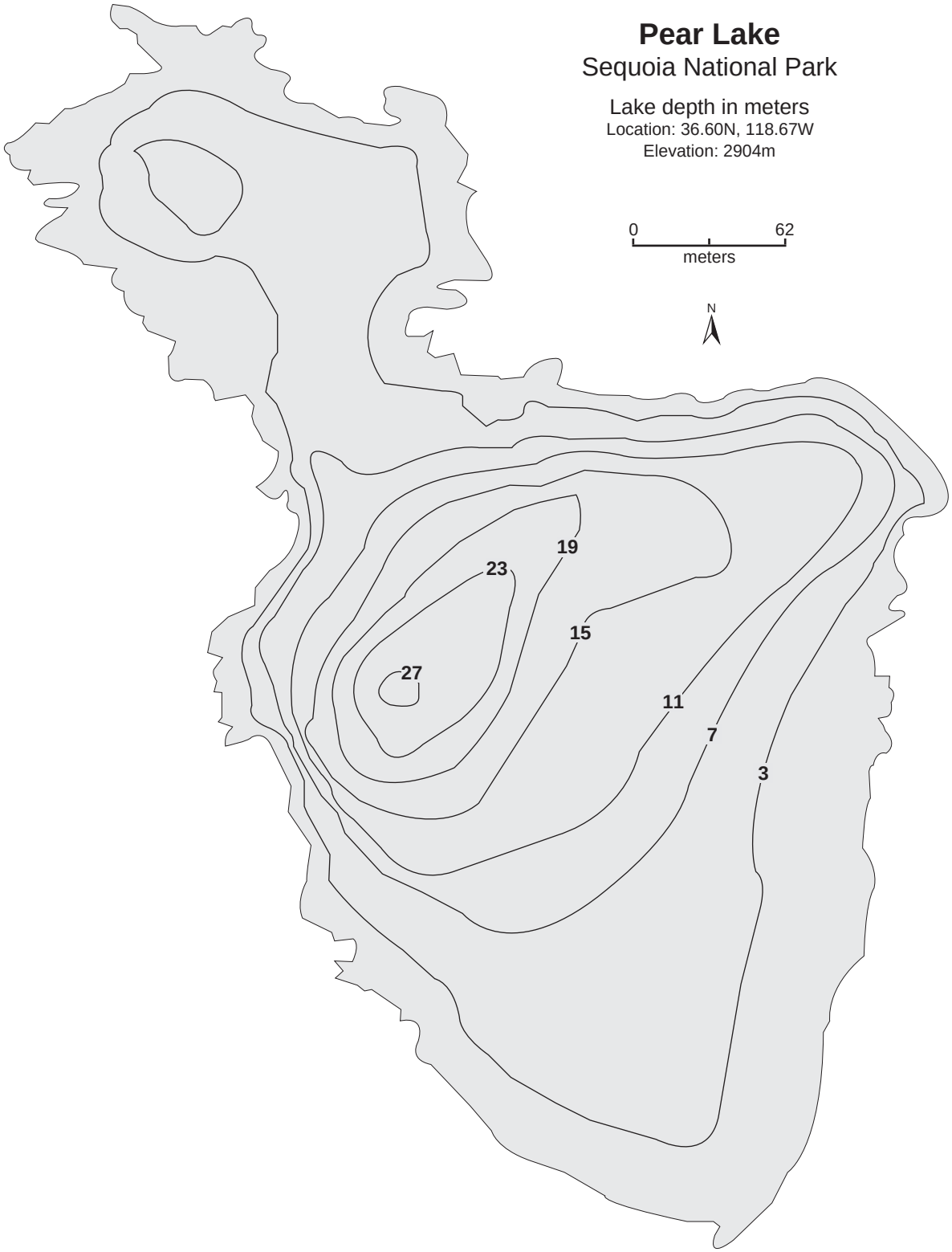
## 1. Pear Lake

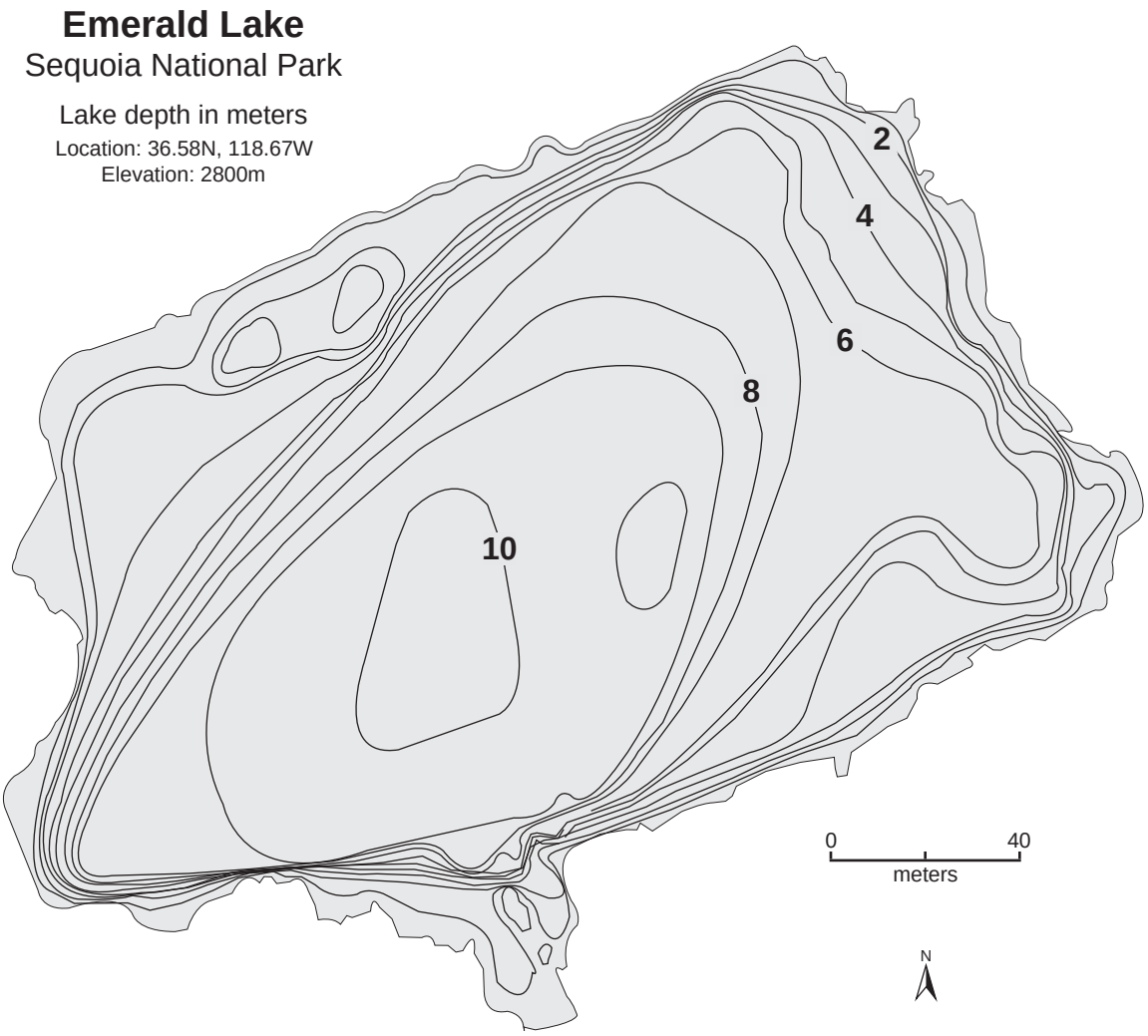
Location: 36.60N, 118.67W
Elevation: 2904m
Fish species: brook trout

## 2. Emerald Lake

Location: 36.58N, 118.67W
Elevation: 2800m
Fish species: brook trout




Pear Lake
Sequoia National Park
Lake depth in meters
Location: 36.60N, 118.67W
Elevation: 2904m
0
62
meters
N
19
23
15
27
11
7
3


Emerald Lake
Sequoia National Park
Lake depth in meters
Location: 36.58N, 118.67W
Elevation: 2800m
2
4
6
8
10
0
40
meters
N

# APPENDIX B: CURRICULUM VITAE OF WACAP SCIENCE TEAM

**Tamara F. Blett** ..... **B-2**
**Donald H. Campbell** ..... **B-4**
**Marilyn M. Erway** ..... **B-6**
**Daniel A. Jaffe** ..... **B-8**
**Michael L. Kent** ..... **B-10**
**Dixon H. Landers** ..... **B-12**
**Linda H. Geiser** ..... **B-14**
**Carl B. Schreck** ..... **B-16**
**Staci L. Simonich** ..... **B-18**
**Howard E. Taylor** ..... **B-20**

**Tamara Franklin Blett**
**Ecologist, Research and Monitoring Branch**
**Air Resources Division, National Park Service**
**Denver, Colorado 80439**
**Phone: 303-969-2011**
**Email: tamara_blett@nps.gov**

**Professional Experience:**

**National Park Service - Air Resources Division from October 2000 to the present: Ecologist.** Focus is on the protection of natural resources in parks from the effects of air pollution, through initiating, synthesizing and interpreting available research and monitoring information on ecological effects and applying these analyses to air quality policy issues.

**USDA Forest Service – Rocky Mountain Region from 1988 through 2000: Air Resource Management Specialist.** Responsible for implementation and oversight of pollution-impacts related monitoring programs for water, soils, flora, fauna, visibility and deposition in the Region. Reviewed industrial air quality permits and environmental impact statements to develop air pollution mitigation recommendations for the proposed projects, and developed and presented training sessions on smoke management and wilderness management topics.

**Colorado State University- Fort Collins, 1986-1988: Graduate Research Assistant, Department of Forest and Wood Sciences.** Conducted fire ecology research project on community dynamics of a subalpine forest ecosystem in the Colorado Rocky Mountains.

**USDA Forest Service – Riverside Forest and Range Experiment Station, Riverside California, 1983 to 1986: Ecologist.** Conducted chamber fumigations and field surveys looking at ozone effects on sequoia and oak seedlings in Sequoia National Park, and conducted data analysis and project planning in Riverside.

**University of California, Los Angeles, 1982 to 1984: Research Assistant, Lab of Biomedical and Environmental Sciences**. Assisted research team in studying acid deposition effects on vegetation at chaparral, forest and subalpine sites in Sequoia National Park. Conducted measurements on vegetation, water relations and soils and prepared data for statistical analysis.

**Education:**

University of California Irvine: B.S. in Biology (1983)
Colorado State University: M.S. in Forest Ecology (1988)

**Selected Publications/Documents:**

- USDA Forest Service, Rocky Mountain Region, 2000. "Screening Methodology for Calculating ANC Change to High Elevation Lakes: User's Guide". January 2000. (Blett, T.)
- USDA Forest Service, Rocky Mountain Region, 1999. "Guidance for Incorporating Air Resource Information into Forest Planning Documents for National Forests in Wyoming." (Blett, T. and T. Maniero)
- Haddow, D., R. Musselman, T. Blett, R. Fisher. 1998. Guidelines for Evaluating Air Pollution Impacts on Wilderness within the Rocky Mountain Region: Report of a Workshop, 1990". Gen.Tech.Rep. RMRS-GTR-4. Fort Collins, CO; U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station.

- Jackson, L., L.Geiser, T. Blett, C.Gries, and D. Haddow. 1996 "Biogeochemistry of Lichens and Mosses in and Near Mt. Zirkel Wilderness, Routt National Forest, Colorado: Influences of Coal-Fired Power Plant Emissions." U.S.Geological Survey Open File Report 96-295.
- USDA Forest Service, Rocky Mountain Region, 1993. "Managing Air Resources in the Rocky Mountain Region. " (Blett, T., L.Dobson, M. Edwards, D. Haddow, K.Wolff)

**Donald H. Campbell**
**Research Hydrologist, U.S. Geological Survey**
**M.S. 415, Denver Federal Center**
**P.O. Box 25046**
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**phone: 303-236-4882 x. 298**
**email: dhcampbe@usgs.gov**

## Research Topics:

Flowpath contols on surface-water chemistry, physical and chemical processes during snow accumulation and melt, edisodic and chronic acidification of alpine and subalpine aquatic ecosystems, nitrogen cycling in high-altitude watersheds, effects of climate on biogeochemical processes in headwater basins, application of stable isotope techniques, atmospheric deposition and fate of mercury and organic pollutants.

## Education

Colorado State University, M.S. Earth Resources, Watershed Science, 1984
Pennsylvania State University, B.S. Life Sciences, Oceanography, 1978

## Professional Experience

1985 to present: Research Hydrologist; U.S. Geological Survey-Water Resources Division, National Research Program and Colorado District, Lakewood, CO.
1995 to present: Affiliate Faculty, Colorado State University, Dept. Earth Resources.
1983 to1984, Hydrologic Field Assistant; U.S. Geological Survey-Water Resources Division, Colorado District, Lakewood, CO.
1984 to 1985: Project Engineer; Tarranto, Stanton, and Tagge, Consulting Engineers, Ft. Collins, CO.
1982 to1983: Research assistant and teaching assistant; Department of Earth Resources, Colorado State University, Ft. Collins, CO.
1978 to1982: Laboratory Specialist and Field Engineer, Departments of Applied Biology and Estuarine Processes, Virginia Institute of Marine Science, Gloucester Pt., VA

## Relevant Publications

Campbell, D.H., Clow, D.W., Ingersoll, G.P., Mast, M.A., Spahr, N.E., and Turk, J.T., 1995, Processes controlling the chemistry of 2 snowmelt-dominated streams in the Rocky Mountains: *Water Resources Research v.31 n.11 p.2811-2821.*

Kendall, C., Campbell, D.H., Burns, D.A., Silva, S.R., Chang, C.C.Y., and Shanley, J.B., 1995, Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate: Tonnessen, K., Williams, M., and Trantner, M., (eds.), ***in: Biogeochemistry of seasonally snow-covered catchments, International Association of Hydrological Sciences Publication No. 228, p.339-348.***

Mast, M.A., Kendall, C., Campbell, D.H., Clow, D.W., and Back, J., 1995, Determination of hydrologic pathways in an alpine-subalpine basin using isotopic and chemical tracers: Tonnessen, K., Williams, M., and Trantner, M., (eds.), *Biogeochemistry of seasonally snow-covered catchments, International Association of Hydrological Sciences Publication No. 228, p.263-270.*

Clow, D.W., Mast, M.A., and Campbell, D.H., 1996, Controls on surface-water chemistry in the Upper Merced River Basin, Yosemite National Park: *Hydrological Processes v. 10, 727-746.*

Baron, J. and Campbell, D. H., 1997, Nitrogen fluxes in a high-elevation Colorado Rocky Mountain Basin: *Hydrological Processes v. 11, 783-799.*

Hauer, F.R., Baron, J.S., Campbell, D.H., Fausch, K.D., Hostetler, S.W, Leavesley, G.H, Leavitt, P.R., McKnight, D.M, and Stanford, J.A., 1997, Assesment of climate change and freshwater ecosystems of the Rocky Mountains, USA and Canada: *Hydrological Processes, v. 11, 903-924.*

Ranalli, A.J., Turk, J.T., and Campbell, D.H., 1997, The use of bulk collectors in monitoring wet deposition at high-altitude sites in winter: Water, Air, and Soil Pollution 95: 237-255.

Turk, J.T. and Campbell, D.H., 1997, Are aquatic resources of the Mt. Zirkel Wilderness Area in Colorado affected by acid depostion and what will emissions reductions at the locat power plants do? ***U.S. Geological Survey Fact Sheet FS-043-97.***

Chang, C.C.Y., Langstrom, J., Riggs, M., Campbell, D.H., Silva, S.R., and Kendall, C., 1999, A method for nitrate collection for d15N and d18O analysis for dilute waters, *Canadian Journal of Fisheries and Aquatic Science 56:1856-1864*.

Brooks, P.D., Campbell, D.H., Tonnessen, K.A., and Heuer, K., 2000, Natural variability in N export from headwater catchments: snow cover controls on ecosystem N retention, *Hydrological Processes 13: 2191-2201*.

Campbell, D.H., Baron, J., Tonnessen, K. A., Brooks, P.D., and Schuster, P.F., 2000, Controls on nitrogen flux in alpine/subalpine watersheds of Colorado, *Water Resources Research 36: 37-47*.

Michel, R.L., Campbell, D., Clow, D., and Turk, J., 2000, Timescales for migration of atmospherically derived sulphate through an alpine/subalpine watershed, Loch Vale, Colorado, *Water Resources Research 36: 27-36*.

Meixner, T., Bales, R.C., Williams, M.W., Campbell, D.H., and Baron, J.S., 2000, Stream chemistry modeling of two watersheds in the Front Range, Colorado, *Water Resources Research 36: 77-87*.

Battaglin, W.A., Kendall, C., Chang, C.C.Y, Campbell, D.H., and Silva, S.R., 2001, Isotopic and Chemical Evidence for Denitrification or Other Nitrogen Loss in the Mississippi River, 1997-1998, *Hydrological Processes* 15: 1285-1300.

Battaglin, W.A., Kendall, C., Chang, C.C.Y., Silva, S.R., and Campbell, D.H., 2001, Isotopic and chemical composition of inorganic and organic samples from the Mississippi River Basin, 1997-1998**, *U.S. Geological Survey Water- Resources Investigation Report* 01-4095.**

Clow, D.W., G.P. Ingersoll, M.A. Mast, J.T. Turk, and D.H. Campbell, 2002, Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: Implications for winter dry deposition, *Atmospheric Environment* 36: 2337-2348.

Michel, R.L, Turk, J.T., Campbell, D.H., and Mast, M.A., 2002, Use of natural 35S to trace sulfphate cycling in a small lake in the Flattops Wilderness Area, Colorado, USA, *Water, Air, and Soil Pollution Focus* 2: 5-18.

Turk, J.T., Taylor, H.E., Ingersoll, G.P., Tonnessen, K.A., Clow, D.W., Mast, M.A., Campbell, D.H., Melack, J.M., 2001, Major ion chemistry of the Rocky Mountain snowpack, *Atmospheric Environment* 35:3957-3966.

Campbell, D.H., Kendall, C., Chang, C.C.Y., Silva, S.R., and Tonnessen, K.A., 2002, Pathways for nitrate release from an alpine watershed: determination using δ15N and δ18O, *Water Resources Research* 38 (5) 10.1029/2001WR000294.

Ingersoll, G.P., Turk, J.T., Mast, M.A., Clow, D.W., Campbell, D.H., and Bailey, Z.C., 2002, Rocky Mountain Snowpack Chemistry Network: History, Methods, and the Importance of monitoring mountain ecosystems, *U.S. Geological Survey Open-File Report 01-466*, 14 p.

Muths, E., D.H. Campbell, and P.S. Corn, Hatching success in salamanders and chorus frogs at two sites in Colorado, USA: effects of acidic deposition and climate, *Amphibia-Reptilia* (in press).

Clow, D.W., Striegl, R.G., Nanus, L., Mast, M.A., Campbell, D.H., Krabbenhoft, D.P., 2002, Chemistry of selected high-elevation lakes in seven national parks in the western United States, *Water, Air, and Soil Pollution*, (in press).

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**Graduate advisor:** John D. Stednick, Colorado State University

**Collaborators (last 48 months):**

R. Bales, J.S. Baron, W. Battaglin, P.D. Brooks, C.C. Chang, D.W. Clow, P.S. Corn, E. Muths, D. Goolsby, G.P. Ingersoll, C. Kendall, C. Kester, D. P. Krabbenhoft, M.A. Mast, T. Meixner, J.M. Melack, R.L. Michel, E. Muths, L. Nanus, R. Rye, P.F. Schuster, S.R. Silva, R. Striegl, H.E. Taylor, K.A. Tonnessen, J.T. Turk, K.P Wickland, M.W. Williams.

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**EDUCATION:**

M.S., Resource Utilization, Plant and Soil Sciences Dept., University of Maine, Orono, 1979
B.S., Botany, University of Maryland, College Park, Maryland, 1974

**PROFESSIONAL EXPERIENCE:**

**Staff Scientist,** Dynamac Corporation, c/o U.S. EPA, National Health and Environmental Effects Research Laboratory (NHEERL)- Western Ecology Division, Corvallis, OR, 1996 to present: Provide logistics coordination and technical support for ecological research activities relating to water and sediment sampling, including the preparation of field implementation plans and quality assurance plans. Responsible for the water chemistry component of a project to evaluate the ecological function and status of off-channel habitat areas in the Willamette River, Oregon. Design and implement sampling activities, establish quality control procedures, organize data, and prepare reports summarizing and presenting data.

**Senior Scientist,** ManTech Environmental Technology, Inc., c/o U.S. EPA, NHEERL- Western Ecology Division, Corvallis, OR, 1987-1996: Designed and coordinated the quality assurance programs for aquatic monitoring projects within the Environmental Monitoring and Assessment Program's Surface Water Resource Group (EMAP-SW). Assisted in the coordination of these projects, conducted on-site technical reviews, and evaluated laboratory performance for long-term monitoring projects. Projects included the Long-Term Monitoring Project and the Sierra Episodes Project.

**Quality Assurance Specialist**, Northrop Environmental Sciences Division, Inc., c/o U.S. EPA, Environmental Research Laboratory, Corvallis, OR, 1986-1987: Provided support for quality assurance (QA) program: reviewed QA project plans and publications to assure compliance with EPA requirements; conducted technical system audits of intramural and extramural projects to assess compliance with project plans; and assisted investigators in developing QA plans.

**Research Associate**, Department of Geological Sciences, University of Maine, Orono, Maine, 1980-1986: Research Laboratory Director; supervised geochemical laboratory supporting the research of Dr. Stephen A. Norton and performing analytical contract work. Research assessed chronology and impact of atmospheric deposition on terrestrial and aquatic ecosystems. Performed chemical stratigraphic analysis of lake sediments and chemical analysis of lake and stream water samples. Coordinated field sampling trips, conducted quality control program, maintained field and analytical equipment, and managed and compiled data.

**REPORTS/PUBLICATIONS:**

Andrus, C.W., D.H. Landers, M.M. Erway, D. Sharps, and S.P. Cline. 1997. Ecological Functions of Off-Channel Habitats, Willamette River, Oregon. EPA/600/R-98/004 U.S. Environmental Protection Agency, NHEERL/WED Corvallis, OR

Newell, A.D. and M.L. Morrison. 1993. Use of overlap studies to evaluate method changes in water chemistry protocols. *Water, Air, and Soil Pollution* 67: 433-456.

Eilers, J.M., D.H. Landers, A.D. Newell, M.E. Mitch, M. Morrison, and J. Ford. 1993. Major ion chemistry of lakes on the Kenai Peninsula, Alaska. *Canadian Journal of Fisheries and Aquatic Sciences* 50:816-826.

Morrison, M.L. 1991. Part I: Quality assurance plan for the long-term monitoring project. In *Data User's Guide to the USEPA Long-Term Monitoring Project: Quality Assurance Plan and Data Dictionary*. EPA/600/3-91/072. Corvallis, OR: U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory.

Morrison, M.L., D. Coffey, and C. Burgeson. 1990. *Watershed Manipulation Project: Quality Assurance Implementation Plan for FY 90-92*. Corvallis, OR: U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory.

Morrison, M.L. and S.A. Norton. 1986. Total metal analysis. In D.F. Charles and D.R. Whitehead, eds. *Paleoecological investigation of recent lake acidification (PIRLA): Methods and project description*. EPRI Report Number EA-4906:10.1-10.5. Palo Alto, CA: Electric Power Institute.

**PRESENTATIONS:**

Erway, M.M., D.H. Landers, J. VanSickle, D. Trobaugh. 1999. Bio-physical and Chemical Characteristics and Relationships of Off-Channel Habitats of the Willamette River, Oregon. Poster session presented at the American Society of Limnology and Oceanography Aquatic Sciences Meeting, Santa Fe, NM, 1-5 February.

Erway, M.M., H. LaVigne, C.W. Andrus, and D.H. Landers. 1998. Water Quality Comparisons between Off-Channel Habitats and the Main Channel of the Willamette River, Oregon. Poster session presented at the joint American Society of Limnology and Oceanography and Ecological Society of America Meeting, St. Louis, MO, 8-12 June.

Erway, M.M., D.H. Landers, J. VanSickle, C.W. Andrus, D. Sharps. 1997. Nutrient Variability in Off-Channel Habitats in the Willamette River, Oregon. Poster session presented at the American Society of Limnology and Oceanography Aquatic Sciences Meeting, Santa Fe, NM, 8-14 February.

*Curriculum Vitae*

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**Education:**

B.S. Chemistry, February 1979, Massachusetts Institute of Technology

M.S. Chemistry, December 1983, University of Washington

Ph.D. Chemistry, June 1987, University of Washington.

**Professional Experience:**

Professor—University of Washington-Bothell, Interdisciplinary Arts and Sciences, September 1997-current.

Adjunct Professor of Atmospheric Sciences, December 1997-current.

Assistant, Associate and Full Professor of Chemistry--University of Alaska Fairbanks, Department of Chemistry/Geophysical Institute, September 1987 - September 1997.

**Selected Peer-reviewed publications (out of approximately 50)**

1. Weiner, R.F .and D.A. Jaffe, A Study of the PSD Permitting Process in EPA Region X, J.Air Pollut. Control Assoc., 33 (8), 797, 1983.
2. Jaffe, D.A., R. E. Honrath, J. A. Herring, S. M. Li, and J. D. Kahl, Measurements of Nitrogen Oxides at Barrow, Alaska During Spring: Evidence for Regional and Northern Hemispheric Sources of Pollution, J. Geophys.Res., 96, 7395-7405, 1991.
3. Jaffe, D.A. and M. D. Zukowski, Nitrate Deposition to the Alaskan Snowpack, Atmos. Env., 27A, 2935-2941, 1993.
4. Jaffe, D.A., E. Leighton, and M.A. Tumeo, Environmental Impact on the Polar Regions. Forum for Appl. Res. and Policy, 9, 65-70, 1994.
5. Jaffe, D.A., B. Cerundolo, J. Rickers, R. Stolzberg, and A. Baklanov, Deposition of Sulfate and Heavy Metals on the Kola Peninsula, Sci. Total Environ., 160/161, 127-134, 1995.
6. Kelley, J.A., D. A. Jaffe, A. Baklanov, and A. Mahura, Heavy Metals on the Kola Peninsula: Aerosol Size Distribution, Sci. Total Environ.,160/161,135-138,1995.
7. Jaffe, D.A., R.E. Honrath, D. Furness, T.J. Conway, E. Dlugokencky, and L.P. Steele, A Determination of the CH4, NOx, and CO2 Emissions from the Prudhoe Bay, Alaska Oil Development, J. Atm. Chem., 20, 213-227, 1995.
8. Jaffe, D.A., T.Berntsen, I.S.A. Isaksen, A Global 3D Chemical Transport Model; 2. Nitrogen Oxides and Non Methane Hydrocarbon Results. J.Geophys.Res. 102, 21,281-21,296, 1997.
9. Beine, H.J., Daniel A. Jaffe, John A. Herring, Jennifer A. Kelley, Terje Krognes, Frode Stordal. High Latitude Springtime Photochemistry Part I: NOx, PAN and Ozone Relationships J.Atm.Chemistry 27, 127-153,1997.
10. Herring, John A., Daniel A. Jaffe, Harald J. Beine, Sasha Madronich, and Donald. R. Blake. High-Latitude Springtime Photochemistry Part II: Sensitivity Studies of Ozone Production J.Atm.Chemistry 27, 155-178,1997.
11. Jaffe D.A., Griffin D., and Ricker J. Analyzing Cigarette Smoke. *The Science Teacher* v.64 (December), 29-33, 1997.
12. Beine H., Jaffe D.A., Stordal F., Engardt M., Solberg S., Schmidbauer N. and Holmén K. NOx during ozone depletion events in the Arctic troposphere at Ny-Ålesund, Svalbard. Tellus 49, 556 - 565, 1997.
13. Jaffe, D.A., Mahura A., Kelley, J., Atkins J., Novelli P.C. and Merrill J. Impact of Asian Emissions on the Remote North Pacific Atmosphere: Interpretation of CO Data from Shemya, Guam, Midway and Mauna Loa. *J.Geophys.Res.* 102, 28,627-28,636, 1997.
14. Jaffe, D.A., L.N. Yurganov, E. Pullman, J. Reuter, A. Mahura, and P.C. Novelli. Measurements of CO and $O_3$ at Shemya, Alaska. *J. Geophys. Res*. 103, 1493-1502, 1998.
15. Yurganov, L. N. ; Jaffe, D. A. ; Pullman, E. ; Novelli, P. C. Total column and surface densities of atmospheric carbon monoxide in Alaska, 1995. *J. Geophys. Res*.103, 19,337-19,347, 1998.

16. Baklanov A., Mahura A.G., Jaffe D., Thaning L., Bergman R., Andres R., and Merrill J. Atmospheric Transport Pathways and Possible Consequences after a Nuclear Accident in Northwest Russia. 11th World Clean Air Congress. Volume 2, E6, 1-6, 1998.
17. Jaffe D.A., Anderson T., Covert D., Kotchenruther R., Trost B., Danielson J., Simpson W., Berntsen T., Karlsdottir S. Blake D., Harris J., Carmichael G. and Uno I. Transport of Asian Air Pollution to North America. *Geophys.Res.Letts.* 26, 711-714, 1999.
18. Anderson, T. L., Covert, D. S., Wheeler, J. D., Harris, J. M., Perry, K. D., Trost, B. E., Jaffe, D. J., and Ogren, J. A. Aerosol backscatter fraction and single scattering albedo: measured values and uncertainties at a coastal station in the Pacific NW, J. Geophys. Res. 104, 26793-26807, 1999.
19. Berntsen T.K., Karlsdottir S. and Jaffe D.A. (1999) Influence of Asian emissions on the composition of air reaching the Northwestern United States. *Geophys.Res.Letts*. 26, 2171-2174, 1999.
20. Lloyd S. et al. (21 coauthors including D. Jaffe). Total Ozone Observations and Trend at Fairbanks during POLARIS. J.Geophys.Res. 104, 26,767-26,778, 1999.
21. Mahura A.G., Jaffe D.A., Andres R.J., and Merrill J.T. Atmospheric transport pathways from the Bilibino nuclear power plant to Alaska. *Atmos. Env*. 33, 5115-5122, 1999.
22. Jaffe D.A. and Chavasse L. Comparing the CO content of cigarette smoke and auto exhaust using gas chromatography. J.College Sci. Teaching, pgs.172-176, Dec. 1999.
23. Jaffe D.A., Anderson T., Covert D., Trost B., Danielson J., Simpson W., Blake D., Harris J. and Streets D. Observations of Ozone and Related Species in the Northeast Pacific During the PHOBEA Campaigns: 1. Ground based observations at Cheeka Peak. J.Geophys.Res. 106, 7449-7461, 2001.
24. Kotchenruther R.A., Jaffe D.A., Beine H.J., Anderson T., Bottenheim J.W., Harris J.M., Blake D. and Schmitt R. Observations of Ozone and Related Species in the Northeast Pacific During the PHOBEA Campaigns: 2. Airborne observations. J.Geophys.Res. 106, 7463-7483, 2001. (Corrected Table 1 published in Vol. 106 (D17), p.20,507.)
25. Husar R.B., et al., (28 coauthors) The Asian Dust Events of April 1998. J.Geophys.Res. 106, 18,317-18,33, 2001.
26. Kotchenruther R.A., Jaffe, D.A. and Jaeglé L. Ozone Photochemistry and the Role of PAN in the Springtime Northeastern Pacific Troposphere: Results from the PHOBEA Campaign. J.Geophys.Res. 106, 28,731-28,741, 2001.
27. Baklanov A., Mahura A., Jaffe D., Thaning L., Bergman R., and Andres R. Atmospheric Transport Patterns and Possible Consequences for the European North after a Nuclear Accident. J. Env.Rad. 60, 23-48, 2002.
28. Jaffe D.A. McKendry I., Anderson T. and Price H. Six 'New' Episodes of Trans-Pacific Transport of Air Pollutants. Accepted for publication in Atmospheric Environment, Oct. 2002.

BIOGRAPHICAL SKETCH

**Michael L. Kent**

Director, Center for Fish Disease Research,
Professor, Departments of Microbiology and Fisheries & Wildlife
Oregon State University, Corvallis, Oregon

## Education:

Humboldt State University, B.S., Fisheries, 1977
San Diego State, M.S., Biology, 1981
University of California, Davis, Ph.D., Comparative Pathology, 1985

## Positions and Honors:

1986-1988. Research Scientist. Battelle Marine Research Laboratory, Sequim, Washington.

1988 – August 1999. Research Scientist IV, Fish Health, Parasitology, and Genetics Section. Aquaculture Division, Department of Fisheries and Oceans, Pacific Biological Station, Nanaimo, B.C

January 1997-August 1999. Head, Fish Health, Parasitology, and Genetics Section, Aquaculture Division, Department of Fisheries and Oceans, Pacific Biological Station, Nanaimo, B.C

September 1999-present. Director , Center for Fish Disease Research. Professor, Departments of Microbiology and Fisheries and Wildlife, Oregon State University, Corvallis, Oregon.

Dr. Kent is a member of the American Society of Parasitologists and Fish Health Section of the American Fisheries Society. He was President of latter society 2000-20001. He was also the Chair of the Professional Standards Committee of this society (1995-1997).

Other board memberships: Past President, Fish Health Section/American Fisheries Society (2000-2001); Technical Advisory Board, Western Regional Aquaculture Consortium. (2000-present); Member of the panel of experts for the Alberta Whirling Disease Action Committee (1997-1999). American Fisheries Society Publications Awards Committee (1998-present); Member of the Editorial Boards of J. Fish Dis. (1999-present) and J. Eukaryt. Microbiol. (2001-present).

Recipient of the Department of Fisheries and Oceans Deputy Minister's Commendation for contributions to the Department - 1997.

**Publications:** 128 reviewed primary articles, 2 books, 7 book chapters, 33 non-peer reviewed papers, and 16 papers in conference proceedings. The following are selected papers and chapters.

**Kent, M.L.,** J. K. Bishop-Stewart, J. L. Matthews, and J. M. Spitsbergen. 2002 .*Pseudocapillaria tomentosa*, a nematode pathogen of zebrafish (*Danio rerio*) kept in research colonies and associated neoplasms. Comp. Med. 52; 362-367.

Ramsay, J. M, D.J. Speare, S.C. Dawe, **M.L. Kent**. 2002. Xenoma formation during microsporidial gill disease of salmonids caused by *Loma salmonae* is affected by host species (*Oncorhynchus tshawytscha,O. kisutch, O. mykiss*) but not by salinity. Dis. Aquat. Org. (in press).

**Kent, M.L.**, M. Moser, A. Marques, J. Lom. Phylum Myxozoa Grassé, 1970. 2002. In: Lee, J., Leedale, G. , Bradbury, P. (ed.). *An Illustrated Guide to the Protozoa Vol. 1.*. Soc. Protozool., Allen Press, Lawrence, Kansas. pp. 127-148.

Brown, A.M.V., and **Kent, M.L.** 2002. Molecular diagnostics for *Loma salmonae* and *Nucleospora salmonis* (Microsporidia). In: Cunningham, C. *Molecular diagnosis of salmonid diseases*. Kluwer Acad. Publ., London, England. pp. 267-283.

Matthews, J J.L., Brown, A.M.V., Larison, K., Bishop-Stewart, J.K., Rogers, P., Kent, M.L. (2001). *Pseudoloma neurophilia* n.g., n.sp., a new genus and species of Microsporidia from the central nervous system of the zebrafish (*Danio rerio).* J. Euk. Microbiol. 48:229-235.

**Kent, M.L.,** Andree, K.B., Bartholomew, J.L., El-Matbouli, M., Desser, S.S., Devlin, R.H., Hedrick, R.P., Hoffmann, R.W., Khattra, J., Hallett, S.L., Lester, R.J.G., Palenzeula, O., Siddall, M.E., Xiao, C. (2001). Recent Advances in Our Knowledge of the Myxozoa. J. Euk. Microbiol. 48:395-413.

Shaw, R.W., **M.L. Kent**, and M.L. Adamson. 2001. Innate phagocytic differences in uptake of *Loma salmonae* (Microsporidia) spores between Atlantic salmon (*Salmo salar*), a resistant host, and chinook salmon (*Oncorhynchus tshawytscha*), a susceptible host. J. Fish Shellfish Immunol. 11: 91-100

Shaw, R.W., **M.L. Kent**, and M.L. Adamson. 2001. Innate susceptibility differences in chinook salmon *Oncorhynchus tshawytscha* to *Loma salmonae* (Microsporidia). Dis. Aquat. Org. 43: 49-53.

Shaw, R.W., **M.L. Kent**, and M.L. Adamson. 2001. Viability of *Loma salmonae* (Microsporidia) under laboratory conditions. Parasitol. Res. 12: 978-981

**Kent, M.L.** 2000. Marine netpen farming and infections with some unusual parasites. Intl. J. Parasitol. 30: 321-326.

**Kent, M.L**. J. Khattra, R.P. Hedrick, R.H. Devlin. 2000. *Tetracapsula renicola* (Myxozoa: Saccosporidae); the PKX myxozoan – the cause of proliferative kidney disease of salmonid fishes. J. Parasitol. 86: 103-111.

**Kent, M.L**., M.S. Myers. 2000**.** Hepatic infection of redstriped rockfish (*Sebastes proriger*) by a putative herpesvirus and associated histopathology. Dis. Aquat. Org. 41:237-239.

Khattra, J.S., S.J. Gresoviac, **M.L. Kent**, M.S. Myers, R.P. Hedrick, and R.H. Devlin. 2000. Molecular detection and phylogenetic placement of a microsporidium from English sole (*Pleuornectes vetulus*) affected by X-cell pseudotumors. J. Parasitol. J. Parasitol. 86:867-871.

Shaw, R., W., **M.L. Kent**. 1999. Fish Microsporidia. In: Wittner, M. (ed.). *Microsporidia and Microsporidiosis*. Am. Soc. Microbiol. Press pp. 418-446.

**Kent, M.L**., S.C. Dawe, D.J. Speare. 1999. Resistance to reinfection in chinook salmon (*Oncorhynchus tshawytscha*) to *Loma salmonae* (Microsporidia). Dis. Aquat. Org. 37: 205-208.

**Kent, M.L**., M. Docker, J. Khattra, C.R. Vossbrinck, D.J. Speare, R.H. Devlin 1999. *Microsporidium prosopium* n.sp. (Microsporidia) from the musculature of the mountain whitefish *Prosopium williamsoni* from British Columbia; morphology and phylogeny. J. Parasitol. (in press).

Gresoviac, S.J., J.S. Khattra, S. A. Nadler, **M.L. Kent**, R.H. Devlin, C.P. Vivares, E. de la Fuente, R.P. Hedrick. 1999. Comparison of small subunit ribosomal RNA gene and internal transcribed spacter region sequences among isolates of the intranuclear microsporidian *Nucleospora salmonis.* J. Euk. Microbiol. 47: 379–387.

Moran, J.D.W., D.J. Whitaker, **M.L. Kent**. 1999. A review of myxosporean genus *Kudoa* Meglistch, 1947, and its impact on the international aquaculture industry and commercial fisheries. Aquaculture 172: 163-196.

Moran, J.D.W., **M.L. Kent**. 1999. *Kudoa thyrsites* (Myxozoa: Myxosporea) infections in pen-reared Atlantic salmon in the eastern north Pacific Ocean, with a survey of potential nonsalmonid reservoir hosts. J. Aquat. Anim. Health. 11: 101-109.

Moran, J.D.W., D.J. Whitaker, **M.L. Kent**. 1999. Natural and laboratory transmission of the marine myxosporean parasite *Kudoa thyrsites* (Gilchrist, 1924) to Atlantic salmon (*Salmo salar*). J. Aquat. Anim. Health. 11: 110-115.

**Kent, M.L.,** J. Khattra**,** D.M.L. Hervio, R.H. Devlin 1998. Ribosomal DNA sequence analysis of isolates of the PKX myxosporean and their relationship to members of the genus *Sphaerospora*. J. Aquat. Animal Health 10: 12-21

*CURRICULUM VITAE - DIXON HAMILTON LANDERS*

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***Education***

Public Schools, Lakewood, Ohio; Rochester, New York
Kansas State University, B. S., Zoology, 1969
Indiana University, M.A.T., Biology, 1974
Indiana University, Ph.D., Zoology (Limnology), 1979

## Professional Experience

**2000 – Present:** Responsible for developing scientific approaches for the National Park Service to assess the impacts of airborne contaminants on remote, western alpine ecosystems. Also leads a research and development effort for EPA/EMAP to develop techniques for evaluating large rivers ecosystems based on habitat and biotic indicators.

**1994 – 2000:** Lead the Large River Off-Channel Habitat Research Project as part of the Pacific Northwest Research Consortium Program. Research efforts were directed toward designing and implementing interdisciplinary projects to evaluate the ecological functions of off-channel habitats of the Willamette River (Oregon) at multiple spatial and temporal scales. The overall goal of this research was to develop tools that can be used in managing ecological systems for various societal objectives. Courtesy Professor and Graduate Faculty, Oregon State University, Department of Fisheries and Wildlife.

**1990 – 1994:** Leader of the Aquatic Monitoring Program and Director of the Arctic Contaminant Research Program: as Program Leader, I lead the development and implementation of EMAP-Surface Waters, Acid Deposition Monitoring for Aquatic Effects and the Arctic Contaminant Research Program. There are approximately 22 scientists and staff involved in this research on-sight. During this period I designed and implemented a research effort to evaluate the distribution, history and ecological effects of contaminants in the Arctic. I forged strong international ties resulting in cooperative projects with researchers pursing similar goals in other Arctic countries, particularly Russia and Canada. Associate Professor (courtesy), Department of Fisheries and Wildlife, Oregon State University.

**1989 – 1990:** Aquatic Team Leader and Director, Aquatic Effects Research Program and Chairperson, Aquatic Effects Task Group for the National Acid Precipitation Assessment Program (NAPAP), U.S. Environmental Protection Agency, Environmental Research Laboratory, Research Environmental Scientist (acting GM-15): as Aquatic Team Leader I designed and implemented interdisciplinary research involving 20 scientists and technical staff; established short and long term research goals; designed, performed and published research; provided national and international leadership and liaison with peer scientists. As director of the EPA's national Aquatic Effects Research Program, I completed seven major State of Science and Technology reports for NAPAP addressing aquatic processes and effects relating to acidic deposition.

**March 1984 to June 1989:** Aquatic Team Leader and Research Director for the National Lake Survey: this position was funded through a cooperative agreement with the Research Foundation of SUNY for 3 years, 1984-1987; I became an EPA employee in June 1987. I directed multidisciplinary scientists and

technical staff to design, implement, and interpret all phases of the National Surface Water Survey and associated projects aimed at evaluating the aquatic effects of acidic precipitation on a regional scale. This pioneering work provided a new approach to evaluate the status, distribution, and assessment of aquatic resources based on a probability sampling framework that provides the means to "scale-up" results to a regional scale with known confidence. I directed all scientific, logistic, quality assurance, quality control, methods development, data management and data analysis issues involving other laboratories and research institutions, foreign and domestic. Results were published, reported and communicated widely. I was awarded both the EPA Bronze Medal and the Silver Medal for leading this research.

***Selected Recent Publications***

Gubala, C. P., D. H. Landers, M. Monetti, M. Heit, T. Wade, B. Lasorsa, and S. Allen-Gil. 1995. The rates of accumulation and chronologies of atmospherically derived pollutants in Arctic Alaska, USA. *the Science of the Total Environment*. Vol. 160-161:347-361.

Wilson, R., S. Allen-Gil, D. Griffin, and D. H. Landers. 1995. Organochlorine contaminants in fish from an arctic lake in Alaska, USA. *the Science of the Total Environment*. Vol. 160-161:511-519.

Landers, D. H. , G. Bangay, H. Sisula, T. Colborn, and L. Liljelund. 1995. Airborne Contaminants in the Arctic: what we need to know. *the Science of the Total Environment*. Vol. 160-161:841-848

Landers, D. H., J. Ford, C. Gubala, M. Monetti, B. K. Lasorsa, and J. Martinson.1995. Mercury in vegetation and lake sediments from the U. S. arctic. *Water Air and Soil Pollution*.Vol.80:591-601.

Landers, D. H. **Guest Editor**. Special Issue of the Science of the Total Environment. 80 research papers from *the International Symposium on the Ecological Effects of Arctic Airborne Contaminants*. Vol. 160-161, pp. 870.

Allen-Gil, S. M., C. P. Gubala, B. Lasorsa, D. H. Landers, and L. R. Curtis. Heavy metal accumulation and effects in freshwater fish in Arctic Alaskan lakes. 1997. *Environmental Toxicology and Chemistry.* 16(4)733-741.

Allen-Gil, S. M., C. P. Gubala, R. Wilson, D. H. Landers, T. L. Wade, J. L. Sericano and L. R. Curtis. 1997. Organochlorine pesticides and polychlorinated biphenlys (PCBs) in sediments and biota from four US arctic lakes. *Arch. Environ. Contam. and Toxicol.* 33:378-387.

Allen-Gil, S. M., D. H. Landers, T. L. Wade, J. L. Sericano, B. K. Lasorsa, E. A. Crecelius and L. R. Curtis. 1997. Heavy metal, organochlorine pesticide and polychlorinated biphenyl contamination in arctic ground squirrels (*Spermaophilus parryi)* in Northern Alaska. *Arctic* . 50(4):323-333.

Landers, D. H., C. Gubala, M. Verta, M. Lucotte, K. Johansson, T. Vlasova, and W. L. Lockhart. 1998. Using lake sediment mercury flux ratios to evaluate the regional and continental dimensions of mercury deposition in arctic and boreal ecosystems. *Atmospheric Environment.* 32(5):919-928.

Landers, D. H., R. M. Hughes, S. G. Paulsen, D. P. Larsen, J. M. Omernik. 1998. How Can Regionalization and Survey Sampling Make Limnological Research More Relevant? *Verh. Int. Verein. Limnol.* 26:2428-2436.

Fernald, A., P. J. Wigington Jr., Dixon H. Landers (2001). Transient storage and hyporheic flow along the Willamette River, Oregon: field measurements and model estimates. *Water Resources Research* 37(6):1681-1694.

Allen-Gil, S. M., J. Ford, B. K. Lasorsa, M. Monetti, T. Vlasova, and D. H. Landers. (In Press). Heavy metal contamination in the Taimyr Peninsula, Siberian Arctic.

Landers, D. H., M. Erway, C. A. Andrus, S. Fernald, S. Cline. (In Review) Spatiotemporal variability of parapotamic habitat indicators in the Willamette River, Oregon, USA.

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# Linda Helen Geiser

## Professional experience

**1993 - present USDA Forest Service Corvallis, OR**
**Ecologist and Air Quality Specialist**
Air quality biomonitoring methods development, implementation, and analysis for the USFS regional air program. Integration of biomonitoring data with data from passive filters, active ozone monitors, and existing instrumental networks (IMPROVE and NADP).
Created a regional field guide to the lichens and provide regional training in lichen taxonomy and monitoring. Helped develop regional survey and management guidelines and a database for rare lichens in the Pacific Northwest
Designed and implemented air pollution assessment studies using lichen communities and tissue analysis of lichens and mosses in Oregon, Washington, Alaska (Arctic National Parks, Denali NPP, Klondike Goldrush Historic NP) Colorado (Mt. Zirkel Wilderness), Vancouver City--British Columbia, and the Alberta Athabasca Oil Sands .
Studied accumulation of organochlorines and metals in lichens and mosses of federally managed lands in the Pacific Rim (Oregon, Alaska, and the Kamchatsky and Primorski Oblasts).

**1989-1993 USDA Forest Service Petersburg, AK**
**Plant Physiologist**
Developed an air quality biomonitoring program for the Tongass and Chugach National Forests using lichen communities and lichen tissue analysis.

## Selected Publications

Geiser, L. and P. Neitlich. 2003. Air quality gradients in western Oregon and Washington indicated by lichen communities and chemical analysis of lichen tissue. Submitted to *Ecological Indicators*.

Fenn, ME, R Haebuer, GS Tonnesen, JS Baron, SG Rossman-Clarke, D Hope, DA Jaffe, S Copeland, LH Geiser, HM Rueth, and JO Sickman. 2003. Nitrogen Emissions, Deposition and Monitoring in the Western United States. *BioScience* (n Press).

Fenn, ME, JS Baron, EB Allen, HM Rueth, KR Nydick, LH Geiser, WD Bowman, JO Sickman, T Meixner and DW Johnson. 2003. Ecological Effects of Nitrogen Deposition in the Western United States. *BioScience* (In press).

Edwards, T, R Cutler and L Geiser. 2003. Assessing rarity and seral stage association of species with low detectability: Lichens in western Oregon and Washington Forests. *Ecological Applications* (In press).

Geiser, LH and R Reynolds. 2002. *Using Lichens as Indicators of Air Quality on Federal Lands*. Workshop Report. USDA-Forest Service Pacific Northwest Region R6-NR-AG-TP-01-02.

Lesher, R, CC Derr, and LH Geiser. 2000. Management Recommendations for Survey and Manage Lichens. USDA-Forest Service and USDI-Bureau of Land Management Regional Ecosystem Office, Report.

Geiser, LH, KL Dillman, CC Derr and MC Stensvold. 1998. Lichens and allied fungi of Southeast Alaska. *In*: *Lichenographia Thomsoniana*: North American Lichenology in Honor of John W. Thomson. Glenn, MG, RC Harris, R Dirig and MS Cole, eds. Mycotaxon Ltd., Ithaca, NY.

McCune, B. and L. Geiser. 1996. *Macrolichens of the Pacific Northwest Forests*. OSU Press, Corvallis, Oregon. 386 pp.

Jackson, L.L., LH Geiser, T Blett, C Gries and D Haddow. 1996. Biogeochemistry of lichens and mosses in and near Mt. Zirkel Wilderness, Routt National Forest, Colorado: Influences of Coal-Fired Power Plant Emissions. USDI-US Geological Survey, Open-File Report 96-295. 162 pp.

Geiser, LH, CC Derr and KL Dillman. 1994. Air quality monitoring on the Tongass National Forest. Methods and baselines using lichens. USDA-FS Alaska Region R10-Technical Bulletin-46.

**Education**

**1980 B.S. Biological Science**, Antioch University, Yellow Springs, OH
**1988 M.S. Soil Science and Plant Nutrition,** University of California at Davis
**1991 Ph.D. Plant Physiology**, University of California at Davis

**Additional professional activities**

Numerous presentations at agency and professional meetings and workshops. Organized a workshop in 2001 for federal managers interested in using lichens to monitor federal lands. Participated in the recent NATO international conference on Lichen Monitoring, in Wales, UK and a Terrestrial Effects Workshop for the Athabasca Oils Sands in 2000.

Lichenologist for the Beringean Fungal Project (1995-2000)

Advanced training in statistical techniques at Oregon State University (five courses)

Advanced training in lichen taxonomy: Crustose lichens of the Pacific Northwest-- Eagle Hill Field Institute, University of Maine (2002) and Arizona State University (1995); Lichens of southeastern Alaska, Canadian National Museum of Natural History, Ottawa (1991) and University of Wisconsin, Madison (1993).

**Professional memberships**

International Association of Lichenologists

American Bryological and Lichenological Society
Northwest Lichenologists, board member
California Lichen Society
British Lichen Society

**Carl B. Schreck**

Leader, Oregon Cooperative Fish and Wildlife Research Unit (U.S.G.S.)
Professor, Department of Fisheries and Wildlife
Oregon State University, Corvallis, OR 97331, USA
541, 737-1961 schreckc@ccmail.orst.edu

**Education:**

A.B. in Zoology--University of California, Berkeley, 1966
M.S. in Fisheries Biology--Colorado State University, 1969
Ph.D. in Physiology/ Biophysics and Fisheries--Colorado State University, 1972

**Employment:**

Virginia Polytechnic Institute and State University--Assistant Professor, 1972-1975

Assistant Leader, Oregon Cooperative Fishery Research Unit, 1975-1977

Leader, Oregon Cooperative Fishery Research Unit, Biological Resources Division, U.S. Department of Interior and Full Professor, Oregon State University, 1997-present

**Present Editorial Boards:**

*Comparative Biochemistry and Physiology*
*Diseases of Aquatic Organisms,* Editor in Chief for AThe Environment@
*Aquaculture*

**PROFESSIONAL RECOGNITION**:

Educator of the Year Award, American Fisheries Society (2000); Earle Price Award for Excellence in Research, Oregon State University (1991); Directors Award for Research Excellence, U.S. Fish and Wildlife Service (1991); Twice winner of the William F. Thompson Award, American Institute of Fishery Research Biologists (1980 and 1989); Governor=s (Oregon) Coastal Salmon Science Team. Independent Multidisciplinary Science Team for the State of Oregon; Others with students and colleagues.
Approx 60 M.S. and Ph.D. theses supervised to date.

**Selected Affiliations:**

International Federation of Fish Endocrinologists-- U.S.A. Representative to Board of Directors and "President" from 2000, 1996-present. International Federation of Comparative Endocrinologists
American Association for the Advancement of Science
American Fisheries Society

**Publications (examples of over 200 total):**

Schreck, C.B. 1992. Glucocorticoids: Metabolism, growth, and development. Pages 367-392. In: M.P. Schreibman, C.G. Scanes, and P.K.T. Pang (Editors). The endocrinology of growth, development and metabolism in vertebrates. Academic Press, New York.

Slater, C.H., M.S. Fitzpatrick, C.B. Schreck. 1995. Characterization of an androgen receptor in salmonid lymphocytes: possible link to androgen induced immunosuppression. General and Comparative Endocrinology 100:218-225.

Schreck, C.B., L. Jonsson, G. Feist, and P. Reno. 1995. Conditioning improves performance of juvenile chinook salmon, *Oncorhynchus tshawytscha*, to transportation stress. Aquaculture 135:99-110.

Maule, A.G., R. Schrock, C. Slater, M.S. Fitzpatrick, and C.B. Schreck. 1996. Immune and endocrine responses of adult chinook salmon during freshwater immigration and sexual maturation. Fish and Shellfish Immunology 6:221-233.

Schreck, C.B. 1996. Immunomodulation: endogenous factors. Pages 311-337. In: G. Iwama and T. Nakanishi (Editors). Hoar and Randall's Fish Physiology, vol. 15. Academic Press, New York.

Schreck, C.B., B.L. Olla, and M.W. Davis. 1997. Behavioral responses to stress. Pages 745-770. In: G.W. Iwama, J. Sumpter, A.D. Pickering, and C.B. Schreck (Editors). Fish Stress and health in aquaculture. Cambridge University Press, Cambridge.

Slater, C.H., and C.B. Schreck. 1998. Season and physiological parameters modulate salmonid leucocyte androgen receptor affinity and abundance. Fish and Shellfish Immunology 8:379-391.

McNabb, A., C. Schreck, C. Tyler, P. Thomas, V. Kramer, J. Specker, M. Mayes, and K. Selcer. 1999. Chapter 3: Basic Physiology. Pages 113-223. In: R.T. DiGiulio and D.E. Tillitt (Editors). Reproductive and Developmental Effects of Contaminants in Oriparous Vertebrates.

Schreck, C.B. 2000. Stress in fish. Pages 149-152. In: G. Fink (Editor). Encyclopedia of Stress. Academic Press, San Diego, Vol. 2.

Schreck, C.B. 2000. Accumulation and long-term effects of stress in fish. Pages 147-158. In: G. Moberg and J. Mench (Editors). The biology of animal stress. C.A.B. International Press, Wallingford, UK.

Clements, S., and C.B. Schreck. 2001. The GABAa agonist muscimol enhances locomotor activity, but does not alter the behavioural effects of CRH in juvenile spring Chinook salmon (*Oncorhynchus tshawytscha).* Fish Physiology and Biochemstry 24:41-48.

Schreck, C.B., W. Contreras-Sanchez, and M.S. Fitzpatrick. 2001. Effects of stress on fish reproduction, gamete quality, and progeny. Aquaculture 197:3-24.

Schreck, C.B., and A.G. Maule. 2001. Are the endocrine and immune systems really the same thing? Pages 351-357. In: H.J.T. Goos, R.K. Rostogi, H. Vaudry, and R. Pierantoni (Editors). Monduzzi Editore, Naples (CD ROM Book).

Crippen, T.L., L.M. Bootland, J.-A. Leong, M.S. Fitzpatrick, C.B. Schreck, and A.T. Vella. 2001. Analysis of salmonid leukocytes purified by hypotonic lysis of erythrocytes. Journal of Aquatic Animal Health. 13:234-245.

Clements, S., C.B. Schreck, D.A. Larsen, and W.W. Dickhoff. 2002. Central administration of corticotropin-releasing hormone stimulates locomotor activity in juvenile chinook salmon (*Oncorhynchus tshawytscha*). General and Comparative Endocrinology 125:319-327.

# Staci L. Simonich

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## EDUCATION

Ph.D. Chemistry, Indiana University, Bloomington, IN – under Distinguished Professor Ronald Hites - 1995

B.S. Chemistry, University of Wisconsin -Green Bay - 1990

## PROFESSIONAL EXPERIENCE

| | | |
|---|---|---|
| 2001 – present | Assistant Professor | Department of Environmental and Molecular Toxicology and Department of Chemistry (Joint Appointment)<br>Oregon State University - Corvallis, Oregon |
| 1999 to 2001 | Senior Scientist | Fabric & Home Care Environmental Safety<br>The Procter & Gamble Company - Cincinnati Ohio |
| 1995 to 1999 | Scientist | Corporate Environmental Science Department<br>The Procter & Gamble Company - Cincinnati Ohio |

## PUBLICATIONS

S.L. Simonich, T. W. Federle, W.S. Eckhoff, A. Rottiers, S. Webb, D. Sabaliunas, W. de Wolf "Removal of Fragrance Materials During U.S. and European Wastewater Treatment" *Environmental Science and Technology* **2002**, 36, 2839-2847.

S.A. Aschmann, J. Arey, R. Atkinson, S.L. Simonich, "Atmospheric Lifetimes and Fates of Selected Fragrance Materials and Volatile Model Compounds" *Environmental Science and Technology* **2001**, *35*, 3595 - 3600.

M.J. Bernhard and S.L. Simonich, "Use of a Bench-Top Photochemical Reactor and Solid-Phase Microextraction to Measure Semivolatile Organic Compound-Hydroxyl Radical Rate Constants" *Environmental Toxicology and Chemistry* **2000**, *19*, 1705 - 1710.

S.L. Simonich, W.M. Begley, G. Debaere, W.S. Eckhoff, "Trace Analysis of Fragrance Materials in Wastewater and Treated Wastewater" *Environmental Science and Technology* **2000**, *34*, 959 - 965.

B.Y. Park, J.W. Bozzelli, M.R. Booty, S.L. Simonich, "Polymer Pyrolysis and Oxidation Studies in a Continuous Feed and Flow Reactor: Cellulose and Polystyrene" *Environmental Science and Technology* **1999**, *33*, 2584 - 2592.

S.L. Simonich and R.A. Hites, "Relationships Between Socioeconomic Indicators and Concentrations of Organochlorine Pesticides in Tree Bark" *Environmental Science and Technology* **1997**, *31*, 999 - 1003.

J.C. Wallace, L.P. Brzuzy, S.L. Simonich and R.A. Hites, "Case Study of Organochlorine Pesticides in the Indoor Air of a Home" *Environmental Science and Technology* **1996**, *30*, 2715 - 2718.

S.L. Simonich and R.A. Hites, "Organic Pollutant Accumulation in Vegetation" *Environmental Science and Technology* **1995**, 29, 2905 - 2914.

S.L. Simonich and R.A. Hites, "Global Distribution of Persistent Organochlorine Compounds" *Science* **1995**, 269, 1851 - 1854.

S.L. Simonich and R.A. Hites, "Importance of Vegetation in Removing Polycyclic Aromatic Hydrocarbons from the Atmosphere" *Nature* **1994**, 370, 49 - 51.

S.L. Simonich and R.A. Hites, "Vegetation-Atmosphere Partitioning of Polycyclic Aromatic Hydrocarbons" *Environmental Science and Technology* **1994**, 28, 939 - 943.

SELECTED AWARDS AND FELLOWSHIPS

| | |
|---|---|
| 2001 | Society of Environmental Toxicology and Chemistry/Roy F. Weston Environmental Chemistry Award |
| 1994 | Graduate Student Award, ACS – Division of Environmental Chemistry |
| 1994 | Graduate Student Paper Award, ACS – Division of Environmental Chemistry |
| 1993-94 | National Institute of Global Environmental Change Fellowship |
| 1993 | Eli Lilly and Company Travel Award |
| 1990 | Outstanding Student in Chemistry Award, American Institute of Chemists |
| 1990 | Outstanding Senior Award, University of Wisconsin – Green Bay |
| 1989-90 | Herbert Fisk Johnson Award for Excellence in Research, University of Wisconsin – Green Bay |
| 1989-90 | Chancellor's Leadership Medallion, University of Wisconsin – Green Bay |

**PROFESSIONAL AFFILIATIONS**

American Geophysical Union
American Chemical Society
American Society for Mass Spectrometry
Society of Environmental Toxicology and Chemistry
Association for Women in Science

Jan 1, 2003

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**CURRENT POSITION:** Research Chemist, GS-15

**EDUCATION:**
Colorado State University, Ph.D., 1970, Analytical Chemistry

Arizona State University, B.Sc., 1967, Chemistry

**PROFESSIONAL EXPERIENCE:**

**PRESENT ASSIGNMENT:** **DATES:** **From:** 1983 **To:** Present
**PROJECT TITLE:** Project Chief of "Inorganic Environmental Analytical Chemistry and Water Quality"

The thrust of this project is three-fold: 1) the development and demonstration of the utilization of field and laboratory techniques for the state-of-the-art measurement of trace metals and other inorganic species in hydrologic systems, with specific focus on surface-water environmental problems; and 2) The study of the occurrence, distribution, fate and chemistry of trace inorganic constituents in surface-water hydrologic systems; and the operation of a common services laboratory for state-of-the-art trace element analyses in support of other NRP projects.

Field and laboratory methods development: This project is designed to develop new and innovative techniques for the determination of trace element constituents in environmental chemistry. Primary areas of interest include: Inductively-coupled argon plasma emission spectrometry, inductively coupled plasma-mass spectrometry, atomic fluorescence spectrometry, differential-pulse anodic stripping voltammetry, atomic absorption spectrophotometry and ion chromatography. Examples of current efforts include development of techniques for rare earth element determinations in hydrologic systems and the development of techniques for the chemical characterization of colloidal suspended sediment (using field flow fractionation-ICP-MS technology).

Occurrence, distribution, fate and chemistry of trace inorganic constituents in surface-water systems: Sub-projects include: Sacramento River metals speciation and transport study; Cache Creek, CA, Hg occurrence and distribution; Bear/Yuba Rivers, CA, Hg occurrence and distribution; Chemical characterization of springs and seeps in Glen Canyon National Recreation Area; Water and sediment quality in Lake Powell, UT; Distribution of trace elements in artificial wetlands: Hemet, CA and Tres Rios, AZ; Water quality in Upper Rio Grande, CO; and Water quality studies on the Yukon River, AL.

**DATES:** **From:** April 1981 **To:** April 1983
**POSITION TITLE:** Laboratory Chief, National Water Quality Laboratory
**ORGANIZATION:** Office of Water Quality, U.S. Geological Survey
**LOCATION:** Arvada, CO

**Faculty Affiliate,** supervising graduate student research studies:
University of Colorado, Department of Geography, 2002 to present
Colorado State University, , Chemistry Department, 1977 to present
University of Colorado, Institute of Artic and Alpine Research, 2001 to present

**PROFESSIONAL SOCIETIES**

American Chemical Society
Society for Applied Spectroscopy (President - Rocky Mountain Section, 1979)
American Geophysical Union
American Association for the Advancement of Science

**SELECTED RECENT PUBLICATIONS** (from 174 technical presentations and 143 published reports):

Moody, J.A., Sullivan, J.F. and Taylor, H.E., 1999, Effects of the Flood of 1993 on the Chemical Characteristics Bed Sediments in the Upper Mississippi River*: Water, Air and Soil Pollution, 76, 120.* (I contributed to the design of the study, the trace element determinations and the trace element data interpretation)

Nordstrom, D.K., Alpers, C.N., Coston, J.A., Taylor, H.E., McCleskey, R.B., Ball, J.W., Ogle, S. and Davis, J., 1999, Geochemistry, toxicity and sorption properties of contaminated sediments and pore waters for two reservoirs receiving acid mine drainage., Morganwalp, D.W. and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 1—Contamination from Hardrock Mining: *U.S. Geological Survey—Water Resources Investigations Report* 99-4018A, p. 289-296.

Verplanck, P.L., Nordstom, D.K., Taylor, H.E., 1999, Overview of rare earth element investigations in acid waters of U.S. Geological Survey abandoned mine lands watersheds, Morganwalp, D.W. and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 1—Contamination from Hardrock Mining: *U.S. Geological Survey—Water Resources Investigations Report* 99-4018A.

Durand, S., Shelley, P.H., Anweiler, R.C. and Taylor, H.E., 1999, Trees, Chemistry, and Prehistory in the American Southwest, *Journal of Archaeological Sciences* , 26, 132. (I directed all of the analytical work and wrote 25 % of the paper)

Alpers, C.N., Taylor, H.E., and Domagalski, J.J., eds., 2000, Metals transport in the Sacramento River, California, 1996-97: Volume 1. Methods and Data: *U.S. Geological Survey Water-Resources Investigations Report* 99-4286, 428 p. (I prepared and edited 30 % of report).

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Taylor, H.E., Antweiler, R.C., Roth, D.A., Brinton, T.I., Peart, D.B., and Healy, D.F., (2001) The Occurrence and Distribution of Selected Trace Metals in the Upper Rio Grande and Tributaries in Colorado and Northern New Mexico, *Archives of Environmental Contamination and Toxicology, 41.* 410-426.

Roth, D.A., Taylor, H.E., Domagalski, J., Dileanis, P., Peart, D.B., Antweiler, R.C. and Alpers, (2001) Distribution of inorganic mercury in Sacramento River water and sediments, *Archives of Environmental Contamination and Toxicology, 40, 161-172.* (I designed the study and wrote the paper)

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# APPENDIX C: PEER REVIEW REPORT

The Western Airborne Contaminants Assessment Project was reviewed by a peer review panel on December 11-12, 2002, in Seattle, Washington. Following is the final report of the peer review panel.

***Peer Review Panelists:***

| | |
|---|---|
| Colin Gray | Head, Research Coordination, Aquatic and Atmospheric Sciences Division, Environment Canada, Vancouver (COLIN.GRAY@EC.GC.CA). |
| Joan Grimalt | Professor, Spanish Council for Scientific Research, Institute of Chemical and Environmental Research, Barcelona, Spain (JGOQAM@IIQAB.CSIC.ES). |
| Steve Kahl (Chair) | Professor of Water Resources and Director, Mitchell Center for Environ. & Watershed Research, University of Maine, Orono, ME (KAHL@MAINE.EDU). |
| Kathy Tonnessen | Research Coordinator, NPS Rocky Mtn. Cooperative Ecosystem Studies Unit, University of Montana, Missoula, MT (KAT@FORESTRY.UMT.EDU). |
| James Wiener | Wisconsin Distinguished Professor, University of Wisconsin-La Crosse, LaCrosse, WI (WIENER.JAME@UWLAX.EDU). |

# Western Airborne Contaminants Assessment Project

**Project Leaders**

**Dixon Landers, EPA-WACAP Technical Director, Corvallis OR**
**Chris Shaver, NPS-WACAP Program Leader, Denver CO**
**Tamara Blett, NPS-WACAP Program Coordinator, Denver CO**

**Final Report of the**
**Peer Review Panel, December 11-12, 2002**

**Seattle, Washington**

*Peer Review Panelists:*

| | |
|---|---|
| Colin Gray | Head, Research Coordination, Aquatic and Atmospheric Sciences Division, Environment Canada, Vancouver (COLIN.GRAY@EC.GC.CA). |
| Joan Grimalt | Professor, Spanish Council for Scientific Research, Institute of Chemical and Environmental Research, Barcelona, Spain (JGOQAM@IIQAB.CSIC.ES). |
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| James Wiener | Wisconsin Distinguished Professor, University of Wisconsin-La Crosse, LaCrosse, WI (WIENER.JAME@UWLAX.EDU). |

December 21, 2002

# Western Airborne Contaminants Assessment Project

Report of the Peer Review Panel, December 11-12, 2002
Seattle WA

## Overview of panel recommendations

The panel recognizes the strengths of WACAP, including:

- A strong research team with appropriate experience
- A clear need for the assessment of long-range airborne contaminants, especially semi-volatile organic compounds (SOCs).
- An appropriate scale and scope for a regional assessment.
- A broad selection of analytes.

The panel suggests the following priority order of analytes based on the availability of existing data: (1) SOCs, Hg, toxaphene; (2) any current-use chemicals not included in SOCs; and (3) other metals. The panel recommends that WACAP drop consideration of fluoridated organic compounds because the analytical methods are not well developed.

The PIs should be cognizant of activities that do not directly address the overarching goal of a reconnaissance assessment project. Accordingly, the Panel recommends that each chapter of the research plan be restructured so that the descriptions of samples and measurements taken, along with the detailed methods applied, follow a subheading stating the specific objective being addressed. This structure will ensure that all objectives can be directly tied to specific methods in the text of the research plan.

The panel characterized the program components into 'core', 'pilot', and 'non-essential' activities. The **core** components, considered to be most important to achieving specified project goals, include the following.

- Annual snow sampling,
- One-time fish sampling,
- One-time sediment coring.

The snow component assumes that snow represents the major input of contamination in these ecosystems. There is no component in the project to test this assumption in the wide variety of parks in the program and the PIs should acknowledge this shortcoming. The panel acknowledges that obtaining data such as concentrations of particulate and gaseous contaminants for the calculation of dry deposition and contaminant loading in rain is unrealistic within the resources of the project.

There are substantial uncertainties on the fish component, that relate to the uncertainty of populations, condition, and type of fish. Piscivorous fish will have the highest concentrations, but fish from the same trophic status should be compared, which will be difficult to control. The same fish should be evaluated for health condition and analyzed for contaminants.

The **pilot** activities are those that are unproven, and do not warrant a multi-year financial commitment until proven. The Panel recommends that the following pilot components be tested in two parks in the first year of sample collection:

- Lichens and willow for SOC and Hg analyses,
- Methylmercury analysis in snow.

Because of the unproven developmental stage of some project components, the panel recommends undertaking these components as one-year pilot studies. The collection of Hg and SOC data via lichens or willows will augment the database and interpretation of results. However, until the PIs know that the receptors actually collect detectable concentrations of target analytes, there is no reason to commit long-term funds to these project components. The PIs should take an iterative approach to subsequent years, carefully learning from the data as it becomes available. This approach will require extra organization and coordination, with a priority placed on rapid laboratory analysis and data availability.

The Panel regards atmospheric modeling as a **non-essential** project component, because it does not directly address the core goal of assessing whether these contaminants are present in detectable concentrations. Contaminant source determination is not included as a project goal in the review draft of the WACAP Study Plan, and this component could be deferred until contamination has been confirmed.

The panel believes that a number of proposed activities will not directly contribute substantively to the overarching WACAP goal:

- N and S in lichens (not toxic contaminants, although inexpensive and potentially helpful in data interpretation)
- Multi-year sampling of lichens within a Park
- The single snow pit at high elevation in each watershed (provides only a second point along a 'gradient', can't assess pattern without three or more locations).
- Lake water analysis for SOCs and metals (uncertainty in the meaning of the results of one sample using a new method).

The panel suggests the workplan be augmented to better assess elevational patterns that are not readily addressed by the lake watersheds themselves due to the correlation (i.e., confounding) of elevation with latitude. The suggested solution is to expand the elevational coverage on transects outside of the watersheds for snow or willow bark, if possible. We recommend that this elevational gradient study be initiated in one park (e.g. Olympic) to determine feasibility and value of the data. The panel suggests that WACAP focus on watershed approach first and then do pilots in a few parks where the elevational gradient hypothesis can be tested if intact snow packs are available.

Other suggested additions/changes include:

- evaluation of the partitioning of substances in snow: total, dissolved, or particulate. This evaluation is a fundamental issue that will drive future research methods.
- Use of a piston sediment corer, rather than a gravity corer, to reduce compaction of the sediment and improve resolution of upper stratigraphy, especially in highly organic sediments.
- Additional meta-data analyses of sediments to aid in data interpretation (e.g., organic C, inorganic C, sulfide)

Event-based back-trajectories will be helpful in assessing the representativeness of each year of snow data. However, if the budget is limited, priority should be given to completing the analyses for priority contaminants. If necessary, the atmospheric modeling can be done after the data collection and analysis are complete.

Because of the potential for data-driven changes in project design, the panel recommends external scientists be closely involved in the project, perhaps via an annual WACAP meeting to which outside scientists are invited to participate and share data.

Lastly, the Panel has no opinion on including moose analysis as part of the tasks within WACAP, but recommends that moose be deleted from the study plan as a specific project component. It is a courtesy analysis for a client group, not a contributor to the goals of the WACAP.

# Western Airborne Contaminants Assessment Project

Report of the
Peer Review Panel, December 11-12, 2002

Final report, December 21, 2002

## Introduction

Long-range, trans-boundary air pollution is a significant global environmental issue. Some airborne contaminants, such as acid rain and mercury, have been intensively studied. Others, such as trace organic substances, are much less well understood because of the difficulty and expense of analysis, the potential for contamination of samples that have ambient concentrations of parts per trillion or quadrillion, and because our recognition of these issues is still developing. These organic substances can have major biological impacts at very low concentrations, ranging from endocrine disruption to reproductive failure especially in wildlife consumers of fish (e.g., mink, otters, osprey).

In the U.S., much of the research and policy attention has been focused east of the Mississippi River, downwind of the major population centers. The western U.S. has been perceived to be less affected, and has received less attention. However, there is increasing awareness of the potential for atmospheric deposition of toxic substances as data become available on the accumulations of substances from global-scale transport. In particular, the deposition of certain contaminants may be enhanced at high elevation due to long-range transport in upper atmospheric air masses and subsequent temperature-dependent condensation. Recognition of ultra long-range transport processes raises the possibility that the sources of contaminants to western areas, included protected National Parks, may be from sources as remote as EurAsia.

This review of the Western Airborne Contaminants Assessment Program (WACAP) program was conducted on December 11 and 12, 2002, in Seattle, Washington. The Principal Investigators presented the WACAP program on the first day, augmenting information contained in the draft of the 116-page WACAP research plan dated November 4, 2002. The panel met in the evening of the first day and the morning of the second day to evaluate the goals and details of the program. The panel verbally presented its recommendations to the NPS managers and the WACAP research team on the afternoon of December 12. The panel presentation was provided electronically to the WACAP research team leader. In addition, each panelist provided written comments and recommendations. This document is the compilation of these individual reviews.

## Overarching Goal

The stated purpose of the Western Airborne Contaminants Assessment Project (WACAP) is to provide the first systematic assessment of the deposition of contaminants to western National Parks. As stated by Christine Shaver (December 11, 2002), Division Chief of the NPS Air Resources Division, the charge to WACAP is to '*conduct a reconnaissance assessment program*

*to determine if there are issues of concern in western parks*' that should receive further in-depth evaluation. An important implicit goal is to collect the appropriate baseline data to provide a foundation for future work, including a monitoring program, if warranted.

The stated overarching goal of WACAP is (review draft, 11/4/02):

> *To design and implement an air toxics monitoring network based in the National Parks of the western US to provide spatially extensive, site specific, and temporally resolved information regarding the exposure, accumulation, and impacts of airborne contaminants in these ecosystems.*

The panel had two suggestions to define the focus of the goal. First, the words '*monitoring network'* should be '*deposition assessment*' because this program is not a network, nor is it establishing a monitoring program. The panel anticipates that the results will point to the wisdom of additional selected data collection in the future, perhaps including a component of monitoring. The panel further recommends deleting the term '*impact*' from the goal statement because determining impacts is a follow-up activity, after the initial assessment. The term *spatially-extensive* may be mis-interpreted because it implies a statistical population, which is not attempted in WACAP. The panel was not sure of the meaning of *temporally-resolved,* with members interpreting it either to refer to sediment core chronology or to the annual sampling of snow.

A *revised* overarching goal suggested by the panel is:

> *To assess the deposition of airborne contaminants in western National Parks, providing regional and local information on exposure and accumulation.*

**Project Components**

The draft WACAP research plan is divided into 10 main chapters, covering laboratory analysis, project coordination, QA/QC, database design, and the main project components listed below. This review is generally organized in the same manner.

Project components:

1) Snow chemistry
2) Contaminants in the food web
    a. fish
    b. lichens
    c. willow bark
    d. moose meat in one to three parks
3) Surface water chemistry
4) Sediment chemistry
5) Atmospheric modeling

**Main Review Questions**

The EPA Principal Investigator posed 7 questions for the panel to consider:

1) Do the objectives of WACAP logically address the overall goal?
2) Is the general program design and approach sufficient to achieve the defined objectives?
3) Are the field and laboratory methods sufficient to meet the objectives of each component?
4) Are the scientists sufficiently experienced to conduct the research components as intended?
5) What improvements should WACAP PIs consider prior to initiating the research, given the limits in funding?
6) Is the coordination and communication strategy within WACAP and between WACAP and NPS sufficient for implementation, completion, and publication of results?
7) What suggestions can the panel offer for prioritizing research elements as 'core components' if funding becomes limiting in the future?

*The panel added an eighth question:*

8) What are the recommendations for revision and distribution of the research plan as an EPA report?

**Supporting background information from the panel**

Potential origin of pollutants. The main goal of WACAP is assessing whether airborne contaminants are an issue for the western National Parks. Inputs from Asia are considered to be important sources of pollutants for the west coast. The panel recognizes that there are some political reasons to focus on Asia as a justification for the research. However, consideration of the global distribution of some pollutants of interest for WACAP project reveals a more complex picture.

In the case of PCBs, Breivick *et al.* (2002) estimated the cumulative global use of these compounds. Europe, Japan and the eastern half of USA were the areas of highest PCB usage (Figure 1). Significant use also occurs in some areas of the West USA coast, including near WACAP Rocky Mountain NP. Asia (except Japan) appears to be highly polluted for other compounds (e.g., Hg and CO as shown by the WACAP research plan), but not overly polluted by PCB (Figure 1). Thus, Asia is not necessarily the source of PCBs found in western Parks.

A similar case can be made for Hg. The eastern US is significantly more contaminated than the west. These two examples are not offered as models for all the possible long-range transport. Rather, they emphasize that examination of the origin of long-range transported pollutants should be considered from a broad perspective, including Asia, eastern USA, Europe, and Central America. Other contributions for some metals, especially an oceanic source of Hg, could also be significant. *Therefore, the panel suggests that WACAP considers Asia as only one of many potential sources of airborne contamination for WACAP parks.* Local sources and episodic reverse trajectory air masses are equally viable *a priori* sources. The inclusion of interior parks (ROMO and GLAC) in the WACAP indicates that the design includes an assessment of local and mid-continental contamination.

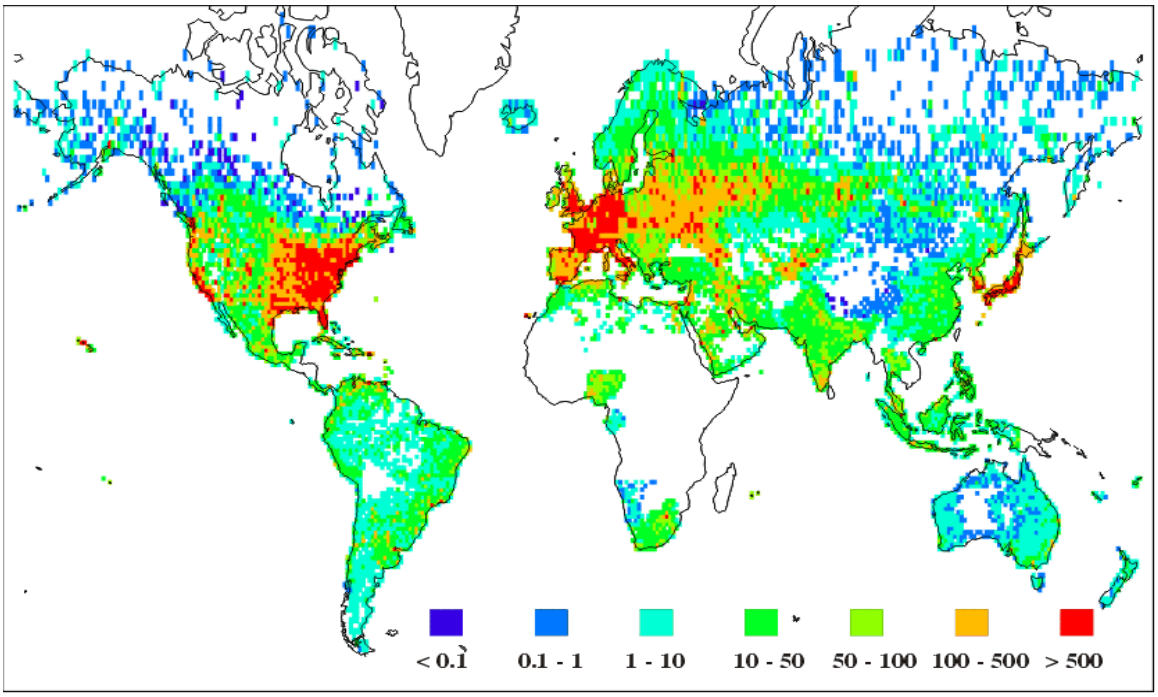



Figure 1. Cumulative global usage of PCBs (in tons) with 1° x 1°resolution (Breivik, K. Sweetman, A., Pacyna, J. M., and Jones, K. C., 2002. *Sci. Total Environ.* 290:181-198.

Altitudinal trends. The Parks selected for study offer a wide range of altitudes (between 0 and 6000 m). The distribution of lakes in the parks (Table 1.1 in the proposal) was selected to address whether some pollutant accumulation patterns follow an altitudinal trend. However, the altitudinal gradient is highly correlated to latitude (Figure 2). Temperature is a key factor determining the accumulation of many of the organic pollutants. Therefore, the latitudinal and altitudinal effects are confounded in the study design and cannot be differentiated. By themselves, the lake watersheds will not serve the intended purpose.

There are alternative approaches to address altitudinal gradients in contamination at WACAP sites, by increasing the number and elevational distribution of the project components designed to address elevation: snow, lichens, or willow bark. These design adjustments are discussed in the questions below.

**Responses to Questions 1-8**

**Question 1: Do the objectives of WACAP logically address the overall goal?**

Yes, the cumulative objectives of the individual project components will address the goal. The panel was nevertheless concerned about two aspects of the objectives. The first is that some objectives exceed the core goal. The interests of individual co-PIs have expanded

some activities beyond the specific (and appropriately limited) goal of the project. Given the apparent limitations on funding, the panel urges the project leaders to evaluate the sub-

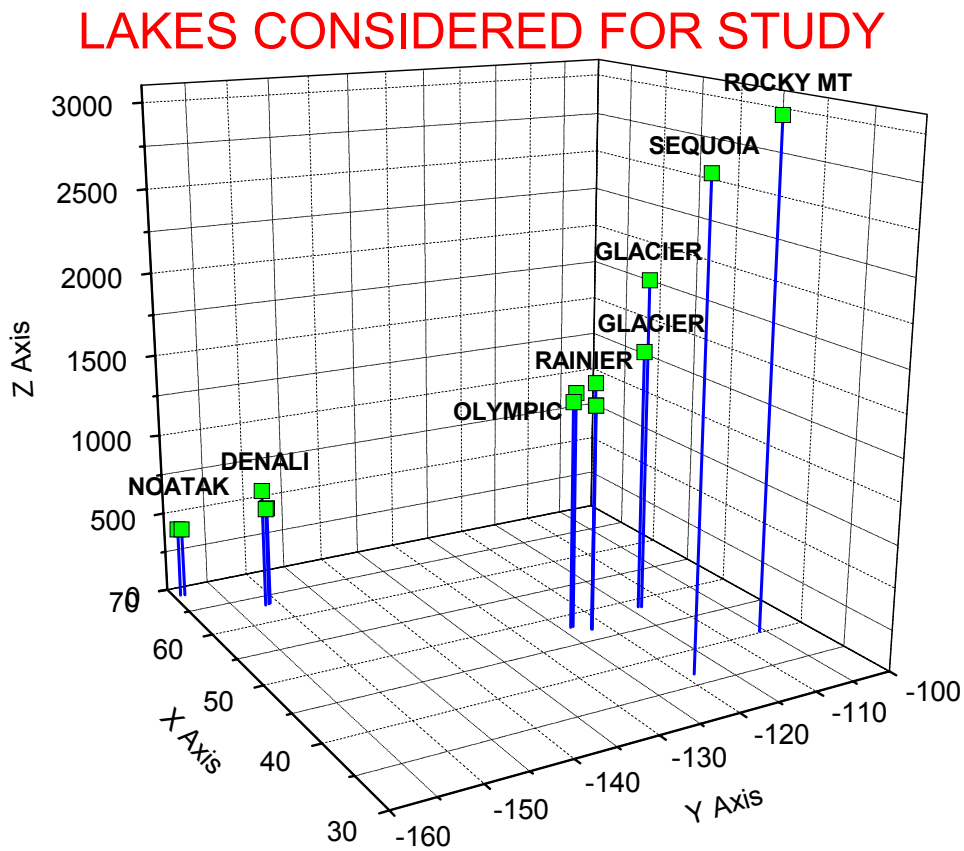



Figure 2. Joint representation of altitude, longitude and latitude of the lakes included in Table 1.1 from the proposal.

objectives in each component to ensure a clear focus on the overarching goal. The panel recommends that each objective be *specifically* addressed in the approach section of each chapter.

The second concern is source determination via the atmospheric modeling component. Source determination is a valid interest of management, but is not essential for achieving the stated project goal *to assess the deposition of airborne contaminants in the National Parks of the western US.* In the view of the panel, a source determination component is not essential until the project has demonstrated that there is significant contamination for which sources need to be identified. The panel recommends minimizing the atmospheric modeling component until the preliminary data have been evaluated and a need for source identification is clear. Event-based trajectory assessment helpful to determine 'representativeness' of each snow year. However, this analysis can be done after the project if necessary, to prioritize the completion of analyses.

There are references in the hypotheses relating to long-distance transport being particularly concerned with trans-Pacific air transport. Preconceived ideas about the sources of air contaminants suggest potential bias and should be deleted from the text.

**Question 2: Is the general program design and approach sufficient to achieve the defined objectives?**

There are many objectives in the various project components. The panel considers the general program design to be sufficient to achieve these objectives. However, the text and the project focus would be sharpened if the authors made an adjustment in the format of each chapter. The panel recommends listing the objectives in the introductory text as already presented. The methods sections should be revised by listing each objective as a subheading, to be followed with the specific activities and methods that will be used to accomplish the specific objective.

One shortcoming of the general design is a lack of consistency in the list of analytes across matrices. The panel recommends the following priority for analytes, and that this priority be maintained for snow, fish, sediments, and flora:

1) SOCs, Hg (and Methyl-Hg in snow), toxaphene;
2) any current-use chemicals not included in SOCs;
3) other metals.

The panel recommended adding toxaphene to the list of analytes because recent surveys of OC pesticides and PCBs in fish from the Columbia And Coast mountains have detected levels of toxaphene above the 6.3 nanogram/gram wet weight guideline for the protection of wildlife consumers of fish (established by the Canadian Council of Environmental Ministers). It was the class of compounds most frequently found close to its guideline.

The data in Figure 1.1 are appropriate as background to establish the need for this study. The authors should expand the inclusion of existing data in the research plan. There are ample sources of appropriate information from Landers, Campbell, Geiser, Jaffe, plus the literature to justify the data needs for this project. In the opinion of the panel, the existing data may help further refine the activities of the project. For example, p. 18 mentions existing snow data for metals and organics along the Continental Divide, yet there is no description of the results that relate to the goals of WACAP. Some questions asked by the research plan may already have answers, if the existing data are carefully examined in advance.

**Question 3: Are the field and laboratory methods sufficient to meet the objectives of each component?**

The panel had a number of questions and concerns with the approach:

- The snow team is highly experienced in interior mountains, but can they reasonably expect to find an intact snowpack at OLYM and MORA, given the prevalence of rain-on-snow events?

- The panel recommends that researchers look at Mercury Deposition Network (MDN) data on Hg and methyl-Hg comparisons at any sites in the snow zone and then consider collecting some snow samples for methylmercury analysis – both for comparison with MDN data and to see if methylmercury deposition at high-elevation sites should be addressed.
- Researchers need to decide what fraction of the melted snow will be used for analysis – melted and digested, dissolved + particulate. And then use this definition for all of the added analysis. They should consider how the Hg and SOC sample analyses could be linked with dissolved major chemical species.
- Lichens: regional data on metals already exist, and the panel recommends that the lichen work be refocused to determine if SOCs are accumulated in lichens via a first year pilot study. Use of lichens to examine elevational transects should be deferred until the suitability of lichens as bioindicators of SOCs is determined.
- If epiphytic lichens are not found in a given target watershed, the panel suggests that the lichens be sampled outside the watershed rather than use terricolous species.
- Analyses of contaminants must be significantly above the detection limit, which may be an issue with low resolution GC/MS. The use of high resolution GC/MS, if necessary, will increase costs by 10-fold. Some extracts or tissue samples should be analyzed at high resolution to enable an assessment of whether the PCB congeners selected adequately capture the Toxic Equivalent Quotients that would be calculated from a larger list of congeners.
- Ensure that biotic response is linked directly to contaminant exposure for the same fish (i.e., analyze the each fish for both sets of variables).
- Consider stratifying samples by total length group, rather than age group, to simplify processing in the field.
- The panel expects that repeated annual sampling at one lake will not be adequate to yield information on interannual effects. The variability in analytical results will be too high due to low concentrations and to variability in fish condition and bioaccumulation and the fact that fish integrate contaminant exposure over their whole lives. Interannual variation may only turn up in young of the year (which may be too small for analysis).
- Many of the details of organic analyses are tentative; many matrices are still to be developed, and new equipment is still being installed. Separate analytical runs for several matrices or analyses will increase costs and time. Is the effort to be spent on chiral analyses appropriate at this time?
- The organic laboratory is expected to be fully committed with determinations of SOCs. The panel recommends that any metal analyses not being done by USGS be done by a proven, external contractor.
- It is inappropriate to say that anomalous SOC concentrations will be discounted at sites accessed by helicopter. Rather, the panel recommends that the helicopter be landed outside the target watershed and that the field crews access the sampling sites on foot.

**Question 4. Are the scientists sufficiently experienced to conduct the research components as intended?**

Yes, a particular strength of the EPA team is experience with multi-investigator, complex, large regional scale projects. The snow team includes the US experts, although they should be careful to consult with local experts familiar with specific terrain. The fish health assessment group is highly experienced.

Despite their strengths, the research team and the project managers should have the appropriate expectations about the many aspects of the project that are still being developed. Processes in development include some aspects of sample collection and the related uncertainty about the ability of the target ecosystem components to sequester the analytes of interest. Most of the sample preparation and analytical methods are in development, and unforeseen problems and delays will occur. The success of fish collection cannot be predicted.

**Question 5. What improvements should WACAP PIs consider prior to initiating the research, given the limits in funding?**

The design for snow sampling does not adequately address the goal of understanding elevational patterns and assessing the cold-condensation hypothesis. The solution is to either drop the single high elevation sample at each watershed, or to expand the transect to adequately address the elevational range. Another way to identify possible elevation gradients is through the use of lichens or willow bark. These matrices are easy to sample and analyze, but are not yet proven as accumulators of SOCs. Before planning extensive studies with these materials it would be advisable to conduct a pilot study during the first year of sampling. This could be performed in the first two watersheds that will be studies in this period. Only after positive trends are observed between altitudinal gradients and concentrations should the pilot effort be extended to the other Parks.

The research plan should define the linkages among the ecosystem~~s~~ components to be sampled. The interrelationships among, and unique contributions from, snow, sediments, fish, and willows may not be obvious to many readers.

Another aspect for consideration is that altitude is, in fact, a surrogate of temperature. Some organochlorine compounds accumulate at higher elevation because these sites are colder and condensation of atmospheric gas phase compounds is enhanced. Thus, determination of annual average air temperatures would be useful.

Additional comments and recommendations follow:

- Consider adding zooplankton analysis (inexpensive) or substitute zooplankton for water as an alternative, and more meaningful indicator of exposure to contaminants. Water concentrations are potentially important for understanding the contribution of gill uptake for some of the compounds. The question is whether analyzing zooplankton and water informs us what to monitor long term or does it allow further analysis of differences in the contaminant patterns. Water concentrations may allow some calculations of equilibrium with the atmosphere for some very volatile compounds. Neither water nor zooplankton are core components.

- Select different organs or tissues for analysis, to focus on areas of highest likely accumulation. For fish, the panel recommends (1) axial muscle (without skin) for total mercury (which will be 95% to 100% methylmercury), PCBs, and organochlorine pesticides and their degradation products and (2) liver tissue be analyzed for PAHs, the more hydrophilic pesticides, and metals other than mercury (possibly cadmium and lead). The remaining carcass could be analyzed for calculation of whole fish body burdens.
- Limit metals to those with biological significance and known bioaccumulation.
- Consider stable isotope (C, N) analyses on fish to estimate trophic position.
- As the surficial sediments are likely to have a high organic and water content, it will be difficult to confirm in the field that sufficient mass of dried sediment has been collected, especially the top 0 to 0.5 and 0.5 to 1 cm sections. This may have to be addressed with extra sampling as a precaution.
- The sediment/water interface environment (physical/chemical/biological) may vary considerably among the lakes and knowledge of these differences may be important in the data interpretation. This should include analyses of water content organic, inorganic carbon, and acid-volatile sulfide.
- The characteristics of the lake drainage basins are highly variable, with respect to geology, soils, vegetation and climatology. Sufficient information on these characteristics will be required to allow the knowledge generated to be applied in other lakes in the National Parks.
- The limnology of each of the lakes will eventually be needed to inform the interpretation of sediment, water column, and air-water interface cycling of the contaminants. It may be important to know what contribution benthic production in the littoral zone makes to the food web and to the associated trophic transfer of contaminants.
- Knowledge of surface sediment concentrations is critical to the understanding of partitioning of SOCs and metals among water, sediment and biotic phases.
- Profiles of sediment concentrations provide long term trends in contaminant sedimentation, which is related by varying degrees to inputs and in-lake processes (degradation, storage in biotic compartments and/or re-volatilization)
- If snow is analyzed for metals, there should be an explicit decision about the form of the samples (dissolved, particulate, total). There should be thought given to how the metals data will be compared across media (including the IMPROVE data set for metals).

**Question 6. Is the coordination and communication strategy within WACAP and between WACAP and NPS sufficient for implementation, completion, and publication of results?**

There are many details to be worked out, but the panel is reasonably confident that the coordination and communication among WACAP researchers will be adequate. There are several recommendations:

- A password-protected web site is needed for investigators and park staff. The site should be updated frequently with methods, schedules, and preliminary data. Existing

background data on the lakes, watersheds, geospatial analyses, and air quality should also be posted.

- Someone not harried by day-to-day logistics could facilitate some aspects of project integration. For example, ARD could hire a graduate student or biotech who could serve as a conduit for technical information, do the web site updates, organize PI meetings, and prepare integrated annual reports for the NPS.
- Continued external scientific input is needed because of the developmental nature of many aspects of the project as well as the rapid pace of discovery in this area of environmental research. The PIs will benefit from outside input as they evaluate results of pilot data to decide whether to expand or drop project components. At a minimum, outside scientists should be invited to present findings at an annual WACAP science workshop. The NPS could consider re-convening a peer review panel after two or three years.

**Question 7. What suggestions can the panel offer for prioritizing research elements as 'core components' if funding becomes limiting in the future?**

The panel characterized the program components into 'core', 'pilot', and 'non-essential' activities. The **core** components, considered to be most important to achieving Project goals, include the following.

- Annual snow sampling,
- One-time fish sampling,
- One-time sediment coring.

The **pilot** activities are those that are unproven, and do not warrant a multi-year financial commitment until proven. The recommendation is to test the pilot components in two parks in the first year of sample collection. Pilot activities include:

- Lichens and willow for SOC and Hg analyses,
- Methylmercury analysis in snow.

The Panel regards atmospheric modeling as a **non-essential** project component, ~~is~~ because it does not directly address the core goal of assessing whether these contaminants are present in detectable concentrations. Contaminant source determination is not included as a project goal in the review draft of the WACAP Study Plan, and this component could be deferred until contamination has been confirmed.

The panel suggests the following priority for analytes, and that this priority be maintained for snow, fish, sediments, and flora:

1) SOCs, Hg (and Methyl-Hg in snow), toxaphene;
2) any current-use chemicals not included in SOCs;
3) other metals

**Question 8. What are the recommendations for revisions and distribution of the research plan as an EPA report?**

- The panel did not see the need for more than a few hard copies of the research plan. The panel's alternative recommendation is to save costs and add substance quickly to the WACAP webpage with the addition of research plan as a PDF file.
- There were significant differences in the level of detail, organization, and clarity of writing among chapters in the draft study plan that should be remedied during revision. An editor is needed for the document. Some draft chapters had extraordinarily long paragraphs, used colloquial language, or were awkwardly constructed.
- The phrase 'if funding permits' should be purged from the study plan and realistic goals and objectives should be based on the objectives and the budget. Costs can be reduced by focusing effort on the three identified core components and by reducing effort on other components.
- The panel recommends that the hypotheses be purged from the document. The hypotheses as stated are largely statements of expectations, not testable hypotheses.
- Leveraged projects should be explicitly and exhaustively listed for political advantage.
- Add ideas or requests for add-on studies (e.g., glacier cores in parks) to the web page.
- A budget summary should be added for each component; this will assist potential collaborators in understanding the scope of the program and would have been helpful for the panel in its deliberations.

**Specific comments on the text**

The List of acronyms does not include WRS laboratory. The panel notes that acronyms are not reader friendly and diminish the effectiveness of the document.

List investigators at the beginning of each chapter to aid the reader.

Include some of D. Landers PowerPoint presentation graphics in the plan document. Example: the Venn diagram of agency involvement.

p. 4, lines 4-5. There are colloquialisms that should be purged from the text. E.g. *setting* these locations *up* to be long term sinks.

p. 6. The PIs could attempt to define relative trophic position of the fish analyzed by stable isotope analysis of co-existing fish and zooplankton, to facilitate the interpretation of fish-contaminant data. Trophic position is just one of many potentially confounding variables that will complicate interpretation of results in this study. Problematic concentrations of biomagnifying contaminants will most likely be found in the highest trophic level to be sampled, which in the WACAP study would presumably be piscivorous fish. The trophic position of the fish sampled is a variable that will not be visually apparent to the field crews and PIs, and examination of the stomach contents of a small number of fish in the field can be misleading due to seasonal changes and other factors affecting diet. Piscivorous fish are desirable for the contaminant analyses, and the fish analyzed should be from the same trophic level.

p. 7. There are some mismatches between the Parks listed in red in Figure 1.3 (those selected for study) and those in the appendix. In the appendix Kings Canyon is not present but Gates of the

Arctic. In Table 1.1 (Pg. 10) there are 8 Parks. Again it shows some differences with the previous Park lists.

p. 11 and elsewhere. Throughout the project sometimes the term Persistent Organic Pollutants (POPs) is used and in other occasions Semi-volatile Organic Compounds (SOCs) is used. Be consistent.

p. 11. In the table: Subsistence, not subsistence

p. 14, line 19. WACAP … *is designed to* answer the following questions.

p. 14, lines 23-32, rephrase for consistency:

- Are concentrations of contaminants detectable in western Parks?
- Where are contaminants accumulating (geographically and by elevation)?
- Which contaminants pose a potential ecological threat?
- Which indicators appear most useful to address contamination…?

p. 14, 28, 48, etc. (each chapter): each section repeats very similar language about publications and data use. This can be done once, in the introduction. Don't overstate the publication potential of a reconnaissance project, but do plan to publish on your methods and method development. The format of this statement on p 57 (water quality) is appropriate for most of the project components.

p. 15. line 16 ~~the 2002~~

p. 15, lines 16-19. Don't apologize.

p. 21. Objective: determine the *continental-scale* spatial variability… This project is not determining local variability due to small number of samples.

p. 24, line 29. Specify what happens if the snowpack is above freezing. Is the entire park not sampled for the year, or does the team dig another pit?

p. 25. Are the samples analyzed in a chilled condition, as written? This would be unusual.

p. 25, line 25. concentrations *are* determined.

P. 26, line 19. 10% of snow sampling will be duplicates and blanks. At 21 samples per year, this is one blank and one replicate per year. These are probably not adequate numbers for meaningful QA.

p. 27. Table 2-1. Add to caption: ….*via ICP-MS at USGS, Boulder CO.*

Section 3 (foodweb). This section needs a technical edit for grammar, construction, and flow.

p. 32, line 7-8. physiological *anomalies* in fish

p. 32, line 21. To assess fish as *indicators of* bioaccumulation….

p. 32. The food web section does not have hypotheses, in contrast to other chapters. The sections should be consistent. Note that the panel does not think that hypotheses are necessary.

p. 33, line 27. *High* WBCs

p. 40. Figure 3.2.2. refers to N in lichens, not to metals

p. 51, lines 9 and 12. *Patterns*, not trends.

p. 65, Figure 5.3. The surface of the sediment core is *horizontal*, not perpendicular.

# APPENDIX D: PEER REVIEW RECONCILIATION MEMO

Following is the reconciliation memo that details the responses of the WACAP science team to the WACAP Peer Review Report.

# WACAP Peer Review Reconciliation Memo

Date: 18 March 2003

Prepared by: Dixon H. Landers

**Background:** On December 12, 2002, the WACAP program was presented to a five-member peer review panel in Seattle, Washington. This review was based on the Draft WACAP Research Plan that was distributed in advance to the review panel. The Peer Review panel prepared a detailed report and submitted this along with oral panel presentations to the National Park Service and assembled WACAP staff and other interested parties. The purpose of this document is to record and document the WACAP responses to each of the major comments made by the peer panel in their report and to act as a guide for the PIs in revising the draft WACAP research plan to a Final plan that will guide the WACAP activities for the next several years.

**Format of the Reconciliation Memo:** The Peer Review panel was specifically charged to consider seven questions and they added an eighth question of their own. These questions are listed here as Q1-Q8 in italics. Specific recommendations and comments from the Peer Review Report are repeated here, with the page number where the recommendation is discussed in the Report. Our responses to each recommendation are provided in all caps in a "RESPONSE/ACTION" section following the recommendation.

1.) pg C-6: Change *monitoring network* to *deposition network* in the goal statement. Delete the term *impact* from the goal statement and consider rewording or deleting *spatially-extensive* and *temporally-resolved* because these might be mis-interpreted and confusing.

**RESPONSE/ACTION:** ACCEPT "DEPOSITION ASSESSMENT" WORDING, LEAVE "IMPACT", AND DROP "SPATIALLY-EXTENSIVE AND TEMPORALLY-RESOLVED" FROM THE GOAL. DO THIS IF NPS-ARD AGREES SINCE SOME OF THIS WORDING CAME FROM THE AK WORKSHOP AND WAS IMPORTANT TO THE NPS. ADD ADDITIONAL TEXT IN THE FINAL RESEARCH PLAN FOLLOWING THE GOAL STATEMENT TO EXPLAN THESE PORTIONS OF THE GOAL.

THE REVISED WACAP GOAL WOULD BE:

***TO ASSESS THE DEPOSITION OF AIRBORNE CONTAMINANTS IN WESTERN NATIONAL PARKS, PROVIDING REGIONAL AND LOCAL INFORMATION ON EXPOSURE, ACCUMULATION, IMPACTS, AND PROBABLE SOURCES.***

2.) pg C-7: The panel thought that the WACAP was biased toward considering air pollution in North American with sources primarily originating in Asia or at least air masses that pass over Asia. The panel suggests that WACAP considers Asia as only one of many potential sources of airborne contamination for WACAP parks.

**RESPONSE/ACTION:** THE PANEL MAKES SOME EXCELLENT POINTS AND UNDERSCORES THE IMPORTANCE OF AN UNDERSTANDING OF WHERE THE ANTICIPATED CONTAMINANTS ORIGINATE AS A KEY ISSUE IN THIS WORK. THE FIRST QUESTION WE WILL BE ASKED AFTER WE REPORT FINDINGS OF ANTHROPOGENIC CHEMICALS IN REMOTE PARK LOCATIONS WILL BE "WHERE IS IT COMING FROM." WE ANTICIPATED THIS BY INCLUDING AN ATMOSPHERIC COMPONENT IN WACAP FROM THE BEGINNING.

WE WILL ADD WORDING REGARDING SOURCES OF CONTAMINANTS IN THE GOAL STATEMENT. FURTHER, IN REVISION OF THE RESEARCH PLAN, BROADER LANGUAGE REGARDING SOURCES OF CONTAMINANTS OTHER THAN ASIA TO THE WESTERN U.S. WILL BE INCLUDED.

***Q1: Do the objectives of WACAP logically address the overall goal?***

3.) pg C-8: The panel had three related comments under Q1:

*a)* The panel recommends that each objective be *specifically* addressed in the approach section of each chapter;

*b)* the panel believes that source determination is outside the scope of the project based on the goal and

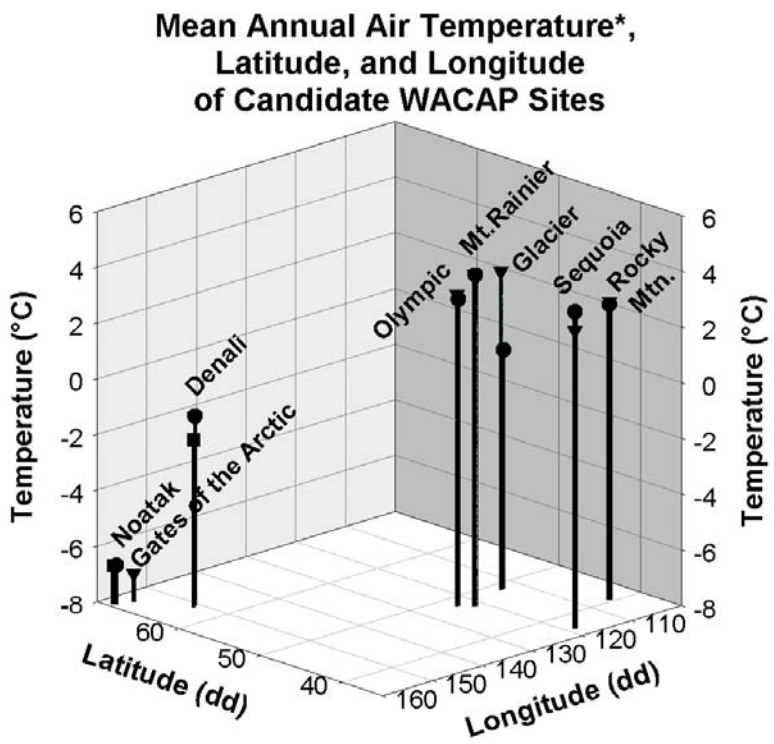
*c)* elevational gradients with regard to contaminants are really designed to look at temperature gradients and these cannot be evaluated given the current WACAP design since elevation and latitude of the WACAP sites are inversely related (cf. Peer Review Report Fig. 2).

**RESPONSE/ACTION:**

a) IN REVISION, EACH SECTION OF THE RESEARCH PLAN WILL BE WRITTEN TO EXPLICITLY ADDRESS THE STATED OBJECTIVES.

b) SOURCE DETERMINATION AND ATMOSPHERIC SCIENCE ISSUE: THE PANEL PREVIOUSLY EMPHASIZED THE IMPORTANCE OF UNDERSTANDING SOURCE APPORTIONMENT (ASIAN VS. OTHER SOURCES) OF CONTAMINANTS (SEE COMMENT #2, ABOVE). THIS IS THE WORK THAT JAFFE'S GROUP IS TO CONDUCT. WE WILL MODIFY THE WACAP GOAL TO INCLUDE SOURCES AND, THUS, JUSTIFY JAFFE'S INVOLVEMENT IF RESOURCES PERMIT.

c) DAN JAFFE'S GROUP CALCULATED TEMPERATURE FOR EACH OF THE WACAP CATCHMENTS BASED ON THE CLOSEST AND MOST REPRESENTATIVE METEOROLOGICAL DATA AND FOUND THAT THERE IS A VERY TIGHT GROUPING OF ESTIMATED TEMPERATURES FOR ALL SITES IN THE COUNTERMINOUS U.S. (CF. FIGURE 1). THUS, THE ALASKAN SITES WILL PROVIDE A MEANS TO COMPARE THE EFFECT OF TEMPERATURE, AND, THEREFORE, THE EFFECTS OF COLD FRACTIONATION. ELEVATION GRADIENTS WILL BE ADDRESSED WITH SNOW AND WILLOW BARK ONLY AS CLARIFIED IN THIS DOCUMENT AND THE FINAL WACAP RESEARCH PLAN.




*Temperature data was estimated from the nearest and most representative locations with long-term meteorological data. In some cases a small correction was made to account for the difference in altitude between the meteorological and lake site. (D. Jaffe, Univ. of Washington-Bothel)

Figure 1. WACAP Site Temperatures, Latitudes and Longitudes

***Q2: Is the general program design and approach sufficient to achieve the defined objectives?***

4.) pg C-10: The panel recommends listing the objectives in the introductory text and then insuring that the methods sections of each section is revised by listing each objective as a subheading, to be followed with the specific activities and methods that will be used to accomplish the specific objective.

**RESPONSE/ACTION:** THIS WILL BE DONE IN REVISION OF THE RESEARCH PLAN.

5.) pg C-10: The panel recommends the following priority for analytes for WACAP: SOCs, Hg (and methyl-Hg, in snow), toxaphene, current-use chemicals, other metals.

**RESPONSE/ACTION:** IF THERE ARE SUFFICIENT RESOURCES WE WILL ADD METHYL HG MEASUREMENTS IN SNOW. HOWEVER, IT IS THE OPINION OF WACAP THAT THIS IS OF AN EXPLORATORY NATURE AND IS NOTAS IMPORTANT AS SOME OF THE OTHER CLASSES OF CONTAMINANTS SINCE TOTAL HG IS ALREADY BEING MEASURED. IT WOULD BE NICE TO MEASURE TOXAPHENE IN SOME FISH SAMPLES AND WE WILL TRY TO DO THIS IF FUNDING PERMITS.

***Q3: Are the field and laboratory methods sufficient to meet the objectives of each component?***

6.) pg C-10: The snow team is highly experienced in interior mountains, but can they reasonably expect to find an intact snowpack at OLYM and MORA, given the prevalence of rain-on-snow events?

**RESPONSE/ACTION:** DURING SOME YEARS, THE MARITIME CLIMATE IN SOME OF THE PARKS MAY CAUSE MIDWINTER SNOWMELT OR RAIN-ON-SNOW EVENTS THAT WASH ACCUMULATED CONTAMINANTS OUT OF THE SNOWPACK AT LOWER-ELEVATION SITES. THE POTENTIAL FOR WASH-OUT WILL BE EVALUATED BEFORE EACH YEAR'S SAMPLING BY EXAMINING METEOROLOGIC AND SNOWPACK DATA FROM NEARBY SITES, AND CONSULTING LOCAL EXPERTS SUCH AS NPS BACKCOUNTRY RANGERS AND SNOW HYDROLOGISTS AT THE NATURAL RESOURCES CONSERVATION SERVICE (NRCS). SAFETY OF FIELD CREWS WILL ALSO BE A CONSIDERATION, ESPECIALLY WITH RESPECT TO AVALANCHE, SNOW, WEATHER, AND TRAIL CONDITIONS. WHEN NECESSARY, ALTERNATE SITES FOR SNOW-SAMPLING WILL BE CHOSEN. IDEALLY, THESE SITES WOULD BE NEAR THE LAKE WATERSHEDS, AND ON THE SAME SIDE OF MAJOR MOUNTAIN RANGES, BUT AT HIGHER ELEVATION AND ON NORTHERLY ASPECTS WHERE SNOW IS LIKELY TO BE COLDER.

7.) pg C-11: The panel recommends that researchers look at Mercury Deposition Network (MDN) data on Hg and methyl-Hg comparisons at any sites in the snow zone and then consider collecting some snow samples for methylmercury analysis – both for comparison with MDN data and to see if methylmercury deposition at high-elevation sites should be addressed.

**RESPONSE/ACTION:** THERE IS LITTLE DATA AVAILABLE ON METHYLMERCURY IN SNOW. IF WE CAN, WE WILL HAVE SOME SAMPLES ANALYZED FOR METHYLMERCURY, HOWEVER THIS IS A RESEARCH QUESTION RATHER THAN A CORE DATA PRIORITY FOR WACAP.

8.) pg C-11: Researchers need to decide what fraction of the melted snow will be used for analysis – melted and digested, dissolved + particulate. And then use this definition for all of the added analysis. They should consider how the Hg and SOC sample analyses could be linked with dissolved major chemical species.

**RESPONSE/ACTION:** WHOLE-WATER SAMPLES (I.E. UNFILTERED) OF MELTED SNOW WILL BE USED FOR HG AND TRACE METALS ANALYSES. RESEARCH TO DATE INDICATES THAT HG IN THE SNOW IS MOSTLY IN THE PARTICULATE PHASE, AND IS CORRELATED WITH CONCENTRATIONS OF PARTICULATE ORGANIC MATTER. MERCURY WAS NOT WELL-CORRELATED TO DISSOLVED MAJOR ION SPECIES IN 2002 SAMPLES FROM THE ROCKY MOUNTAIN REGION, HOWEVER, SITES AFFECTED BY LOCAL SOURCES OF EMISSIONS MAY BE EXPECTED TO HAVE HIGH VALUES OF SULFATE AND NITRATE AS WELL AS MERCURY.

9.) pg C-11: Lichens: regional data on metals already exist, and the panel recommends that the lichen work be refocused to determine if SOCs are accumulated in lichens via a first year pilot study. Use of lichens to examine elevational transects should be deferred until the suitability of lichens as bioindicators of SOCs is determined.

**RESPONSE/ACTION:** WE DISAGREE THAT REGIONAL LICHEN DATA ALREADY EXIST – IT DOESN'T EXIST AT THE HIGHER ALTITUDE SITES PLANNED FOR WACAP.

WE DO NOT INTEND TO USE LICHENS FOR ELEVATIONAL TRANSECTS AT THIS TIME AND, THEREFORE, WE WILL ONLY CONDUCT SOC WORK ON LICHENS IF THE WILLOW BARK RESULTS WITH REGARD TO SOCs DEMONSTRATES THAT THIS MATRIX IS NOT USEFUL FOR OUR INTENDED PURPOSE AND SUBSEQUENT METHODS DEVELOPMENT WORK WITH LICHENS IS DEEMED NECESSARY.

AT THIS POINT, GIVEN THE UNCERTAIN NATURE OF FULL FUNDING FOR WACAP, WE PROPOSE TO DISCONTINUE FUTURE WORK ON LICHENS UNLESS SUFFICIENT FUNDING IS SECURED. WE BELIEVE THERE IS MERIT IN OBTAINING LICHEN SAMPLES FROM THE WACAP CATCHMENTS AND ANALYZING THEM FOR

METALS, N AND S. HOWEVER, CLEARLY THE PEER REVIEW PANEL INDICATED THAT THIS COMPONENT OF THE PROPOSED WORK WAS OF LESSER IMPORTANCE THAN OTHER "CORE" COMPONENTS. N IS AN IMPORTANT EMERGING POLLUTANT TO ALPINE AREAS AND CAN BE DEVASTATING WITH RESPECT TO CHANGES IN FLORA AND POSSIBLY THE ENTIRE ALPINE ECOSYSTEM. MOREOVER, METALS, S AND N PROVIDE LINKS TO PREVIOUS LICHEN WORK IN THE U.S. AND ELSEWHERE IN THE WORLD. THEREFORE, IF SUFFICIENT FUNDING BECOMES AVAILABLE, WE PROPOSE TO CONTINUE ANALYSES ON LICHENS COLLECTED IN THE SITE CATCHMENTS.

10.) pg C-11: Analyses of contaminants must be significantly above the detection limit, which may be an issue with low resolution GC/MS. The use of high resolution GC/MS, if necessary, will increase costs by 10-fold. Some extracts or tissue samples should be analyzed at high resolution to enable an assessment of whether the PCB congeners selected adequately capture the Toxic Equivalent Quotients that would be calculated from a larger list of congeners.

**RESPONSE/ACTION:** THE PCB CONGENERS LISTED IN TABLE 6.1 WERE SELECTED AS WACAP TARGET ANALYTES BECAUSE THEY OVERLAP WITH THE CONGENERS MEASURED IN EMERGE AND BY CANADIAN RESEARCHERS STUDYING HIGH ELEVATION ECOSYSTEMS. THEY ALSO REPRESENT SOME OF THE MOST PREVALENT PCB CONGENERS FOUND IN THE ENVIRONMENT AND A SIGNIFICANT FRACTION OF THE PCB TEQ FOUND IN THE ENVIRONMENT. TWO CONGENERS WERE CHOSEN TO REPRESENT THE PHYSICAL-CHEMICAL PROPERTIES ASSOCIATED WITH EACH LEVEL OF CHLORINATION, RANGING FROM DICHLORO- TO HEPTACHLORO-PCBS. THE PURPOSE OF WACAP IS TO ASSESS DEPOSITION, NOT TO CONDUCT RISK ASSESSMENTS FOR THE ECOSYSTEMS. IF A MORE DETAILED ASSESSMENT IS NEEDED IN THE FUTURE, EXTRACTS MAY BE ANALYZED BY A CONTRACT LABORATORY FOR FULL PCB CONGENER ANALYSIS BY GC/HRMS (ANALYSIS COST OF ~ $1,000/EXTRACT).

11.) pg C-11: Ensure that biotic response is linked directly to contaminant exposure for the same fish (i.e., analyze each fish for both sets of variables).

**RESPONSE/ACTION:** WE HAVE DECIDED TO ALTER THE METHODS SO THAT THE SAME FISH WILL BE USED FOR BOTH CHEMISTRY AND PATHOLOGY/PHYSIOLOGY FOR THE FOLLOWING REASONS:

a) AS RECOMMENDED BY THE REVIEWERS, THIS WILL ALLOW US TO CORRELATE CHEMICAL BURDENS DIRECTLY WITH HEALTH CHANGES ON INDIVIDUAL FISH.

b) THIS WILL LIKELY REDUCE THE OVERALL NUMBER OF FISH COLLECTED AT EACH LAKE. THIS MAY BE VERY IMPORTANT AT LAKES WITH SPARSE POPULATIONS.

c) EXAMINATION OF THE SAME FISH FOR PATHOLOGY AND CHEMISTRY IS CONSISTENT WITH THE EMERGE PROGRAM.

WE WILL, THEREFORE, SAVE PIECES OF INDIVIDUAL ORGANS FROM FISH FOR PATHOLOGY/PHYSIOLOGY STUDIES, AND SAVE THE REMAINING CARCASS FOR CHEMICAL ANALYSIS. PATHOLOGY/PHYSIOLOGY WILL REQUIRE ABOUT 10% OF THE BLOOD, 50% OF THE KIDNEY, THE ENTIRE SPLEEN (AT LEAST FOR SMALLER FISH), AND ABOUT 25% OF THE LIVER. FOR OTHER ORGANS (E.G., GILLS, SKIN, MUSCLE, GI TRACT) ONLY 10-20% OF THESE ORGANS ARE NEEDED. WE WILL CALCULATE THE OVERALL % OF TOTAL WEIGHT REMOVED FROM THE FISH DUE TO THESE PATHOLOGY PROCEDURES.

THE REMAINING CARCASS WILL BE SAVED FOLLOWING PROCEDURES RECOMMENDED BY DR. SIMONICH TO AVOID CHEMICAL CONTAMINATIONS IN THE FIELD. WHEN POSSIBLE, ADDITIONAL FISH WILL BE COLLECTED AND SAVED WHOLE AS ADDITIONAL SAMPLES FOR CHEMISTRY.

12.) pg C-11: Consider stratifying [FISH]samples by total length group, rather than age group, to simplify processing in the field.

**RESPONSE/ACTION:** WE AGREE WITH THIS NOTION, AND THAT IS WHAT WE HAD INTENDED AS A SURROGATE FOR AGE. IT IS NOT PRACTICAL TO AGE FISH IN THE FIELD, SO OUR AGE CLASSES WILL HAVE TO BE BASED ON LENGTH FREQUENCIES OF THE FISH COLLECTED. HOWEVER, AGE CAN BE MORE IMPORTANT THAN LENGTH WITH OLDER FISH BECAUSE FISH MAY GROW VERY SLOWLY IN COLD, ALPINE LAKES WITH LIMITED FOOD SUPPLY AND OLDER FISH WOULD HAVE MORE TIME TO BIOACCUMULATE TOXIC SUBSTANCES. WHILE THE SAMPLES OF FISH RETAINED FOR ANALYSES WILL BE BASED ON SIZE DISTRIBUTIONS, ALL INDIVIDUALS WILL BE AGED IN THE LABORATORY .

13.) pg C-11: The panel expects that repeated annual sampling at one lake will not be adequate to yield information on interannual effects. The variability in analytical results will be too high due to low concentrations and to variability in fish condition and bioaccumulation and the fact that fish integrate contaminant exposure over their whole lives. Interannual variation may only turn up in young of the year (which may be too small for analysis).

**RESPONSE/ACTION:** CERTAIN PATHOLOGICAL ENDPOINTS REFLECT CHRONIC, ONGOING DAMAGE. THESE INCLUDE INCREASES IN MACROPHAGE AGGREGATES, AND OTHER CHRONIC LESIONS (E.G., NEOPLASMS, GILL HYPERPLASIA, ETC.). THEREFORE, ALTHOUGH EACH YEAR WILL BE A 1 DAY "SNAP SHOT", CERTAIN PATHOLOGICAL END POINTS WILL REFLECT CHRONIC, CUMULATIVE EXPOSURE. WHILE WE AGREE WITH THE GENERALITY OF THE PANEL'S COMMENT, OUR EXPERIENCE WITH BOTH CONTAMINANT CONCENTRATIONS AND PHYSIOLOGICAL AND PATHOLOGICAL ASSESSMENTS OF FISH CONDITION BASED ON REPEATED SAMPLING OVER YEARS FROM THE SAME

SITE WITH SMALL SAMPLE NUMBERS HAS EXPOSED CONSIDERABLE INTERANNUAL VARIATION.

14.) pg C-11: Many of the details of organic analyses are tentative; many matrices are still to be developed, and new equipment is still being installed. Separate analytical runs for several matrices or analyses will increase costs and time. Is the effort to be spent on chiral analyses appropriate at this time?

**RESPONSE/ACTION:** THE CHIRAL ANALYSES WILL BE DONE AT NO ADDITIONAL COST TO WACAP AND IS EXPLORATORY RESEARCH FOR THE PI'S LABORATORY. NO ADDITIONAL SAMPLE PREPARATION IS REQUIRED AND THE ANALYSES HAVE POTENTIAL TO ADD ADDITIONAL UNDERSTANDING WITH REGARD TO SOURCE AGE (RECENT OR HISTORICAL USE OF THE CHEMICAL) AND BIOLOGICAL TRANSFORMATION WITHIN THE ECOSYSTEMS.

15.) pg C-11: The organic laboratory is expected to be fully committed with determinations of SOCs. The panel recommends that any metal analyses not being done by USGS be done by a proven, external contractor.

**RESPONSE/ACTION:** AGREE. THE USGS NATIONAL RESEARCH PROGRAM LAB IN BOULDER, CO HAS AGREED TO CONDUCT ALL METALS ANALYSES FOR WACAP USING ICP-MS. THIS LABORATORY HAS AN EXCELLENT RECORD AND REGULARLY PARTICIPATES IN AN INTERNATIONAL PERFORMANCE EVALUATION PROGRAM.

16.) pg C-11: It is inappropriate to say that anomalous SOC concentrations will be discounted at sites accessed by helicopter. Rather, the panel recommends that the helicopter be landed outside the target watershed and that the field crews access the sampling sites on foot.

**RESPONSE/ACTION:** WE AGREE THAT CARE NEEDS TO BE TAKEN IN SAMPLING AND INTERPRETATION OF SNOW COLLECTED WITH THE USE OF HELICOPTER ACCESS. HOWEVER THE RECCOMENDATION OF THE PANEL MAY NOT BE WORKABLE. INSTEAD, WE INTEND TO PAY CLOSE ATTENTION TO WIND DIRECTION AND DISTANCE TO THE SAMPLING SITE AND TO DOCUMENT THIS FOR EACH COLLECTION. FURTHERMORE, THE SURFACE OF THE SNOW (TOP 2-5 CM) WILL BE DISCARDED TO REMOVE ANY CONTAMINATION.

***Q4: Are the scientists sufficiently experienced to conduct the research components as intended?***

17.) pg C-12: A particular strength of the EPA team is experience with multi-investigator, complex, large regional scale projects. The snow team includes the US experts, although they should be careful to consult with local experts familiar with specific terrain. The fish health assessment group is highly experienced.

Despite their strengths, the research team and the project managers should have the appropriate expectations about the many aspects of the project that are still being developed. Processes in development include some aspects of sample collection and the related uncertainty about the ability of the target ecosystem components to sequester the analytes of interest. Most of the sample preparation and analytical methods are in development, and unforeseen problems and delays will occur. The success of fish collection cannot be predicted.

**RESPONSE/ACTION:** THE WACAP TEAM FORESAW THE NEED TO SCHEDULE AN ENTIRE YEAR TO CONDUCT PILOT WORK AND IS EFFICIENTLY EXECUTING THIS PLAN. RESULTS OF THIS WORK WILL BE PRESENTED, DISCUSSED, DOCUMENTED AT THE SPRING (JUNE 2003) WACAP PI MEETING. RESULTS WILL BE USED TO FINALIZE APPROACHES TO THE WACAP.

***Q5: What improvements should WACAP PIs consider prior to initiating the research, given the limits in funding?***

18.) pg C-12: The design for snow sampling does not adequately address the goal of understanding elevational patterns and assessing the cold-condensation hypothesis. The solution is to either drop the single high elevation sample at each watershed, or to expand the transect to adequately address the elevational range. Another way to identify possible elevation gradients is through the use of lichens or willow bark. These matrices are easy to sample and analyze, but are not yet proven as accumulators of SOCs. Before planning extensive studies with these materials it would be advisable to conduct a pilot study during the first year of sampling. This could be performed in the first two watersheds that will be studied in this period. Only after positive trends are observed between altitudinal gradients and concentrations should the pilot effort be extended to the other Parks.

**RESPONSE/ACTION:** WACAP WILL DROP THE "EXTRA" HIGH ELEVATION SITE FOR SNOW IN EACH CATCHMENT THAT HAD BEEN CONSIDERED. VEGETATION/SOCS WORK HAS BEEN DISCUSSED PREVIOUSLY. ADDITIONAL SNOW SAMPLES WILL BE COLLECTED TO EVALUATE ENVIRONMENTAL FACTORS AFFECTING DEPOSITION OF CONTAMINANTS TO SNOW. THESE WOULD BE COLLECTED OPPORTUNISTICALLY RATHER THAN IN EVERY PARK IN EVERY YEAR. ELEVATIONAL TRANSECTS WILL BE SAMPLED WHEN THE SEASONAL SNOWPACK EXTENDS OVER A WIDE RANGE OF ELEVATION WITH ACCESSIBLE

SITES. MULTIPLE SNOWPITS WITHIN A SINGLE WATERSHED WILL BE SAMPLED TO EVALUATE THE EFFECTS OF SNOW TEMPERATURE, SOLAR RADIATION, AND ORGANIC MATTER CONTENT IN THE SNOWPACK ON CONTAMINANT ACCUMULATION.

19.) pg C-12: The research plan should define the linkages among the ecosystem~~s~~ components to be sampled. The interrelationships among, and unique contributions from, snow, sediments, fish, and willows may not be obvious to many readers.

**RESPONSE/ACTION:** WE WILL ADD A "LINKAGES" SECTION ON INTERRELATIONSHIPS AMONG THE WACAP COMPONENTS TO THE INTRODUCTION OF THE RESEARCH PLAN.

20.) pg C-12: Another aspect for consideration is that altitude is, in fact, a surrogate of temperature. Some organochlorine compounds accumulate at higher elevation because these sites are colder and condensation of atmospheric gas phase compounds is enhanced. Thus, determination of annual average air temperatures would be useful.

**RESPONSE/ACTION:** DONE, SEE FIGURE 1 OF THIS DOCMENT.

21.) pg C-12: Consider adding zooplankton analysis (inexpensive) or substitute zooplankton for water as an alternative, and more meaningful indicator of exposure to contaminants. Water concentrations are potentially important for understanding the contribution of gill uptake for some of the compounds. The question is whether analyzing zooplankton and water informs us what to monitor long term or does it allow further analysis of differences in the contaminant patterns. Water concentrations may allow some calculations of equilibrium with the atmosphere for some very volatile compounds. Neither water nor zooplankton are core components.

**RESPONSE/ACTION:** WE PROPOSE TO CONTINUE WITH THE WATER SAMPLING AS PLANNED BECAUSE MANY OF THE CURRENT USE CHEMICALS ARE HYDROPHILLIC AND MAY BEST BE FOUND IN WATER. UPTAKE OF THESE COMPOUNDS BY ZOOPLANKTON MAY OR MAY NOT OCCUR. WE DO NOT INTEND TO CONDUCT THE ZOOPLANKTON SAMPLING PROPOSED ON A ROUTINE BASIS BUT MAY DO SOME WORK IN THIS AREA IF METHODS ARE ROBUST, SIMPLE AND WE CAN AFFORD TO CONDUCT THE ANALYSES.

22.) pg C-13: Select different organs or tissues for analysis, to focus on areas of highest likely accumulation. For fish, the panel recommends (1) axial muscle (without skin) for total mercury (which will be 95% to 100% methylmercury), PCBs, and organochlorine pesticides and their degradation products and (2) liver tissue be analyzed for PAHs, the more hydrophilic pesticides, and metals other than mercury (possibly cadmium and lead). The remaining carcass could be analyzed for calculation of whole fish body burdens.

**RESPONSE/ACTION:** CHEMISTRY PROTOCOLS DICTATE WHOLE FISH FOR ANALYSIS. HOWEVER, WE WILL SAVE PIECES OF INDIVIDUAL ORGANS FROM FISH USED FOR PATHOLOGY/PHYSIOLOGY STUDIES FOR ADDITIONAL CHEMICAL ANALYSIS IF WARRANTED. ALTHOUGH PATHOLOGY/PHYSIOLOGY WILL REQUIRE MOST OF THE TISSUES FROM THE KIDNEY AND SPLEEN, MORE THAN 70% OF THE GILL, LIVER, MUSCLE AND SKIN WILL BE SAVED FOR CHEMISTRY FROM THESE FISH. THEREFORE, IF LESIONS OR OTHER CHANGES ARE DETECTED, DR. SIMINOICH'S GROUP WILL HAVE THE OPPORTUNITY TO ANALYZE THE GILLS, MUSCLE, SKIN AND LIVER FROM THE SAME FISH.

23.) pg C-13: Limit metals to those with biological significance and known bioaccumulation.

**RESPONSE/ACTION:** WE ALREADY HAVE DONE THIS IN THE SHORT LIST OF METALS PROPOSED FOR ANALYSIS. HOWEVER, BECAUSE USGS WILL NOW BE DOING ALL THE METAL WORK, WE WILL GET THE SAME EXTENSIVE SUITE OF METALS THAT WILL BE MEASURED IN SNOW – ANALYZED AT THE SAME LABORATORY.

24.) pg C-13: Consider stable isotope (C, N) analyses on fish to estimate trophic position.

**RESPONSE/ACTION:** ASSUMING THAT THE QUESTION IS WHETHER THE FISH TROPHIC WEB IS OF TERRESTRIAL OR AQUATIC ORIGIN, TO BE CERTAIN ONE WOULD NEED TO COLLECT ALGAE (SESTONIC AND BENTHIC), AND AQUATIC OR TERRESTRIAL INVERTEBRATES. TERRESTRIAL SIGNATURES FOR CARBON $\delta^{13}C$ ARE RATHER PREDICTABLE AND PERHAPS LITERATURE VALUES COULD BE USED TO DENOTE TERRESTRIAL SOURCES. AQUATIC CARBON ISOTOPE VALUES ARE DEPENDANT UPON INORGANIC CARBON AVAILABILITY AND THEREFORE CAN CHANGE FROM LAKE TO LAKE. THE TERRESTRIAL SIGNATURES FOR THESE HAVE BEEN RATHER WELL WORKED OUT, AND LITERATURE VALUES COULD BE USED TO HELP STRENGTHEN THE CONCLUSIONS RELATIVE TO INPUTS FROM TERRESTRIAL SOURCES. NITROGEN ISOTOPE VALUES ($\delta^{15}N$) CAN ALSO VARY BETWEEN LAKES AND THEREFORE CONCLUSIONS THAT INPUTS ARE AQUATIC WOULD BE LESS ROBUST. HOWEVER, $\delta^{15}N$ CAN INFORM US OF THE TROPHIC CHAIN IN THE LAKES, THEREBY HELPING INTERPRET THE $\delta^{13}C$ VALUES.

STABLE ISOTOPES WILL BE MEASURED TO PROVIDE INFORMATION ON THE ORIGIN OF THE COMPONENTS OF THE TROPHIC WEB CONTRIBUTING TO FISH PRODUCTION IN THE LAKES. WE HOPE TO BE ABLE TO ASCERTAIN THE IMPORTANCE OF TERRESTRIAL VERSUS AQUATIC NUTRIENTS CONTRIBUTING TO FISH PRODUCTION. SUCH INFORMATION WILL BE OF USE IN ESTABLISHING THE ROUTE(S) WHEREBY CONTAMINANTS MAY FIND THEIR WAY INTO FISH TISSUES. SUCH AN APPROACH HAS BEEN USED SUCCESSFULLY IN THE PAST TO TRACK TROPHIC RELATIONSHIPS IN FOOD WEBS OF LAKES (Campbell et al., 1997; Pinnegar

and Polunin, 1999; Vander Zanden et al., 1999; Vander Zanden et al., 2000; Dufour and Gerdeaux, 2001; Grey, 2001; Johnson et al., 2002; Vander Zanden and Vadeboncoeur, 2002) AND THE TRANSFER OF CONTAMINANTS THROUGH THE FOOD CHAIN (Kiriluk et al., 1995; Schindler et al., 1995; Kiriluk et al., 1996; Garcia and Carignan, 2000; Fisk et al., 2001).

WE WILL COLLECT TISSUE FROM FISH FOR STABLE ISOTOPE ANALYSIS AS WELL AS FROM POTENTIAL AQUATIC AND TERRESTRIAL BASAL AND PREY SOURCES. TERRESTRIAL INVERTEBRATES WILL BE COLLECTED BY SWEEP NETS, AND ALGAE AND INVERTEBRATES WILL BE COLLECTED FROM THE LAKES WITH PLANKTON NETS AND DIP NETS. TISSUES WILL BE ANALYZED FOR $\delta^{13}C$ AND $\delta^{15}N$ BY A COMMERCIAL LABORATORY SUCH AS AT THE UNIVERSITY OF GEORGIA.

25.) pg C-13: As the surficial sediments are likely to have a high organic and water content, it will be difficult to confirm in the field that sufficient mass of dried sediment has been collected, especially the top 0 to 0.5 and 0.5 to 1 cm sections. This may have to be addressed with extra sampling as a precaution.

**RESPONSE/ACTION:** AGREE, BUT OTHERS HAVE DONE THESE ANALYSES OF HIGH ELEVATION LAKES ON SMALL SAMPLES. OUR PILOT WORK SHOULD BE INFORMATIVE. ADDITIONAL "BACK-UP" CORES WILL BE TAKEN, SLICED AND ARCHIVED. MOREOVER, WE ARE LOOKING INTO USING A LARGER CORING DEVICE. SOME RESEARCHERS EFFECTIVELY COMBINE SLICES FROM SEVERAL CONSECUTIVE DEPTHS TO REACH THE APPROPRIATE CONCENTRATIONS FOR DETECTION. EACH CORE WILL BE TREATED AS ITS OWN UNIQUE PROBLEM AND APPROPRIATE MEASURES TAKEN TO ACQUIRE GOOD DATA.

26.) pg C-13: The sediment/water interface environment (physical/chemical/biological) may vary considerably among the lakes and knowledge of these differences may be important in the data interpretation. This should include analyses of water content organic, inorganic carbon, and acid-volatile sulfide.

**RESPONSE/ACTION:** THE RESEARCH PLAN WILL BE MODIFIED TO NOTE THAT WE <u>DO</u> PLAN TO MEASURE DRY WEIGHT (I.E. WATER CONTENT) AND, LOI (I.E. ORGANIC CARBON CONTENT). WE WILL LOOK INTO PERFORMING INORGANIC CARBON AND A-V SULFIDE ANALYSES BUT ANTICIPATE THAT THIS WILL INVOLVE INCREASED SAMPLE SIZE WHICH WE WOULD PREFER TO USE FOR SOCs.

27.) pg C-13: The characteristics of the lake drainage basins are highly variable, with respect to geology, soils, vegetation and climatology. Sufficient information on these characteristics will be required to allow the knowledge generated to be applied in other lakes in the National Parks.

**RESPONSE/ACTION:** WE DO PLAN TO COLLECT BASIC WATERSHED INFORMATION BUT DEVELOPING A MODEL TO LINK OUR WACAP SITES TO OTHER SITES WITHIN NATIONAL PARKS IS OUTSIDE OF THE SCOPE OF THE CURRENT PROJECT. IT SHOULD BE NOTED THAT ANY APPLICATION OF THIS INFORMATION TO OTHER LAKES OR PARKS MADE IN THE FINAL REPORTS WILL BE SPECULATIVE, AS WE DO NOT PLAN TO DEVELOP A MODEL TO DO THIS.

28.) pg C-13: The limnology of each of the lakes will eventually be needed to inform the interpretation of sediment, water column, and air-water interface cycling of the contaminants. It may be important to know what contribution benthic production in the littoral zone makes to the food web and to the associated trophic transfer of contaminants.

**RESPONSE/ACTION:** WE DO NOT BELIEVE THAT THESE ADDITIONAL LIMNOLOGICAL PARAMETERS ARE NECESSARY TO ANSWER THE BASIC WACAP QUESTION "IS THERE A PROBLEM." AGAIN, THIS COULD COME INTO PLAY IN DEVELOPING A MODEL RELATING FINDINGS TO BROADER SPATIAL COVERAGE OF WESTERN NATIONAL PARKS.

29.) pg C-13: Knowledge of surface sediment concentrations is critical to the understanding of partitioning of SOCs and metals among water, sediment and biotic phases.

**RESPONSE/ACTION:** AGREE. BUT THE FOCUS ON PARTIONING IS NOT THE WACAP GOAL. NONETHELESS, WE PLAN TO DEVELOP GOOD CONCENTRATION DATA IN THE SURFICIAL SEDIMENTS.

30.) pg C-13: Profiles of sediment concentrations provide long term trends in contaminant sedimentation, which is related by varying degrees to inputs and in-lake processes (degradation, storage in biotic compartments and/or re-volatilization)

**RESPONSE/ACTION:** AGREE. THESE PROCESSES ARE ALSO INFLUENCED GREATLY BY TROPHIC STATUS OF THE SYSTEM WHICH IS WHY WE WILL BE CONDUCTING EMAP ANALYSIS OF THE WATER FROM EACH SYSTEM. THIS INFORMATION WILL PROVIDE DATA THAT CAN BE USED, COLLECTIVELY, TO SORT THE LAKES BY RELATIVE LEVELS OF PRODUCTIVITY.

31.) pg C-13: If snow is analyzed for metals, there should be an explicit decision about the form of the samples (dissolved, particulate, total). There should be thought given to how the metals data will be compared across media (including the IMPROVE data set for metals).

**RESPONSE/ACTION:** SNOW WILL BE ANALYZED FOR METALS AND WE AGREE THAT THE FRACTION OF SNOW IN WHICH WE MEASURE METALS NEEDS TO BE EXPLICIT AND BUILD ON RECENT ANALYSES CONDUCTED BY USGS. WHOLE-

WATER (I.E., UNFILTERED) SAMPLES OF THE SNOW WILL BE USED FOR METALS ANALYSIS. IF POSSIBLE, SOME SAMPLES MAY ALSO BE ANALYZED FOR DISSOLVED AND PARTICULATE FRACTIONS, BUT THIS ADDRESSES RESEARCH QUESTIONS OUTSIDE THE CORE WACAP MISSION.

***Q6: Is the coordination and communication strategy within WACAP and between WACAP and NPS sufficient for implementation, completion, and publication of results?***

32.) pg C-13: A password-protected web site is needed for investigators and park staff. The site should be updated frequently with methods, schedules, and preliminary data. Existing background data on the lakes, watersheds, geospatial analyses, and air quality should also be posted.

**RESPONSE/ACTION:** GOOD IDEA. NPS-ARD PLANS TO SET THIS UP AND MAINTAIN IT.

33.) pg C-14: Someone not harried by day-to-day logistics could facilitate some aspects of project integration. For example, ARD could hire a graduate student or biotech who could serve as a conduit for technical information, do the web site updates, organize PI meetings, and prepare integrated annual reports for the NPS.

**RESPONSE/ACTION:** THIS IS A GOOD IDEA. WACAP WILL LOOK INTO THIS POSSIBILITY.

34.) pg C-14: Continued external scientific input is needed because of the developmental nature of many aspects of the project as well as the rapid pace of discovery in this area of environmental research. The PIs will benefit from outside input as they evaluate results of pilot data to decide whether to expand or drop project components. At a minimum, outside scientists should be invited to present findings at an annual WACAP science workshop. The NPS could consider re-convening a peer review panel after two or three years.

**RESPONSE/ACTION:** WE PROPOSE AN INTERNATIONAL SYMPOSIUM AT ONE OF THE WESTERN NATIONAL PARKS IN THAT WOULD INCLUDE EUROPEAN, CANADIAN AND OTHERS ALONG WITH WACAP PIs TO PRESENT AND DISCUSS FINDINGS. THE BEST TIME FOR THIS WOULD BE IN THE WINTER OF 2004-2005. IN ADDITION, WE WILL CONSIDER INVITING OUTSIDE SCIENTIST TO OUR ANNUAL DATA MEETING TO PRESENT DATA AND INTERACT WITH OUR INTERIM FINDINGS.

***Q7: What suggestions can the panel offer for prioritizing research elements as 'core components' if funding becomes limiting in the future?***

35.) pg C-14: The panel characterized the program components into 'core', 'pilot', and 'non-essential' activities. The **core** components, considered to be most important to achieving Project goals, include the following.

- Annual snow sampling,
- One-time fish sampling,
- One-time sediment coring.

**RESPONSE/ACTION**: GENERALLY AGREE

36.) pg C-14: The **pilot** activities are those that are unproven, and do not warrant a multi-year financial commitment until proven. The recommendation is to test the pilot components in two parks in the first year of sample collection. Pilot activities include:

- Lichens and willow for SOC and Hg analyses,
- Methyl mercury analysis in snow.

**RESPONSE/ACTION:** WE GENERALLY AGREE BUT THINK THAT WILLOW BARK IS MUCH MORE FEASIBLE THAN LICHENS WITH REGARD TO SOCs (AS THERE IS EXTANT LITERATURE ON SOCS IN BARK) AND WE WILL PURSUE THIS METHOD IN A PILOT MODE DURING 2003. THE EFFICACY OF MEASURING METHYL HG IN ADDITION TO TOTAL HG WAS POORLY EXPLAINED AND JUSTIFIED BY THE PEER PANEL. THEY VERBALLY INDICTED THAT IT WOULD BE VERY INTERESTING AND NOT MUCH OF THIS TYPE OF ANALYSIS EXISTS. WE PERCEIVE THIS TO BE MORE OF A NON-ESSENTIAL ADDITION AND WILL TREAT IS SO AS EXPLAINED EARLIER.

37.) pg C-14: The Panel regards atmospheric modeling as a **non-essential** project component because it does not directly address the core goal of assessing whether these contaminants are present in detectable concentrations. Contaminant source determination is not included as a project goal in the review draft of the WACAP Study Plan, and this component could be deferred until contamination has been confirmed.

**RESPONSE/ACTION:** AS PREVIOUSLY MENTIONED, WE HAVE CHANGED THE WACAP GOAL TO INCLUDE *SOURCES* BUT WE WILL FUND THIS PORTION IN 2003 ONLY IF SUFFICIENT FUNDS EXIST SINCE THIS TYPE OF WORK COULD BE COMPLETED AT A LATER DATE. THERE IS INTEREST IN DEVELOPING THIS PIECE OF WACAP ALONG WITH THE REST OF THE PROGRAM SO THAT SOURCE APPORTIONMENT WORK COULD BE COMPLETED AS THE REST OF THE WACAP PROGRAM IS FINALIZED.

38.) pg C-14: The panel suggests the following priority for analytes, and that this priority be maintained for snow, fish, sediments, and flora:

1) SOCs, Hg (and Methyl-Hg in snow), toxaphene;
2) any current-use chemicals not included in SOCs;
3) other metals

**RESPONSE/ACTION:** WE GENERALLY AGREE BUT PLAN TO ROUTINELY ANALYZE "OTHER METALS" IN SEDIMENTS, SNOW AND FISH BECAUSE THESE ARE STANDARD ANALYSES AT THE USGS BOULDER LABORATORY.

***Q8: What are the recommendations for revisions and distribution of the research plan as an EPA report?***

39.) pg C-15: The panel did not see the need for more than a few hard copies of the research plan. The panel's alternative recommendation is to save costs and add substance quickly to the WACAP web page with the addition of research plan as a PDF file.

**RESPONSE/ACTION:** GOOD IDEA. WE WILL "PUBLISH" IT, HOWEVER, AS AN EPA REPORT WITH A SMALL RUN OF HARD COPIES.

40.) pg C-15: There were significant differences in the level of detail, organization, and clarity of writing among chapters in the draft study plan that should be remedied during revision. An editor is needed for the document. Some draft chapters had extraordinarily long paragraphs, used colloquial language, or were awkwardly constructed.

**RESPONSE/ACTION:** WE WILL ACQUIRE THE SERVICES OF A PROFESSIONAL EDITOR TO ASSIST IN THE FINAL DEVELOPMENT OF THE RESEARCH PLAN.

41.) pg C-15: The phrase 'if funding permits' should be purged from the study plan and realistic goals and objectives should be based on the objectives and the budget. Costs can be reduced by focusing effort on the three identified core components and by reducing effort on other components.

**RESPONSE/ACTION:** THE PROBLEM, AS POINTED OUT BY CHRIS SHAVER, IS THAT THE FUNDING LEVEL IS UNCERTAIN AND WILL REMAIN SO. WE WILL PURGE THE WORDS "IF FUNDING PERMITS" BUT THE CONCEPT AND ITS REALITY WILL NOT GO AWAY.

42.) pg C-15: The panel recommends that the hypotheses be purged from the document. The hypotheses as stated are largely statements of expectations, not testable hypotheses.

**RESPONSE/ACTION:** AGREE, GOOD IDEA!

43.) pg C-15: Leveraged projects should be explicitly and exhaustively listed for political advantage.

**RESPONSE/ACTION:** AGREE.

44.) pg C-15: Add ideas or requests for add-on studies (e.g., glacier cores in parks) to the web page.

**RESPONSE/ACTION:** WE COULD DO THIS – SEEMS TO BE A LOWER PRIORITY.

45.) pg C-15: A budget summary should be added for each component; this will assist potential collaborators in understanding the scope of the program and would have been helpful for the panel in its deliberations.

**RESPONSE/ACTION:** A DECISION TO DO THIS WOULD BE UP TO THE NPS-ARD. THIS SEEMS MOOT AT THIS POINT.

**Specific comments on the text: THESE ITEMS WILL BE FIXED IN THE FINAL RESEARCH PLAN.**

The List of acronyms does not include WRS laboratory. The panel notes that acronyms are not reader friendly and diminish the effectiveness of the document.

List investigators at the beginning of each chapter to aid the reader.

Include some of D. Landers PowerPoint presentation graphics in the plan document. Example: the Venn diagram of agency involvement.

p. 4, lines 4-5. There are colloquialisms that should be purged from the text. E.g. *setting* these locations *up* to be long term sinks.

p. 6. The PIs could attempt to define relative trophic position of the fish analyzed by stable isotope analysis of co-existing fish and zooplankton, to facilitate the interpretation of fish-contaminant data. Trophic position is just one of many potentially confounding variables that will complicate interpretation of results in this study. Problematic concentrations of biomagnifying contaminants will most likely be found in the highest trophic level to be sampled, which in the WACAP study would presumably be piscivorous fish. The trophic position of the fish sampled is a variable that will not be visually apparent to the field crews and PIs, and examination of the stomach contents of a small number of fish in the field can be misleading due

to seasonal changes and other factors affecting diet. Piscivorous fish are desirable for the contaminant analyses, and the fish analyzed should be from the same trophic level.

p. 7. There are some mismatches between the Parks listed in red in Figure 1.3 (those selected for study) and those in the appendix. In the appendix Kings Canyon is not present but Gates of the Arctic. In Table 1.1 (Pg. 10) there are 8 Parks. Again it shows some differences with the previous Park lists.

p. 11 and elsewhere. Throughout the project sometimes the term Persistent Organic Pollutants (POPs) is used and in other occasions Semi-volatile Organic Compounds (SOCs) is used. Be consistent.

p. 11. In the table: Subsistence, not subsistence

p. 14, line 19. WACAP … *is designed to* answer the following questions.

p. 14, lines 23-32, rephrase for consistency:

- Are concentrations of contaminants detectable in western Parks?
- Where are contaminants accumulating (geographically and by elevation)?
- Which contaminants pose a potential ecological threat?
- Which indicators appear most useful to address contamination…?

p. 14, 28, 48, etc. (each chapter): each section repeats very similar language about publications and data use. This can be done once, in the introduction. Don't overstate the publication potential of a reconnaissance project, but do plan to publish on your methods and method development. The format of this statement on p 57 (water quality) is appropriate for most of the project components.

p. 15. line 16 ~~the 2002~~

p. 15, lines 16-19. Don't apologize.

p. 21. Objective: determine the *continental-scale* spatial variability… This project is not determining local variability due to small number of samples.

p. 24, line 29. Specify what happens if the snowpack is above freezing. Is the entire park not sampled for the year, or does the team dig another pit?

p. 25. Are the samples analyzed in a chilled condition, as written? This would be unusual.

p. 25, line 25. concentrations *are* determined.

P. 26, line 19. 10% of snow sampling will be duplicates and blanks. At 21 samples per year, this is one blank and one replicate per year. These are probably not adequate numbers for meaningful QA.

p. 27. Table 2-1. Add to caption: ….*via ICP-MS at USGS, Boulder CO.*

Section 3 (foodweb). This section needs a technical edit for grammar, construction, and flow.

p. 32, line 7-8. physiological *anomalies* in fish

p. 32, line 21. To assess fish as *indicators of* bioaccumulation….

p. 32. The food web section does not have hypotheses, in contrast to other chapters. The sections should be consistent. Note that the panel does not think that hypotheses are necessary.

p. 33, line 27. *High* WBCs

p. 40. Figure 3.2.2. refers to N in lichens, not to metals

p. 51, lines 9 and 12. *Patterns*, not trends.

p. 65, Figure 5.3. The surface of the sediment core is *horizontal*, not perpendicular.

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