**North Coast and Cascades Network**

**Protocol:** Deposition Monitoring

**Parks Where Protocol will be Implemented:**
MORA, NOCA, OLYM

**Justification/Issues being addressed:**
Three parks within the NCCN are designated Class I areas. Comprehensive scientific information is essential to understand and document air quality conditions and effects of air pollution on park resources. Parks within the NCCN are subject to regional long-distance transport of air pollutants (sulfur and nitrogen oxides, ozone, particulates and toxic pollutants) from various mobile and stationary sources, from as far north as Vancouver BC, and south to Portland OR. Canadian sources from the Lower Fraser River Valley also affect air quality in NOCA and possibly SAJH. Most stationary and mobile sources are in metropolitan Seattle-Tacoma and Portland regions. Trans-Pacific transport of persistent organic pollutants is also occurring but little is known about how park resources will be affected.

Deposition of nitrogen and sulfur to protected Class I high elevation park resources in the Pacific Northwest is believed to be exceeding acceptable levels in many locations, particularly downwind of urban and industrial areas. Some evidence of ecosystem change has been seen from lichen community disturbance. Lichen species are selectively sensitive to both sulfur and nitrogen deposition. Some evidence of atmospheric inputs to very sensitive aquatic ecosystems has also been noted. The higher elevation watersheds in the Cascade Range of the PNW are known to be some of the most sensitive known anywhere in the world. A number a alpine lakes have near zero acid neutralizing capacity (ANC) and approximately 25% have ANC of 50 μeq/liter or less.

Deposition inputs accumulate from three major inputs: rainfall, dry fall (fine particulate settling), and fog or cloud water. Estimates of deposition rates in NCCN parks are made from limited low elevation precipitation dispersion models. These estimation models each have uncertainties associated with them. The NPS currently monitors deposition from rainfall (NADP) and dry fall (CASTNET) at MORA, NOCA, and OLYM. Fog and cloudwater deposition is not monitored because the measurements are intensive and expensive. However, cloudwater deposition is likely to be a significant portion of total atmospheric deposition in these parks. Throughfall measurements may be used to estimate total atmospheric deposition of sulfur and nitrogen that incorporates wet, dry and cloudwater deposition. Given the uncertainty of available funding for the existing monitoring of dry deposition, and the lack of information on cloudwater, the NCCN has partnered with the USGS-BRD, NPS-ARD, and the USFS to develop throughfall protocols.

## Objectives and Basic Approach:

| Category | Objective | Basic Approach |
|---|---|---|
| Wet Deposition | 1. Determine the natural variation and temporal(event, weekly, seasonal, annual, decadal) trends in wet deposition chemistry (precipitation) for sulfate, nitrate, ammonium, H+, Cl-, base cations, Ca, Mg, K, conductivity, PO4 (weekly, event sampler with NADP.NTN at three low elevation sites; and | Utilize existing NADP monitoring stations and protocols |
| | 2. Determine the natural variation and temporal(event, weekly, seasonal, annual, decadal) trends in wet deposition chemistry (precipitation) for sulfate, nitrate, ammonium, H+, Cl-, base cations, Ca, Mg, K, conductivity, PO4 (weekly sample) at one high elevation site in the NCCN (MORA). | Utilize existing bulk deposition monitoring protocols. Get peer review from USGS-WRD (Campbell, Clow and others) |
| | 3. Determine the natural variation and temporal (annual, decadal) trends in snow deposition chemistry for sulfate, nitrate, ammonium, H+, Cl-, base cations, Ca, Mg, K, conductivity, at two high elevation sites in the NCCN (MORA, NOCA).[1] | Develop snowpack deposition protocols as described in detail in Landers et al.,2003. Briefly, a snowpit is excavated to the ground, physical characteristics are measured, and a column of the entire depth of snow is sampled from a clean face of the snowpit. Quantitative sampling of the snow is done using clean techniques to fill large Teflon bags with snow yielding 40-60 liters of meltwater. Chemical analysis is conducted by certified lab. |
| | 4. Determine the natural variation and temporal(seasonal, annual, decadal) trends in throughfall deposition chemistry ( for sulfate, nitrate, ammonium, H+, Cl-, base cations, Ca, Mg, K, conductivity, within the forested zones at two NCCN parks (NOCA, MORA), and add OLYM if additional funds become available, or the | Develop throughfall deposition protocols using the ion exchange resin (IER) throughfall collectors that have been developed and used extensively over the past four years, as described in Fenn et al., 2002; Fenn and Poth, 2004. |

[1] The seasonal snowpack at OLYM is difficult to sample given the difficult access to high elevation areas and the more frequent rain on snow events that occur there.

[2] The OLYM site was eliminated because of park decisions made to fund other higher priority Vital Signs. If additional funding is available, this remains a high priority atmospheric vital sign protocol to implement.

| Category | Objective | Basic Approach |
|---|---|---|
| | anticipated costs to implement protocols is reduced[2] | |
| Dry Deposition | Determine the temporal (seasonal, annual and decadal) trends in dry deposition chemistry (TSO4, TNO3, TNH4) at two sites (MORA, NOCA). | Utilize existing CASTNET sites in MORA and NOCA (ARD removed the OLYM CASTNET site in 2005 and may remove the NOCA site in FY06 or 07. The future status of the MORA CASTNET site is also uncertain. |
| Mercury | Determine the temporal (seasonal, annual and decadal) flux of mercury in MORA, NOCA and OLYM | Recommendations TBD at end of WACAP and PNW snow deposition studies. Recommendations for add'l protocols to be developed at the completion of the WACAP study. However, NCCN funding is not currently available to implement. |
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| Contaminants: | Determine the spatial and temporal trends in semi-volatile organic compounds in MORA, NOCA, OLYM | Recommendations and protocols to be developed at completion of WACAP study However, NCCN funding is not currently available to implement. |
| Deposition in Aquatic Ecosystems | Determine the spatial and temporal trends in sulfate, nitrate, ammonium, H+, Cl-, base cations, Ca, Mg, K, conductivity, PO4 in montane lakes (see Montane Lakes protocol ) | Water chemistry,, plankton, amphibians, (in Montane Lakes protocol) |
| Mercury in aquatic systems | – see aquatic protocol (analysis of fish/amphibian tissue in high lakes) | Recommendations and protocols to be developed at completion of WACAP study However, NCCN funding is not currently available to implement. |
| Deposition in Terrestrial Ecosystems | Recommendations for vegetation and soils to be developed at the completion of the WACAP study and Critical Loads studies being conducted in other NPS and USFS areas. | Recommendations for long term monitoring in vegetation and soils from impending WACAP and other study results. However, NCCN funding is not currently available to implement. |

**Principal Investigators and NPS Lead:**
Snow Deposition Protocols: Don Campbell, USGS-WRD Colorado
Throughfall Protocols: Mark Fenn, USFS Research Lab, Riverside, CA
Bulk Precipitation: Dr. Anne Johansen, Central Washington University

NCCN Lead :Barbara Samora (MORA), Elizabeth Waddell (PNWRO) will work with Ellen Porter, NPS-ARD to compile the NPS existing programs (NADP, CASTNET).
Others: Jon Riedel (NOCA);
Aquatic Ecosystems: Barbara Samora, Reed Glesne, Steve Fradkin (Montane Lakes/water quality protocols).

**Development Schedule and Expected Interim Products:**

- NADP protocol developed and available for peer review in December, 2005.
- Bulk wet deposition developed and available for peer review FY06.
- Dry deposition protocol element completed in FY05.
- Snow deposition protocol completed FY06 (developed by USGS-WRD in Colorado, via Campbell)—pilot field work, etc. FY05, writing, review and completion FY06.
- Throughfall deposition field work initiated FY05, protocol completed FY08 (cost share with ARD, USGS-BRD 4 year project).

**Literature Cited**

Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O. 2003. Nitrogen emissions, deposition, and monitoring in the western United States. BioScience 53:391-403.

Fenn, M.E., and Poth, M.A. 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: A field test in the San Bernardino Mountains. J. Environ. Qual. 33: In Press; Nov/Dec issue).

Landers, D.H., S.L. Simonich, D.H. Campbell, M.M. Erway, L.H. Geiser, D.A. Jaffe, M.L. Kent, C.B.Schreck, T.F. Blett, and H.E. Taylor. 2003. Western Airborne Contaminants Assessment Program Research Plan. EPA/600/R-03/035. U.S. Environmental Protection Agency, Office of Research and Development, NHEERL, Western Ecology Division, Corvallis, Oregon.

*For Appendices in the back of Phase 3*

**Existing Deposition Protocols**
The Clean Air Status and Trends Network (CASTNET) and the National Atmospheric Deposition Program (NADP) were developed to monitor dry and wet acid deposition, respectively. Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNET also includes measurements of rural ozone and the chemical constituents of PM 2.5.

**CASTNET Objectives**
CASTNET provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone and other forms of atmospheric pollution.

**CASTNET Methods**
Atmospheric concentration data are collected at each site with open-faced, 3-stage filter packs. The filter pack contains a teflon filter for collection of particulate species, a nylon filter for nitric acid and a base-impregnated cellulose (Whatman) filter for sulfur dioxide. Filter packs are exposed for 1-week intervals (i.e., Tuesday to Tuesday) at a flow rate of 1.5 liters per minute (3.0 liters per minute for western sites), and sent to the Harding ESE, Gainesville, FL laboratory for chemical analysis.

The teflon filter is extracted in deionized water with sonication and shaking, then analyzed for sulfate, nitrate and ammonium ions. Nylon filters are extracted in IC eluent with 0.05 percent hydrogen peroxide and then analyzed for sulfate and nitrate. The Whatman filter is extracted in deionized water with 0.05 percent hydrogen peroxide and analyzed for sulfate and nitrate. Atmospheric concentrations are then calculated based on the mass of analyte in each filter extract and the volume of air sampled. The sulfate, nitrate and ammonium in teflon filter extract are interpreted as particulate species (listed below as TSO4, TNO3 and TNH4, respectively). The nitrate in the nylon filter extract is interpreted as nitric acid (listed below as NHNO3). The sum of sulfate in the nylon and cellulose filter extracts is interpreted as sulfur dioxide (listed below as SO2). Nitrate in cellulose filter extracts is not interpreted, since it likely represents a host of oxidized nitrogen species.

**National Atmospheric Deposition Program (NADP) Objectives**
The NADP was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, electric utilities, and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Collection of weekly wet deposition samples began in 1978. The size of the NADP Network grew rapidly in the early 1980s when the major research effort by the NAPAP called for characterization of acid deposition levels. At that time, the network became known as the NADP/NTN (National Trends Network). By the mid-1980s, the NADP had grown to nearly 200 sites where it stands today as the longest running national atmospheric deposition monitoring network.

**NADP Methods**
The NADP analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The NTN measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by the NADP's Central Analytical Lab at the Illinois State Water Survey. A new subnetwork of the NADP, the Mercury Deposition Network (MDN), measures mercury in precipitation.

**Throughfall Methods**
The approach will be to use the ion exchange resin (IER) throughfall collectors within the forested zones of each of the three large parks (MORA, NOCA, OLYM) that have been developed and used extensively over the past four years, as described in Fenn et al., 2002; Fenn and Poth, 2004. However, for this study, a larger funnel opening size will be used to increase the sampling efficiency of the collectors. The current collectors are 10 cm in diameter without the snow tubes installed and 7.4 cm in diameter with snow tubes in place (Fenn and Poth, 2004). A 20 cm diameter collector is proposed, which will increase the collection surface

area from 79 to 314 $cm^2$. The collector size recommended by the European ICP Forests monitoring program is 20 cm (Bleeker et al., 2003).

The IER collectors are ideally suited for throughfall monitoring in remote locations because ions in throughfall or precipitation solutions are captured on the IER columns as the solutions percolate through the columns. Samplers can be left in place for as long as a year at a time, based on intensive field tests in the San Bernardino Mountains, although the IER columns are normally changed out every 6 months as a conservative measure. At the end of the sampling period, the IER columns are brought back to the laboratory, extracted with KCl or KI and the extracts are then analyzed for ionic content using standard ionic chemistry techniques. From these chemical analyses, the cumulative deposition of the measured N and S ions is calculated based on the surface area of the collector openings. These collectors have worked very well in capturing high levels of $NH_4^+$ and $NO_3^-$ in throughfall at the Camp Paivika study site, largely as a result of frequent fog exposure (Fenn and Poth, 2004). Likewise, the collectors worked well in the northern Sierra Nevada where N deposition levels are relatively low (Fenn et al., 2003).