# IMPROVE Steering Committee Meeting Summary October 28-29, 2008

# Administration Building; Okefenokee National Wildlife Refuge, GA by Gloria Mercer

#### Overview

The Steering Committee met at the Administration Building in Okefenokee National Wildlife Refuge, GA, on October 28-29, 2008. A copy of the agenda and meeting participants is attached.

#### Major topics included:

- Aerosol, optical, and scene operation update
- Ion, carbon, and XRF analysis update
- Laboratory audits
- Estimates of MDLs
- > Role of fire in Okefenokee
- Exceptional events and data
- Air quality issues and SIPs in the West
- Chemical Speciation Network update
- > ROMANS nitrogen issue
- Estimating contribution of haze from fire
- > Canadian visibility program update
- > Urban visibility and secondary standard

The following summarizes meeting discussions in greater detail as shown in the agenda.

#### October 28

#### Welcome and introductions

The meeting started with Jim Burkhart, Visitor Services Chief, who welcomed the group. He introduced Refuge Manager George Constantino who provided a few facts about the Okefenokee National Wildlife Refuge. Meeting attendees then introduced themselves.

#### **Network Review**

## **Aerosol monitoring**

A map of the current network shows little change from last year. The Omaha site (OMAH1) in Nebraska was removed in July due to lack of funding, and the Breton Island site (BRIS1) in Louisiana was reinstalled in January at a slightly different location after its destruction by hurricane Katrina in 2005. The Breton Island site now has two PM<sub>10</sub> modules as part of the collocated sampler program. The sampler was removed temporarily for Hurricanes Gustav and Ike in 2008 but was reinstalled promptly once the threat had passed. Also new this past year is the Pack Monadnock site (PACK1) in New Hampshire, and the Gates of the Arctic National Park (GAAR1) site will be installed next week in Bettles, in northcentral Alaska. This site will be serviced by an NPS employee in Bettles. A backup operator can fly in from Fairbanks if an emergency arises.

There is a new protocol for secondary quartz filters; the number of sites that operate secondary filters increased from 6 to 12, and all quartz field blanks in the network are now collected at these 12 sites. All front filters are analyzed, but only 5 out of every 7 secondary filters and blanks are analyzed, to conserve funding. The 2007 sample recovery rates for the entire network, for Module A are: 94%, 95%, 94%, 93%, and 94% (for Q1, Q2, Q3, Q4, and annual period, respectively). In 2006 the annual recovery rate was also 94%. The 2007 sample recovery rates for the entire network, for all modules are: 92%, 94%, 91%, 91%, and 92% (for Q1, Q2, Q3, Q4, and annual period, respectively). In 2006 the annual recovery rate was also 92%. Sample loss in 2007 was due to a variety of equipment problems, operator problems, power problems, and other such issues. Regional Haze Rule requirements for complete data sets were provided. Sites failing the RHR requirements for 2007 are:

- Cohutta, GA samples lost due to equipment problems and operator problems
- Douglas, AZ samples lost due to equipment problems and operator problems
- North Absaroka, WY the site, destroyed by wind in 2007, was reinstalled in January 2008
- Phoenix, AZ a pump failure due to poor ventilation in the pump box was the cause of missing data; vents were installed in the pump box to avoid future problems
- Queen Valley, AZ samples lost due to equipment problems and operator problems
- Sierra Ancha, AZ samples lost due to equipment problems and the operator being called off on firefighting duties
- Virgin Islands, VI samples lost due to electrical problems; the entire system was rewired

UC-Davis currently has 25 samplers in spare inventory and there are no plans to purchase any new ones.

To alleviate lengthy periods of data loss, UC-Davis has begun to make weekly telephone calls to backup operators to ensure that they are successfully collecting samples while filling in for the primary operators. Since filter boxes are shipped every three weeks, laboratory technicians don't have to wait until a shipment arrives before finding out there's a problem.

A new sampler program is being tested prior to installation in the network. The code was rewritten by ARS for the new CSN URG-3000N carbon sampler, and was then revised for the IMPROVE network. The program includes new features such as diagnostic information, unlimited flexibility in sampling schedules (for special studies), and cleaner code which will provide fewer compromised flashcard files.

Aerosol data are expected to be available soon for January 2007 through June 2008. The 2007 data are being held awaiting a new XRF calibration protocol. UC-Davis is nearing a six-month lag time in data delivery, dual Cu XRF systems have allowed achievement of this goal. The new SQL database was in development during 2007-2008 and now includes flowrate data as well as other new information. UC-Davis can now track and document changes to data and software in secure files. The new SQL database is also readily accessible and sortable. UC-Davis also developed a new Intranet that includes a forum, calendar, and project management software for users.

IMPROVE data advisories are located on the IMPROVE Web site. These advisories alert data users to changes in systems or procedures and address deviations that are not incorporated into reported statistical uncertainties. Eight advisories have been posted since Summer, 2007. Revised aerosol SOPs have also been posted to the Web site for site selection and for data processing and validation. A revised XRF SOP will be added soon. The SOPs state when they are effective and with what data they should be applied.

UC-Davis maintains more detailed information on data and metadata than users would likely need access to, such as filter lot information, blank filter values, changes in the filter manufacturing process, etc. We should document this aerosol history for possible future use. The committee also created a subcommittee to recommend which metadata to store in a publicly accessible format and which can reside with the contract laboratories.

→ IMPROVE Metadata Task Force: Marc Pitchford, Bret Schichtel, Eva Hardison, Warren White, Chuck McDade, John Molenar, and Judy Chow.

The discussion turned to the question of "Should the IMPROVE Program continue to produce a network report (i.e. report in 1993, 1996, 2000 and 2006)?" Participants concurred that we should prepare a report produced by scientists who are connected with the program and not rely solely on others to interpret IMPROVE data obtained through VIEWS. Though it requires a significant commitment of time and resources, the preparation of a new report is a good idea. It should include a chapter on procedural and quality history of the sampler and protocols. The group set 2010 as the target date for the next report.

## **Optical and Scene Monitoring**

The program currently has 48 optical monitors. The network is slowly decreasing, mostly due to decommissioning in the Midwest. The Arizona network is retrofitting all their nephelometers with a LED light source. The LED nephelometers require less maintenance than incandescent lamp nephelometers. Optical and scene SOPs are reviewed annually. Nephelometer data are available 90 days after the quarter and transmissometer data are available on an annual basis, after annual calibration is performed. For scene monitoring, a new partnership has been formed between the National Park Service and Olympus USA, to help pick up where NPS budget cuts left off. Olympus now has a three-year contract with the NPS and will provide new cameras and system upgrades, and technical support to all 15 NPS Web-camera monitoring sites. New Web-camera sites may start up soon at Mesa Verde NP, CO; Hawaii Volcanoes NP, HI; and Cape Cod National Seashore, MA.

Shell Oil Company has funded ammonia monitoring in Upper Green River Basin, WY (Boulder area) since December 2006. Rapid natural gas development has taken over the area, which is adjacent to the Bridger Wilderness (Class I area). Filter samples are collected on a 3-4 day schedule. The data indicate ammonia below detectable limits (essentially 0) from late November to Early April. Ammonia peaks in the summer. Yearly average ammonia concentration is 0.3 ppb, much less than the FLAG default

value of 1.0 ppb. The winter has large peaks in nitric acid and particulate nitrate. Sulfate ion is also measured. An acidic sulfate episode occurred in May 2007. Nephelometer scattering and relative humidity also peaked. When the relative humidity fell, aerosol scattering remained elevated showing the expected large hysterisis of an acidic sulfate aerosol. An intensive monitoring experiment was performed during August 22-29, 2008. This monitoring showed nitric acid peaks during the day and particulate sulfate peaks at night. ARS will perform another study in the Boulder area this winter and believes that the amount of snow cover may be a factor in elevated pollutant concentrations. LADCO will perform a similar study in Milwaukee (urban location) and Mayville (rural location) this winter.

#### **Laboratory Review & Methods Development**

#### **Carbon Analysis**

DRI will attempt to have carbon analysis complete for April 1 through June 30, 2008 data by December 2008. DRI staff working on IMPROVE carbon analysis now consists of three full-time and two part-time lab technicians and one part-time maintenance technician. DRI also purchased two additional Model 2001 analyzers. One was received in September and the other is expected in November 2008. The SQL server has also been upgraded for data retrieval.

Replicate analysis has been performed on the Model 2001 analyzers. For January 2005 through April 2008, approximately 7,000 pairs of samples were analyzed for replicate and original analysis. Data were plotted in a time series of daily absolute relative differences. The absolute differences were 2-4 mg/filter for Total Carbon (TC) and Organic Carbon (OC), and 1-2 mg/filter for Elemental Carbon (EC). Relative differences were 5%-10% for TC and OC, and 10%-30% for EC. Relative differences were worst for OC1, which is usually very low. 10%-20% relative differences resulted for OC2, OC3, and OC4. EC1 resulted in 10%-20% difference. Replicate and relative differences were consistent for all data for the period. OC and TC median relative differences were 5%. Median relative differences for EC were 10%. Flow rate is not included in the relative uncertainties. Discussion followed.

#### **IMPROVE-CSN Carbon Analysis Workshop**

UC-Davis hosted a workshop January 22-23, 2008, with 18 attendees from EPA, UC-Davis, DRI, RTI, NPS, NOAA, and Washington University. The workshop discussed PM carbon monitoring for the IMPROVE and CSN programs and how to make their carbon data more comparable. Carbonaceous species concentrations have greater uncertainties than other PM species, is important to both health and visibility affects assessment, and is generally either the most or second most abundant of the PM components. Currently available information is not sufficient to adequately understand and reduce these uncertainties. Workshop goals were to:

- Develop an action plan (12-24 months) to gather useful additional information
- Develop a consistent approach to adjust for sampling artifacts
- Create algorithms to relate the IMPROVE to the CSN data
- Create algorithms to relate the old to the new analyzer for IMPROVE data

A challenge in doing these is that neither program has identified any new resources to conduct additional measurements or studies. CSN is changing their network sampler for carbon to the URG-3000N, which is identical in most regards to the IMPROVE module C sampler. Papers and presentations from the workshop are available on <a href="http://vista.cira.colostate.edu/improve/Publications/Workshops/Workshops.htm">http://vista.cira.colostate.edu/improve/Publications/Workshops/Workshops.htm</a>. The plan developed at the workshop includes the following action items:

- Reanalyze selected archived filters.
- Use the new IMPROVE analysis method to investigate historic variations in EC/OC trends and at six CSN sites.
- Recalculate OC/EC for CSN filters collected prior to July 8, 2003 using the new Sunset Labs software.
- Increase the number of IMPROVE sites from 6 to 12 that collect backup filters used for artifact correction.

# Ion Analysis

RTI is celebrating its 50<sup>th</sup> anniversary this year. Approximately 18,000 samples are analyzed at the lab every year. A performance evaluation was made for ion analyses using sample results from five labs (RTI, NAREL, and three other labs). Analyses included extracting spike recoveries for June 2008.

There are peaks apparent in sample chromatograms from the Trinity, CA, site for unknown ions. They were compared to fluoride, chlorite, bromate, and organic acids. The lab spiked filters with these chemicals to see how much is recovered. The peaks may be due to the inclusion of smoke from nearby fires in the area as they were not apparent in all samples. The same peaks were also seen in Lassen Volcanic NP and Columbia River Gorge (nearby sites to Trinity), as well as Denali NP, AK; Everglades NP, FL; Cape Romain NS, SC; and others. The lab also performed an anion/cation comparison for UC-Davis quality assurance samples, and proposed several experiments:

- Prepare and analyze standards of possible ions and compare retention times of unknown peaks in sample extracts.
- Compare peak abundances with total mass and OC/EC measurements.
- Investigate historical record of fire events.
- Check ionic balance to apportion the mass contribution of unknown ions, and
- Run organic acid/nitrite/nitrate solutions to check for conversion in control experiments.

# **XRF Analysis**

A new aerosol generation chamber was built at UCD to permit generation of samples with known composition to test XRF analysis on filters used by IMPROVE at typical areal concentration levels. Micromatter standards that are used to calibrate the XRF analyzers generally have single elements at higher concentrations on substrates (Mylar or Nuclepore) unlike those used by IMPROVE for ambient sampling. A photograph of the mixing chamber was shown. This should help us address issues such as the varying long-term trends in the ratio of sulfur to sulfate across the network.

Upcoming work will be to:

- Compare the atomizer to a TSI atomizer and characterize results.
- Prepare samples using components other than ammonium sulfate.
- Assess possible handling artifacts that affect weighing.
- · Verify expected molar ratios.
- Assess sample homogeneity using SEM.

#### **Crustal Element Sampling**

Collocated measurements in Phoenix have shown sporadic poor comparability for crustal elements. Differences are episodic and unpredictable and can remain for several months. This appears mostly with the crustal elements of fine mass on Module A. It is clearly not a flow issue because sulfur is well-behaved. Tests are underway to limit the influence of coarse particles. To test if it's a problem of coarse particle breakthrough of the 2.5µm cut-point cyclone, Module A units were added to each of the samplers at Phoenix, with a PM<sub>10</sub> inlet placed on each. This configuration was also placed on a sampler at the UC-Davis test site for use in special tests.

## **Carbon PM Special Studies at UCD**

To investigate carbon loss from filters prior to their transport from the field, UCD has used a Sunset Labs carbon analyzer available on campus and has programmed it to mimic the IMPROVE\_A analysis applied by DRI to network module C quartz filter samples. The on-campus analyzer was used so samples collected in their roof-top special study site could be analyzed promptly without shipping and the usual handling. Samples were collected in Davis in groups of 12 and were divided into four groups:

- 3 samples would be analyzed immediately.
- 3 samples would be heated to 40-degrees C for 24 hours then analyzed.
- 3 samples would be heated for 48 hours then analyzed, and.
- 3 samples would be heated for 96 hours then analyzed.

Results indicated that 40% - 60% of OC1 (the lowest temperature, most volatile carbon fraction) was lost off the filters in 24 hours and 30%-40% of OC1 was lost in 12 hours. IMPROVE does not ship the filters to and from the field cold and this study validates that approach, since a substantial amount of the volatile organic material is lost before the filter is even removed from the sampler.

In a separate study, experiments are underway at UCD to better quantify the uncertainty inherent in IMPROVE's approach of subtracting quartz secondary values from the primary filter values to account for a presumed positive (gas adsorption) organic carbon sampling artifact. Combinations of denuders and secondary filters, sampling concurrently, will provide estimates of both positive and negative artifacts. The testing is in progress now and will be completed by Fall 2009.

Finally, extensive California wildfires during Summer 2008 provided an opportunity for collecting special samples at the test site on the UC-Davis roof. To minimize clogging of the filters during these fire events, laboratory staff collected 8-hour samples. The 15-minute flowrate data from these events will be examined carefully to understand sampler behavior (especially clogging) during smoke events. The data will also be analyzed, along with meteorological data and aerial photographs, to assess the sources of the haze.

#### **Lab Audits**

NAREL's quality assurance activities were summarized including performance test samples which are prepared at NAREL and then distributed to participating laboratories that routinely analyze speciation samples. Each PT study administered by NAREL includes the following design elements:

- Understand the analytical methods of each test lab.
- · Prepare several replicate samples for each technique being tested, and
- Check the quality of the replicates before study begins.

Seven participating labs involved in the performance tests were: CARB, DRI, Oregon DEQ, RTI, UCD, NAREL, and EPA's National Exposure Research Lab (NERL) which served as a reference lab for this study. A photograph was shown of the air sampling site at NAREL with collocated Met One samplers used to generate the replicate samples. For XRF analysis tests each of the seven labs received 8 filters for analysis; comparison graphs were shown using normalized stacked bar graphs with various colored bands for each lab and each species concentration being tested. Some of the XRF replicates were also analyzed at ICP/MS labs. Results from the ICP/MS analysis were presented at the meeting although they will not be included in the final EPA report. For the thermal/optical carbon analysis using the STN/TOT method, NAREL showed far more pyrolitic carbon than the other labs, and no explanation could be offered at this time. NAREL has promised to pursue an explanation for this problem just as soon as time permits. For IC analysis tests each of the seven labs received 6 filters for analysis; results showed nitrate was much less on Teflon® filters than on nylon filters. This is not a new finding.

#### **Data Processing & Distribution**

#### **Data Advisories**

UC-Davis occasionally issues data advisories to address specific biases, discrete changes in behavior, and other identifiable anomalies. Two specific examples were presented, both related to masked Teflon® filters. The first example concerned 22 sites that operated with masks during 2005-06. Light absorption data were incorrectly calculated using the unmasked filter area, so an advisory was issued, to remain in effect for data downloaded until the data have been correctly resubmitted. The second example data advisory concerned observations of sulfur data at individual sites before and after masks were removed from the network, evident since 2002. Unmasked sites have generally reported about 5% more sulfur than masked sites at a given measured sulfate

concentration, and the sulfur reported from masked sites has typically risen by about 5% when they have converted to unmasked operation.

#### **IMPROVE Estimates of Detection Limits**

Minimum Detectable Limits (MDLs) and uncertainties are currently based on different techniques for each module. Collocated sampler measurements, begun in 2003, have shown these module-specific values to be underestimated for many species, especially for many XRF elements. An approach has been proposed to be more consistent across modules and more consistent with international guidance. MDLs will be determined from field blank values (secondary filters for carbon), and uncertainties will incorporate contributions from field blanks and from collocated sampler. UC-Davis also proposes to start reporting OC, EC, and TC with their uncertainties and MDL for carbon, whereas only the carbon component values have been reported in the past. Work is underway to develop the details of these proposed improvements. Once this development work is completed, the changes will be implemented at a calendar year break.

#### **VIEWS and EPA DSS (Decision Support System)**

Over the past year the IMPROVE and VIEWS websites have added a number documents including gray literature, data advisories, QA/QC reports, IMPROVE activities and educational material. It also contains all of the most up to date IMPROVE aerosol and optical data. Over the course of the next year the VIEWS 2.0 website will be released expanding the data visualization and analysis capabilities. John Huddleston has recently been added to the CIRA IT team which maintains and develops VIEWS and other on-line decision support systems at CIRA. John is a retired federal employee and spent most of his years with USDA Soil Conservation Service and his last two years with NOAA National Centers for Environmental Prediction. John holds a PhD from Colorado State University in Geophysics, an MSCE from Rutgers School of Engineering, and a BA from Rutgers College. He has been a registered professional engineer since 1982. He has extensive experience in the application of geographic information systems to solve natural resource problems.

## **Data Comparability & Interpretation**

#### **NASA ROSES**

In conjunction with the Uma Shankur at the University of North Carolina and other, the VIEWS team has won a NASA ROSES contract to expand the capability of VIEWS and the WRAP Technical Support System (TSS) by incorporating satellite data and chemical transport modeling data. New tools to visualize and analyze these data and perform model evaluation will be developed. Dr. Duli Chand, from the University of Washington has been hired to work on this project and will begin in February.

# **EC** to Absorption

EPA has an interest in estimating historical concentrations of "elemental carbon" (EC) from already-exposed Teflon® filters. A proven estimation method would allow new epidemiological and source-attribution analyses to tap the substantial filter archives generated by regulatory monitoring of PM<sub>2.5</sub> mass concentrations. IMPROVE has been making such measurements from its beginning. In 1994 we converted from an integrating plate method which only measured transmittance to a technique know as

hybrid-integrating plate/sphere (HIPS) that has the unique feature of measuring both transmittance and reflectance so it does not require a pre-sampling blank measurement to determine sample absorption.

There appears to be a systematic relationship between the ratio of transmitted/reflected light and Elemental Carbon (EC) data. Adjustments to absorption thickness (AT) were developed that improved correlations of collocated measurements. The effect of high iron (Fe) on the AT measurement was noted. Regional differences in EC/AT ratio were found indicating non-uniform absorption/mass ratios ranging from less than 9 to greater than 12.

# **Regional Issues**

#### Role of Fire In Okefenokee

The Okefenokee National Wildlife Refuge was established in 1936 to "preserve the swamp" and is one of the few, last wilderness places in the southeast. The refuge usually receives 300,000-400,000 visitors annually but in 2007 it received only about 250,000 visitors. It has the benefits of about 250 volunteers to assist the refuge employees. The swamp changes over time from wet lands to shrubs and trees – a process which does not reverse unless fire comes and regenerates the swamp. A massive drainage attempt and timber harvest occurred during the early 20<sup>th</sup> century. In 2006-2007 drought hit the refuge and greater Georgia region. It receives 10,000-20,000 lightning hits per year, some of which ignite wild land fires.

The Red Cockaded Woodpecker is endangered and roosts in the trees of Okefenokee. The refuge protects 300 such trees in case of fire and creates defensible space around them. Refuge biologists protect the diversity and health of animal species in the refuge. Their goal is to restore the ecosystem; the swamp/watershed, and longleaf pine uplands habitat management. The longlieaf pine is "extremely resilient" to fire. Fire management is performed to clear out and replant for forest habitat improvement and includes prescribed burning. Refuge staff built a fire buffer between the swamp and their rural neighbors after the 1954-1955 series of fires which lasted for 18 months. At that time a perimeter road was constructed all around the swamp for fire access and protection.

The large fire that began April 16, 2007, was caused by two power lines crossing outside of the refuge; 100 bulldozers built a fire line around the edge but couldn't keep up with the progressing fire which increased massively each day due to drought conditions. Federal teams were called immediately and three teams responded. The fire engulfed about 560,000 acres and was the largest fire in Georgia history. It was declared "out" in June and residual cleanup occurred until August. The Greater Okefenokee Association of Landowners was created and are partners in fire protection for the refuge and surrounding areas.

# Exceptional Events - AQ Management, Policy, and Demonstration Tools

The discussion of the 2007 Okefenokee fire prompted a presentation and discussion of the new EPA Exceptional Events rule. An Exceptional Event is defined as an event that affected air quality, can be natural or human-caused, and is not controllable nor preventable. Data may be excluded from valid data sets if it is influenced by an exceptional event. Four criteria must be met to be considered an exceptional event:

- It must satisfy the definition of an Exceptional Event.
- A clear, causal relationship must exit between the measurement and the event.
- The event must be associated with a measured concentration in excess of normal historical fluctuations, and
- No exceedance or violation of standards must occur, "but for" the event.

Online tools are available for such analyses; see <a href="http://www.epa.gov/pmdesignations/2006standards/index.htm">http://www.epa.gov/pmdesignations/2006standards/index.htm</a>.

EPA concurred that May 22, 27, and 31, 2007, the PM<sub>2.5</sub> data should not be used for nonattainment status at certain sites in the southeast that were impacted by the Okefenokee region.

# Regional Air Quality Issues in the West Beyond Haze

 $SO_2$  and  $NO_x$  increases are projected in the West due to increased marine shipping and oil and gas development. Canada and Mexico have much more  $SO_2$  than the western U.S., but the West sees a high proportion of PM carbon than other areas of the U.S. EPA has modeled ozone and as shown on a map, counties predicted to violate the new standard by 2020 are mostly in southern California. However, WRAP modeling shows violation of the new ozone standards are likely over large rural/remote portions of seven western states.

# <u>Current & Future Interactions with Other Programs/Studies</u>

# Changes to Carbon Measurements in the CSN

The Chemical Speciation Network (CSN) includes 53 Trends sites and 150 SLAMS sites. The new carbon sampler is the URG-300N with mass controller, and filters are analyzed with the IMPROVE\_A Thermal Optical Reflectance (TOR) method. The CSN utilizes cold filter shipping to and from their monitoring sites. The network has begun a changeover to the new carbon samplers and anticipates the entire network to be changed in three phases. Phase I converted 56 sites in May 2007. Phase II is currently underway and will convert 61 sites in late 2008. Phase III will convert the remaining 76 sites; funding is in progress for this phase and the network anticipates sampler installation in late 2009. See <a href="http://www.epa.gov/ttn/amtic/specurg3000.html">http://www.epa.gov/ttn/amtic/specurg3000.html</a>. Linear regression data plots were shown using the old CSN (SASS samplers) vs. the IMPROVE samplers. EC was higher in the SASS than the IMPROVE samplers, but now EC is lower than IMPROVE in the URG samplers. After the change in CSN carbon samplers and analysis, data are expected to be consistent with measurements by the IMPROVE program.

#### **Regional Haze SIPs in the West**

State Implementation Plans (SIPs) were due December 2007 but not many states filed them. The Environmental Defense Fund filed a lawsuit in October 2008 because of this failure to file. Five western states (Arizona, New Mexico, Oregon, Utah, and Wyoming) submitted Section 309 plans in December 2003. EPA never responded to these plans

and considered these five states to have had a "failure to submit"). The states without a SIP will ultimately be covered by a Federal Implementation Plan (FIP) that EPA would have to prepare. EPA may withhold portions of the Section 105 grand funding to prepare the FIPs. EPA regions will begin preparation of the FIPs once findings are made concerning the submitted SIPs.

#### **ROMANS** and Nitrogen Issues

Visibility degradation and changes in ecosystem function in Rocky Mountain National Park (RMNP) are occurring because of emissions of nitrogen and sulfate species along the Front Range of the Colorado (CO) Rocky Mountains, as well as sources farther east and west. The nitrogen compounds include oxidized, reduced, inorganic, and organic nitrogen. The Rocky Mountain Atmospheric Nitrogen and Sulfur study (RoMANS) was initiated to better understand the origins of sulfur and nitrogen species as well as the complex chemistry occurring during transport from source to receptor. This included a source apportionment assessment to identify the relative contributions to atmospheric sulfur and nitrogen species in RMNP from within and outside of the state of CO; from emission sources along the Colorado Front Range; as well as the relative contributions from mobile sources, agricultural activities, and large and small point sources within CO.

As part of the study, a monitoring program was conducted for two 5-week periods, one during the spring, the other during late summer. Monitoring data of ammonium/ammonia, nitrogen oxide/nitrates, and sulfur dioxide/sulfates were combined with tracers of opportunity and modeled releases of conservative tracers from source regions around the United States to apportion these species to their respective sources, using a variety of receptor modeling tools. The preliminary results show that during the spring a larger fraction of nitrogen and sulfur species came from sources within CO than during the summer. Specifically, during the spring, sources within CO contributed more than 80% of the ambient NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, HNO<sub>3</sub>, and particulate NO<sub>3</sub><sup>-</sup>; 50% of SO<sub>2</sub> and 30% of particulate SO<sub>4</sub><sup>=</sup> came from sources within CO. During the summer period CO sources contributed to about 75% of the ambient NH<sub>3</sub> and 55–60% of the NH<sub>4</sub><sup>+</sup> and HNO<sub>3</sub>; 30% of SO<sub>2</sub>, and 20% of particulate SO<sub>4</sub><sup>=</sup>.

# **Estimating the Contribution of Haze from Fire Types**

Smoke from fire emissions can be a significant contributor to fine particulate matter (PM2.5) and haze. In order to meet air quality regulations, state and federal regulators are beginning to explore reducing the impacts from smoke. To develop meaningful control strategies, federal land managers and policymakers need retrospective tools to apportion daily measurements of PM2.5 to smoke from natural, e.g., wildfire, and anthropogenic fires, e.g., some prescribed fire, as well as mobile and industrial sources. This is complicated by the fact that more than half of the carbonaceous material can be secondary organic aerosols (SOA) and some of this SOA is indistinguishable from vegetation SOA. Traditionally, source attribution is conducted using chemical transport models (CTM) or receptor models. However, a new hybrid-receptor model has been developed that directly incorporates a-priori CTM modeling results, either as source attribution estimates or emission tracer species, into the CMB equation. The CTM results act as an additional constraint on the receptor model and aid in the identification

and separation of the different source types. In the current version, the expanded CMB equation is solved for the source attribution results and source profiles using the PMF receptor model which using a robust, constrained, weighted, least-square optimization technique where the individual measured concentrations and prior source attribution estimates are weighted by their uncertainty.

The system has been tested using synthetic data where the "truth", prior CTM source attribution, and measured data were known by using results from two CTM models and incorporating additional errors. The modeled smoke contributions were adjusted so that about 30% was SOA. The incorporation of the CTM results in the receptor model significantly reduced the systematic and random errors in the source attribution results compared to the CTM model results or receptor models alone. On average the hybrid-receptor model results had little bias indicating that the model was able to reproduce the large SOA contributions.

# **Other Topics**

#### Field site tour

Ron Phennerton site operator hosted the tour. He showed us the aerosol sampler shelter and the sampler, as well as other meteorological instrumentation at the site operated by other programs. Biologist Sarah Aicher provided a tour of burned areas of the refuge and how vegetation and animals have come back so far.

#### **WRAP TSS**

A short presentation was made of the WRAP Technical Support System (TSS) that showed the types of information available to federal, state and tribal users for providing technical assessment products to support the Regional Haze Rule SIP development process. Also a short presentation of the WRAP Fire Emissions Tracking System (FETS) was shown.

#### **PM NAAQS Review and Canadian Visibility**

Canada and the U.S. have an Air Quality Accord. Each country has agreed to do what is necessary to support the other with respect to meeting its federal air quality regulation. For example Canada would need to assure that its emissions do not violate the prevention of significant deterioration in US class I areas. Canada-wide standards for PM and ozone contain provisions for continuous improvement and keeping clean areas clean. Canada wants to update the understanding of visibility science and to develop the information that would be needed to plan for visibility monitoring in Canada. Their goal would be to produce data that is comparable to IMPROVE at Canadian sites. Canada currently has two independent networks (similar to the U.S.); the networks are the Canada Air and Precipitation Monitoring Network – CAPMon, a rural network, and the National Air Pollution Surveillance network – NAPS, an urban network. Canada and U.S. measurements agree well on mass and sulfur at the one IMPROVE-comparison site currently located at Egbert, Ontario. Environment Canada official are in contact with IMPROVE concerning their interest in acquiring a second IMPROVE comparison site in the Canadian Rockies.

#### NAAQS Urban visibility-based secondary standard

During the last review of the PM National Ambient Air Quality Standard (NAAQS), a separate, more stringent secondary standard that focused on visibility improvement in urban areas, was proposed but in 2006 it was not approved. The PM NAAQS are being reviewed again and the possibility of a secondary standards to protect urban visibility is again being considered. An urban visibility perception and valuation workshop was held in Denver, CO, October 6-8, 2008 to explore the types of additional information that would be needed to advise EPA on such a decision. One of the tools that are needed in future focus group and surveys is a way to display urban haze levels. WinHaze has been used in the past for this purpose and is being modified to better display sky color and to add cloud appearance as a way to explore the possibility that these may be sensitive to perceived visibility changes resulting from PM concentration changes. Also a review of the IMPROVE algorithm for estimating light extinction from PM speciation data to determine its appropriateness for urban situation will soon begin. In setting a different secondary standard based on urban visibility, EPA could choose a non-PM mass indicator for a proposed secondary standard (e.g., light extinction).

## **Budget**

Fiscal Year July 1, 2008 to June 2030, 2009. EPA funds are \$7.4 million and non-EPA contributions are nearly \$2 million for the year.

#### **IMPROVE Calendars and Newsletters**

CIRA staff collect the information and produce the yearly calendar. ARS staff distribute it. The 2009 calendar is expected to be ready for distribution the first week of December. Costs are approximately \$7,000 (plus labor) for 1,000 calendars. One of the challenges in producing the calendars is the preparation of articles describing IMPROVE activities, facilities, sites and their operators. It was suggested that the size of the calendar be reduced to reduce printing and shipping costs, but to continue to include relevant technical articles, though perhaps shorter ones.

ARS is responsible for production and distribution of the IMPROVE quarterly newsletter. The newsletter is distributed to approximately 400 individuals and 180 site operators (who receive their newsletter in a filter shipment). Cost to print and mail is \$950 per quarter. Like the calendar, a major challenge for the newsletter is the preparation of articles. The staff encourages contributed articles and ideas for article to the newsletter.

#### **Next Meeting**

The group suggested that it was the National Park Service's turn to host the next meeting (i.e. Fish and Wildlife Service hosted the current meeting and the Forest Service and Bureau of Land Management the prior one). Locations discussed included the upper Midwest, but could be elsewhere (avoiding regions with recent meetings) Dave Maxwell will research possible, suitable locations, perhaps Isle Royale in Michigan's Upper Peninsula.

-- end --

# IMPROVE Steering Committee Meeting Agenda October 28-29, 2008 Administration Building; Okefenokee National Wildlife Refuge, GA

<u>Time</u>		sday, October 28	Discussion Leader		
8:30am	Welcome		George Constantino		
8:45am	Introductions and agenda		Marc Pitchford		
		etwork Review			
9:15am	Aerosol monitoring		Chuck McDade		
10:15am	Break				
10:30am	Optical & scene monitoring		John Molenar		
11:00am	Quality assurance field au-		Jeff Lantz		
Laboratory Review & Methods Development					
11:30am	Carbon analysis		Judy Chow		
12:00pm	Lunch				
1:00pm	Carbon analysis workshop	summary	Marc Pitchford		
1;15pm	lon analysis		Eva Hardison		
1:45pm	XRF analysis		Chuck McDade		
2:15pm	Sampling systems		Chuck McDade		
2:45pm	Laboratory audits		Jewell Smiley		
3:15pm	Break				
·	Data Pro	cessing & Distribution			
3:30pm	Data advisories	_	Warren White		
3:45pm	Revised quality metrics		Warren White		
4:00pm	VIEWS & EPA DSS		Brett Schichtel		
Data Comparability & Interpretation					
4:30pm	Elemental carbon to absor	rption & CSN to IMPROVE	Warren White		
5:00 Adjourn for the day					
5:15pm	Dinner (for those who sign	ı up)			
6:00pm	Sunset boat tour (for those	e who sign up)			
Wednesday October 29					
	R	egional Issues			
8:30am	Role of fire in Okefenokee	NWR	George Constantino		
9:30am	Western regional issues be	eyond haze	Tom Moore		
Current & Future Interactions with Other Programs/Studies					
9:45am	CalNex 2010 Study (air qu	uality/climate)	Tom Moore		
10:00am	Break				
10:15am	NASA including AERONE	Т	Bret Schichtel		
10:30am	RHR implementation statu	IS	Tom Moore		
10:45am	Atmospheric nitrogen issue	es	Bill Malm		
11:15am	Hybrid receptor modeling		Bret Schichtel		
11:45am	PM NAAQS review & Cana	adian visibility	Marc Pitchford		
12:15pm	Lunch	•			
1:15pm	Monitoring site tour (site	e operator Ron Phennerton)	Chuck McDade		
•	•	Other Topics			
2:00pm	IMPROVE budget summa		David Maxwell		
2:15pm	IMPROVE Newsletter & ca		Gloria Mercer		
2:30pm	Next meeting location & tir		Marc Pitchford		
2:45pm	Meeting adjourned	•			
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# IMPROVE Steering Committee Meeting Participants October 28-29, 2008 Administration Building; Okefenokee National Wildlife Refuge, GA

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