INTERAGENCY MONITORING OF PROTECTED VISUAL ENVIRONMENTS

IMPROVE

1st Quarter 2012 | The IMPROVE Newsletter | Volume 21 / Number 1

Monitoring update

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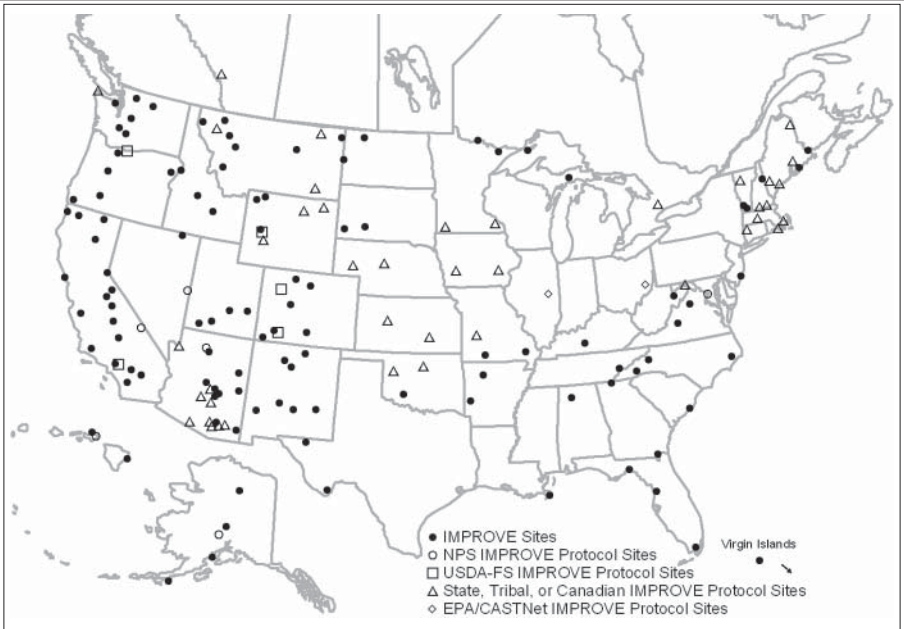
Network operation status

The IMPROVE (**I**nteragency **M**onitoring of **Pro**tected **V**isual **E**nvironments) Program consists of 110 aerosol visibility monitoring sites selected to provide regionally representative coverage and data for 155 Class I federally protected areas. Instrumentation that operates according to IMPROVE protocols in support of the program includes 53 additional aerosol samplers, optical instrumentation (nephelometers and transmissometers), scene instrumentation (Webcamera systems), and interpretive displays.

IMPROVE Program participants are listed on page 8. Federal land management agencies, states, tribes, regional air partnerships, and other agencies operate supporting instrumentation at monitoring sites as presented in the map below. Preliminary data collection statistics for the 1st Quarter 2012 (January, February, and March) are:

- Aerosol (channel A only) 95% collection
- Aerosol (all modules) 95% completeness
- Optical (nephelometer) 98% collection



IMPROVE and IMPROVE Protocol Sites
1st Quarter 2012

Data availability status

Data and photographic spectrums are available on the:

- IMPROVE Web site
  http://vista.cira.colostate.edu/improve/Data/data.htm
- VIEWS Web site
  http://vista.cira.colostate.edu/views
- Federal Environmental Database (FED)
  http://views.cira.colostate.edu/fed/Default.aspx

Aerosol data are available through December 2010. Nephelometer and transmissometer data are available through December 2011 and December 2010, respectively.

Webcamera real-time images and associated air quality data are available on agency-supported Web sites:

- National Park Service
  http://www.nature.nps.gov/air/WebCams/index.htm
- U.S. Forest Service
  http://www.fsvisimages.com
- CAMNET (Northeast Camera Network)
  http://www.hazecam.net
- Midwest Haze Camera Network
  http://www.mwhazecam.net
- Wyoming Visibility Network
  http://www.wyvisnet.com
- Phoenix Visibility Network
  http://www.phoenixvis.net

The U.S. Environmental Protection Agency AIRNow Web site *http://airnow.gov* includes many of these same images, as well as additional visibility-related Webcameras from 33 states and the District of Columbia. Click on "Visibility Cameras" at the AIRNow home page.

***Monitoring update** continued on page 3....*

Visibility news

Visibility and air pollution conference to have something for everyone in September

The Air & Waste Management Association (A&WMA) is holding a weeklong technical conference this coming September. The Aerosol and Atmospheric Optics: Visibility and Air Pollution Conference will be held September 24-28, 2012, in Whitefish, MT, home to Glacier National Park. Several peripheral activities are also scheduled for those with varying interests.

Conference presentations currently being solicited include the following topics:

- Emission sources, atmospheric conditions, and aerosol characteristics associated with haze and aerosol urban visibility.
- Regional haze.
- Climate forcing.
- Innovative aerosol, haze, and radiation balance monitoring assessments and modeling methods.
- Urban and regional haze and aerosol climate forcing policy, regulatory, and economic issues related to implementation of U.S. EPA standards and rules.

Special sessions on black carbon particulate and nitrogen deposition are also being planned. In addition to conference proceedings, attendees can also participate in:

- A field trip to nearby Glacier National Park.
- A night sky / astronomy program.
- A visibility photo contest.

To participate in the photo contest, submit your best photos of spectacular visibility, impaired visibility, unusual optical effects, visibility instrumentation, or people engaged in visibility research or protection. E-mail your photo entry to *Kristi.gebhart@colostate.edu* by September 10, 2012, and bring an 8"×10" print to the conference.

Details are still being planned for this fall conference. For more information visit http://visibility.awma.org.

PESA hydrogen analysis discontinued

The IMPROVE Steering Committee has decided to discontinue Proton Elastic Scattering Analysis (PESA) effective with samples collected in January 2011. PESA has provided a measurement of hydrogen in $PM_{2.5}$ samples collected on Teflon® filters. It was performed using a proton beam in the cyclotron at Crocker Nuclear Laboratory at UC Davis.

Budget constraints sparked the decision to discontinue PESA. The hydrogen measurement is not needed for the Regional Haze Rule visibility analysis nor for most analyses of long-term aerosol trends or source apportionment. PESA data have been used primarily as a secondary quality control check on other data, but its use requires applying some rather crude assumptions. Hence, eliminating PESA seemed to be a logical choice for trimming the budget. It will save the IMPROVE Program approximately $250,000 per year.

The PESA apparatus and its dedicated beamline at the UC Davis cyclotron will be retained. Therefore, the infrastructure will exist if, in the future, there is a desire to restore PESA for routine measurements or to use it for limited special studies.

The PESA method was developed at UC Davis in 1984 to determine the total hydrogen content of samples in the National Park Service Network that preceded IMPROVE. Since the Teflon® filter material contains very low concentrations of hydrogen, the measured value is solely due to the hydrogen in the sample deposit. The use of the PESA data has relied principally on applying assumptions about the amount of hydrogen associated with other measured species. By estimating, for example, the amount of hydrogen associated with measured sulfate and nitrate, one can associate the remaining hydrogen with organic material and therefore obtain an estimate of organic mass.

For more information contact Chuck McDade at the University of California-Davis. Telephone: 530/752-7119. Fax: 530/752-4107. E-mail: cemcdade@ucdavis.edu.

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1901 Sharp Point Drive,
Suite E
Fort Collins, CO 80525

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Gloria S. Mercer, Editor
Telephone: 970/484-7941 ext.221
Fax: 970/484-3423
E-mail: Gmercer@air-resource.com

IMPROVE Newsletters are also available on the IMPROVE Web site at *http://vista.cira.colostate.edu/improve/Publications/news_letters.htm.*

IMPROVE committee to meet at Lake Tahoe

The IMPROVE Steering Committee will hold their annual technical and administrative meeting in Incline Village, NV, October 23-24, 2012. The meeting will include discussions about network status and other administrative aspects of the program, as well as technical presentations by laboratory and university researchers who analyze and use collected data from the monitoring program. A complete agenda will be prepared later this summer.

The meeting will be held at the University of California's Tahoe Environmental Research Center (TERC), on the north shores of Lake Tahoe. A field trip to the local IMPROVE monitoring site at Bliss State Park will also be part of the agenda.

The U.S. Forest Service sponsors the Bliss monitoring site, which has monitored Lake Tahoe area aerosols since 1990. IMPROVE committee members will listen to and present the latest information and research efforts concerning regional haze and visibility throughout the nationwide program.

For more information contact Scott Copeland at the U.S. Forest Service. Telephone: 307/332-9737. Fax: 307/332-0264. E-mail: copeland@CIRA.colostate.edu.

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Monitoring update

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Operators of distinction

You don't need a lot of experience being an IMPROVE site operator to be a good one. Daniel Brese has proven this, as he is quick to troubleshoot and correct problems, sometimes before UC Davis technicians can offer advice. Daniel, an Environmental Technical Specialist for the Air Pollution Control Division at the Vermont Agency of Natural Resources, has maintained the Proctor Maple Research Center (PMRF1) air quality monitoring station in northern Vermont for about 15 months.

The center focuses its research on the sugar maple tree, its sap, and its syrup. "The tree and its products are economically important to our state," said Daniel, "it is also culturally significant here and in Canada." The air monitoring station at the center is equipped with an IMPROVE aerosol sampler as well as a variety of gaseous, particulate, air toxics, and heavy metal samplers. The station is located in a rural area that can be difficult to visit. "Circumstances may change drastically overnight, and a 30-inch snowfall can make hiking into the station a challenge," said Daniel.

He is also responsible for operation of three other stations in the state's air monitoring network, and his efforts help in real-time assessment of criteria air pollutants in the region. Another of Daniel's current projects is finalizing the relocation of the state's air quality laboratory, which sustained heavy flood damage last August. "Literally everything was washed away," said Daniel. "The lab is important in maintaining the integrity of our air program and our goal is to have it fully operational again."

Daniel holds a BS in biology and an MS in ecology, and has studied conservation in various parts of the country including remote western prairies in Oregon and Kansas, alpine tundra in New Mexico, and eastern forests. He is a Vermont native who moved back to the state to be closer to family and live the lifestyle he enjoys with all its outdoor richness.

In his free time, Daniel likes to ski and run. A recent venture in hard cider-making has proven successful, and a cold, bubbly, hard cider is choice after a long day's work.

IMPROVE site operator Daniel Brese maintains a growing interest in our environment and the many resources that co-exist in it.

Monitoring update continued on page 7....

Feature article

Changes to the UC Davis sample handling facility and XRF laboratory

(by Chuck McDade, University of California-Davis)

IMPROVE operations at Crocker Nuclear Laboratory (CNL) at UC Davis underwent big changes during 2011. New instrumentation was obtained for x-ray fluorescence (XRF) elemental analysis and for filter weighing, and the sample handling operations were moved to new quarters to put all of the filter operations under one roof.

The biggest change was the transition to new XRF instruments. XRF is used to quantify the concentrations of 24 chemical elements on the A-module $PM_{2.5}$ filters. The new instrument in the lab at UC Davis is the PANalytical Epsilon 5, shown in Figure 1. This new XRF system provides a number of benefits, including enhanced stability of the chemical results, better equipment reliability, a modern and secure data handling system, and strengthened traceability of the data to support regulatory applications.

The old XRF systems at UC Davis had been in use since the early years of IMPROVE, and had become outdated and increasingly unreliable. They were controlled by VAX computers that were over 20 years old and still ran legacy software code written for an even earlier generation of hardware. It became evident that new equipment would be needed to maintain the sample throughput and data quality needed for IMPROVE.

The design of the Epsilon 5 provides improvements over CNL's legacy XRF systems. Unlike the CNL systems, the Epsilon 5 has a three-dimensional optical geometry that yields a polarized beam. Polarization reduces unwanted spectral background, thereby producing cleaner spectra. Cleaner spectra enhance the ability to investigate physical phenomena with minimal interference from instrumental artifacts.

Figure 1. UC Davis' new PANalytical Epsilon 5 XRF system offers increased data stability, data handling, and data traceability.

The Epsilon 5 uses secondary x-ray excitation, in which primary x-rays from a single x-ray tube excite a series of elemental targets, each of which then emits characteristic x-rays that are used to excite the aerosol samples. Each element in a sample is most efficiently excited by x-rays within a fairly narrow energy range. Furthermore, the multiple targets allow tailoring of the energy spectrum to fluoresce certain elements without fluorescing others that could interfere, making it easier to discriminate the peak of interest. By offering a series of targets, the Epsilon 5 allows quantification of each element using excitation x-rays in its optimal range, thereby maximizing the sensitivity of the measurement. Typically, up to about a half dozen elements in a sample are quantified using a single target. The Epsilon 5 differs from CNL's custom-built XRF systems which used primary emissions from only two anodes, copper and molybdenum, to excite the samples. Primary emission has the advantage of strong x-ray flux, but it has the disadvantage of providing only two excitation energies so that many elements are being excited far from their optimal regions.

To enhance the usefulness of the Epsilon 5, the design engineer and machinists at CNL have worked with PANalytical to custom design a modified sample holder for IMPROVE's 25 mm filters that increases the instrument's capacity from 48 to 126 filters without reloading. A specially designed vacuum head, shown in Figure 2, picks up each filter from its holder and places the filter in the x-ray chamber for analysis. This CNL-designed modification to the Epsilon 5 gives the instrument the filter capacity needed to accommodate a large network such as IMPROVE without the time-consuming and labor-intensive sample changing required by standard commercial instruments.

Another laboratory improvement during 2011 was the transition to new balances for filter weighing. The choice to obtain new balances was straightforward. The IMPROVE balances at CNL had been in use for over 20 years and were increasingly prone to failure. They were an old, fragile hanging-pan design and were occasionally damaged by the student operators. Hence they required a great deal of maintenance and repair, and sporadic failures impacted the sample throughput.

Figure 2. Special vacuum head places filter in analysis chamber.

Figure 3. The Mettler XP6 filter weighing unit.

The aging balances were replaced with the Mettler XP6, a state-of-the-art unit well suited to filter weighing. The precision of the Mettler XP6 routinely falls within ± 3 µg, which is well within CNL's stated uncertainty of ± 5 µg. As an added advantage, the settling time of the Mettler XP6 is under 10 seconds, compared to over a minute for the old balances, so the weighing process is faster. The XP6 is shown in Figure 3.

Concurrent with the switch to new balances and new XRF systems was the switch to Teflon® filters with a small barcode and serial number etched onto the support ring of each filter. Engineers at CNL worked with the filter manufacturer, Pall Corporation, to perfect a barcode design and to select an optical code reader that is compatible with the new weighing and XRF systems. Testing of barcoded filters has indicated that the barcodes do not affect the sampling characteristics of the Teflon® filters. The barcode does not use ink but is laser etched onto the support ring and does not change the Teflon® filter material.

Barcodes provide the advantage of unique identification of each filter. In the past, with non-coded filters, filter identification was achieved through the labeled filter holder, either a cassette during field sampling or a slide mount during analysis. Data review suggested that filters were occasionally being swapped during transfer from cassette to slide mount in the laboratory, but there was no mechanism for verifying each filter's true identity. Barcodes and serial numbers eliminate that uncertainty by providing unique identification throughout each filter's entire life cycle.

New instrumentation and new procedures provided an opportunity to reconfigure the sample handling and analytical facilities at CNL. In the past, filter weighing had been conducted in a small annex adjacent to CNL. Filters needed to be boxed up and transported outdoors to the main CNL building nearby. Now, all of the facilities are in the main CNL building so that everything is under one roof. Figure 4 shows a photograph of the new sample handling facility.

For more information contact Chuck McDade at the University of California-Davis. Telephone: 530/752-7119. Fax: 530/752-4107. E-mail: cemcdade@ucdavis.edu.

Figure 4. UC Davis' new sample handling facility, which was moved from another building to the main Crocker Nuclear Laboratory building.

Visibility news continued from page 3 ....

Some uncertainties found in the Chemical Speciation and fine particle monitoring networks (CSN and IMPROVE)

The Environmental Protection Agency (EPA) and the federal land management community (National Park Service, United States Fish and Wildlife Service, United States Forest Service, and Bureau of Land Management) operate extensive particle speciation monitoring networks that are similar in design but are operated for different objectives. Compliance (mass only) monitoring is also carried out using federal reference method (FRM) criteria at approximately 1,000 sites. The Chemical Speciation Network (CSN) consists of approximately 50 long-term trend sites, with about another 150 sites operated by state and local agencies. The sites are located in urban or suburban settings. The Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring network consists of about 170 sites, all in nonurban locations.

Each monitoring approach has its own inherent monitoring limitations and biases. Determination of gravimetric mass has both negative and positive artifacts. Ammonium nitrate and other semivolatiles are lost during sampling, while on the other hand, measured mass includes particle-bound water. Furthermore, some species may react with atmospheric gases, further increasing the positive mass artifact. Estimating aerosol species concentrations requires assumptions concerning the chemical form of various molecular compounds, such as nitrates and sulfates, and organic material and soil composition.

Comparing data collected in the various monitoring networks allows for assessing uncertainties and biases associated with both negative and positive artifacts of gravimetric mass determinations, assumptions of chemical composition, and biases between different sampler technologies. All these biases are shown to have systematic seasonal characteristics. Unaccounted-for particle-bound water tends to be higher in the summer, as is nitrate volatilization. The ratio of particle organic mass (POM) divided by carbon mass (Roc) is higher during summer and lower during the winter seasons in both urban and nonurban areas; however, Roc is lower in urban than nonurban environments.

Figure 1 shows that there is a rather dramatic seasonal difference in Roc factors, with winter and summer being at about 1.3–1.4 and 1.6–1.8, respectively. Spring and fall have intermediate values as compared to winter/summer. Because of less photochemistry during winter months, one might expect POM to be less oxygenated and have lower Roc factors than summer months. Also, because urban areas are likely sources of organic carbon (OC), it might be expected that a "young" urban organic aerosol would have a lower Roc factor than a more aged rural or remote aerosol. Figure 2 shows that these differences, if they exist, are not large. The center city Roc factors are systematically lower than either suburban or rural sites, but only by about 5–15%. Interestingly, suburban and rural Roc factors are about the same. Because the Roc factors between IMPROVE and CSN Met One monitoring systems are nearly the same, in spite of a 20% loss of OC using the IMPROVE system, it seems reasonable to hypothesize that the Roc factor of the volatilized speciated volatile organic compounds (SVOC) is about the same as the OC that is retained.

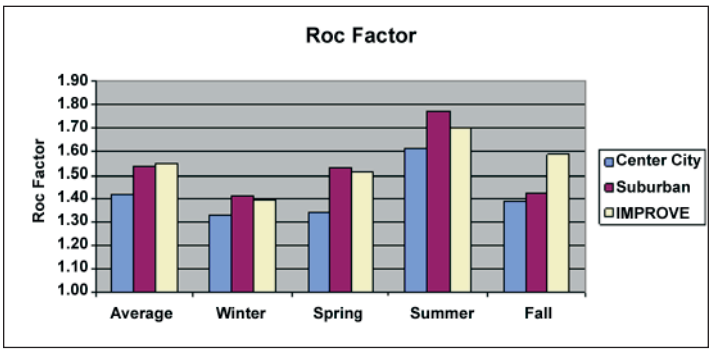

Figure 1. Roc factor for the IMPROVE and CSN monitoring networks.

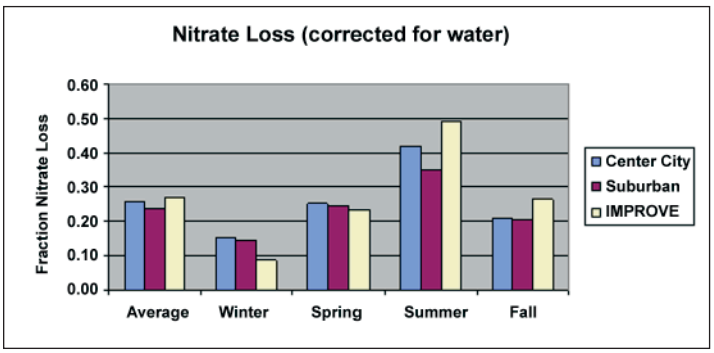

Figure 2. Average fraction of nitrate lost from a Teflon® filter for the IMPROVE and CSN monitoring networks.

Estimated seasonal variability of nitrate volatilization from a Teflon® filter is consistent with literature values. In Figure 2, winter fractional loss of nitrate is about 10%, while during the summer the average loss is estimated to be 40–50%, with spring and fall loss being intermediate compared to summer/winter. There is very little difference of nitrate volatilization between urban and nonurban sites.

For more information contact Bill Malm at the Cooperative Institute for Research in the Atmosphere. Telephone: 970/491-3679. E-mail: malm@CIRA.colostate.edu.

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Outstanding sites

Data collection begins with those who operate, service, and maintain monitoring instrumentation. IMPROVE managers and contractors thank all site operators for their efforts in caring for IMPROVE and IMPROVE Protocol networks. Sites that achieved 100% data collection for 1st Quarter 2012 are:

Aerosol (Channel A) - 50% of all sites

Acadia	Great Basin	Proctor Research Cntr.
Badlands	Great River Bluffs	Quabbin Reservoir
Bliss	Great Sand Dunes	Queen Valley
Boulder Lake	Guadalupe Mtns.	Rocky Mountain
Boundary Waters	Haleakala	Saguaro West
Bridger	Hawaii Volcanoes	San Gabriel
Bridgton	Hells Canyon	San Gorgonio
Brigantine	Hercules-Glades	San Pedro Parks
Bryce Canyon	Indian Gardens	Seney
Cabinet Mountains	Isle Royale	Sequoia
Caney Creek	James River	Shamrock Mines
Casco Bay	Joshua Tree	Sula
Chassahowitzka	Lake Sugema	Theodore Roosevelt
Cherokee	Lassen Volcanic	Three Sisters
Chiricahua	Linville Gorge	Tonto
Cloud Peak	Londonderry	Tuxedni
Columbia Gorge East	Lye Brook	Upper Buffalo
Crater Lake	Makah	Virgin Islands
Crescent Lake	Mammoth Cave	Voyageurs
Death Valley	Mesa Verde	Weminuche
Denali	Mingo	Wheeler Peak
Dolly Sods	Monture	White Pass
Douglas	Organ Pipe	Wichita Mountain
El Dorado Springs	Pack Monadnock	Wind Cave
Flat Tops	Phoenix	Yellowstone
Gila	Pinnacles	Yosemite
Grand Canyon	Presque Isle	

Nephelometer - 47% of all sites

Big Bend	Glacier	Shenandoah
Dysart	Mount Rainier	Vehicle Emissions
Estrella	Rocky Mountain	

Sites that achieved at least 95% data collection for 1st Quarter 2012 are:

Aerosol (Channel A) - 18% of all sites

Bondville	Frostburg Reservoir	Pasayten
Canyonlands	Ft. Peck	Petrified Forest
Capitol Reef	Haleakala Crater	Quaker City
Cedar Bluff	Ike's Backbone	Simeonof
Craters of the Moon	Kalmiopsis	Snoqualmie Pass
Dome Land	Lostwood	Starkey
Egbert	Martha's Vineyard	Trapper Creek-Denali
Ellis	Mohawk Mountain	Trinity
Everglades	Mount Hood	Washington DC
Flathead	North Absaroka	White Mountain

Nephelometer - 41% of all sites

Acadia	Great Smoky Mtns.	Mammoth Cave
Grand Teton	Indian Gardens	South Pass
Great Basin		

Transmissometer - 100% of all sites

Bridger

Sites that achieved at least 90% data collection for 1st Quarter 2012 are:

Aerosol (Channel A) - 17% of all sites

Barrier Lake	Lava Beds	Puget Sound
Big Bend	Medicine Lake	Redwood
Birmingham	Mount Baldy	San Rafael
Breton	Mount Zirkel	Sawtooth
Cape Romain	Nebraska	Shenandoah
Gates of the Arctic	North Cascades	St. Marks
Gates of the Mtns.	Okefenokee	Sycamore Canyon
Great Gulf	Olympic	UL Bend
Jarbidge	Penobscot	Viking Lake

Nephelometer - 12% of all sites

Cape Romain	National Capital

Monitoring Site Assistance:

Aerosol sites: contact University of California-Davis
telephone: 530/752-1123 (Pacific time)

Optical/Scene sites: contact Air Resource Specialists, Inc.
telephone: 970/484-7941 (Mountain time)

IMPROVE

The IMPROVE Newsletter

Air Resource Specialists, Inc.
1901 Sharp Point Drive, Suite E
Fort Collins, CO 80525

TO:

First Class Mail

IMPROVE STEERING COMMITTEE

IMPROVE Steering Committee members represent their respective agencies and meet periodically to establish and evaluate program goals and actions. IMPROVE-related questions within agencies should be directed to the agency's Steering Committee representative.

U.S. EPA
Neil Frank
US EPA MD-14
Emissions, Monitoring and Analysis Div.
Research Triangle Park, NC 27711
Telephone: 919/541-5560
Fax: 919/541-3613
E-mail: frank.neil@epa.gov

NPS
Bret Schichtel
Colorado State University
CIRA - Foothills Campus
Fort Collins, CO 80523
Telephone: 970/491-8581
Fax: 970/491-8598
E-mail: schichtel@cira.colostate.edu

USFS
Scott Copeland *
USDA-Forest Service
Washakie Ranger Stn / 333 E. Main St
Lander, WY 82520
Telephone: 307/332-9737
Fax: 307/332-0264
E-mail: scott.copeland@colostate.edu
* Steering Committee Chair

USFWS
Sandra Silva
US Fish and Wildlife Service
7333 W. Jefferson Avenue
Suite 375
Lakewood, CO 80235
Telephone: 303/914-3801
Fax: 303/969-5444
E-mail: sandra_v_silva@fws.gov

BLM
David Maxwell
USDI BLM National Operations Center
Resource Services - Mail Stop OC-520
Denver Federal Center - Building 50
PO Box 25047, 205ST
Denver, CO 80225-0047
Telephone: 303/236-0489
Fax: 303/236-3508
E-mail: david_maxwell@blm.gov

MARAMA
David Krask
Maryland Dept. of the Environment
MARAMA/Air Quality Planning and Monitoring
1800 Washington Blvd.
Baltimore, MD 21230-1720
Telephone: 410/537-3756
Fax: 410/537-4243
E-mail: dkrask@mde.state.md.us

NESCAUM
Rich Poirot
VT Agency of Natural Resources
103 South Main Street
Building 3 South
Waterbury, VT 05676
Telephone: 802/241-3807
Fax: 802/244-5141
E-mail: rich.poirot@state.vt.us

WESTAR
Robert Lebens
715 SW Morrison
Suite 503
Portland, OR 97205
Telephone: 503/478-4956
Fax: 503/478-4961
E-mail: blebens@westar.org

NACAA
Gordon Andersson
State of Minnesota
Pollution Control Agency
520 Lafayette Road North
St. Paul, MN 55155
Telephone: 651/757-2197
E-mail: gordon.andersson@state.mn.us

NOAA
Rick D. Saylor
NOAA/ARL/Atmospheric Turbulence & Diffusion Division
456 South Illinois Ave.
Oak Ridge, TN 37830
Telephone: 865/576-0116
E-mail: rick.saylor@noaa.gov

ASSOCIATE MEMBERS
Associate Membership in the IMPROVE Steering Committee requires operation of at least one IMPROVE protocol site, openly share data, and participate in technical review and oversight of the IMPROVE Program. Associate and International Associate Member representatives are:

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