

The Monitor

CASTNET

Clean Air Status and Trends Network

Spring 2007

The Newsletter for Air Quality Station Operators



National Park Service (NPS)
Gaseous Pollutant Monitoring Program



Environmental Protection Agency (EPA)
CASTNET program

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NETWORK NEWS

What's old and new

CASTNET currently consists of 88 sampling stations and the majority of these sites (over 80%) have been operating for at least 15 years. Many sites have original equipment and shelters which are showing their age. To avoid compromising data quality, the EPA has begun to invest in upgrading the

sites in many areas. The following 10 sites have received new ozone analyzers (Thermo Environmental 49i):

- ROM206 - Rocky Mountain, CO (collocated)
- SAN189 - Santee Sioux, NE
- CVL151 - Coffeerville, MS
- ALH157 - Alhambra, IL
- SAL133 - Salamonie Reservoir, IN
- QAK172 - Quaker City, OH
- MCK131/231 - Mackville, KY (2 sites)
- BEL116 - Beltsville, MD
- PAL190 - (new site, April 2007) Palo Duro Canyon State Park, TX

In addition, starting in late 2006 EPA CASTNET sites are being outfitted with new laptop computers. Currently, over half of the 61 EPA-sponsored sites have received new computers with the remaining sites to receive one by the end of 2007. MACTEC personnel will also be upgrading several additional sites over the course of this year. Sites scheduled for major upgrades to infrastructure and general maintenance this month include:

- CKT136 - Crockett, KY
- PNF126 - Cranberry, NC
- ESP127 - Edgar Evins, TN
- CDR119 - Cedar Creek, WV

Station operators can help by providing a list of items that should be checked, repaired, or replaced to the Tuesday call-in personnel or the on-site repair technicians.

In addition to installing new ozone analyzers, EPA-sponsored CASTNET sites with newer ozone instruments will be switching from weekly zero/span/precision (z/s/p) checks to every other day. This protocol change will provide more frequent checks of instrument performance and is part of a larger effort to make CASTNET ozone monitoring more consistent with 40 CFR, Part 58 ozone quality assurance requirements which state, local, and tribal agencies follow. The complete transition will occur over the next couple of years and will likely include more frequent multi-point calibrations, site audits or accuracy checks, and certain data validation changes. More information will be provided in the next issue of *The Monitor*.

NETWORK NEWS continued on page 2....

NETWORK NEWS continued from page 1....

POMS plans for 2007

Portable ozone monitoring systems (POMS) have been used the past five summer ozone monitoring seasons by the National Park Service and its cooperating researchers. These small, relocatable systems developed by the NPS and Air Resource Specialists, Inc. (ARS) include a low-power ozone monitor (2B Technologies, Inc.), meteorological measurements, and at 3 of the 12 stations CASTNET-style filter pack sampling. All the stations are powered by batteries charged with solar panels. Data are collected via satellite modem. The purpose of the stations is to provide air quality measurements at sites (some remote) without the initial expense and infrastructure support required for a traditional air quality station.

The station locations are occasionally moved from park to park to satisfy evolving measurement needs and strategies. For example, measurement needs have been satisfied over the past five seasons at Lake Mead National Recreation Area, and that station will be moved to Mojave National Preserve, located in central California. The NPS and ARS wish to recognize and thank retirees' Ray Selinsky and Bob Porzio for their many years of supporting the POMS at Lake Mead. These individuals will continue to service the IMPROVE site located where they live near Meadview, Arizona.

Also in 2007, two stations will receive the new ozone calibrator recently developed by 2B Technologies, Inc. This low power device is capable of generating stable concentrations of ozone and will be used to perform periodic precision and span checks of the POMS analyzer. Although this equipment is not EPA-certified equivalent, the data are considered accurate and are valuable additions to the regional air quality database.

The 15 POMS monitoring locations for 2007 are:

- Abraham Lincoln Birthplace National Historic Site, KY
- Assateague Island National Seashore, MD/VA
- Carlsbad Caverns National Park, NM
- Colorado National Monument, CO
- Cuyahoga Valley National Park, OH
- Dinosaur National Monument, CO
- Joshua Tree National Park - Pinto Wells, CA
- Mojave National Preserve, CA
- Natchez Trace Parkway/National Scenic Trail, MS/AL/TN
- Olympic National Park, WA
- Padre Island National Seashore, TX
- Rocky Mountain National Park, CO



Portable ozone monitoring station (POMS) operating at the Tahoma Woods site in Mount Rainier National Park, Washington.

- Yosemite National Park - School Yard, CA
- Yosemite National Park - Tioga Pass, CA
- Undetermined at this time

Staffing changes around the program

Brian Lee joined EPA in October 2006, to enhance CASTNET's monitoring capabilities and ensure the scientific integrity of collected data. Since coming onboard as an environmental scientist with EPA, Lee has been studying monitoring principles, new technologies, and new monitoring techniques.

Before joining the EPA, Lee designed and operated an air quality monitoring network in the Philippines. He holds a Ph.D. in Inorganic Chemistry from the University of California - Santa Barbara.

Mark Hodges is now leading MACTEC's Gainesville, FL, office ambient air group. He is managing and maintaining schedules for all ambient air projects, including CASTNET, and works closely with all members of the CASTNET field operations group. His role is to ensure that network repairs are handled promptly and that the necessary personnel are scheduled to perform instrument repairs, site installations, and regular maintenance and calibration tasks.

At ARS, Kelly Sutton transferred from the Information Management Center to ARS' environmental compliance division, and Christian Kirk filled the vacated position as data analyst. Kirk is experienced in data collection and analysis and has a background in chemistry.

NETWORK NEWS continued on page 7....

STATION OPERATOR FOCUS

Station maintenance just part of the plan at Connecticut Hill

Proper instrument and station maintenance is critical to any monitoring program, but at Connecticut Hill, NY (CTH110), it is just part of the effort that Tom Butler puts forth as a CASTNET site operator.

Tom has been with the CASTNET program since the inception of the Connecticut Hill station in 1987. Because he is an air quality researcher at nearby Cornell University and also at the Institute of Ecosystems Studies, his involvement with the program doesn't end with station maintenance. "We have over 30 years of deposition data," said Tom, "we were collecting wet deposition data before the National Acid Deposition Program even existed and we're now looking into alternative monitoring methods and parameters to sample."

Tom is also involved with other monitoring programs, including the Southern Ontario Ammonia Passive Sampler (SOAPS) network, nitrogen deposition in the Upper Susquehanna Watershed project, and an intensive ammonia study last June. Researchers have found that ammonia can be a significant component of nitrogen dry deposition, and Tom is working with others to develop future ammonia monitoring for the CASTNET program.

Tom began working at Cornell University in 1976 and at the Institute of Ecosystems Studies in 1984. He holds an M.S. degree in Marine Sciences from Louisiana State University and is currently vice chairman of the National Atmospheric Deposition Program.

Being involved with many aspects of the monitoring program helps Tom see the bigger picture. All components of a program are important, but it begins with proper site operations and maintenance.

Tom has a wife and two children who are in college. He cross-country skis, gardens, hikes, and canoes in his spare time, which allows him to experience the air and surrounding landscapes in his free time as well as during work.

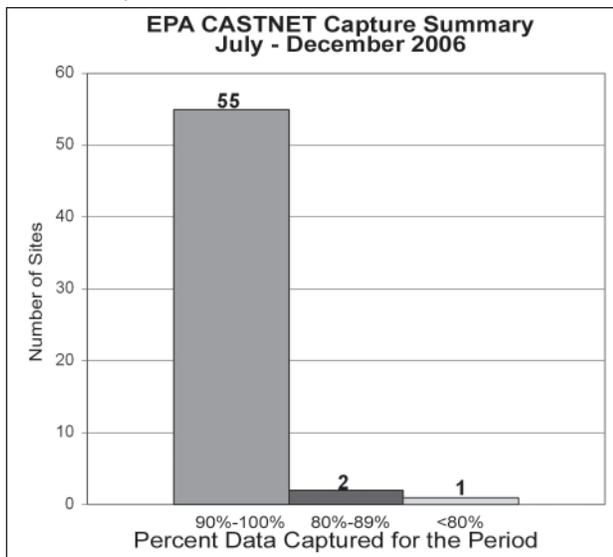


Air quality researcher and CASTNET site operator Tom Butler, points out his site, Connecticut Hill, New York, 15 miles distant.

DATA COLLECTION SUMMARY

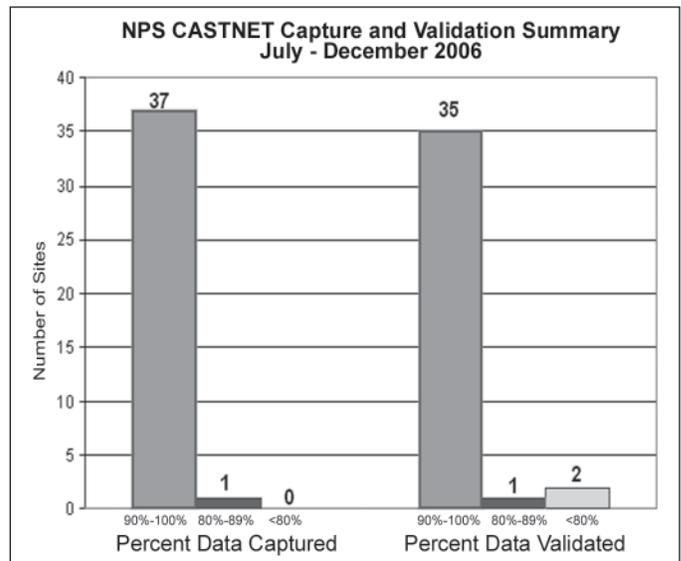
EPA Site Data Capture Summary

Data capture for the EPA CASTNET sites for July through December 2006 are summarized in the graph below. The network achieved an average 96% collection for the period. Data validation statistics for the period will not be available until mid-July 2007.



NPS Data Capture and Validation Summary

Data capture for the NPS CASTNET and GPMP sites for July through December 2006 achieved an average of 97% collection as illustrated in the graph below. Data validation for the same sites and period are also shown. The network achieved an average 95% final validation for the period.



FEATURE ARTICLE

The total picture: wet and dry nitrogen deposition in the West (by K. Morris, National Park Service)

Atmospheric deposition is how pollutants enter an ecosystem and is made up of dry and wet portions. Dry deposition of pollutants, as particles and gases, is monitored by CASTNET. Wet deposition of pollutants in precipitation is monitored by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). When dry portions and wet portions of a pollutant are summed together, it is referred to as “total” deposition. Figure 1 shows total deposition of nitrogen measured at collocated CASTNET and NADP sites across the western United States. Deposition in the West ranges from 1.3 to 5 kg/ha/yr, with proportions of wet and dry deposition varying from site to site.

The feature article in the last issue of *The Monitor* showed that sulfur and nitrogen deposition have decreased at sites in the East over the past 20 years. Average nitrogen deposition decreased from 8 kg/ha/yr in 1990 to about 6 kg/ha/yr in 2005. Figure 2 shows that average nitrogen deposition for 17 sites in the West decreased only slightly, from 2.4 kg/ha/yr in 1998 to 2.1 kg/ha/yr in 2005, however, some individual sites still showed increases in nitrogen deposition. (Western sites do not have as long of a record.)

Because wet nitrogen deposition is a function of concentration and precipitation amount, and therefore directly influenced by climate, scientists often track changes in pollutant concentrations. Published trends analyses show that at many sites in the West, since 1985, concentrations of nitrate in precipitation have increased (Figure 3), and concentrations of ammonium have increased dramatically (Figure 4).

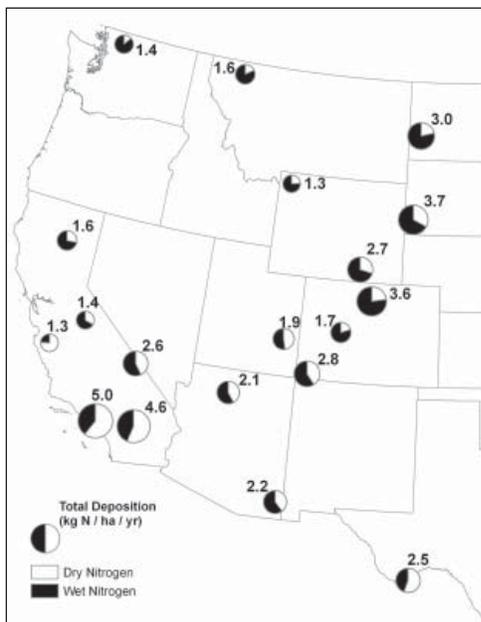


Figure 1. 2005 total nitrogen deposition at collocated CASTNET/NADP sites across the western U.S., showing proportions of dry and wet deposition.

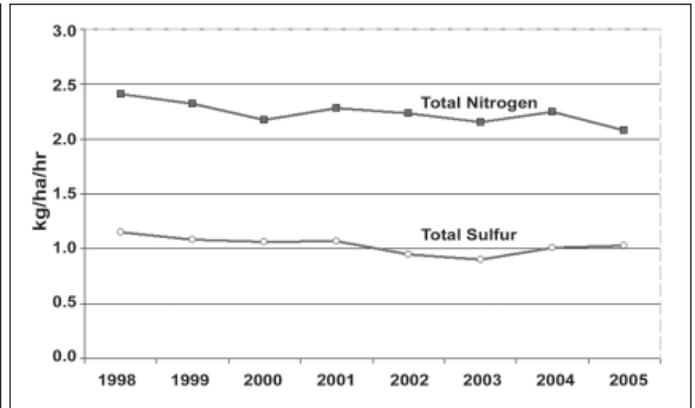


Figure 2. Total deposition at 17 collocated CASTNET/NADP sites in the West.

Deposition in the western U.S. is a concern because many high-elevation ecosystems are sensitive to even small inputs of nitrogen. One example is Rocky Mountain National Park, CO, where nitrogen deposition has increased and ecosystems are particularly vulnerable to fertilization caused by increases in nitrogen deposition. This is because these ecosystems have evolved under low nitrogen deposition conditions, they have granitic bedrock and shallow soils that provide limited chemical buffering, and short growing seasons that limit the amount of time plants have to absorb nitrogen for growth during the year. Over the past 20 years, researchers at the park have documented changes in both the type and abundance of aquatic plant species, chronically elevated levels of nitrate in surface waters, elevated levels of nitrogen in spruce trees, and the accumulation of excess nitrogen in forest soils.

Figure 5 shows the composition of nitrogen deposition at Rocky Mountain National Park. The majority of nitrogen deposition is wet, and is split almost evenly between nitrate and ammonium. Dry deposition is dominated by gaseous nitric acid, with smaller contributions from particulate ammonium and particulate nitrate.

However, one important piece of the puzzle is missing, and that is the contribution of gaseous ammonia (NH_3). Currently, ammonia is not measured routinely by a national network. However, atmospheric models have predicted that as much as 30% of total nitrogen deposition is from ammonia. Several efforts are currently underway to begin measuring ammonia on a national scale in conjunction with the national deposition monitoring networks, either with enhanced filter packs, passive samplers, or continuous instruments. Stay tuned for more information on measuring ammonia, as plans and protocols develop.

¹ Lehmann, C.M.B., V.C. Bowersox, S.M. Larson, 2005, Spatial and Temporal Trends of Precipitation Chemistry in the United States, 1985-2002, *Environmental Pollution*, 135: 347-361.

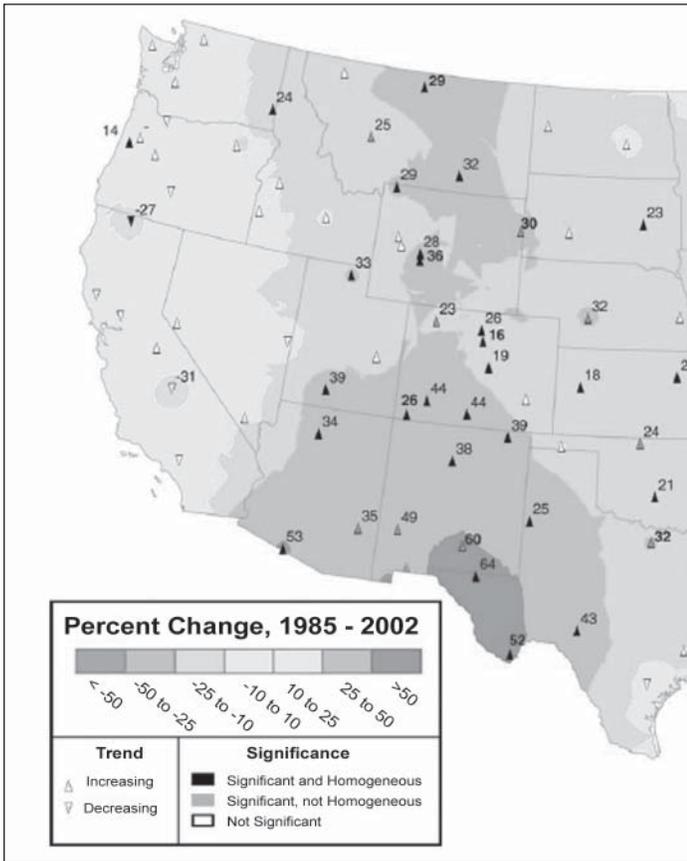


Figure 3. Change in nitrate concentrations in precipitation over time (adapted from Lehmann et al., 2005').

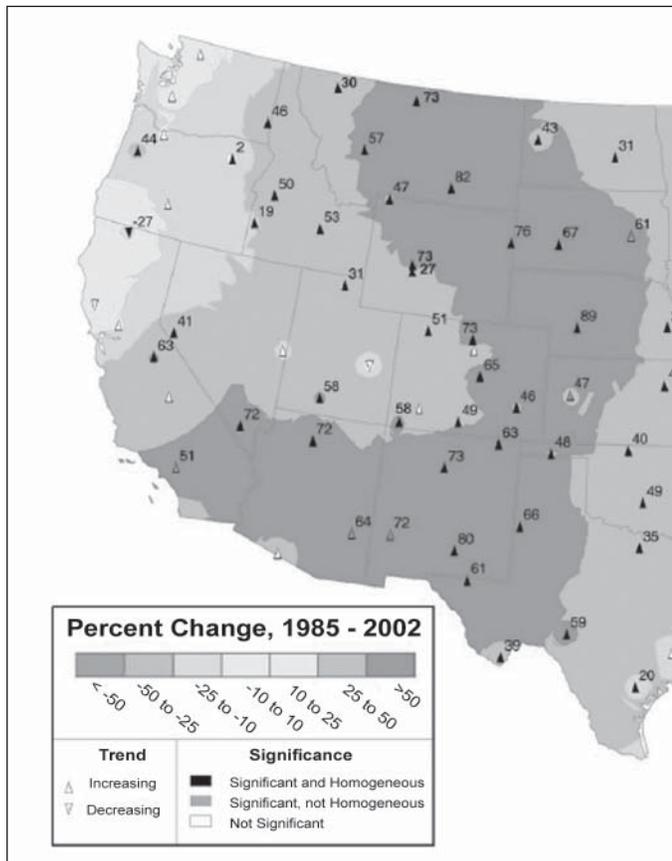


Figure 4. Change in ammonium concentrations in precipitation over time (adapted from Lehmann et al., 2005').

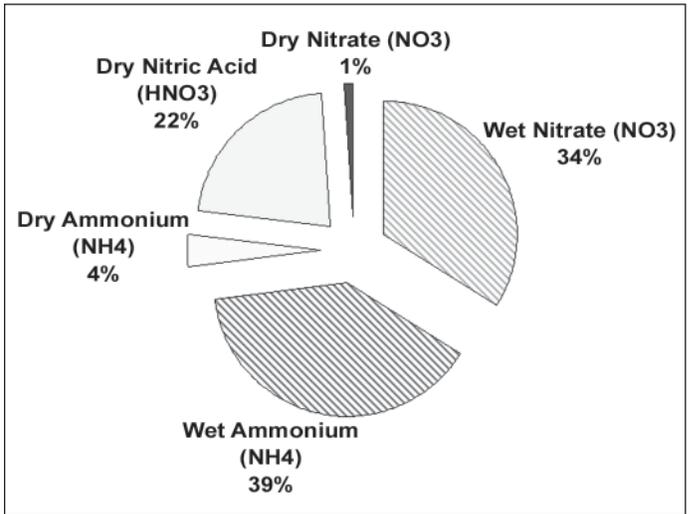


Figure 5. Composition of nitrogen deposition at Rocky Mountain National Park from 2002-2004 (CASTNET ROM406/NADP CO98).

OPERATOR'S TOOLBOX

STP: station temperature



With spring now upon us, it is critical to maintain proper station (shelter) temperature. As the transition seasons come and go, it may be necessary to readjust your station thermostat settings.

When working properly, stations automatically maintain a temperature of between 20°C and 30°C (68°F and 86°F). Shelter temperature (STP) is one of the datalogger-measured parameters and must be maintained in the above range for gaseous data to be considered valid according to EPA regulations. You may view the STP channel on your station's datalogger to get a recent value, or if you're an NPS-sponsored station, look at a DataView stackplot with the STP parameter to get a multi-day view of the temperature range within your shelter during that period.

If, during a station visit, you notice that both the heating and cooling systems are on at the same time, a malfunctioning heater or air conditioner relay is probably the culprit. Give ARS or MACTEC a call immediately to report this or any other temperature control problem. ARS or MACTEC will work with you to troubleshoot and isolate the problem and affect repairs.

Review a more detailed look at proper station temperature in the Fall 2005 issue of *The Monitor*, or log onto the GPMP Project Web site to view the article from the "Articles from The Monitor" link.

LAB TALK

Filter pack analysis: Ion chromatography



CASTNET air monitoring sites utilize a three-stage filter pack to measure the sulfur and nitrogen pollutants in the air we breathe. Each filter within the filter pack collects certain analytes or pollutant species. As discussed previously in “Lab Talk,” the filter from each stage of the filter pack provides only part of the captured pollutant picture for each sample. Teflon® filters trap the particulate phase, while gaseous analytes, such as nitric acid (HNO₃), are trapped by the nylon filter. The cellulose filters in the third stage collect sulfur dioxide (SO₂) gas, a neutral compound which reacts with the carbonate coating on the cellulose filters and water vapor from the atmosphere. When the filter is extracted, sulfite, bisulfite, and sulfate are all present in solution. The sulfites are converted to sulfate by an acidified hydrogen peroxide (H₂O₂) extraction solution before analysis. Some SO₂ is also captured by the nylon filter. Sulfur dioxide concentrations are determined from the combined sulfate results from these two filter types.

So how does the laboratory obtain its measurements from the filters? The CASTNET laboratory uses three different analytical methods: ion chromatography (IC), inductively coupled argon plasma-atomic emission spectrometry (ICP-AES), and automated colorimetry (AC). The method discussed in this article is IC, and it is the method used to determine the concentrations of the negatively charged pollutant species (see Figure 1). Pollutants with negative ions (anions) that are collected on CASTNET filters include sulfate, nitrate, and chloride.

The name chromatography is fittingly taken from the Greek *chromatos* (color) and *graphein* (to write) and translates to “color writing.” A botanist first used liquid chromatography to separate plant pigments, producing bands of color in his separation medium. Most laboratory techniques require separate portions of sample to be analyzed for each individual analyte; chromatography, however, can be used to separate and quantitate multiple analytes simultaneously.

The exposed filters are extracted (as described in the previous edition of “Lab Talk”). After extraction, a portion of the sample is pushed into a fluid medium called an eluent stream and onto a column containing an anion exchange resin similar to those commonly found in water-softening units. Pollutants are separated based on a combination of charge density and size, with larger, more highly-charged ions traveling more slowly than the smaller, less-charged ions. The sample stream then flows to a conductivity detector cell before passing into a waste stream.

The detector is monitored continuously, and a plot of the conductivity readings over time produces a chromatogram containing a series of peaks, each representing an analyte (see Figure 2). The time an analyte takes to travel the length of the column to the detector cell is referred to as the retention time and is the identifying characteristic of each peak. Calibration curves are then calculated using the peak areas of solutions with known concentrations. Concentrations of pollutants in each sample are determined by comparing the peak area for each analyte to its respective calibration curve. While the primary analytes of interest determined by IC are chloride, nitrate, and sulfate, any negatively charged species present in the sample will produce a peak in the resulting chromatogram.

Ion chromatography continued on page 7...

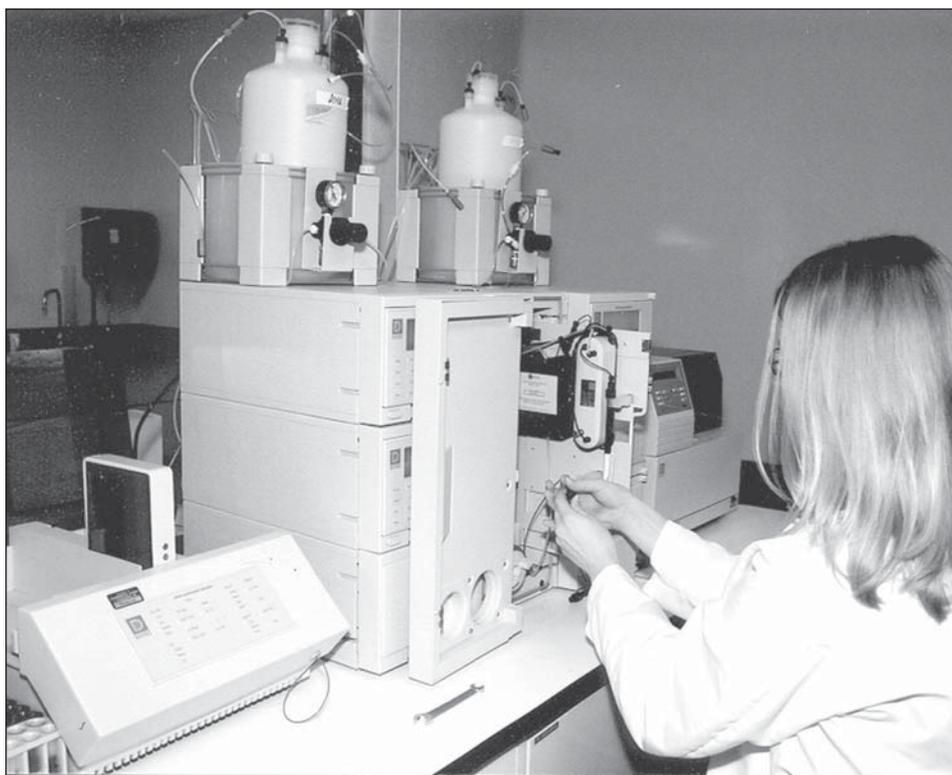


Figure 1. Technician operating the ion chromatograph.

Ion chromatography continued from page 6...

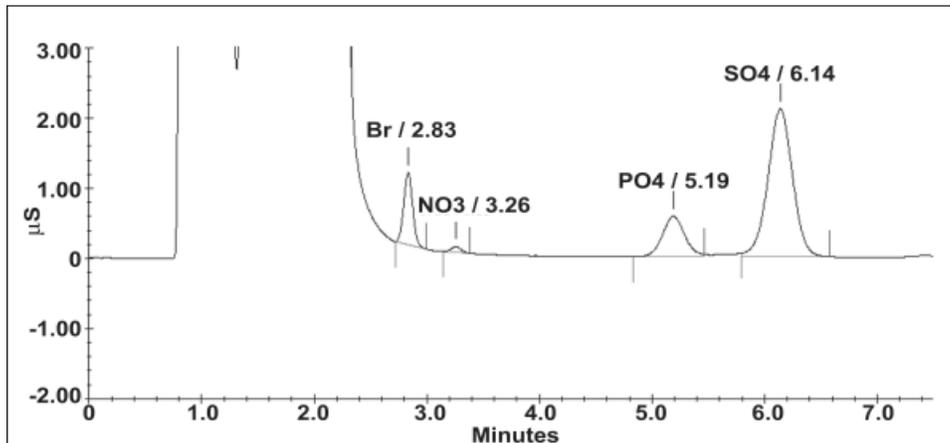


Figure 2. Example chromatogram: Whatman cellulose filter from Claryville, NY (CAT175).

All of the analytes of interest are very commonly found at high levels on exposed surfaces including hands, and any direct contact with the filter itself, or with the parts of the filter pack that are in contact with the filter, can result in contamination that produces falsely elevated results for

that sample. Thus, careful handling of the filter pack using the disposable gloves and bags provided is vitally important to obtaining accurate results. Smoke from nearby fires can also cause interferences. Organic solvents, such as those found in pesticide and herbicide sprays, can also be absorbed and affect analysis. While smoke and absorbed organics do not cause the same sort of bias as direct contact, the resulting peak broadening can affect the calculation of the peak areas for that sample, and any unusual and extraneous peaks can potentially obscure the peaks produced by the analytes of interest. Accurate and

complete site narrative logs are, therefore, important to obtaining meaningful results.

For more information on chromatography and its history, please see <http://www.lcgcmag.com/lcgcl/data/articlestandard/lcgcl202003/56954/article.pdf>.

NETWORK NEWS continued from page 2....

Is there a star out there?

The NPS ARD and ARS have begun preparing the *Annual Data Summary 2006* for the NPS' Gaseous Pollutant Monitoring Program. If you recall, last year's data summary sported a new look and format, and contained numerous photographs of scenic park locations, as well as air monitoring station photographs.

We ask station operators to send in any high-resolution photographs (300 dpi or better) that are scenic views of their park or monitoring location, or good photographs of their monitoring shelter/station. All photographs used in the data summary will include a caption containing the name of the site as well as name of the photographer.

Don't be shy! This is your chance to show off your amateur photography skills as well as your monitoring station! E-mail your photographs to Gmercerc@air-resource.com.

Monitoring Site Assistance:

NPS CASTNET sites: contact Air Resource Specialists
telephone: 1-800/344-5423 (Mountain Time)

EPA CASTNET sites: contact MACTEC
telephone: 1-888/224-5663 ext. 3611 (Eastern time)

GPMP project Web site enhancements

Several changes to the GPMP project Web site have taken place or will very soon occur. One important change involved moving the Web site to a new server. To access the site from this new server, you'll need to change your bookmark on your browser as your old bookmark will no longer work. In your Internet browser, type in the Web address, <http://ard-request.air-resource.com/project>. After reaching the project's login screen, add the site to your browser bookmarks. Login information (user name and password) remain the same.

Also note some new links and information under the site's Network Configuration folder. Contact information is provided for a variety of network-related personnel. Panoramic photographic views (360-degrees) are also available for each monitoring location.

Expected to come online before May is detailed information about each monitoring site. This information will include site location specifications, an aerial photograph, and a topographic description of the general monitoring area.

If you haven't visited the GPMP project Web site lately, check it out and see what it can offer you.

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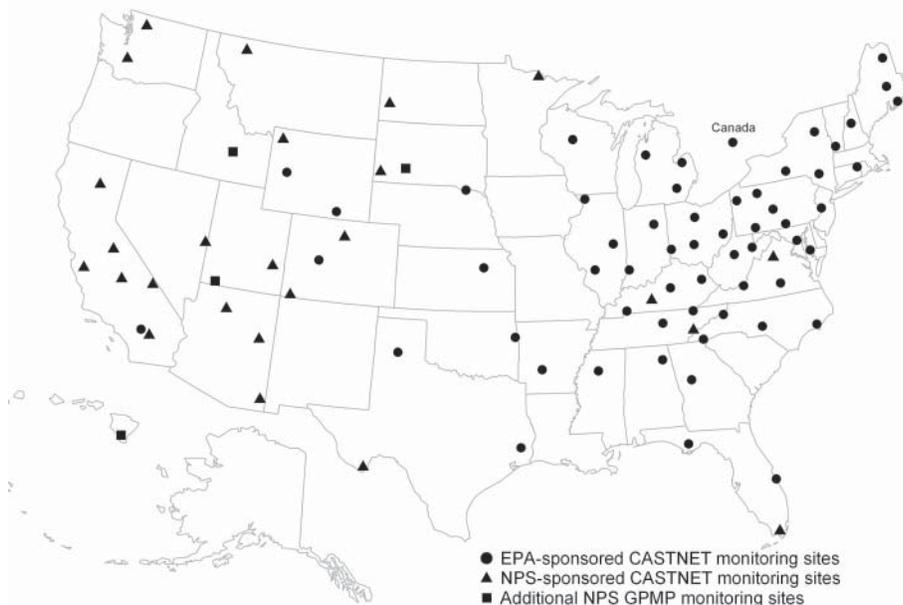
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CASTNET Monitoring Program Locations



EPA Clean Air Status and Trends Network
(<http://www.epa.gov/castnet>)

NPS Gaseous Pollutant Monitoring Program Network
(<http://www2.nature.nps.gov/air/monitoring/index.cfm>)