RICHARD MARCHBANKS/NOAA

AIRBORNE NOAA chemist Andrew Langford monitors a light-scattering instrument that is mapping aerosol and ozone plumes around Sacramento from an agency plane in June 2010. The plane is unpressurized, so personnel must wear cannulas to get oxygen.

MONITORING THE SKIES

FIELD CAMPAIGNS target the chemistry behind air quality and climate

JYLLIAN KEMSLEY, C&EN WEST COAST NEWS BUREAU

SCAFFOLD TOWERS sprang up in spots around California in late spring of last year. Up to six stories tall, they were soon festooned with mysterious-looking scientific gadgets and tubes. At their bases emerged trailer encampments loaded with additional instruments. Aircraft decorated with odd protuberances flew in, and the research vessel *Atlantis* cruised the coastline, laden with its own array of analytical devices.

Behind all this activity was a coordinated set of three field campaigns to analyze physical and chemical processes in the atmosphere. In all the debates over pollution, air quality, and climate change, one thing is undeniable: If we don't know what chemicals are put into the atmosphere, whether from nature or human activity, and how those chemicals react with each other, we won't be able to predict their effect on air quality and climate. Air analysis therefore plays a basic and critical role in understanding atmospheric processes and predicting their outcomes, both short and long term.

Scientists use two methods to analyze the air. In one technique, they place sensors in certain locations to look for specific things—say, ozone, methane, or particles of a specific size—and track them long term. But such an approach is necessarily selective because it would be prohibitively expensive to look for everything in the air all the time, says Eileen McCauley, manager of atmospheric processes research at the California Air Resources Board (CARB), part of the state's Environmental Protection Agency.

Even so, sometimes scientists need to try to measure everything, if only for a few weeks. For example, this kind of big-picture strategy is required to determine not just the concentration of particulates in the air but also their size distribution, what chemicals they start as, what gets added to them over hours or days, and whether they'll absorb or reflect sunlight or seed clouds. Such is the goal of atmospheric monitoring field campaigns, including the three that took place in California and Mexico in May and June 2010. Early results from the campaigns indicate that there are still new things to learn in our ever-evolving understanding of the atmosphere.

Although field campaigns study emissions and chemistry in a particular spot, their results can reveal poorly understood as well as entirely new atmospheric chemistry with repercussions beyond the local area, says David D. Parrish, who heads the tropospheric chemistry program within the National Oceanic & Atmospheric Administration's (NOAA's) Earth System Research Laboratory.

During a 2006 campaign in coastal Texas, for example, researchers discovered that chloride ions in aerosolized sea salt can react at night with N_2O_5 to form $ClNO_2$. In the morning, the $ClNO_2$ is photolyzed to form NO_2 and $Cl^•$, both of which are involved in photochemical ozone production. This chemistry has since also turned up inland, perhaps driven by HCl emissions from burning coal, biomass, and waste, as well as industrial processes such as semiconductor and petroleum manufacturing (C&EN, March 15, 2010, page 10).

DATA FROM field campaigns can also drive air-quality policy decisions. A decade ago, Houston was battling increasing levels of ozone, which forms from photochemical reactions of hydrocarbons or NO_x compounds, and Texas was considering what Parrish calls "draconian" controls on NO_x emissions. An air-quality field campaign in 2000, however, demonstrated that amounts of volatile organic compounds emitted from petrochemical refineries in the Houston Ship Channel region were 10 to 100 times as high as previously realized. Ozone levels could therefore be reduced by a less expensive combination of hydrocarbon controls and more moderate NO_x controls, the state concluded.

THE RECENT CALIFORNIA campaigns brought together a multitude of scientists and analytical techniques from universities, companies, and government agencies to tackle a host of scientific problems. The main focus of one of the campaigns, the Carbonaceous Aerosols & Radiative Effects Study (CARES), in the Sacramento area, was to look at the evolution of various carbon-rich aerosols. Such aerosol particles can be directly emitted from vehicles, industrial processes, and biomass burning, in which case they're called primary aerosols. Alternatively, they can be nucleated from gaseous chemicals, in which case they're known as secondary organic aerosols (C&EN, July 12, 2010, page 32). Both kinds of aerosols are of interest for air quality and human health because they are respiratory irritants and can cause cardiovascular problems. They also play a role in global climate by absorbing or scattering sunlight, depending on their composition, and seeding clouds.

"One of the least understood parts of air-quality and climate models is aerosols," says Rahul Zaveri, a chemical engineer at Pacific Northwest National Laboratory and the lead scientist for CARES. "We wanted to measure all the different types of aerosols and precursor gases, see what's partitioning between the gas and particulate phases, and characterize the optical and cloud-nucleating properties of freshly emitted and cloud-nucleating aerosols," he says, noting that such data could improve atmospheric modeling.

CARES placed researchers at two ground sites—one in Sacramento and the other in Cool, a community in the foothills of the Sierra Nevada Mountains. Scientists were therefore able to monitor both precursor gases and aerosol particles as they were emitted in Sacramento, then were able to see how the aerosols evolved and aged as the air was transported north and east to Cool. Instruments aboard aircraft based at the Sacramento airport provided additional, complementary data from higher in the atmosphere. The Department of Energy sponsored CARES and provided most of its roughly $2.5 million budget.

A second campaign, CalNex, involved two ground sites—one at Pasadena in the coastal Los Angeles Basin and the other at Bakersfield in the inland San Joaquin Valley. *Atlantis* cruised along the coast from San Diego to the Los Angeles harbor, and then up to San Francisco Bay and Sacramento. Research aircraft, based near Los Angeles in Ontario, flew missions over the ocean, Los Angeles Basin, San Joaquin Valley, and east to Nevada. NOAA provided $12.6 million, and CARB gave $5 million for CalNex; some scientists also used their own grant money to participate.

One of the goals of CalNex was to assess the emissions inventories for the area; another was to study aerosol chemistry, akin to CARES. A third goal had regulatory overtones: to illuminate the differences between air in Los Angeles and San Joaquin Valley. Although state pollution controls have worked well to reduce ozone levels in Los Angeles Basin, those same controls have not led to improved air quality in San Joaquin Valley. No one understands why not, says Ronald C. Cohen, director of the Atmospheric Science Center at the University of California, Berkeley, and one of the principal investigators at the Bakersfield site.

Hypotheses for the underlying reasons include reactive aldehydes emitted from open piles of wet, fermenting cattle feed and emissions from farm vehicles or growing plants. More data from the valley and a comparison to those collected for Los Angeles Basin should help clarify the source of the problem and direct future control policies, Cohen says, noting that a solution might be as simple as covering feed corn to keep it dry.

CalNex also followed up on a 2009 California regulation requiring ships to switch from bunker fuel—what remains of crude oil after gasoline and distillate fuel oils are extracted—to low-sulfur diesel within 24 nautical miles of the coast. CalNex worked with both a second research vessel and a Maersk Line cargo ship, tracking the ships as they switched fuel types to see how emissions changed.

The third field campaign, Cal-Mex, focused on atmospheric chemistry in the California-Mexico border region. Emissions in the area come from motor vehicles, including a high proportion of older, more pollution-prone vehicles; power plants; industrial facilities; agricultural operations; mining; dust from unpaved roads; and open trash burning, says Luisa T. Molina, president of the Molina Center for Energy & the Environment, in La Jolla, Calif., and leader of the Cal-Mex campaign.

Scientists involved in Cal-Mex planned to characterize emissions in the area, including the identity, concentrations, and variability of the gaseous chemicals and particulates involved. They also wanted to look at the transport and chemical processing of emissions. The effort included a central ground site, several downwind sites, and mobile sites—vans circulating in various locations. The project's $1.2 million budget came from the U.S. Environmental Protection Agency, the National Science Foundation, and the Mexican Ministry of the Environment.

THE THREE CAMPAIGNS collectively brought together a dizzying array of analytical instrumentation. These instruments measured light absorption, light scattering, fluorescence, chemiluminescence, particle hygroscopicity, and other properties. Researchers also used ion and other chromatography and mass spectrometry to help identify atmospheric components.

DESTINED FOR ORBIT

Satellite Will Eye Earth's Aerosols

Another tool will be added to the atmospheric-monitoring toolbox on Feb. 23, when a new Earth-observing satellite, *Glory,* is set to launch from California's Vandenberg Air Force Base. *Glory* includes two instruments, one of which will be the first in space to measure atmospheric aerosol morphology and composition. Data from *Glory* should yield a better picture of global and seasonal variability of aerosol properties.

Glory's Aerosol Polarimetry Sensor (APS) will collect visible and infrared light scattered from aerosols and clouds and determine the size, shape, and refractive index of particles. From that information, scientists hope to extract the composition and possibly even the origin of particles, although getting clear information on heterogeneous, nonspherical aerosols might be challenging, says Michael I. Mishchenko, a scientist at the National Aeronautics & Space Administration's Goddard Institute for Space Studies. Nevertheless, APS will provide a new global view of aerosols and their role in Earth's climate.

Glory's second instrument is the Total Irradiance Monitor (TIM), which will continue a 32-year, multisatellite record of monitoring total solar irradiance and its short- and long-term fluctuations.

Glory will join what's known as the "A-Train," a current set of four satellites containing 15 separate instruments that orbit together to provide coordinated and complementary views of Earth's atmosphere and surface: *Aqua* measures temperature, water vapor, and rainfall; *CloudSat* and *Calipso* use laser and radar instruments to map the vertical distribution of clouds and aerosols; and *Aura* produces vertical maps of some greenhouse gases and other atmospheric chemicals.—JYLLIAN KEMSLEY

Additional instruments collected meteorological data, such as temperature, humidity, and wind speed and direction.

Scientists used the technology to measure primary pollutants, such as CO_2, NO_x compounds, NH_3, SO_2, organic compounds, and black carbon particles, as well as secondary species formed from atmospheric reactions, including O_3, formaldehyde, sulfate, radical species, and aerosols. They also used trace metals in the air to track emissions sources—vanadium comes from ship combustion and potassium from biomass burning, for example. "If you can measure it, we probably looked for it," says Jochen Stutz, a professor of atmospheric and oceanic sciences at the University of California, Los Angeles, and one of the lead scientists at the CalNex Pasadena ground site. Some analysis happened in real time, even during takeoffs and landings on vibrating airplanes. In other cases, samples were collected for later analysis.

The assortment of techniques was designed to be complementary and, in some cases, redundant, Stutz says. If one person sees something odd or unusual in their data, it can be hard to determine whether it was an instrument issue or an actual atmospheric phenomenon. If multiple instruments pick up something similar, however, that provides the reproducibility needed for scientific rigor. Data sharing began almost immediately—a trailer at the Pasadena site was plastered floor to ceiling during the campaign with preliminary graphs—and various teams of scientists met frequently during the campaigns to go over early results. Periodic data analysis workshops continue to encourage communication and collaboration.

It will take some time for the scientists involved in CARES, CalNex, and Cal-Mex to learn all they can from the data collected, but some early results presented at the American Geophysical Union meeting in San Francisco in December 2010 give a taste of the findings to come.

Patrick Veres presented measurements of airborne organic and inorganic acids taken during CalNex, when he was a graduate student at the University of Colorado, Boulder, working in collaboration with the Cooperative Institute for Research in Environmental Sciences (CIRES) Fellow Joost de Gouw. Organic acids, in particular, are something that atmospheric chem-

INSTRUMENTATION

Aerodyne Spectrometers Ease Particle Research

Research into atmospheric aerosol particles has accelerated in the past decade, propelled in part by advances in reliable and portable instruments from Billerica, Mass.-based Aerodyne Research.

According to Charles E. Kolb, president of Aerodyne, about 100 of the firm's aerosol mass spectrometers (AMSs) are now used around the world. Some are so small they can be deployed on airplanes, installed in mobile labs, or shipped off and set up in the Siberian tundra to evaluate real-time atmospheric conditions. Larger lab-based instruments can be used for in-house atmospheric chamber studies.

"The first academic paper citing our AMS appeared in 2000," Kolb says. And since then, the firm's AMSs have received more than 400 additional citations, he says. Many of the articles examine not only the role of particles in cloud formation but also their impact on the phenomenon of global warming.

Depending on their size and sophistication, the instruments cost between \$150,000 and \$450,000, Kolb says. The more expensive versions of the firm's AMSs come equipped with a time-of-flight mass spectrometer from the German firm Tofwerk for detailed particle-size and composition studies.

Key to Aerodyne's spectrometers is a patented nozzle system, known as the aerodynamic lens, that collects a beam of fine particles from the air and feeds it into the AMS for analysis. Aerodyne licensed the technology from its developer, Peter H. McMurry, a mechanical engineering professor at the University of Minnesota, Minneapolis.

Twenty years ago, studying such atmospheric particles involved collecting them on a filter, scraping them off, and then analyzing them, Kolb says. Results took days and the analyses were often inaccurate because the process didn't capture many volatile elements. The aerodynamic lens, along with today's faster mass spectrometers, allows more complete capture of volatile elements and delivers results in real time.

"Particle collection is critical" in atmospheric research, notes Richard C. Flagan, a professor of environmental science and engineering at California Institute of Technology. The aerodynamic lens is an "elegant and simple" solution to collecting particles and an important element in the commercial success of Aerodyne's AMSs, he says. Researchers have used instruments from other makers, such as TSI and Aerosol Dynamics, for particle research, Flagan adds, but because Aerodyne's AMSs are relatively easy to operate and widely used, new researchers "can get started fast" with the firm's instruments.

Aerodyne started out in 1970 as a contract R&D firm that worked for the U.S. military solving problems such as tracking rockets and space vehicles in Earth's atmosphere. Kolb, who has a Ph.D. from Princeton University in physical chemistry, joined the firm a few years later.

Kolb helped expand the firm's work into atmospheric chemistry, combustion chemistry, and pollution formation. He became president of privately held Aerodyne, which he now owns, in the mid-1980s.

Aerodyne still does some of the tracking research it was founded to do, but it now has \$18.5 million in annual revenues, mostly from atmospheric-chemistry-related work that Kolb calls his "passion." About half of the firm's revenues come from the sale of instruments including AMSs.

Today, the firm employs about 60 people, including 40 Ph.D.s, Kolb says. It also hosts collaborators, including postdoctoral researchers, visiting professors, and national lab researchers.

The firm not only does contract research with academic partners but also works with a number of government agencies to accurately track and analyze airborne particles with the aim of ultimately helping reduce man-made pollutants. "Important problems are complicated," Kolb says. "We need special tools, facilities, and the right people to solve them."—MARC REISCH ists don't understand well, Veres says. Results from negative-ion proton-transfer chemical-ionization mass spectrometry demonstrated that rapid photochemical production of compounds such as formic, acrylic, pyruvic, and isocyanic acids took place in Pasadena air during the campaign. The findings point to a need to reevaluate modeling of organic acids in the atmosphere and the role they might be playing in secondary organic aerosol formation, Veres says.

ANOTHER PRESENTATION, by NOAA and CIRES research scientist Harald Stark, looked at nighttime gas-phase photochemical reactions. Aboard the NOAA WP-3D aircraft, Stark and colleagues usually use an actinic flux spectroradiometer to measure the intensity of sunlight, and the aircraft has detectors on the top and bottom of the plane to measure both direct and reflected light.

At one point during a night flight, however, one of the pilots asked Stark whether he could detect anything when the plane flew over a brightly lit stadium. Stark decided to turn on the instrument and found that he could detect stadium and city lights. He also found that the lights have wavelengths and intensities that can drive $NO_3^{\bullet}$ photolysis, reducing nighttime levels of the radical in the Los Angeles atmosphere by as much as 7%. The consequences, chemically, are increased primary and decreased secondary pollutants, plus a shift in NO_x equilibria that could result in higher daytime ozone concentrations. Different types of street lamps give different photolysis rates, Stark calculates. As cities and states grapple with meeting ever-stricter air-quality controls, nighttime lighting might be another factor to consider, Stark says.

CARES, CalNex, and Cal-Mex won't be the last field campaigns, of course. Already in the planning stages is a study in the Midwest to look at short-lived climate-forcing agents such as black carbon and some halocarbons. "Perhaps if we control those, then we can control or at least abate climate change more rapidly than we can if our only target is CO_2 emissions," NOAA's Parrish says.

Another upcoming campaign aims to look at secondary organic aerosol formation in the southeastern U.S. in the summer, when there are strong biogenic carbon emissions. Although researchers have historically viewed secondary organic aerosols as anthropogenic in origin, isotopic data indicate that the carbon in aerosols comes from living plants rather than fossil fuels. "In the southeastern U.S., we can go to a location where there are strong biogenic emissions and not much anthropogenic and begin to sort that out," Parrish says.

The latest campaigns also signal a shift in thinking among atmospheric scientists and regulators, says CARB's McCauley. Rather than seeing air quality and climate as things to be studied separately, people are recognizing that the two are interconnected and need to be considered jointly. And "the atmosphere is so incredibly complex" that understanding its physical and chemical processes will be an ongoing effort, McCauley says. ■