Tracking down the menace in Mexico City smog

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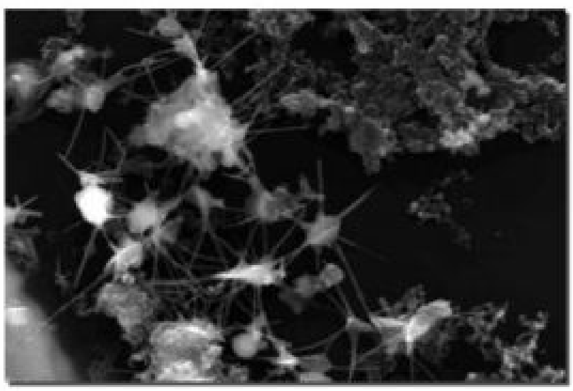

Needle-like particles containing lead, zinc, and chlorine were among the several forms of metallic particles collected at the T0 site during the MILAGRO Campaign. Credit: Brian Moffet, Lawrence Berkeley National Laboratory, MILAGRO Campaign

A new report by scientists who are part of the international MILAGRO Campaign indicates that some of the most harmful air pollution in Mexico City may not come from motor vehicles but instead originates with industrial sources – and that the culprit may be garbage incineration.

The MILAGRO Campaign (Megacity Initiative: Local and Global Research Observations) monitored air quality in the Mexico City Metropolitan Area throughout the month of March, 2006. Headed by the

Molina Center for Energy and the Environment in La Jolla, California, MILAGRO – the acronym means "miracle" in Spanish – is an international scientific collaboration supported by the U.S. Department of Energy, the National Science Foundation, NASA, and other agencies in the U.S., Mexico, and Europe. Five DOE labs contributed to the study, including Lawrence Berkeley National Laboratory.

Beamline 11.0.2 at Berkeley Lab's Advanced Light Source (ALS) was used for scanning transmission x-ray microscopy (STXM) of aerosol particles, in work led by Mary Gilles of the Lab's Chemical Sciences Division. Ryan Moffet, now a Seaborg Postdoctoral Fellow at Berkeley Lab, was a member of a team monitoring a rooftop collection station at the Mexican Institute of Petroleum in the northern part of Mexico City, a site designated T0 (T-zero); the evidence gathered there was among that analyzed by Gilles and her colleagues.

"The T0 site is in the industrial heart of the city, but the neighborhood is also a densely populated residential area. Children who live here have 11 percent higher levels of lead in their blood than children from the opposite side of town," says Moffet, who was a doctoral student at the University of California at San Diego during the MILAGRO Campaign. Moffet is first author of a report in Environmental Science & Technology on the research at the T0 site. "Although researchers had noted the high levels of lead, no one before us had analyzed the aerosol compounds for clues to its origins."

Airborne particles of varying size, shape, and chemical composition are an important constituent of the smog in Mexico City, one of the largest cities in the world and one of the most polluted. The aerosols come from motor vehicles, industries, and residences; their sources include the burning of fossil fuels and biomass, and industrial emissions. Because of the city's high elevation in a basin walled by mountains, air pollution in the metropolitan area is often trapped in the basin and chemically altered by ultraviolet radiation and other processes.

Metal-containing aerosols in particular are implicated in adverse effects on health. Size and solubility affect their mobility in the body; for example, small particles with compact shapes penetrate deep into the lungs, where they are likely to stay. Soluble compounds readily enter the bloodstream. And a metal's oxidation state affects its toxicity.

Measuring airborne particles

Many different instruments were used to collect the aerosol samples at several sites: one, a Davis Rotating Drum, captured particles of three different sizes on Teflon tapes; another, a Time Resolved Aerosol Impactor, collected single particles. In situ measurements were made with an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), which sucked particles into a vacuum chamber, determined their size, and analyzed the mass spectra of their constituent chemicals on the fly, by zapping each with a laser pulse.

Spectra from tens of thousands of particles were stored for later analysis. The rotating drum and ATOFMS yielded time series, allowing the researchers to determine how size, shape, chemical composition, and the changing mix of chemicals in the aerosol particles varied with the time of day and other factors like weather.

"When we started the study, we were interested in what fraction of the aerosols was from traffic, since many scientists believed that traffic was the worst source of the pollution," says Moffet. "But when I looked at the mass spectrometry data, the first thing that jumped at me was the lead spikes. We wondered what the source of the lead was. Lead has been completely banned in gasoline sold in the city since 1997, which meant the aerosols were coming from something else."

Many anthropogenic (human caused) sources contribute to the metal-containing aerosols in Mexico City air. Nickel and vanadium are associated in particles from fossil-fuel burning. Smelting and other metallurgical processes produce emissions rich in heavy metals. Burning waste emits particles containing lead, zinc, and many other metals, plus chlorine. Activities like construction and traffic stir up dust and send large metal-containing particles into the atmosphere. All these sources can be identified by their characteristic compositions.

"In many of the spikes the lead was associated with chlorine and zinc," Moffet says. "The nature of the chemical associations of these metals could give us valuable clues as to the origin of the particles and their subsequent processing."

Mass spectrometry results were available on the spot, while additional informative data came from later laboratory analyses, including proton-induced x-ray emission and computer-controlled scanning electron microscopy directed by Alexander Laskin at the W. R. Wiley Environmental Molecular Sciences Laboratory at DOE's Pacific Northwest National Laboratory in Washington State, the STXM studies by Mary Gilles at Berkeley Lab's ALS, and other researchers using additional techniques.

Narrowing the suspects

By comparing the mixing of lead, zinc, and chloride in the T0 particles to previous studies characterizing the sources of metal-containing aerosols, clues to the source of the Mexico City particles quickly emerged. Both nonferrous (non-iron) smelters and municipal waste incinerators emit particles that contain lead and zinc, and both have similar compositions – except that smelter particles do not contain phosphorus and chlorine, while incinerator particles do.

The particles that contained lead and zinc in the T0 aerosols did contain phosphorus and chlorine, and had other species in common with incinerator samples, including soot. Particles from smelting typically have more iron; moreover, smelter emissions do not have large amounts of chlorine but do have high concentrations of sulfates, which were missing in the T0 samples.

ALS beamline 11.0.2 helped further zero in on the chemical makeup of particles containing zinc. Incinerators produce metal chlorides, which in the atmosphere can react with acidic gases and become other species like nitrates: many of the zinc-containing particles from T0 were zinc nitrates, suggesting their origin in incinerator emissions. Zinc oxides were also among the particles collected at T0; nitrates, chlorides, and sulfates are partitioned on zinc oxide surfaces, and all are found in the lead and zinc-rich aerosols from T0.

The occurrence of lead and zinc particles at different times of day – and even different days of the month – added more evidence for incineration as the principal source of the airborne metals. On most days, metal-rich particles at the T0 site peaked early in the morning, as early morning air masses from the northeastern part of the city carried them to other neighborhoods. The lag time of metal nitrates behind metal chlorides matched the time needed for reactions with nitric acid in the air. Perhaps most telling, during the month-long collection, the lowest concentration of metal-rich particles occurred on a holiday weekend when most industrial processes were shut down.

The lead-bearing aerosol particles found in Mexico City are small, many of them needle-shaped, making them easy to inhale and likely to stay in the lungs. As time passes, the initial metal chlorides are converted to lead nitrates, which are soluble and readily enter the blood stream.

Can garbage incineration be unequivocally identified as the source of the worst pollution in the Mexico City Metropolitan Area? Not quite yet, says Moffet.

"At present the government is not keeping track of emissions from incinerators, and incineration is not even listed in the emissions inventory for the metropolitan area," he says, "although we saw garbage incinerators in the northern part of Mexico City. But even short of absolute proof of bad health effects, incineration – especially of discarded electronics, which are loaded with heavy metals and chlorine – is a dangerous process and a growing problem in developing countries."

Source: Lawrence Berkeley National Laboratory