PARTICULATE MATTER

# Getting a Handle on Air Pollution's Tiny Killers

Mention particulate pollution, and most people think of soot from smokestacks and diesel buses. But there is another source of particles in urban air that is just as important: gases and vapors that come from evaporated or partially burned gasoline and solvents in paints, among other sources. In the presence of sunlight, these gases react with nitrogen oxides and other chemicals in the air and condense onto bits of dust to form very fine particles. These create a major public health problem—and a vexing puzzle for scientists, who have been hard pressed to figure out how these particles form and interact.

Results on page 96 of this issue may dispel some of the uncertainty. A team of engineers and atmospheric chemists describes how they simulated particle-forming processes in the laboratory to devise a mathematical model that predicts how hydrocarbons from gasoline are transformed into particles. The work, by Jay Odum and others in John Seinfeld's lab at the California Institute of Technology in Pasadena, should help regulators get a better handle on how to reduce levels of fine particles, especially in areas where motor vehicles are a big contributor to air pollution. "It's a real move forward," says Roger Atkinson, an atmospheric chemist at the University of California, Riverside.

Researchers and regulators began paying close attention to fine particles in urban air some 5 years ago, when studies in cities such as Steubenville, Ohio; Provo, Utah; and Philadelphia showed that hospital visits for asthma and other respiratory illnesses rose and fell with the levels of these particles. On a smoggy day in Los Angeles, up to 20% of the mass of particulate matter of less than 2.5 micrometers in diameter can come from hydrocarbons in evaporated and burned gasoline, among other sources.

This summer, the U.S. Environmental Protection Agency (EPA) is planning to issue its first-ever limits on the levels of these particles, called PM2.5. But to come up with specific steps to meet those goals—proposed measures range from limiting backyard barbecues to fitting diesel vehicles with new emissions-control equipment—regulators need good models for predicting the contribution of different hydrocarbon compounds in particle formation. That is what the Seinfeld group's work may help them to do.

In earlier laboratory work with single hydrocarbons such as xylene, the researchers developed the first equation to describe accurately the process by which hydrocarbons oxidize and condense on seed particles: More condense if there is a higher mass of seed particles in the air. In the lab, they also found that different hydrocarbons did not interact much, so the contributions of the various compounds in the test chamber could simply be added up to predict the total level of particles. Finally, they noticed that in a mixture of hydrocarbons containing heavier aromatics and lighter compounds, only the aromatics seemed to attach themselves to soot. Together, these findings made it possible for the researchers to predict the amount of particles that would form from hydrocarbons, at least in the neat world of a test chamber.

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**Dark matter.** On a smoggy day in Los Angeles *(above)*, up to 20% of the fine particles in the air come from organic compounds condensing on bits of dust.

But that didn't mean their equations would work for the much more complex mixture of hydrocarbons in urban air. For that, the researchers decided to investigate particle formation from hydrocarbons in gasoline—a soup of hundreds of compounds that the researchers say serves as a good proxy for the cocktail of exhaust products, evaporated gasoline, paint solvents, and other human-made hydrocarbons in city air. "We [hoped that] if we could do two compounds, we would be able to do 200," Odum says.

The researchers tested 12 different kinds of gasoline (each with different mixtures of aromatics) in a gigantic smog chamber—a Teflon bag about the size of a two-car garage, which they filled with seed particles (ammonium sulfates); the gasoline of interest; nitrogen oxides; and a chemical called a photoinitiator, which gets particle-forming reactions started. While the bag baked in the sun, they sampled its contents at regular intervals with gas chromatographs and mass spectrometers to track the transformation of hydrocarbons into particles.

Through several test runs with the different gasolines, the researchers found that they could, indeed, predict from the gasoline's aromatic content the amount of particulate matter that would form. Moreover, just as with the simple mixtures of hydrocarbons tested in the lab, the contributions of the hundreds of hydrocarbons in gas turned out to be additive.

Other researchers caution that Seinfeld's group still needs to show that its model will work with the whole gamut of particle-forming hydrocarbons in urban air, especially because in many eastern cities, compounds from pine trees and other vegetation can dominate. Still, "this is a clear breakthrough in our understanding," says Steven Japar, an atmospheric chemist at Ford Motor Co.

According to John Bachmann of EPA's Office of Air Quality Planning and Standards, the agency expects to use Seinfeld's results to improve its latest air-pollution models and to help figure out, for instance, whether gasoline with a lower aromatics content could help reduce PM2.5 in some areas. "These are the kinds of advances we really need [in order] to do a better job of modeling and specifying control alternatives," Bachmann says.

Seinfeld's group also found some unexpected good news. To reduce ground-level ozone, an important ingredient in smog, regulators in recent years have required gasoline manufacturers to remove some of the aromatics from their products. This has had the side benefit of cutting down on particulate matter. Being able to describe the links between gasoline and the formation of ozone and particles will be of great help in developing cost-effective pollution-control strategies, Bachmann says.

Seinfeld is now weaving this new hydrocarbon model into an overall computer model for urban airsheds—one that includes sulfates and nitrates, which also form particles in the air. He hopes that having cleared up this murky spot in the air pollution picture, the team will be able to bring the whole thing into sharper focus.

–Jocelyn Kaiser