I can see (more cl

early now

By Kimm Fesenmaier

Sitting in his office on an average Pasadena afternoon, atmospheric chemist John Seinfeld can glimpse the San Gabriel Mountains, a commanding reminder of the geological cards the L.A. Basin has been dealt. When he arrived at Caltech in 1967, there would have been few days when he would have been able to take in such a view—at that time, a pall of brownish-gray smog would have often obscured the mountains.

"If you were here in the late 1960s, the smog was pretty thick, and this was a calling card for Los Angeles," Seinfeld says. "Had I gone to another university as a faculty member, I probably never would have gone into this field." In fact, having recently completed his doctorate in chemical engineering at Princeton University, the young Seinfeld had never dabbled in environmental studies.

But when he arrived on campus, Caltech was already home to several leading researchers in the air-quality field who had been shaking things up—fighting industry and, in some cases, policy makers for a decade or more. (See "The Award Goes To," page 29.) After talking with some of them, Seinfeld joined the effort—and he's never looked back. Today, he and Caltech scientists such as Richard Flagan, Paul Wennberg, and Mitchio Okumura are carrying the air-quality torch forward, providing insight into the atmosphere and the ways human activities affect it.

Indeed, it would be no exaggeration to say that the air we breathe today would be very different if not for the work that Caltech researchers have engaged in since the late 1940s. They have helped build the scientific foundation that has led policy makers to adopt everything from the first statewide air-quality standards and the original Clean Air Act, to that act's more recent revisions and to ever-stricter controls on factory and vehicle emissions.

A 30-BILLION-TON REACTOR

Before Caltech biochemist Arie Haagen-Smit started working on the air-pollution problem in 1948, no one even knew what smog was. Through a series of investigations, he showed that two of the products that come out of the incomplete combustion of gasoline in cars—volatile organic compounds and oxides of nitrogen—combine in the atmosphere in the presence of sunlight to produce ozone and other nasty by-products. He estimated that to make significant improvements to L.A.'s smog situation, nitrogen oxide emissions would need to be reduced by about 90 percent.

"It was a good starting point, but there is much more to the problem than he knew at the time," says Flagan, another chemical engineer whose research focuses on the control of air pollutants. "The basic chemistry gives you some clues as to what you need to do, but to know how far you need to go, you need to fill in the gaps in the science and then build models. Caltech's huge impact has been that of going beyond the science to the engineering of air quality—to actually understanding it well enough that you could start tweaking the system to start cleaning up the air."

It was this push toward a deeper understanding that led to Seinfeld becoming fascinated with the idea of the atmosphere as one big chemical reactor. It was also how he decided to start building a mathematical model of the air above Los Angeles—one that would incorporate emission levels and sources, as well as the details of the chemistry that was taking place, the atmospheric circulation patterns . . . the whole shebang. With his training as a chemical engineer, Seinfeld had plenty of experience describing what transpires in reactors. So he tapped into that experience to begin writing equations to describe the fundamental physics and the chemical reactions that take place in L.A.'s atmosphere.

It was Glen Cass (PhD '78), another young Caltech researcher at the time, who ended up doing the grunt work of determining everything that might contribute to emissions throughout Los Angeles—from oil refineries and factories to diesel trucks and automobiles. Chemical engineer Sheldon Friedlander worked out a way to verify those inventories—determining where smog was likely to be coming from based on existing data about atmospheric chemical composition.

Seinfeld combined all of their efforts and everything that was known of atmospheric chemistry into the first model of an urban atmosphere—the grandfather of the models that all states are required by the federal Clean Air Act to use today in planning for air-pollution control.

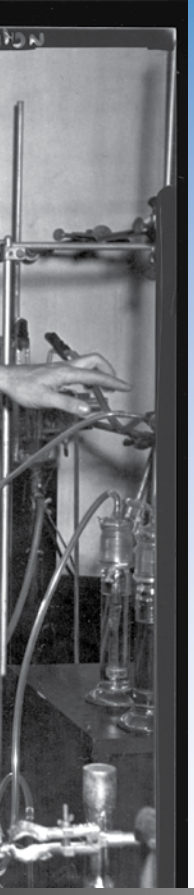
Even before the modeling work truly began, Seinfeld, Friedlander, and their colleagues knew they would need to bring more depth to the pool of existing knowledge about atmospheric chemistry. Take aerosols, for example. In the early 1970s, only basic size and composition information was known about these suspensions of minuscule particles in the air, which are largely responsible for the obscuring haze of smog. Today, researchers know that aerosols are harmful to human health, affect global climate by reflecting solar radiation, and are incredibly complex. "The particles everywhere on Earth are little microscopic chemistry laboratories," Seinfeld says. "They contain a kitchen sink of chemicals."

Aerosols fall into a couple of categories—those emitted directly into the atmosphere and those, called secondary aerosols, that form after emissions react chemically with oxidants like the hydroxyl radical and ozone in the atmosphere. Secondary organic aerosols, a subclass of secondary aerosols, form when oxidized organic gases glom onto particles. These carbon-containing compounds make up roughly half of all aerosols in the atmosphere, yet researchers are still trying to work out all of the molecular details and the life cycle of these particles.

From the beginning of their efforts, Seinfeld and his colleagues knew that in order to investigate aerosols, they needed to find new experimental methods to study what was actually happening to particles in the air. "You can't study the chemistry of the air when it is flowing by," he says. "You measure it at one point, and then it is gone."

Above: Caltech biochemist Arie Haagen-Smit, known as the father of air-pollution control, in the lab.

Below: John Seinfeld, Richard Flagan, and their colleagues inside the new atmospheric chamber in the Linde + Robinson Laboratory.



And so he began using an outdoor reactor created by Friedlander—an atmosphere in a bag, if you will. For about 15 years, Seinfeld, Flagan, and their students ran experiments on the roof of the Keck building to determine the chemistry of trapped particles. Pumping huge Teflon bags full of carefully selected gases, they exposed the bags to sunlight and studied the chemical changes that took place over time.

Later the outdoor experiments were enclosed, and the group spent a decade using that facility on the roof of the Keck building, jump-starting the chemistry with artificial sunlight. Today, these so-called chamber experiments have a shiny new home in the Linde + Robinson Laboratory, and multiple researchers use the technique to study atmospheric chemistry.

This approach may be commonplace now, but it was Seinfeld and his colleagues who were first to use these chamber experiments, which also allowed them to become the first to reveal the mechanism by which some volatile organic compounds—those that evaporate quickly and easily at regular temperatures—become less volatile and condense onto atmospheric particles. More recently, his team has been investigating organic compounds called alkanes, which are emitted in combustion processes. The team is trying to trace the various chemical pathways that these alkanes and their oxidized products follow so as to end up as aerosols.

WHERE DOES HE GET THOSE MARVELOUS TOYS?

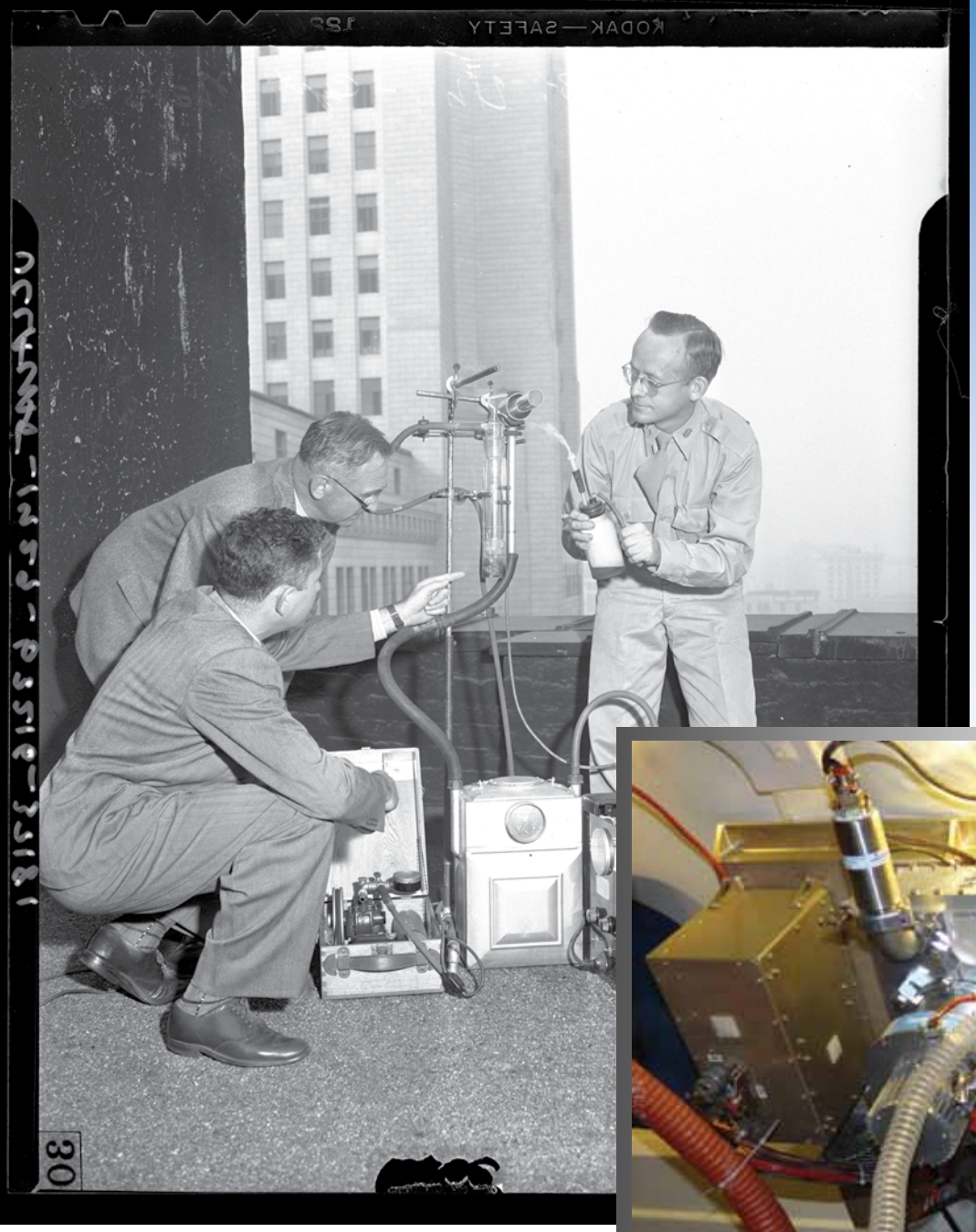
To track the molecular details of the reactions that take place in chambers or in the atmosphere, researchers need quality analytical tools. Making and improving such devices is the forte of Flagan and environmental scientist Paul Wennberg.

"Much of what I've done over the years has been focused on questions of getting data where we couldn't get it before," Flagan explains. He devised the first scanning mobility particle sizer (SMPS)—an instrument that measures minute aerosol particles in the air—while teaching an aerosol-measurements laboratory course at Caltech in the mid-1980s. "One day I gave my students a lecture on an instrument that didn't exist," he laughs. "I had them using it two weeks later." Today, the SMPS and its descendants are used by researchers around the world.

For their part, Paul Wennberg and his students have been building specialized mass spectrometers to analyze the chemistry of the atmosphere both in chamber experiments and out in the field. They are able to charge, or ionize, fragile gas molecules in the air, rather than needing high-energy electrons, which is the norm for mass spectrometry. "If we used the standard technique on these atmospheric gases, we'd end up with an uninterpretable mess," Wennberg says.

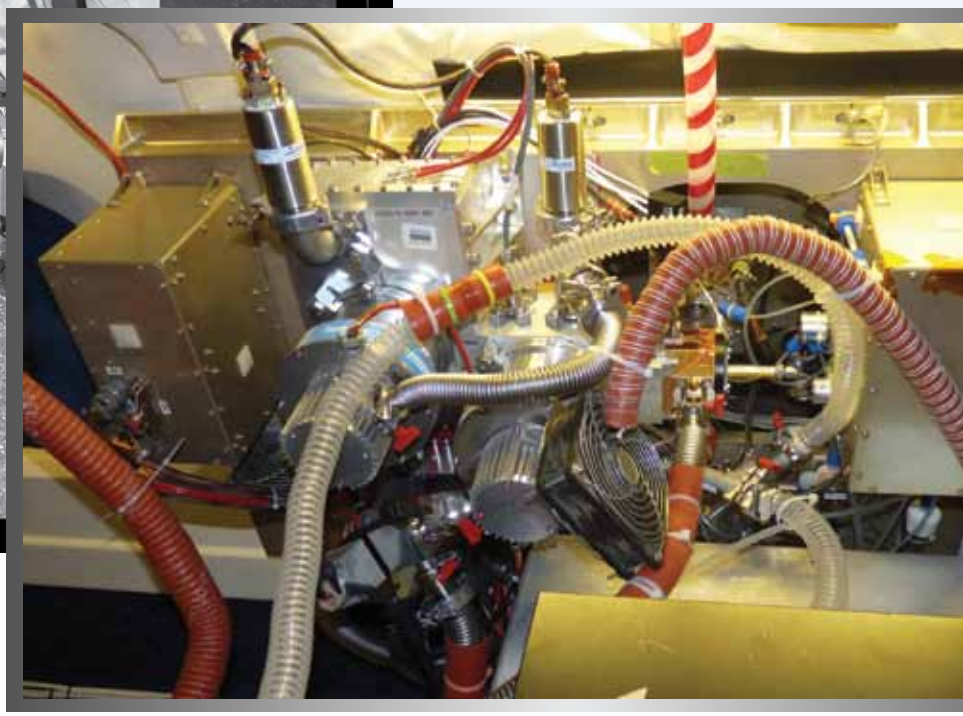
Wennberg and Seinfeld have used the mass spectrometers to study isoprene—the most abundant nonmethane hydrocarbon in the atmosphere, which is only emitted by plants. The chemistry of isoprene and related compounds is responsible for the haze and pollution of Atlanta and other cities in the Southeast. Using the new analytical methods developed in Wennberg's laboratory, the researchers discovered that the cascade of chemical changes triggered by the oxidation of isoprene in the atmosphere leads to the formation of epoxides. Chamber experiments revealed that these epoxides act as nature's glue, sticking to particles and producing secondary organic aerosols.

This summer, one of Wennberg's mass spectrometers was deployed on a National Science Foundation/NASA survey to look at air chemistry in the southeastern United States. His group has also deployed instruments in California's Sierra Nevada to study the air upwind of Sacramento. As Wennberg explains, this kind of fieldwork is one of three legs of atmospheric chemistry research: "First, you do a series of



hydroxyl radicals and nitrogen dioxide are critical molecules in the reactions that create ozone.

Okumura and Sander used an advanced chemical reactor at JPL to measure the rate of the reaction. At Caltech they used a relatively new analytical method, called cavity-ringdown spectroscopy, to observe the products as they were being formed. They could then measure how the amounts of nitric acid stack up against a less-stable product of the reaction of nitrogen dioxide and the hydroxyl radical, called HOONO (pronounced WHO-no). Rather than removing the reactants from the ozone cycle, HOONO dissociates and puts the reactants back *into* the atmosphere. The scientists determined how much HOONO was being produced but



controlled laboratory experiments. Then you plug your findings into a large model of the atmosphere and the chemistry within it. Finally, you go into the field to test if your description of the chemical environment is accurate."

Chemical physicist Mitchio Okumura uses ultrasensitive laser techniques in laboratory experiments that quantify key steps in the individual chemical reactions included in large models of the atmosphere. He and his colleagues also use quantum chemistry techniques to ensure that they understand the detailed molecular basis for each reaction. "That way," he says, "it's not just that we measure a number but that we know *why* it's that number."

In a study published in 2010, Okumura and his JPL collaborator Stan Sander (MS '75, PhD '80) were able to use these techniques to characterize the different pathways nitrogen dioxide and the highly reactive hydroxyl radical can take in the atmosphere. They examined a key reaction that produces nitric acid, a relatively stable molecule that essentially takes its reactants—i.e., the hydroxyl radical and nitrogen dioxide—out of play in the atmosphere. It's an important reaction in terms of reducing air-pollution levels because, left to their own devices, not accounted for by then-current models, suggesting that the models used to predict air quality could have been underestimating ozone levels by between 10 and 15 percent for the most polluted areas of Los Angeles on the most polluted days.

IT'S A SMALL WORLD, AFTER ALL

The combined product of these and many other efforts on campus has been the piecemeal creation of a much clearer picture of the atmospheric dynamics in the Los Angeles Basin.

That is not to suggest the air-quality problem is now solved. Take Los Angeles, for instance. It consistently earns top billing on the list of cities with the filthiest air. And the California Air Resources Board estimates that about 9,000 Californians die prematurely every year due to exposure to fine particles in the air.

But to be fair, Los Angeles is at a significant disadvantage. It has all of the necessary ingredients to whip up a particularly bad batch of air, what with its sunshine and its position in a basin that's shaped something like a bowl with an inversion layer for a lid, trapping smoggy air up against those commanding mountain ranges. Still, it's not all about geography: the iconic Angeleno obsession with cars and with shipping goods is also part of the recipe.

That said, Los Angeles is still a great example of how far we've come as a country in terms of air quality. Back in the 1940s, for instance, the air in Los Angeles was toxic, and air-quality standards were unheard of. Factory and refinery emissions were just starting to be regulated. People burned garbage in their backyards. No one knew that the exhaust spewing from tail pipes contributed to smog. What people *did* know was that the air made their eyes water, smelled slightly of bleach, ruined cherished views, damaged plants, and seemed to eat holes in rubber. Ah, the good old days.

By 1976, the first year for which detailed ozone air-quality data are available, the South Coast Air Quality Management District reported that ozone measurements exceeded health advisory levels on 166 days. There was obviously room for improvement: By 2010, there was not a single day when the ozone reached such levels.

Today, Caltech's air-quality researchers know they can't rest on their laurels; they also know they no longer have the luxury of focusing solely on the Los Angeles Basin.

"Back in the days of Haagen-Smit, one thought of air pollution as being confined to a city," Seinfeld says. "We've learned over the years that the atmosphere is in a sense one big backyard. Emissions from Asia are routinely sensed crossing the west coast of the U.S., and likewise emissions from the U.S. can be tracked in Europe. So we have had to broaden the focus of our research accordingly."

The global focus is especially important when looking at the link between air particles and global climate. After all, water droplets condense on particles in the air to form clouds. In fact, if our atmosphere were devoid of particles, Earth would have no clouds. And since clouds reflect about 20 percent of incoming solar radiation, both the planet and its climate would be drastically different without them.

Scientists still don't understand precisely how particles and clouds—those diaphanous, ever-changing players in the water cycle—interact with one another, nor how that intricate dance influences climate. What will happen to Earth's clouds, for instance, if more particles enter the atmosphere as a result of human activity?

One hypothesis holds that a higher number of particles will yield smaller cloud droplets, and that those smaller droplets will produce clouds that are more opaque and reflect more sunlight than clouds made of larger droplets.

Seinfeld and Flagan have seen this cloud-brightening effect from their flying laboratory, a Navy-owned plane now managed by the National Science Foundation. In a series of experiments, they collected samples of low-lying clouds—some visibly being fed exhaust from the smokestacks of large container ships and some not. Using a collection

Above: A 1945 demonstration of an electrostatic precipitator—a device once known as a "smog catcher."

Below: A chemical ionization mass spectrometer developed by Paul Wennberg's group. This instrument measures atmospheric acids and peroxides.

THE AWARD GOES TO . . .

It was inventor and long-time Caltech trustee Arnold Beckman (PhD '28) who originally pulled Arie Haagen-Smit—the biochemist known today as the father of air-pollution control—into the study of smog. Beckman, then chairman of the L.A. Chamber of Commerce's scientific committee, reached out to Haagen-Smit because of his skill in microchemical analysis, the study of minute concentrations of chemicals—a skill he developed working in plant physiology.

Beckman later said he felt guilty about pulling Haagen-Smit away from his research to work on the smog issue—but it was Haagen-Smit who couldn't walk away from the problem. As he said then, "The fly has trapped the fly paper." Once he figured out the chemical recipe for smog and determined that the mighty automobile was a major contributor to L.A.'s ever-dirtier air, he became embroiled in a battle with the oil and car industries, which tried to discredit his work. The plan backfired; he became more motivated to produce new and better scientific evidence, which eventually convinced first the state and then the federal government to establish air-quality standards and set controls for motor-vehicle emissions.

For his work, Haagen-Smit was honored in 1974 with the first Tyler Prize for Environmental Achievement, an honor regarded as the highest distinction in environmental science, environmental health, and energy research. In 1995, Caltech geochemist Clair Patterson won the Tyler Prize for his work in investigating mineral isotope concentrations and his recognition that lead from man-made sources had been contaminating Earth's air, land, and water since the Industrial Revolution. That work, and his many testimonies to policy makers, led the United States to ban leaded gasoline in 1986, despite the vociferous objection of industry proponents.

This year, John Seinfeld became the third Caltech faculty member to receive the Tyler Prize. "When I began doing research on the atmosphere, I read Haagen-Smit's early papers and got to know him," Seinfeld says. "I never would have imagined at that time that the work I would do would someday lead to my recognition with the same prize that both Haagen-Smit and Patterson received for their work." e&s

of onboard analytical instruments, they measured everything from aerosol size and composition to the size, concentration, and chemistry of each cloud's droplets. Their results showed that the exhaust-filled clouds are usually brighter than the others, but not always—a testament to the maddening complexity of cloud physics.

Such studies are needed to inform global climate models, where the magnitude of global cooling from aerosols remains a focal point. To understand why it's so important, consider that the concentration of aerosols in the atmosphere has increased two or three times since the Industrial Revolution but has leveled off in recent decades. Since no one knows how large a cooling effect to attribute to aerosols, it's hard to say how global climate will respond in the future if they remain at roughly the same levels while greenhouse-gas emissions rise.

"We've come from something that was a regional issue and fairly exclusively a chemical problem—smog in L.A.—to one that is global and involves other disciplines like fluid dynamics, microphysics, and biology," explains environmental scientist Tapio Schneider, who directs the Ronald and Maxine Linde Center for Global Environmental Science. "As a result, we have to be much broader in our studies than in the past. We all have to work together to ultimately reduce uncertainties about climate and how it works."

Caltech is well equipped to do such interdisciplinary work, he says, noting that these problems are naturally appealing to researchers—not just because the science is fascinating and complex, but because it addresses important issues we can all relate to on some level.

"How can we improve the air we breathe? How much does cloud cover increase or decrease as Earth's climate warms? These are important problems that matter for society," he says. "And with the analytical instrumentation, computational tools, and satellite data that are now available, we, unlike past generations, have a good chance of solving them."

Schneider has good reason to feel that way. After all, for six decades now,

Caltech air-quality researchers have provided information used by policy makers to pass laws and update standards. "The focus of the research in air quality here at Caltech is on providing *the* best scientific basis for policy making," says Paul Wennberg. "It's focused on actually understanding the processes that are influencing atmospheric composition and then trying to better diagnose what the future might be if various decisions are made."

And the future, he says, is becoming clearer. E&S

***John Seinfeld** is the Louis E. Nohl Professor and professor of chemical engineering. His work is funded by the National Science Foundation (NSF), the Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA), the Office of Naval Research (ONR), and the National Oceanic and Atmospheric Administration (NOAA).*

Richard Flagan is the Irma and Ross McCollum–William H. Corcoran Professor of Chemical Engineering and professor of environmental science and engineering, as well as the executive officer for chemical engineering. His work is funded by the NSF, the DOE, the EPA, the ONR, NOAA, the Davidow Discovery Fund, and the Wallis Foundation.

Paul Wennberg is the R. Stanton Avery Professor of Atmospheric Chemistry and Environmental Science and Engineering. He receives funding from the NSF, NASA, the Camille and Henry Dreyfus Foundation, and the Davidow Discovery Fund.

Mitchio Okumura is a professor of chemical physics. His work is funded by the NSF, NASA, and the Camille and Henry Dreyfus Foundation.

Tapio Schneider is the Frank J. Gilloon Professor of Environmental Science and Engineering and director of the Ronald and Maxine Linde Center for Global Environmental Science.