

# Ozone Depletion's New Environmental Threat

By JANET RALOFF

The seeds of future stratospheric ozone depletion have already been sown. Not only have many of the ozone-attacking chemicals — such as chlorofluorocarbons — been irretrievably dispersed into the atmosphere, but the global rate at which such chemicals are emitted continues to grow annually. As a result, atmospheric chemists no longer talk about whether stratospheric ozone depletion will occur, but rather how much will be lost. In fact, the first apparent evidence that measurable depletion has already occurred was reported earlier this year (SN: 6/28/86, p.404).

Until recently, most predictions of the environmental hazards posed by this ozone depletion focused on the direct effects — such as human skin cancers — of bathing the earth's living things in a more intense field of solar ultraviolet radiation, or on the climate change that might occur as many of the ozone-destroying "greenhouse gases" initiated a global warming (SN: 5/18/85, p.308).

But the recent findings of a pair of atmospheric chemists have added two new dimensions. Declines in stratospheric ozone, they say, could exacerbate not only smog but also the acid rain with which urban areas may have to contend. Details of their preliminary estimates of such effects — based on air quality data from Philadelphia, Nashville and New York — were circulated in a discussion paper last week in Amsterdam at a meeting of the United Nations Coordinating Committee on the Ozone Layer.

One of the chief benefits of earth's stratospheric ozone layer is its ability to filter out much of the sun's biologically harmful ultraviolet radiation. But as air pollutants such as the chlorofluorocarbons CFC-11 and -12 reach the stratosphere and begin destroying that ozone, increased ultraviolet levels will penetrate to the lower atmosphere, the troposphere. There, the higher ultraviolet levels will begin driving subtle perturbations in tropospheric chemistry. A computer model to simulate those tropospheric chemistry changes and their potential impacts on the human environment is being developed by Gary Z. Whitten and Michael Gery of Systems Applications Inc. in San Rafael, Calif.

"We see about a 2 percent increase in smog ozone from a 1 percent decrease in stratospheric ozone," says Whitten. Ultraviolet increases the rate of ozone formation — a process that occurs only during daylight hours. Whitten says this means not only that there is the potential for an

overall increase in how much smog ozone is produced from reactions involving combustion pollutants such as hydrocarbons and nitrogen oxides ( $\text{NO}_x$ ), but also that ozone production will peak earlier in the day.

The latter could have serious implications for human exposure to ozone — the primary irritant in smog. Both smog production and human activity tend to be concentrated around industrial urban centers. If smog production peaked after many of the urban workers had commuted home to the suburbs, relatively few individuals would be exposed to the most intense smog. However, if, as the new Whitten-Gery simulations suggest, smog peaks in early to mid-afternoon, far more people could be exposed to serious smog-ozone pollution than most future projections would indicate.

But smog ozone is not the only hazard. Another potentially serious effect of more efficient smog ozone production is a dramatic increase in the production of hydrogen peroxide, a key chemical precursor to acid rain. The generation of hydrogen peroxide — also a product of ultraviolet-driven reactions between derivatives of hydrocarbons and  $\text{NO}_x$  — only occurs after ozone production shuts down, explains Whitten. "If the ozone process is still going when the sun goes down, you won't make any hydrogen peroxide. But if the ozone process finishes at noon," he says, "you have the whole rest of the day to make hydrogen peroxide."

Based on preliminary analyses of their data for Nashville, Gery says it appears there could be "about an 80 percent increase in hydrogen peroxide production for each 1 percent decrease in stratospheric ozone." Moreover, in contrast to smog ozone formation, the ultraviolet-induced changes in hydrogen peroxide are nonlinear — for each successive unit of stratospheric ozone depletion there is a disproportionately larger increase in hydrogen peroxide generation.

In their computer modeling calculations, Whitten and Gery tried to account for whether the city being studied would be enacting major controls on the emission of hydrocarbons and  $\text{NO}_x$  in the future to limit smog and acid rain production. But when they accounted for the increased tropospheric ultraviolet levels that would correspond to an 8 percent depletion of stratospheric ozone, Gery says, these cities all but lost the benefit of the expensive hydrocarbon- and  $\text{NO}_x$ -control measures in controlling acid rain precursors. Their analyses indicate that levels of hydrogen peroxide would increase dramatically — roughly to levels that



At right is a damaged leaf grown in an environment rich in sulfur dioxide and ozone. At left is a healthier leaf that grew in carbon-filtered air.

match those forming under today's lower tropospheric-ultraviolet levels and no emissions controls.

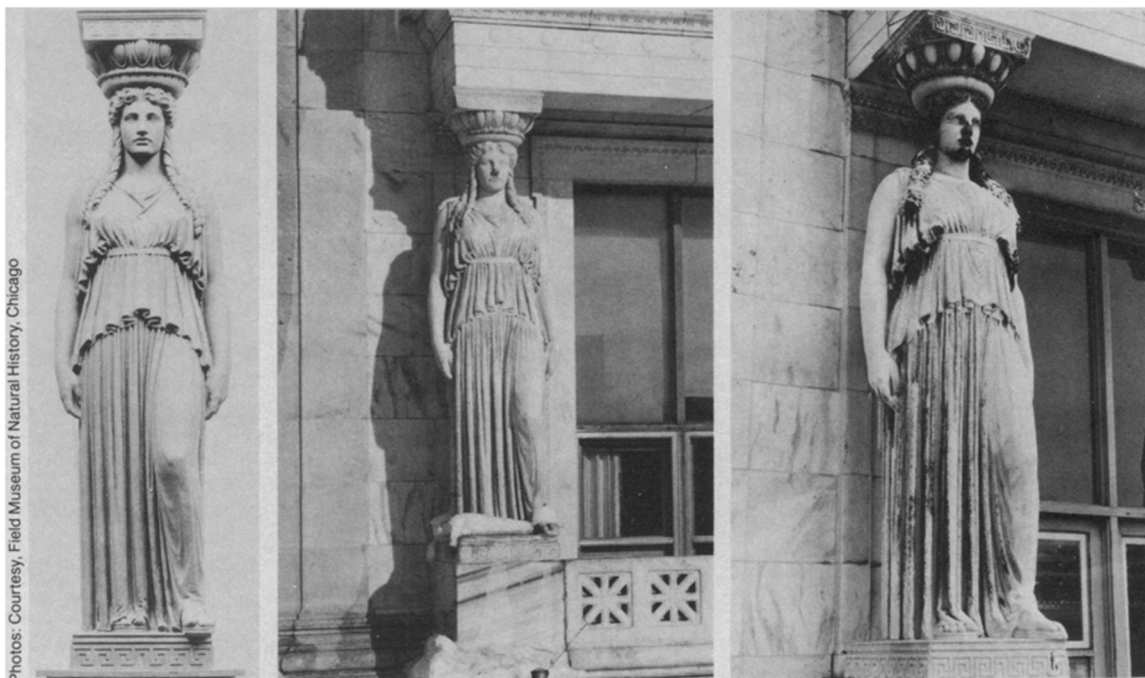
"The implications of this for people who do smog simulation studies," he says, "is that if they use today's stratospheric ozone figures they may end up dramatically underestimating not only the future amount of smog ozone that is going to form, but also the cost of [hydrocarbon and  $\text{NO}_x$ ] control measures they're going to need" to meet federal pollution standards.

Humans are not the only victims in this scenario. The Agriculture Department's National Crop Loss Assessment Network estimates that ozone damage already costs U.S. farmers \$2 billion annually in reduced crop yields. Some commercially important trees also appear sensitive to ozone.

For example, according to a new field study by researchers at the Yale School of Forestry and Michigan Technological University's forestry department, a 16 to 19 percent stunting was measured in the growth (dry mass) of young hybrid poplars, cottonwoods and black locusts exposed to outdoor ozone levels that were generally well within the current federal air-quality limit. Ironically, write the authors in the November ENVIRONMENTAL SCIENCE AND TECHNOLOGY, although the effect was serious, it was generally masked by the fact that there were no pathological symptoms in the ozone-affected trees; even their stunted growth was virtually invisible.

Explains Deane Wang, one of the authors (and now working at the University of Washington's Center for Urban Horticulture in Seattle), it wasn't that the

*Solid marble caryatid figure outside the Field Museum of Natural History in Chicago shows decades of damage caused by acid rain. Photo dates from left to right: circa 1920 (pre-installation), January 1967, June 1981.*



Photos: Courtesy, Field Museum of Natural History, Chicago

ozone-stunted trees were much shorter, so much as that they had fewer branches and somewhat fewer leaves on their branches. Wang described this subtle change in the "architecture" of the tree as being a possible sign that the tree's energy was being severely sapped — perhaps so severely that it might not have enough energy to fight additional stressors, like pests. Because the ozone produced no overt signs of ill health, the study's authors report, "it is probably prudent to conclude that ozone effects on forest ecosystems are more widespread and intensive than indicated by visible symptomatology alone."

The reduced plant productivity indicated by this study, taken together with ozone's current toll on crops, suggests that all who depend on forestry and agriculture may bear a much higher cost if the emissions of pollutants that destroy stratospheric ozone are not regulated soon, says Daniel J. Dudek, senior economist for the Environmental Defense Fund in New York City.

And, adds David Doniger, a senior attorney with the Natural Resources Defense Council in Washington, D.C., ozone-depletion-initiated "increases in smog production threaten to make it harder for cities to meet the ambient ozone standard [SN: 6/28/86, p.405]." He says, "We've mentioned this to as many . . . state air-pollution-control officials as we can. We've been telling them they ought to become concerned about fluorocarbon emissions because they're going to make the smog problem worse down here."

Donald Stedman, an atmospheric chemist at the University of Denver, describes the Whitten-Gery link between stratospheric ozone depletion and tropospheric environmental chemistry as "extremely exciting and very interesting. It

puts together a couple of fields of researchers who haven't been talking to each other — those who work on photochemical smog and those who work on stratospheric ozone."

Jack G. Calvert of the Boulder, Colo.-based National Center for Atmospheric Research and chairman of the National Academy of Sciences panel that authored "Acid Deposition: Atmospheric Processes in Eastern North America" (SN: 7/2/83, p.7), has a note of caution about attempts to interpret the new findings. "I would be a little skeptical about its numbers," he says — in part because the computer model used to simulate the atmospheric chemistry is, of necessity, rather simplistic. Moreover, he adds, the quantity of hydrogen peroxide present is not the only factor in determining whether acid rain production will increase.

Inside cloud water, hydrogen peroxide reacts with sulfur dioxide to form sulfuric acid. Maximum acid production occurs when there are roughly equal quantities of each precursor. Calvert points out that if there is already enough hydrogen peroxide to react with all of the sulfur dioxide, adding more hydrogen peroxide to the atmosphere will not increase acid rain production.

However, Stedman notes, because there is usually a relative shortage of hydrogen peroxide in urban air during the winter, this season would likely be susceptible to the most dramatic increases in acid rain production as tropospheric levels of ultraviolet radiation increase.

**B**ut even if there were no summer shortage of hydrogen peroxide, Stedman believes more prodigious hydrogen peroxide generation in cities could still have a profound effect on the

environment. First, he says, if there were enough of it present to oxidize all of the sulfur dioxide — before that airborne sulfur dioxide got a chance to drift away from cities — more of the production and deposition of acid would occur closer to pollution sources. Under this scenario, he says, the city that generates the acid precursors would suffer more from acid rain than it does today, and the forests downwind would suffer relatively less.

Second, he points out that it's not yet clear whether ozone and acid rain are the primary actors accounting for forest losses downwind of industrial centers. One of the better of several new, competing theories, Stedman says, is that hydrogen peroxide may by itself be directly responsible for injuring the leaves of trees.

To date the Whitten-Gery projections are based on only several days' worth of air pollution data collected at three cities. Within the next six months, the researchers expect to run simulations based on data from nine additional cities and more than 100 days of air pollution readings. By that time, Gery also expects to have completed a three-day simulation of an air mass traveling from West Virginia into the Adirondacks. It will contain an acid rain model he's developed to account for how changes in the ultraviolet-light field might affect acid formation.

In the end, Gery says, the precise numbers of ozone and hydrogen peroxide increases they've calculated thus far may not hold up. But the researchers do not expect the type of effects they're reporting today to change much, Gery says, because "what we see is a definite trend in the data" toward increased urban ozone and "dramatically increased" acid rain precursors. Considering the strength of this trend, he says, there's no reason to believe it won't continue. □