New Chemical Model, New Ozone Fear

More disconcerting news about the ozone layer: The same kinds of chemical reactions causing the yearly Antarctic ozone "hole" may be gnawing at the global veil of ozone, according to recent laboratory experiments.

Stratospheric ozone shields Earth's surface from harmful ultraviolet radiation, and scientists have observed with concern that worldwide ozone concentrations dropped by several percent over the last decade. While natural fluctuations have played some part in this trend, an international panel of experts concluded earlier this year that chlorine from human-made chemicals is destroying stratospheric ozone and causing part of the noticed drop. Curiously, though, the ozone losses have greatly exceeded those predicted by computer models based on the known amount of chlorine in the atmosphere, even when natural swings in ozone are taken into account (SN: 3/19/88, p.183).

Laboratory experiments conducted this year may help explain the extra ozone decrease. Margaret Tolbert and her colleagues at SRI International in Menlo Park, Calif., report in the August GEOPHYSICAL RESEARCH LETTERS that tiny droplets of sulfuric acid and water, which are ubiquitous in the stratosphere, can help chlorine destroy ozone. In the laboratory – and perhaps in the actual atmosphere – these droplets provide a surface for chemical reactions that convert relatively innocuous chlorine compounds into ozone-eating forms.

Atmospheric researcher Susan Solomon, who served as co-associate editor of the journal's special issue on polar ozone, says, "[Tolbert's] paper may be one of the most important ones to hit the streets in the last five years."

Reactions involving liquid or solid surfaces and gas molecules fall into a special category, called heterogeneous chemistry, that is currently occupying the minds of many atmospheric researchers. Until three years ago, when the scientific community first grappled with the alarming ozone losses over Antarctica, stratospheric experts had concentrated mostly on reactions occurring strictly in the gas phase. For this reason, most computer models do not yet incorporate heterogeneous chemistry.

The ozone hole, however, caught everyone by surprise – including the computer models – and prodded scientists to consider the importance of surface reactions. They discovered that in the cold polar stratosphere, frozen cloud particles allow heterogeneous reactions that are necessary for the wholesale destruction of ozone. Without these frozen particles, most chlorine remains locked in "passive" molecules, and only a small amount is free to break apart ozone.

Outside of the Antarctic and Arctic regions, where stratospheric temperatures drop below the crucial value of -80°C, the stratosphere is generally too warm to form frozen particles. But within the last two years researchers have proposed that pervasive sulfuric acid-water droplets may also support heterogeneous reactions – a theory bolstered by the recent experiments.

Sulfuric acid in the stratosphere comes from sulfur compounds produced at the surface by plants, microbes, fossil-fuel combustion and volcanic eruptions.

The SRI researchers found that sulfuric acid-water droplets promote reactions involving chlorine nitrate, hydrogen chloride and water – all molecules that normally do not break down ozone. Without any available surfaces, these molecules seldom react. But with droplets in the chamber, the chlorine chemicals begin to split into more destructive forms.

Still, particles of sulfuric acid and water don't hold a candle to the frozen cloud pieces found in the stratosphere near the Arctic and Antarctic. According to laboratory experiments, ice particles are more than 10 times more efficient as reaction surfaces than are liquid acid-water droplets. And observations show the polar stratosphere houses the greatest concentration of particles, far more than exists elsewhere.

All these findings support what scientists generally assume: that chemical ozone destruction should be far less effective outside the Earth's polar regions. Indeed, measurements show that the high southern and northern latitudes do suffer the greatest ozone loss, especially in winter. Earlier this year, investigators in Greenland detected signs of Arctic ozone loss caused by chlorine chemistry (SN: 6/11/88, p.383).

Because the SRI experiment is the first to measure heterogeneous reactions on sulfuric acid-water droplets, it is far from clear how important these reactions might be in the actual atmosphere, says Tolbert. More tests will have to determine how temperature and particle number affect the reactions before computer models can assess the damage from these reactions. *– R. Monastersky*

Mutant hamsters: Running a little early

A family of hamsters with oddly timed biological clocks is providing new clues about the genetics of circadian rhythms. The restless rodents may someday help explain why some people seem to need more sleep than others, or prefer to be more active at different times of the day.

The pattern of inheritance observed in the animals suggests the behavioral abnormality – which leaves the affected hamsters living 20-hour instead of 24-hour days – is the result of a single mutant gene. If confirmed, it would be the first such gene discovered in a vertebrate animal.

Michael Menaker and Martin R. Ralph, then at the University of Oregon in Eugene, charted activity periods for the nocturnal rodents by recording the time spent on exercise wheels, and traced the inheritance of abnormal patterns through numerous breeding experiments. Normal hamsters, even when reared in total darkness, spontaneously start exercising every 24 hours and stay active for several hours. But the researchers' purebred mutants showed 20-hour cycles, and hybrids became active every 22 hours. "It's a textbook case of a semi-dominant gene," says Menaker. The researchers, now at the University of Virginia in Charlottesville, report their results in the Sept. 2 SCIENCE.

Scientists already have identified a handful of genes that affect daily behavioral rhythms and mating-call frequencies in lower organisms such as fruit flies. In mammals, daily biological rhythms have long been recognized, and brain areas regulating them have been identified. But the genetics of these phenomena have remained a mystery.

"The value of [the mutant hamsters] is that you can start getting at the genes and the proteins and the actual building blocks involved in making this clock run – what the gears are," says Mitchell Dushay, a circadian-rhythm researcher at Brandeis University in Waltham, Mass. With a genetic defect now identified in a mammal, he adds, "I think the field is going to take off."

"There are some people who have trouble synchronizing to the day/night cycle, and we have no idea why," Menaker says. "The clock is no doubt a very complicated mechanism, and we are not going to fully understand it by figuring out what this gene makes. But it may give us a handle that we can use for further exploration." *– R. Weiss*