Atmosphere may cleanse itself better than previously thought

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A research team from Purdue University and the University of California, San Diego has found that the Earthâ€™s atmosphere may be more effective at cleansing itself of smog and other damaging hydrocarbons than was once thought.

Scientists, including Joseph S. Francisco, have learned that some naturally occurring atmospheric chemicals react with sunlight more effectively than previously thought to produce substances that "scrub" the air of smog. This group of chemicals, after absorbing energy from sunlight, is able to break down smog and other pollutants into far less harmful components.

While many such chemicals have long been known to behave in this way â€“ producing natural air cleaners called OH radicals â€“ the chemicals the team studied have for the first time been observed to produce air-scrubbing OH radicals at low ultraviolet wavelengths. This observation has eluded science primarily because photochemistry at these wavelengths has been difficult to study.

"Thanks to an innovative laser technique that at last allows us to observe these chemicals in action, we now theorize that the atmosphere may produce up to 20 percent more OH radicals from these chemicals than we once thought," said Francisco, who is a professor of both earth and atmospheric sciences and chemistry in Purdueâ€™s College of Science. "We now have a better understanding of an atmospheric process that could be giving our pollution-weary lungs more breathing room."

Francisco's research, which he performed at the University of California, San Diego with two of that institution's scientists, lead author Amitabha Sinha and graduate student Jamie Matthews, appears in this week's (May 9â€”13) online early edition of the journal Proceedings of the National Academy of Sciences. It will appear in the print edition on May 24 (vol. 102, issue 21).

Much air pollution consists of chemicals called hydrocarbons, which are produced when we burn organic matter such as wood or fossil fuels. The atmosphere has three main ways to cleanse itself of such pollutants, two of which are relatively direct: either water droplets in clouds absorb them and rain them out, or sunlight strikes them and the energy breaks the molecules apart.

"The third way is the one we are concerned with here, the way that involves breaking these hydrocarbons down chemically," Francisco said. "For that, the atmosphere relies on a reactive group of chemicals called OH radicals that attach themselves to hydrocarbons and rip them into inert pieces."

OH radicals arise naturally from many atmospheric constituents, and the effect they have on pollution has long been factored into models that describe the atmosphere and attempt to predict how it will react to increasing quantities of hydrocarbon pollutants, which generate smog. But these models do not always function well, Francisco said, in part because OH radicals are in some ways an unknown quantity.

"One of the biggest questions in our field concerns the amount of OH radicals the atmosphere holds," he said. "It's tough to get a handle on them because they are so reactive â€“ which means they vanish fast â€“ and also because we don't have complete knowledge of all the sources that produce them yet."

The experiments, which Sinha and Matthews performed at UCSD, used a laser technique that allowed the team to look at the OH radical-producing molecules in a new way. More precisely, it allowed the researchers to observe a portion of the spectrum that the molecules absorb â€“ a portion that has been something of a blind spot for scientists, who often detect chemical reactions by perceiving the telltale light frequencies that certain reactions are known to emit or absorb. Many sources of OH radicals strongly absorb UV light, making them easily detectable. However, the weak absorptions in the lower region of the ultraviolet spectrum, from wavelengths of about 360 nanometers to 630 nanometers, has been more challenging.

"It's usually difficult to detect what's going on in that spectral region because the molecular systems of interest frequently have weak spectral features there, so they're tough to see," said Francisco, who contributed the study's computations. "The upshot is that a lot of atmospheric models ignore this region altogether, assuming that because nothing can be seen, nothing must be happening."

The laser technique, however, enabled the team to characterize the minute quantities of radiation absorbed by a substance called methyl hydroperoxide when it breaks up in sunlight and forms OH radicals. Methyl hydroperoxide is one of the substances that can absorb light in the lower UV spectrum, and the team theorizes that the sensitive laser technique, called action spectroscopy, could reveal OH radical production from other chemically related molecules as well.

"This study is important because it shows that the atmosphere could be generating far more OH radicals than we thought before because the models are underestimating the amount of chemistry thatâ€™s happening," said Sinha, who is an associate professor of chemistry and biochemistry. "It could imply that the atmosphere is more effective at breaking down pollution than models have shown. We hope the results will improve our understanding of how the atmosphere works."

Sinha cautioned, however, that the results do not mean we can now safely ignore atmospheric pollution.

"This study in no way implies that we are out of the woods with regard to atmospheric pollution," he said. "What it means is that we need to do a much more careful job with our measurements in order to accurately account for all the reactive chemicals present in the air."

Francisco said he hopes the study also would encourage other refinements to atmospheric models.

"Models are only as good as the information we put into them, and we must always keep a cautious perspective about the results models return," he said. "Sometimes things are happening that you can't see using standard methods. Now we hope to take this improved understanding of the atmosphere and include it in future models â€“ thatâ€™s the next step."

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