Study shows skin-aging radicals age naturally formed particles in the air

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Pine trees are one of the biggest contributors to air pollution. They give off gases that react with airborne chemicals – many of which are produced by human activity – creating tiny, invisible particles that muddy the air. New research from a team led by Carnegie Mellon University's Neil Donahue shows that the biogenic particles formed from pine tree emissions are much more chemically interesting and dynamic than previously thought. The study provides the first experimental evidence that such compounds are chemically transformed by free radicals, the same compounds that age our skin, after they are first formed in the atmosphere.

These findings, published in the *Proceedings of the National Academy of Sciences*, can help make climate and air quality prediction models more accurate, and enable regulatory agencies to make more effective decisions as they consider strategies for improving air quality.

"We have been able to show conclusively that biogenics are chemically transformed in the atmosphere. They're not just static. They keep going, they keep changing, and they keep growing," said Donahue, professor of chemistry, chemical engineering, engineering and public policy, and director of Carnegie Mellon's Center for Atmospheric Particle Studies. "Quite a few atmospheric models, which are commonly used to inform research and policy, have been assuming that that doesn't happen. What we really need to have in the models is an accurate representation of what's really going on in the atmosphere, and that's what this lets us do."

The air that we breathe is chock-full of particles called aerosols. These tiny liquid or solid particles come from hundreds of sources including trees, volcanoes, cars, trucks and wood fires. The small particles influence cloud formation and rainfall, and affect climate and human health. In the United States each year, 50,000 premature deaths from heart and lung disease are attributable to excess concentrations of aerosols, especially particles less than 2.5 micrometers in diameter.

"There's a very, very strong body of data that establishes that fine particles in the air we breathe have a significant bad effect on people. What is less well understood is how the size and chemical composition of those particles influences that effect," Donahue said.

What complicates matters is that the atmosphere is a highly oxidizing, highly reactive place, which means that aerosols are transformed very rapidly into particles that can have completely different chemical compositions. Donahue and colleagues in the Center for Atmospheric Particle Studies were the first to describe the chemical processes involving free radicals that transform aerosols emitted by man-made sources like diesel exhaust. But this mechanism didn't explain what happens to natural compounds when they enter the atmosphere.

"It was too aggressive and made too much stuff, so the modelers simply turned off biogenic aging entirely. This seemed a little extreme," Donahue said. He suspected that the biogenic particles would age too, but in a different way.

Donahue, together with colleagues in Germany, Sweden, Denmark and Switzerland, set out to test this hypothesis using fake atmospheres called smog chambers, which contain several cubic meters of air in an enclosed space in the laboratory. They fed alpha-pinene, an aerosol released by pine trees, and ozone into the smog chambers and then added hydroxyl (OH) radicals, which are naturally-occurring, highly-reactive molecules

that drive reactions with other chemicals present in the air. The researchers gathered data from four different smog chambers and fed it into a computer model that they developed. They discovered that OH ages the particles, altering their properties and concentrations and producing three times more particulate matter than what was originally released into the atmosphere.

"The most intriguing part is that humans may influence the way that chemistry plays out," Donahue said. "The trees emit the stuff, but since human activity changes the chemistry taking place in the atmosphere, those changes can affect the amount and properties of the natural aerosols. There is a lot of evidence that, even when organic gases come from natural sources, the aerosol levels that come from them are controlled by human activity. Our work shows one of the ways this can happen."

Provided by Carnegie Mellon University