Using nighttime air chemistry to track ozone impact

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St. Louis summers can be hot, hazy, and tough for people with respiratory issues. New research from Washington University in St. Louis takes a new look at nighttime air chemistry, and how it can affect ozone levels the next day.

It is well known that the dog days of summer in St. Louis are hot, humid and hazy. On the warmest of these days, the air arrives from the south, bringing with it high temperatures, moisture and natural forest emissions of chemicals, known as hydrocarbons, from the Ozark Plateau. The hydrocarbons can interact with human-influenced emissions, and in the presence of sunlight, create a cocktail of pollutants—including ozone—that are hazardous to human health.

A team of engineers in the School of Engineering & Applied Science at Washington University in St. Louis collaborated with researchers at the University of Minnesota to study the late-summer air quality in the St. Louis area. They found that the way that isoprene, a natural hydrocarbon compound emitted from broadleaf deciduous trees, such as oak, is processed in the atmosphere at night can have a big impact on the ozone in the atmosphere the next day.

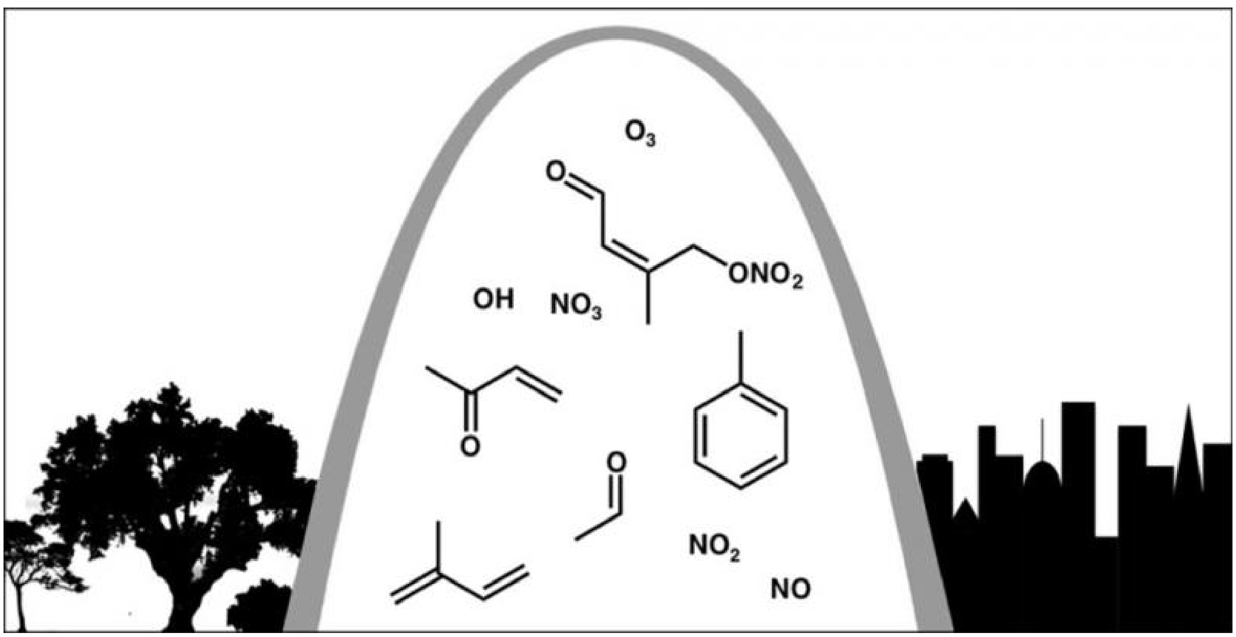
Brent Williams, the Raymond R. Tucker Distinguished I-CARES Career Development Assistant Professor, and Jay Turner, associate professor of energy, environmental & chemical engineering, both in the School of Engineering & Applied Science; and Dylan Millet, associate professor in the Department of Soil, Water, and Climate at the University of Minnesota, and other members of their research teams discovered the phenomenon after studying data from the St. Louis Air Quality Regional Study (SLAQRS), which took place in 2013 at the St. Louis-Midwest Supersite core monitoring station in East St. Louis, Ill.

Results of the study were recently published online in *Environmental Science & Technology* and are the first to show this phenomenon.

"Here we are looking at ground-level ozone, which is different than the ozone high up in the stratosphere that protects us from UV radiation," Williams said. "What often isn't talked about is that we do need a little ozone here on the ground as well to kick start chemical reactions that clear pollutants out of the atmosphere.

"However, too much ozone will damage materials and even your lungs. That's why the U.S. Environmental Protection Agency has set limits for ozone concentrations in the atmosphere, which can't exceed 70 parts per billion averaged over an eight-hour period."

The EPA considers April 1-Oct. 31 "ozone season" for the St. Louis region, when ozone pollution is more of a problem because of the sunlight and heat. Ozone forms from the combination of nitrogen oxides emitted from combustion sources such as vehicles or power plants, hydrocarbons from natural or human-influenced sources and sunlight. Ozone concentrations generally peak when temperatures are highest during the afternoon hours.



Isoprene, emitted at night by some trees, can have a big impact on St. Louis' ozone levels the following morning.

Trees in forests emit isoprene, an organic hydrocarbon tied to photosynthesis strongly dependent on light and temperature and emitted during the daylight hours. St. Louis is downwind of the deciduous forests of the Ozark Plateau, a major isoprene source region nicknamed the "isoprene volcano," because it has the largest emission rates of isoprene in the U.S., Williams said. Turner and collaborators previously conducted a field study that examined the isoprene emissions from the isoprene volcano.

During the SLAQRS study, southerly winds brought to St. Louis emissions from the Ozark region, however, isoprene had largely underwent chemical reactions and had faded away prior to arriving in St. Louis during the daylight hours. Isoprene that was emitted at the end of the day did not react away and was transported into St. Louis overnight.

The team found that if human-influenced emissions of nitrogen oxides were in low abundance in the air at night, isoprene remained in the atmosphere until daybreak, when it reacted with the sunlight and created a burst of ozone production, in stark contrast to the typical peak of ozone levels in mid-late afternoon and extending the daily high-ozone period. That pushed the ozone measurement over 70 parts per billion for a short period, increasing the potential for ozone standard exceedances, Williams said.

However, on nights when nitrogen oxides were in large abundance in the atmosphere, they reacted with ozone left over from the daytime and created nitrate radicals. When the sun rose the next morning, those nitrate radicals had reacted with the isoprene overnight to eliminate it—and ozone—from the atmosphere. In this case, the presence of nighttime nitrogen oxides prevents excess ozone formation the next morning, whereas daytime nitrogen oxides still produce ozone.

The phenomenon likely applies to other cities downwind of forests.

Nitrogen oxides still contribute to daytime ozone formation and should be controlled to limit ozone formation, but regulatory agencies should be aware of this nighttime chemistry that influences morning ozone levels, Williams said.

"We have to control what we can to prevent detrimental health impacts," Williams said. "With the three key ingredients to ozone production, we can control nitrogen oxides and some of the hydrocarbons from combustion sources, but we can't do anything about the hydrocarbons that forest is emitting, nor should we attempt to change the amount of sunlight.

"An understanding of this chemistry will help to predict elevated morning ozone periods and could even be factored into air quality alerts and awareness efforts," Williams said.

More information: Dylan B. Millet et al. Nighttime Chemistry and Morning Isoprene Can Drive Urban Ozone Downwind of a Major Deciduous Forest, *Environmental Science & Technology* (2016). DOI: 10.1021/acs.est.5b06367

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