NOx emissions from urban centers mix with emissions from vegetation, facilitating $PM_{2.5}$ formation in many parts of the world, including downwind of Atlanta, GA (pictured here).

EPA Study Shows Combustion Emissions Influence Rate and Amount of PM from Vegetation

by Carrie Holz and Emily Smith

Results from a study that examined how atmospheric oxidation from vegetation influences the formation of fine particulate matter.

Recent research led by the U.S. Environmental Protection Agency (EPA) examined how the rate of atmospheric oxidation of volatile organic compounds (VOCs) influences the formation of fine particulate matter ($PM_{2.5}$). The team's research included laboratory experiments, atmospheric observations, and model calculations, and found that when nitrogen oxides (NOx)—which is dominantly man-made and comes from combustion activities—is reduced, there is a corresponding reduction in how quickly VOCs from vegetation form $PM_{2.5}$. This, in turn, reduces the amount of $PM_{2.5}$ in that region.

The research estimates that a quarter of the decreases in organic $PM_{2.5}$ seen over the past 20 years in the southeastern United States are likely due to reductions in NOx emissions. This means that air quality mitigation strategies targeting reductions in ozone and inorganic $PM_{2.5}$ formation have also led to decreases in organic $PM_{2.5}$ formation.

The study, published in the *Proceedings of the National Academy of Sciences (PNAS)*,[1] focuses on a class of compounds from vegetation called monoterpenes, which are chemicals emitted from certain types of plants. Monoterpenes all have the same chemical formula, but can have different structures. This study focused specifically on the "alpha-pinene" structure, which is one of the major species emitted from pine trees that gives rise to their pine scent. Prior research showed that monoterpene chemistry is responsible for most of the organic component of $PM_{2.5}$ in the southeastern United States.[2]

"Since monoterpenes are emitted in the gas phase, chemistry is required to process them into lower-volatility forms that can enter $PM_{2.5}$," said Havala Pye, EPA scientist and lead author of the study. "This study was unique, in that it focused on the mechanism by which NOx affect $PM_{2.5}$ and was able to verify the mechanism with experimental data."

The research team used datasets developed from laboratory environmental chamber experiments to understand the chemical interactions taking place. Pye noted that the study was motivated by concern about a "NOx penalty" that could potentially increase $PM_{2.5}$ as NOx emissions are reduced.

"Monoterpenes are known to undergo a unique type of reaction called autoxidation, which leads to efficient $PM_{2.5}$ formation," she explained. "Autoxidation exhibits a NOx penalty in terms of $PM_{2.5}$ yield when NOx emissions decline, since NOx generally acts to suppress autoxidation reactions."

To determine the atmospheric impact of NOx, researchers first showed that autoxidation reactions were the main driver of $PM_{2.5}$ for monoterpenes by building a chemical mechanism that would describe in detail what was taking place at each stage of the chemical reaction. The highly detailed mechanism, consisting of hundreds of reactions and products, was able to reproduce $PM_{2.5}$ concentrations observed in previous lab experiments.

Researchers then looked at the mechanism in the context of changing NOx emissions. "While the NOx yield penalty was indeed present, the mechanism indicated that oxidant abundance was actually more important for dictating the $PM_{2.5}$ from monoterpenes," Pye said. "In fact, oxidant reductions due to decreasing NOx emissions can overcome the yield penalty from autoxidation."

Models, including EPA's Community Multiscale Air Quality Modeling (CMAQ; https://www.epa.gov/cmaq/learn-about-cmaq) System, and data from a 2013 Southeast Nexus (SENEX; https://www.esrl.noaa.gov/csd/projects/senex/) field study were also used to confirm the research team's understanding of how $PM_{2.5}$ changes in the ambient environment.

During the SENEX study, an aircraft was flown in and out of the urban plume downwind of Atlanta, measuring the effects of NOx. Researchers noticed that inside the plume, NOx concentrations, ozone, organic PM, and monoterpene autoxidation products were enhanced. Outside the plume, in the regional background, autoxidation products were lower in concentration, which confirmed that emissions from human activities were enhancing $PM_{2.5}$ from monoterpene autoxidation.

According to Pye, research dating back to the 1990s has proposed that monoterpenes were important for $PM_{2.5}$ formation, but that science is only now beginning to reveal the nuances of this relationship. She says there's still much work to be done before researchers will fully understand monoterpene chemistry.

"The abundance of monoterpene secondary organic aerosol and interaction with NOx is only now being elucidated and quantified," Pye said. "Mechanisms offer a path forward to determine robust associations of biogenic VOCs with anthropogenic emissions and the resulting implications for air quality today, and in the future."

About the Collaborators

EPA scientists collaborated on this study with scientists from the University of Washington; Pacific Northwest National Laboratory; National Oceanic and Atmospheric Administration; and University of Colorado, Boulder. The research was made possible by a Presidential Early Career Award for Scientists and Engineers (PECASE; https://obamawhitehouse.archives.gov/the-press-office/2017/01/09/president-obama-honors-federally-funded-early-career-scientists) award to Havala Pye. The PECASE award is the highest honor bestowed by the U.S. government on science and engineering professionals in the early stages of their independent research careers. The award comes with a financial stipend that allows investigators to pursue questions of high societal importance to protecting public health and the environment. Advances in this work provide the scientific underpinnings of future National Ambient Air Quality Standards and air quality management strategies to achieve them. **em**

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More Information

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