Refining atmospheric climate models

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The fresh scent of pine may end the search for missing sources of organic molecules in the air—which, it could well turn out, aren't missing after all. In work appearing in this week's Proceedings of the National Academy of Sciences Early Edition Online, researchers found that particles containing compounds such as those given off by pine trees evaporate more than 100 times slower than expected by current air-quality models

(PhysOrg.com) -- A long, frustrating search for the source of "extra" aerosols seen in field experiments but not in models might have come to an end when scientists at Pacific Northwest National Laboratory and Imre Consulting discovered the particles aren't what people thought. The particles are not liquids. Instead, the aerosols, known as secondary organic aerosols (SOA), are solid and evaporate more than 100 times slower than expected. What researchers previously thought takes seconds actually takes days.

"This work could resolve the discrepancy between field observations and

models," said principal investigator Dr. Alla Zelenyuk, a chemist at PNNL. "The results will affect how we represent organics in climate and air quality models, and could have profound implications for the science and policy governing control of submicron particulate matter levels in the atmosphere."

In predicting the impact of different scenarios on the planet's climate, atmospheric scientists want to use the most accurate models possible. This study gives scientists the information they need to properly represent secondary organic aerosols in the models, more accurately reflecting what is measured in the environment.

For a couple of decades, researchers have interpreted lab and field measurements under the assumption that secondary organic aerosols are liquid droplets that evaporate quickly, to establish equilibrium with their surroundings, which is central to the way these particles are modeled. Secondary organic aerosols are tiny particles of chemically modified organic compounds floating in the air. They absorb, scatter or reflect sunlight, and serve as cloud nuclei, making them an important component of the atmosphere. However, researchers have failed to explain the high amounts observed in real-world measurements.

So, researchers at PNNL and Imre Consulting used equipment that could study the particles under realistic conditions. Zelenyuk developed a sensitive and high-precision instrument called SPLAT II that can determine the composition, count, size, and measure the evaporation characteristics of these particles at room temperature. The instrument is located in EMSL.

To establish their methodology the researchers made particles from other, well-understood organic molecules that are known to form solids or liquid droplets, such as one called DOP and demonstrated that they behaved precisely as expected.

They then created secondary organic particles in the lab by oxidizing alpha-pinene, the molecule that makes pine trees smell like pine. Oxidation of this and similar volatile organic compounds is what happens in the atmosphere and results in formation of secondary organic aerosols.

Monitoring the various particles with SPLAT II for up to 24 hours, the research team found that while DOP particles behaved as expected, the pinene-based particles did not. About 50 percent of their volume evaporated away within the first 100 minutes. Then it slowed. Only another 25 percent of their volume dissipated in the next 23 hours. In addition, this fast-slow evaporation occurred similarly whether the particle was big or small, indicating the particles were not behaving like a liquid.

In the world, the secondary organic aerosols from pinene are formed in the presence of many other organic molecules, and some of these molecules slam into the particle and get incorporated, forming coatings. Experiments with the co-mingled secondary organic aerosol precursors and other organic compounds showed the researchers that these coated particles evaporate even slower than single-source secondary organic aerosols.

This lack of evaporation could put to the rest an intense effort by many scientists focused on finding other sources of atmospheric organics. "Our findings indicate that there may, in fact, be no missing SOA," said Zelenyuk.

The team then tested how close to reality their lab-based secondary organic aerosols were. By sampling the ambient air in Sacramento, Calif., they found the behavior of atmospheric secondary organic aerosols (whether from trees and shrubs or anthropogenic pollution) paralleled that of the co-mingled pinene-derived aerosols in the lab and

did not behave like liquids.

The results suggest that in the real atmosphere, secondary organic aerosols evaporation is so slow that scientists do not need to include the evaporation in models. The researchers believe that incorporating this information into atmospheric models will improve the understanding of aerosols' role in the climate.

The scientists are continuing their research into measuring the properties of secondary organic aerosols and working with modelers on properly representing the aerosols' properties and their impact on the environment and atmospheric models.

More information: Vaden TD, et al. 2011. "On the Evaporation Kinetics and Phase of Laboratory and Ambient Secondary Organic Aerosol." *Proceedings of the National Academy of Science USA*, Early Edition. Online the week of January 24, DOI: 10.1073/pnas.1013391108

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