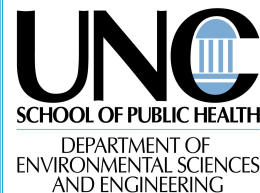




Secondary Organic Aerosol Formation in the Presence of Diesel Soot Exhaust

Sangdon Lee, Myoseon Jang, Richard M. Kamens

Department of Environmental Sciences and Engineering, School of Public Health, The University of North Carolina at Chapel Hill



Abstract

Organic aerosols that forms in the atmosphere as a consequence of atmospheric reactions, are often called SOAs. The resulting aerosols have the potential to influence climate change by altering the earth's radiative balance and by acting as cloud condensation nuclei. They may also have adverse health effects associated with respiratory and circulatory diseases. These atmospheric SOAs can be produced by the gas phase oxidation of a class of compounds called terpenes (e.g. α -pinene, β -pinene, d-limonene, etc.) that come from biogenic sources, alkanes from biogenic and anthropogenic sources, and aromatics (toluene, xylene, etc) which come only from anthropogenic sources.

SOA formation usually occurs in the presence of preexisting particles because they are ubiquitous in the atmosphere. α -Pinene was chosen in this study because it is one of the most abundant monoterpenes and its atmospheric oxidative reactions are well-known. Freshly emitted diesel soot particles were selected as preexisting seed particles, because these particles are mostly composed of long-chain alkanes and alkanic acids, which have very different polarities from oxygenated SOA products. Atmospheric experiments were carried out in a large outdoor Teflon film smog chamber. Results from this work show some of the possible impacts of the preexisting particulate matter on SOA formation from the α -pinene-NOx photo-oxidation reaction system. First, dilute diesel exhaust photo-oxidation by itself generates significant amounts of SOA. This has not been previously reported or quantified. Second, α -pinene SOA results in a dramatic alteration of the diesel particle chemical composition, as the air mass ages in the chamber. These observations suggest that the composition of urban combustion related particulate matter, due to atmospheric chemical reactions, may be dramatically different from that based just on the estimates of source related emissions.

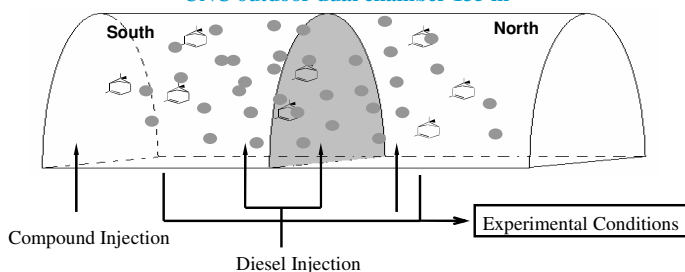
Objectives

Determine the stability of non-polar compounds on diesel particles as they age in the atmosphere and the interaction between non-polar diesel soot particles and polar SOA gas phase products

- Monitor the partitioning behavior of diesel soot particle components during SOA formation.
- Monitor the partitioning behavior of α -pinene oxidation products.
- Compare the observed partitioning behavior of alkanes and α -pinene products as diesel soot particles age in the chamber with theoretical estimation.

Experiments were performed in a large outdoor dual smog chamber in the daytime.

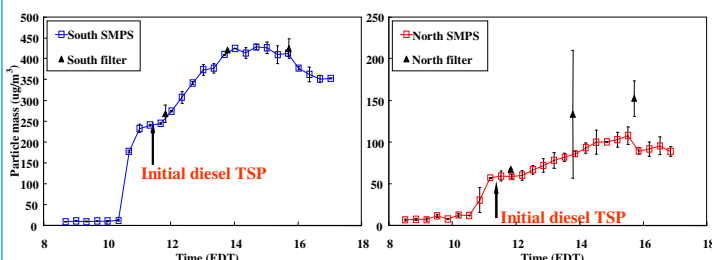
UNC outdoor dual chamber 135 m³



Results and Discussion

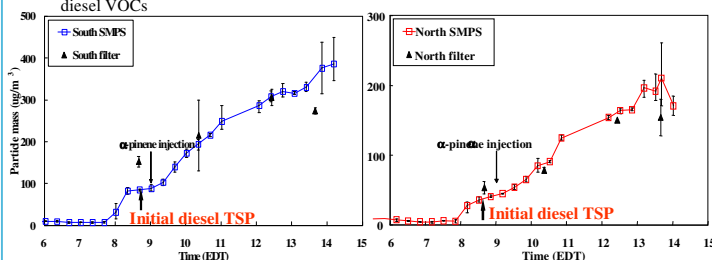
1. SOA formation from diesel exhaust by itself

Two experiments on the same day under sunlight in the dual chamber started with 250 $\mu\text{g}/\text{m}^3$ particles (south) and with 50 $\mu\text{g}/\text{m}^3$ particles (north) + associated diesel VOCs



2. SOA formation from diesel exhaust + α -pinene (0.14 ppmV)

Two experiments on the same day under sunlight in the dual chamber with 0.14 ppmV α -pinene started with 100 $\mu\text{g}/\text{m}^3$ particles (south) and with 50 $\mu\text{g}/\text{m}^3$ particles (north) + associated diesel VOCs



With just diesel exhaust by itself and diesel exhaust with α -pinene, particle mass increased by factors of 2 and 4 respectively.

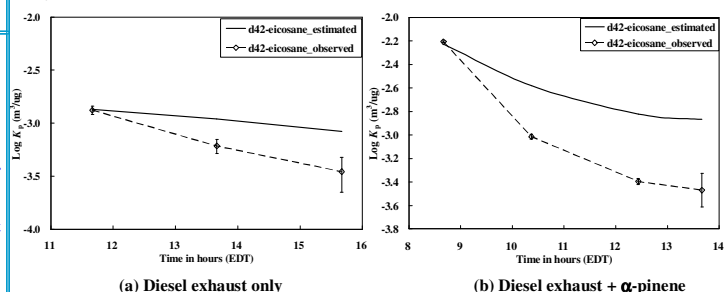
This result suggests that for SOA to increase, polar products must condense onto the non-polar diesel particle phase and the polarity of aged non-polar diesel particles increases with time.

3. Diesel soot particle polarity increase

As a tracer for this process, deuterated long-chain alkanes (d_{42} -eicosane) were added to the system to monitor the apparent polarity change from the deuterated alkane partitioning behavior. The partitioning behavior of d_{42} -eicosane was compared with the estimated values obtained from Eq 1.

$$K_p = \frac{C_p}{C_g \cdot TSP} = \frac{7.501RTf_{om}}{10^9 MW_{om}^i \gamma_{om}^i P_L^0} \quad (\text{m}^3 \mu\text{g}^{-1}) \text{ Eq 1}$$

MW_{om}^i : average molecular weight (g mol^{-1}) of liquid organic medium (om),
 f_{om}^i : mass fraction of organic material, T : ambient temperature (K), R : ideal gas constant,
 γ_{om}^i : activity coefficient of a compound i , P_L^0 : vapor pressure (mmHg) of compound i .



K_p of d_{42} -eicosane decreased by a factor of 2 for just (a) diesel exhaust system and a factor of 4 for (b) diesel exhaust + α -pinene system.

Tracking the partitioning behavior of tracer d_{42} -eicosane in the diesel exhaust system corroborates that SOA produced from diesel exhaust photo-oxidation by itself is more polar than the freshly emitted diesel soot particles.

When α -pinene SOA formed in the presence of diesel exhaust, a dramatic alteration of the diesel particle polarity was observed as the air mass ages in the chamber.

4. Acid-catalyzed heterogeneous reaction of α -pinene oxidation products in diesel soot particle

Acid-catalyzed heterogeneous reactions are plausible in the presence of diesel soot particles because they contain indigenous sulfuric acid which seems to provide sufficient acidity for heterogeneous reactions¹.

1. Experimental K_p values for the major products with aldehyde functional groups were abnormally high compared to theoretically estimated values (see Table). This is consistent with recently published acid-catalyzed heterogeneous reactions of these aldehyde products^{2,3}.

Compounds	Exp. K_p / Predicted K_p
<i>cis/trans</i> -pinonaldehyde	258
<i>cis</i> -pinonic acid	3
pinalic-4-acid	3720
<i>cis/trans</i> -10-hydroxypinonaldehyde	288

- cis/trans* Isomers for pinonaldehyde and 10-hydroxypinonaldehyde
- 5-dimethyl-7-oxo-2-octenal, acid-catalyzed heterogeneous reaction product from *cis*-pinonaldehyde, was tentatively identified.

This evidence for acid-catalyzed heterogeneous reactions all agreed with the previously proposed study by Jang *et al*³.

Acknowledgements

This study was supported by a grant from National Science Foundation (ATM 0097462 and ATM-0314128) to the University of North Carolina at Chapel Hill. We thank Di Hu for helping with the chamber experiments.

References

- Tobias, H., Beving, D.E., Ziemann, P.J., Sakurai, H., Zuk, M., McMurray, P.H., Zarling, D., Waytulo-nis, R., Kittelson, D.B., 2001. Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA/Thermal Desorption Particle Beam Mass Spectrometer. *Environmental Science and Technology* 35, 2233-2243.
- Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions. *Science* 298, 814-817.
- Jang, M., Carroll, B., Chandramouli, B., Kamens, R.M., 2003b. Particle Growth by Acid-catalyzed Heterogeneous Reactions of Organic Carbonyls on Pre-existing Aerosols. *Environmental Science and Technology* 37, 3828-3837.