The Role of Biogenic and Anthropogenic Hydrocarbons in Aging of Atmospheric Soot

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A. Motivation

Soot is a byproduct of incomplete fossil fuel combustion and biomass burning, generated at a rate of 12-24 Tg/yr annually. Fine soot particles are a major atmospheric pollutant. Their presence in urban air degrades visibility, enhances accumulation of other pollutants, and negatively impacts human health. Atmospheric soot also contributes to climate change, and in many megacities worldwide solar heating by soot particles is comparable to heating caused by the greenhouse gases. In the atmosphere, soot is subjected to aging, which modifies the composition, properties, and impacts of soot particles. An important aging process involves the interaction of soot with semi-volatile and low volatility oxidation products of Volatile Organic Compounds (VOCs).

VOCs are emitted from a variety biogenic and anthropogenic sources. A significant fraction of anthropogenic VOCs are represented by aromatic hydrocarbons, such as toluene. Biogenic VOCs are dominated by monoterpenes, such as isoprene and a-pinene, emitted in large quantities by deciduous and coniferous trees. Emission of isoprene, estimated to be 600 Tg year$^{-1}$, dwarfs the emissions of all other hydrocarbons.

It is well established that anthropogenic and biogenic hydrocarbons are precursors of Secondary Organic Aerosols (SOA). What role do these hydrocarbons play in the aging of primary aerosols? Are they all or are there differences in their ability to modify the properties of fractal soot aggregates?

B. Experimental setup and methodology

Photochemical aging experiments: UV photolysis of 5 ppm H$_2$O, in the presence of 340 ppb isoprene, 250 ppb toluene, and/or 0.317 ppb NO, NO$_2 = 1.5$) in a collapsible fluoropolymer chamber at 20% RH.

Dark aging experiments: reaction of 40 ppb isoprene with 20 ppb ozone at 8% RH.

Derived properties:
- Organic mass fraction, $f_{org} = 1 - 1/12(m)$
- Effective density, $\rho_{eff} = \frac{m_{org}}{V_{org}}$
- Inherent density, $\rho_{in} = \frac{m_{org}}{V_{org}} + (1 - \rho_{in})/\rho_{in}$
- Volume equivalent diameter, $D_v = \sqrt{m_{org}/\rho_{in}}$
- Coating thickness, $\delta_{cat} = (\rho_{cat} - \rho_{soot})/\rho_{soot}$
- Particle number concentration, $N$

Directly measured properties:
- Diameter growth factor, $G_D = D/D_0$
- Mass growth factor, $G_m = m/m_0$
- Critical supersaturation, $S_c$
- Scattering and extinction coefficients, $b_{sc}$ and $b_{ext}$

C. Particle size and mass growth

80 nm
100 nm
150 nm

D. Particle properties and morphology

Isoprene	Toluene	\(\alpha\)-Pinene

Significant changes in morphology of soot aggregates upon coating and subsequent humidification

E. Modified direct and indirect radiative impacts

Light absorption and scattering

- Light absorption shows complex behavior with aging
- Thermal desorption cannot be used to restore particles to their nascent state to derive the absorption enhancement factor, e.g., Cappa et al., Science 2012, 337 (6095), 1078-1081.

F. Summary and relevant publications by research group

- The aging of soot from oxidation of biogenic and anthropogenic hydrocarbons transforms initially hydrophobic particles into efficient CCN, the rate of aging increases in the presence of nitrogen oxides, a common co-pollutant of soot.
- The fastest internal mixing occurs for \(\alpha\)-pinene, which is known to produce SOA in a high yield. Coatings formed on soot from oxidation of isoprene are relatively thin because of low SOA yield, but their impacts on particle properties are profound and comparable to those from sulfuric acid coatings.
- In addition to sulfuric acid, biogenic and anthropogenic hydrocarbons play a major role in the transformation of anthropogenic soot, shortening its atmospheric lifetime and considerably altering its impacts on air quality and climate.

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