The Photoreactivity of Atmospheric Dust: Quantifying Hydroxyl Radical Production Using Molecular Probes

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Introduction

- Every year, an estimated 1,600 Tg of mineral dust is emitted into the atmosphere to be transported long distances.
- Dust can impact Earth’s atmosphere in several ways: it can affect the radiative budget by both scattering or absorbing radiation, influence cloud formation, impact air quality, and act as a reactive surface for heterogeneous photochemistry.
- Certain components of dust, such as TiO$_2$ and Fe$_2$O$_3$, are photoactive and produce radical species (e.g. hydroxyl radicals) when illuminated.
- Since dust originating from different locations contains varying amounts of photoactive minerals, each dust has unique photoactive properties.
- The goal of our project is to develop a molecular probe technique to quantify the amount of OH radicals produced by different dusts when illuminated.
- These quantities can be used as a proxy for comparing overall reactivity of dust of various origins, and how dust reactivity changes with transport.

Experimental Method

- Arizona Test Dust (ATD), Niger sand, and Saharan Desert Cape Verde Dust (SDCV Dust) were used for analysis.
- Aqueous probe solutions of benzoic acid, coumarin, umbelliferone, methanol and benzene were placed in a cuvette with dust samples and illuminated under a solar simulator for 5 to 120 minutes.
- Quantification of products from the reaction of hydroxyl radicals with probes were analyzed with an Agilent 1260 HPLC with UV detection or a PTI fluorimeter.
- To verify whether the intensity from the solar simulator is uniform throughout the samples, we used 2-nitrobenzaldehyde as an actinometer.
- The calculated values for the rate constant are uniform throughout our nine samples.

Coumarin and Umbelliferone as Probes

- Coumarin acts as a hydroxyl radical probe to form highly fluorescent umbelliferone. Umbelliferone was also used as a probe, by monitoring its decomposition.
- As shown in Figure 2, the SDCV accelerates the decomposition of umbelliferone above its background photolytic loss, whereas Niger sand does not.
- The increase in OH radical production of depositional dust over source sand indicates that as dust gets transported, it is more reactive.
- During the coumarin experiments, Figure 3 shows the hydroxyl radical production is higher under more acidic conditions.
- Increased reactivity at low pH implies higher reactivity in urban areas than in less polluted environments.

Methanol as a Probe

- Methanol reacts with OH radicals to form formaldehyde, derivatized with DNPH and detected via HPLC-UV at 360 nm.
- Figure 6 shows background formaldehyde formation, possibly originating from oxidation of organics in solution or on the dust surface, which cannot be distinguished from formaldehyde production caused by the ATD.

Benzene as a Probe

- Benzene reacts with OH radicals to form phenol, which can be quantified using HPLC with fluorescence detection.
- Figure 7 depicts the linearity of the fluorescence signal at low concentrations, while Figure 8 shows an increased production of phenol in the presence of dust against background production.

Benzoic Acid as a Probe

- As seen in Figure 4, there is an increase in fluorescent salicylic acid produced from reaction between benzoic acid and OH radicals.
- We would expect that as the benzoic acid concentration increases, the amount of salicylic acid produced would plateau once all the OH is captured.
- As shown in Figure 2, this is not the case, indicating that the benzoic acid is influencing the photochemical system.

Conclusions / Future Directions

- Preliminary results show there is a dependence for dust reactivity on transport, dust origin and environmental conditions.
- Benzene is a suitable probe molecule for this system.
- Investigate dust reactivity as a function of particle size.

References