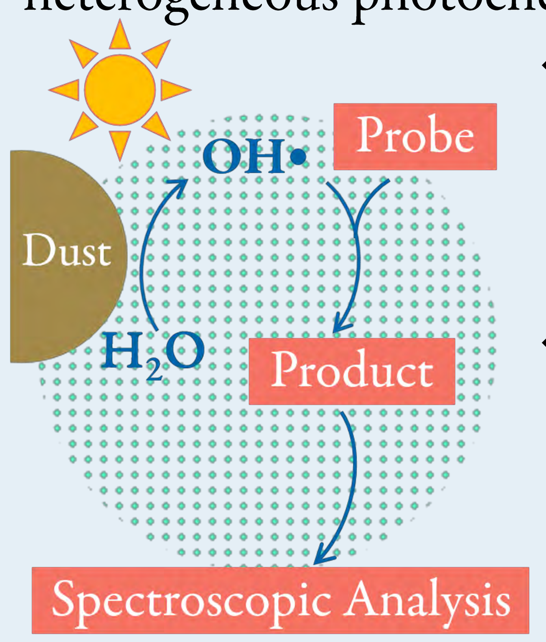
The Photoreactivity of Atmospheric Dust: Quantifying Hydroxyl Radical Production Using Molecular Probes

Stephanie R. Schneider, Sherry Gao, Chelsea D. Cote, Thomas H. H. Chou, Sarah A. Styler

Styler Research Group
University of Alberta Department of Chemistry
URi Undergraduate Research Initiative

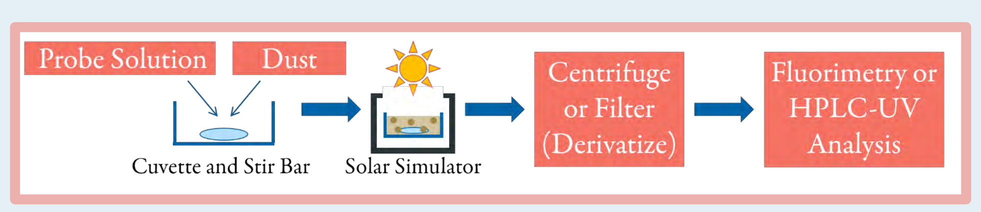
Introduction

- Every year, an estimated 1,600 Tg of mineral dust is emitted into the atmosphere[1] to be transported long distances[2]
- 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[3]



- Certain components of dust, such as TiO_2 and Fe_2O_3, are photoactive and produce radical species (e.g. hydroxyl radicals) when illuminated [3,4]
- Since dust originating from different locations contains varying amounts of photoactive minerals, each dust has unique photoactive properties[1]
- 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

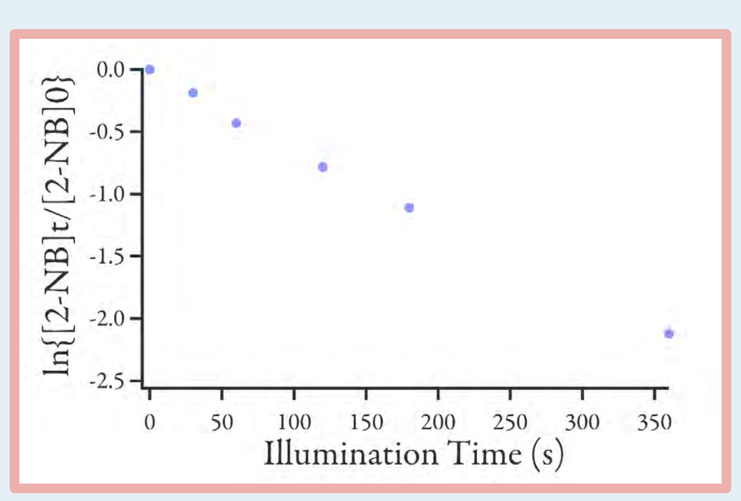
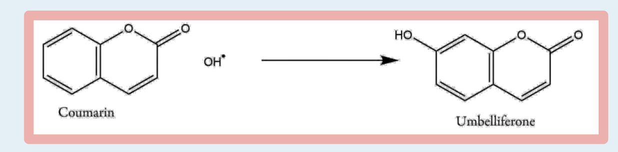


Figure 1

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[5]

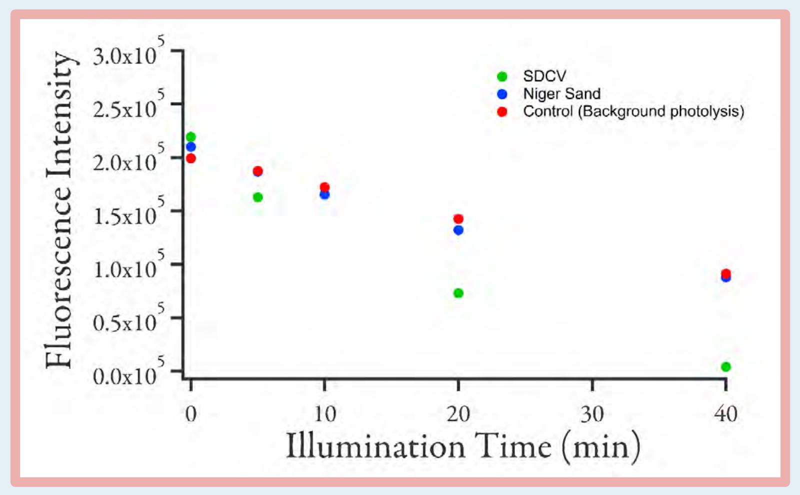


Figure 2

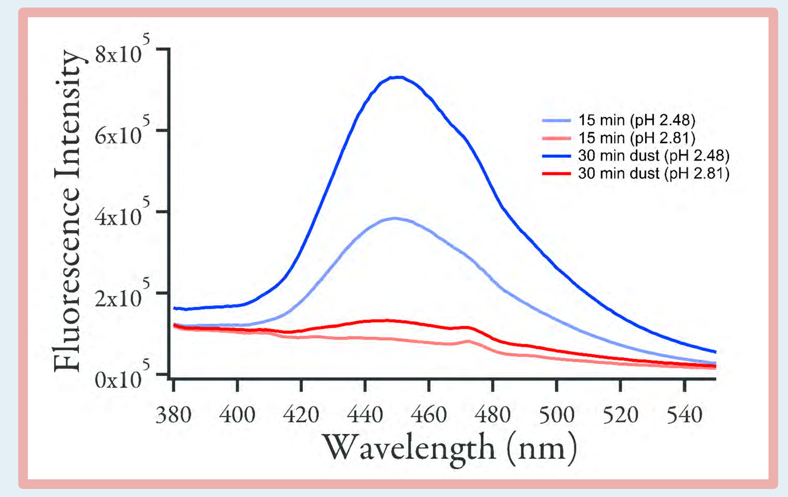
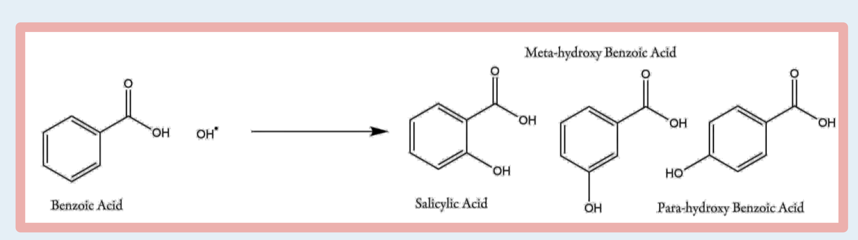


Figure 3

- 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

Benzoic Acid as a Probe



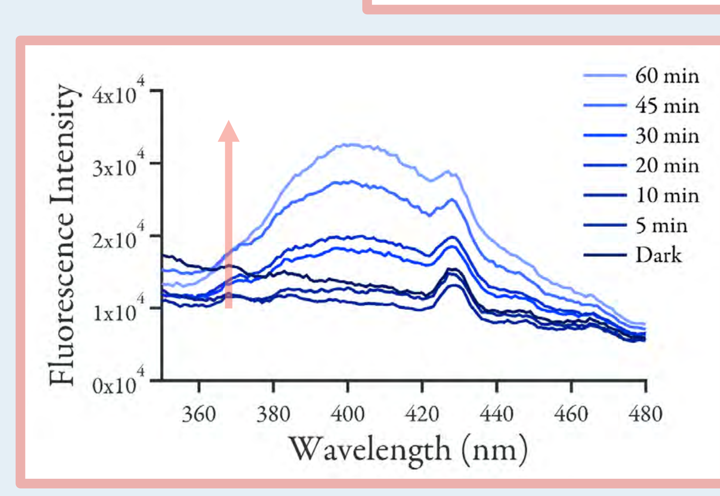


Figure 4

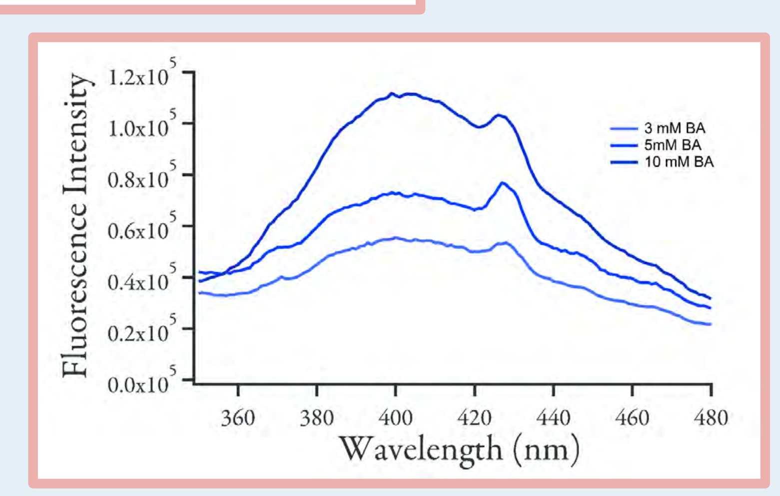
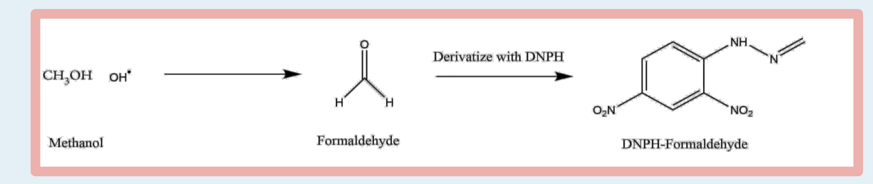


Figure 5

- As seen in Figure 4, there is an increase in fluorescent salicylic acid produced from reaction between benzoic acid and OH radical[6]
- 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

Methanol as a Probe



- Methanol reacts with OH radicals to form formaldehyde, derivatized with DNPH and detected via HPLC-UV at 360 nm[7]

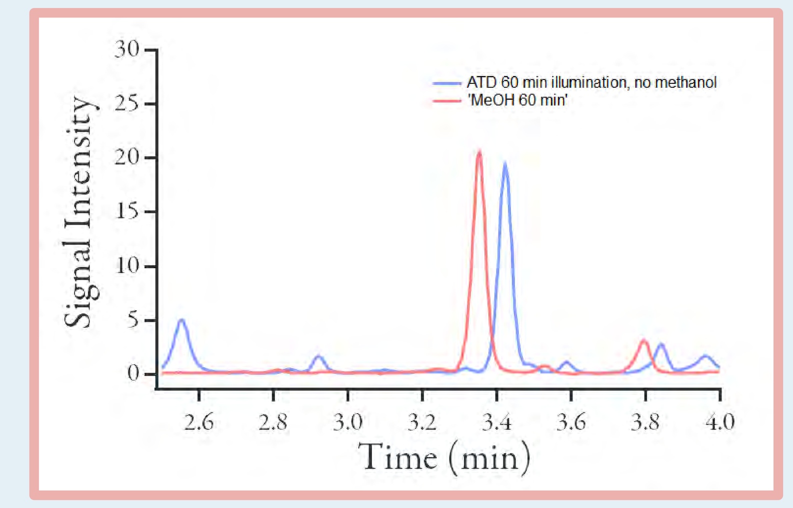


Figure 6

- 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 HLPC 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

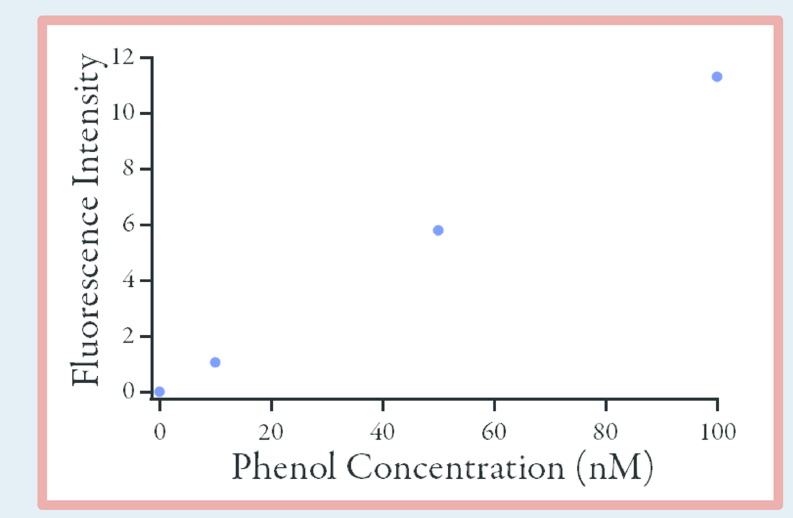


Figure 7

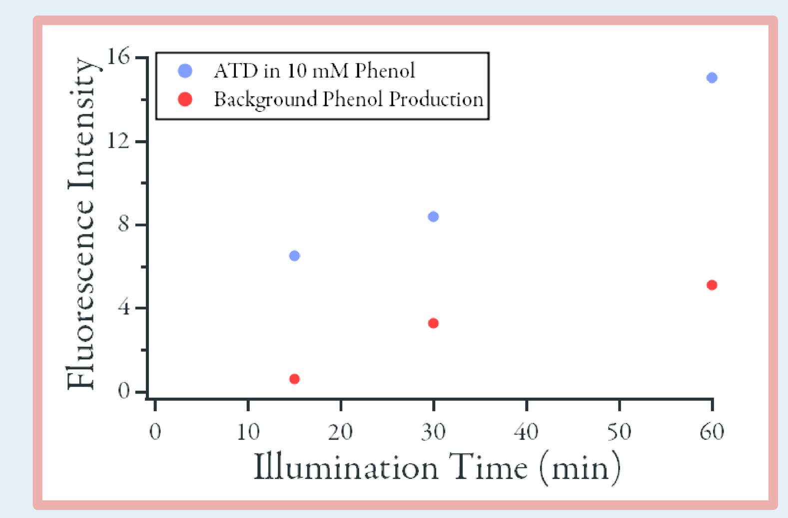


Figure 8

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

1. M. O. Andreae, D. Rosenfeld, *Earth-Science Reviews* **2008**, *89*, 13-41 10.1016/j.earscirev.2008.03.001.
2. Y. H. Tang, G. R. Carmichael, G. Kurata, I. Uno, R. J. Weber, C. H. Song, S. K. Guttikunda, J. H. Woo, D. G. Streets, C. Wei, A. D. Clarke, B. Huebert, T. L. Anderson, *Journal of Geophysical Research-Atmospheres* **2004**, *109*, 10.1029/2003jd003806.
3. C. George, B. D'Anna, H. Herrmann, C. Weller, V. Vaida, D. J. Donaldson, T. Bartels-Rausch, M. Ammann, in *Atmospheric and Aerosol Chemistry*, ed. by V. F. McNeill, P. A. Ariya, **2014**, Vol. 339, pp. 1-53.
4. H. H. Chen, C. E. Nanayakkara, V. H. Grassian, *Chemical Reviews* **2012**, *112*, 5919-5948 10.1021/cr3002092.
5. J. Zhang, Y. Nosaka, *Journal of Physical Chemistry C* **2013**, *117*, 1383-1391 10.1021/jp3105166.
6. C. Anastasio, K. G. McGregor, *Atmospheric Environment* **2001**, *35*, 1079-1089 10.1016/s1352-2310(00)00281-8.
7. K. Mopper, X. L. Zhou, *Science* **1990**, *250*, 661-664 10.1126/science.250.4981.661.