

# Laboratory Investigation of the Relative Humidity Dependence of Light Extinction by Mixed Organic/Sulfate Particles

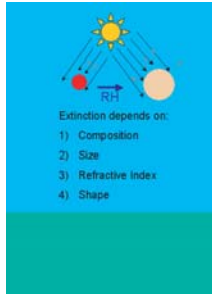
Melinda R. Beaver<sup>1,2</sup>, Tahllee Baynard<sup>3</sup>, Rebecca M. Garland<sup>1,2,4</sup>, Christa Hasenkopf<sup>2,5</sup>, A.R. Ravishankara<sup>1,3</sup>, and Margaret A. Tolbert<sup>1,2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA; <sup>2</sup>CIRES, Boulder, CO, USA

<sup>3</sup>NOAA Earth Systems Research Laboratory, Chemical Sciences Division, Boulder, CO, USA; <sup>4</sup>now at Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany

<sup>5</sup>Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO, USA

## Background and Motivation



Biomass burning contributes a large amount of organic particulate matter, ranging from soluble sugars to slightly soluble aromatic compounds.

Research Question: How does humidity affect the light extinction by particles of limited solubility, representative of biomass burning?

## Experimental Methods

### Tandem Cavity Ring-Down Aerosol Extinction Spectrometer (CRD-AES)

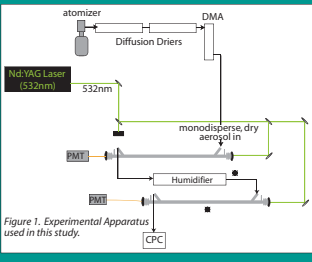


Figure 1. Experimental Apparatus used in this study.

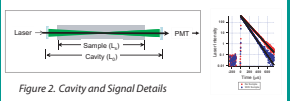


Figure 2. Cavity and Signal Details

Extinction by particles can be measured by cavity ring-down spectroscopy.

In the technique, a pulse of laser light decays exponentially within the cavity due to losses (i.e. particle extinction). A fit to this decay determines the time constant,  $\tau$ .

Extinction ( $\text{cm}^{-1}$ ) can be calculated from the time constants  $\tau$  and  $\tau_0$  (with and without sample),  $R$  (ratio of optical to sample length), and the speed of light,  $c$ , according to Eqn 1.

$$\sigma_{\text{ext}} = \frac{R}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

Extinction measurements taken at different relative humidities (RH) can be ratioed to determine optical growth factors,  $fRH_{\text{ext}}(\text{RH}, \text{Ref})$ , in Eqn 2.

$$fRH_{\text{ext}}(\text{RH}, \text{Ref}) = \frac{\sigma_{\text{ext}}(\text{RH})}{\sigma_{\text{ext}}(\text{Ref})} \quad (2)$$

### Experimental Approach:

- 1) Atomize particles
- 2) Dry particles
- 3) Size select, using DMA
- 4) Measure extinction of dry particles,  $[\sigma_{\text{ext}}(\text{dry})]$
- 5) Expose particles to  $\text{RH} > 95\%$  to ensure deliquescence.
- 6) Measure extinction of humidified particles,  $[\sigma_{\text{ext}}(80\% \text{RH})]$
- 7) Count particles using CPC

### Organics Studied:

Organic Compound	Water Solubility (at 25 deg C)	Growth Factor (dry)	$fRH_{\text{ext}}(80\% \text{RH}, \text{Dry})$ ( $\sigma_{\text{ext}} = 335 \text{ nm}$ )
phthalic acid	0.6 wt%	$1.19 \pm 0.04$	$1.27 \pm 0.07$
pyromellitic acid	N/A	$1.12 \pm 0.05$	$1.16 \pm 0.11$
4-hydroxybenzoic acid	0.5 wt%	0.97 <sup>c</sup>	-

## Results

### Validation Studies:

#### $Q_{\text{ext}}$ of PSLs and Ammonium Sulfate

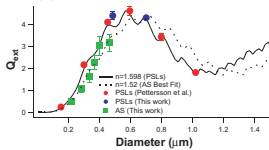


Figure 3. Comparison of calculated and measured  $Q_{\text{ext}}$  for polystyrene spheres (PSLs) and ammonium sulfate.

Two sizes of PSLs were analyzed to determine their extinction efficiency. These data agree well with  $Q_{\text{ext}}$  calculated using Mie theory and  $n=1.598$ .

Dry ammonium sulfate over a range of sizes was measured. The best fit for  $n=1.52$ , similar to the values found in the literature ( $n=1.53$ ).

Assumes spherical particles for Mie calculation.

#### $fRH_{\text{ext}}$ Ammonium Sulfate

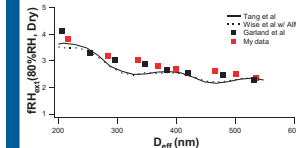


Figure 4. Comparison of measured  $fRH_{\text{ext}}(80\% \text{RH}, \text{Dry})$  for ammonium sulfate from this study, Garland et al. (2007), and GF from Tang (1996).

Data from new CRD-AES instrument agree well with data taken using another instrument, under similar conditions (Garland et al., 2007).

$D_{\text{eff}}$  was determined by using the measured  $C_{\text{ext}}$  and Mie calculations to determine the effective optical diameter (accounts for multiply charged particles).

### Optical Properties:

#### Extinction Efficiency of Organics

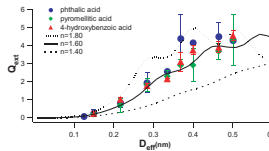


Figure 7. Extinction efficiencies measured for the organics studied. Curves calculated using Mie theory, assuming spherical particles, and no absorption.

The optical constants of these organic compounds are not known, and are often assumed to have  $n=1.40-1.45$ . By measuring the extinction ( $\text{Mm}^{-1}$ ) and the particle concentration ( $\text{cm}^{-3}$ ),  $C_{\text{ext}}$  and  $Q_{\text{ext}}$  can be determined.

Upon inspection of the data, it appears these organic compounds have larger real refractive indexes than the commonly assumed 1.45. The data and fit details are shown in the next panel.

#### Determination of Refractive Index

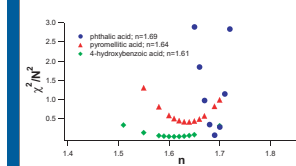


Figure 8. Determination of best fits for the real refractive index for the organic compounds studied.

Minimization of the merit function  $\chi^2/N^2$  as in Riziq et al (2006) was conducted to determine the best fits of the real refractive index,  $n$ . The error was taken as the std. dev of the measurement, and  $N$  is the number of experimental data points.

$$\chi^2 = \sum_{i=1}^N \left( \frac{Q_{\text{ext},i} - Q_{\text{ext},i}(\text{fit})}{\sigma_{Q_{\text{ext},i}}} \right)^2 \quad (3)$$

Each organic studied has a refractive index higher than 1.45. The values of 1.69, 1.64, 1.61 are closer to the refractive indexes of Benzene ( $n=1.51$ ) and Naphthalene ( $n=1.60$ ) at 560 nm.

### $fRH_{\text{ext}}$ Measurements:

#### Optical Growth of Organics

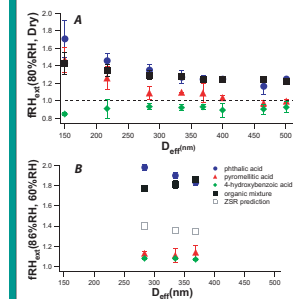


Figure 5. Measurements of A)  $fRH_{\text{ext}}(80\% \text{RH}, \text{Dry})$  and B)  $fRH_{\text{ext}}(80\% \text{RH}, 60\% \text{RH})$  for the pure organic compounds and a mixture of them.

Overall, the organic compounds studied take up much less water at 80%RH than ammonium sulfate.

Continuous water uptake was observed for the organics (i.e. no deliquescence).

At smaller sizes, the  $fRH_{\text{ext}}$  for 4-hydroxybenzoic acid was  $< 1.0$ . A similar trend was observed by Mochida et al. (2004) when measuring GF for the same compound with HTDMA.

Water uptake amongst organic compounds does not appear to follow the ZSR approximation.

#### Dependence on Percent Organic

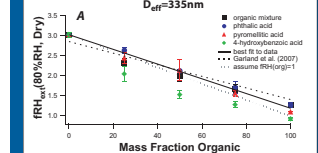


Figure 6. Variation of A)  $fRH_{\text{ext}}(80\% \text{RH}, \text{Dry})$  and B)  $fRH_{\text{ext}}(80\% \text{RH}, 60\% \text{RH})$  with mass fraction organic for particles with an effective optical diameter of 335 nm.

In order to study more atmospherically relevant scenarios, mixtures of these compounds with ammonium sulfate were investigated at sizes ranging from 150 nm - 501 nm.

Phthalic acid and pyromellitic acid exhibited additive water uptake.

4-hydroxybenzoic acid exhibited a depression in water uptake.

However when comparing extinction at two humidified conditions, the suppressions disappears, implying shape/density issues.

## Summary and Conclusions

The sparingly soluble organic compounds investigated have much smaller optical growth factors than inorganics such as ammonium sulfate.

Phthalic acid and pyromellitic acid exhibit similar water uptake to the very soluble DCAs studied by Garland et al (2007).

Optical growth of 4-hydroxybenzoic acid was less than or equal to 1.0 over the size range studied.

Refractive indexes for the organics studied have been determined, and are larger than 1.45.

Phthalic and pyromellitic acids mixtures with ammonium sulfate exhibit additive water uptake, adhering to the parameterization determined by Garland et al (2007).

4-Hydroxybenzoic acid when mixed with ammonium sulfate exhibits a depression in optical growth factor.

A shape/density issue is thought to be responsible for the behavior of 4-hydroxybenzoic acid.

### References:

- Pettersson, A., et al., *J. Aerosol Sci.*, 35, 995-1011, 2004.
- Baynard, T., et al., *Geophys. Res. Lett.*, 33, L06813, doi:10.1029/2005GL024898, 2006.
- Garland, R. M., et al., *J. Geophys. Res.*, doi:10.1029/2006JD008179, in press, 2007.
- Brooks, S. D., et al., *Atmos. Environ.*, 38, 1859-1868, 2004.
- Mochida, M., and Kawamura, K., *J. Geophys. Res.*, doi:10.1029/2004JD004962, 2004.
- IPCC Working Group 1 Report, <http://ipcc-wg1.ucar.edu/wg1/wg1-report.html>, 2007.
- Riziq, A. A., et al., *Atmos. Chem. Phys.*, 6, 1523-1536, 2006.
- Tang, I. N., *J. Geophys. Res.*, 101, 10245-10250, 1996.

### Acknowledgements:

The authors acknowledge financial support from NASA under grant # NNG06G79G. MRB was supported by an EPA STAR Graduate Fellowship. The research described in this poster has been funded in part by the United States Environmental Protection Agency (EPA) under the Science to Achieve Results (STAR) Graduate Fellowship Program. EPA has not officially endorsed this publication and the views expressed herein may not reflect the views of the EPA. The authors acknowledge Dr. Steve Brown and Dr. Meg Greeneslade for helpful discussions.