

Supplementary Information for: “Organic Aerosol Formation in Urban and Industrial plumes near Houston and Dallas, TX”

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A) Supplementary Text:

D) Validation of the AMS dataset

Uncertainty analysis on AMS mass concentrations

As described previously [Allan *et al.*, 2003; Jimenez *et al.*, 2003; Alfarra *et al.*, 2004; Canagaratna *et al.*, 2007], the following dependencies are used in calculating non-refractory mass concentration of species measured by the AMS:

$$mass_{species} \propto \frac{1}{IE_{NO_3}} \cdot \frac{1}{RIE_{species}} \cdot \frac{1}{CE} \cdot \frac{1}{Q}$$

IE_{NO_3} : Ionization efficiency of nitrate- determined in routine calibrations (10% uncertainty)

$RIE_{species}$: Ionization efficiency of species relative to nitrate

- for ammonium: determined in routine calibrations (10% uncertainty)

- for sulfate: determined in previous laboratory experiments and computational results (15% uncertainty) [Jimenez *et al.*, 2003; Alfarra *et al.*, 2004; Canagaratna *et al.*, 2007]

- for organics: determined for various types of organics in previous laboratory experiments and literature values, an average value is used (20% uncertainty) [Jimenez *et al.*, 2003; Alfarra *et al.*, 2004; Canagaratna *et al.*, 2007]

CE: Collection efficiency, determined based on previous laboratory experiments with mixed sulfate-nitrate particles (30% uncertainty) [Quinn *et al.*, 2006; Matthew *et al.*, 2008]

Q: measured continuously and calibrated with NIST-traceable flow meters (<0.5% uncertainty)

The above uncertainties lead to 33% overall uncertainty for ammonium and nitrate, 35% uncertainty for sulfate, and 37% uncertainty for organics.

Transmission (TE) tests of ammonium nitrate particles have shown $100\% \pm 20\%$ efficiency in the size range of 70-500 nm, with a significant fraction of the scatter being due to noise in these challenging experiments [Bahreini *et al.*, 2008]. Considering a 10% uncertainty for TE increases the uncertainty to 34% for ammonium and nitrate, 36% for sulfate, and 38% for organics. This leads to uncertainty of 20-35% in total AMS mass, depending on the flight. When comparing AMS total mass to fine mass, we assume an uncertainty of 30% for the AMS total mass data.

Comparisons with estimated fine mass measurements

In order to compare AMS total mass concentrations with mass estimates from fine volume measurements (which have ~30% uncertainty, [Brock *et al.*, 2008]), mass-weighted density of particles, based on the measured mass concentrations of individual species and their corresponding densities, is calculated. In this calculation, a 10% uncertainty in the assumed density of organics leads to 7% uncertainty in the overall density.

Fine volume data have been averaged on AMS saving time of 10 s or 15 s, depending on the flight.

Considering the uncertainties in the AMS total mass (30%), fine volume (30%), and aerosol density (7%), the uncertainty in the ratio of AMS mass to estimated fine mass is estimated to be 43%.

Figure S1 shows the histogram of the ratio of AMS mass to fine mass for all the data archived for the TexAQS-2006 study. The FWHM of the Gaussian fit to the histogram is 0.41, which is comparable to the overall uncertainty in the ratio. Scatter plot of AMS mass vs. fine mass (Figure S2) also shows that the two measurements are well correlated with overall slope of 0.90 and correlation coefficient of $r^2 = 0.86$. The gray area in both plots represents the area covered by $\pm 43\%$ uncertainty in the ratio; 94% of the data falls within this range.

Within occasional concentrated plumes of ammonia from industrial sources, AMS ammonium nitrate mass concentrations were lower, respectively, by a factor of 1.3-2.5 and 1.3-5 than expected based on comparisons with particle size distributions and observed removal of gas-phase nitric acid- assumed to form particulate ammonium nitrate (*J.B. Nowak et al.*, Gas-to-particle conversion: observations of ammonium nitrate formation above Houston, manuscript in preparation, 2009). The source of the discrepancy between expected and measured ammonium nitrate concentrations in this situation has not been determined, but the problem is believed to be absent in the plumes analyzed here and appears to be limited to few isolated ammonia-rich plumes in the whole project.

Figures S3-S6 show the scatter plot of the ratio of AMS mass to estimated fine mass vs. transport age for the plumes analyzed in the manuscript. The gray area represents the area covered by $\pm 43\%$ uncertainty in the ratio. The data in these figures indicate that the ratio stays relatively constant from one transect to another within these plumes.

II) Cumulative histograms

We provide an overview of concentrations, mixing ratios, and values of different parameters observed in the Houston plumes analyzed in this manuscript as cumulative histograms in Figures S7-S18.

III) Tables of background values of OA and CO in each transect

In Table S1 we provide background values (\pm standard deviation) of OA ($\mu\text{g sm}^{-3}$) and CO (ppbv) on the east and west side of the plumes in each transect. Values are not reported if aircraft altitude changed immediately after a plume (n/a values).

IV) Effect of background consideration on $\Delta\text{OA}/\Delta\text{CO}$ values in the urban-influenced plumes on 27 Sept.

As discussed in Section 3.1, due to recirculation of older plumes to the west of Houston area on 27 Sept., background levels on the west side of Houston were higher than background levels on the east side of the Ship Channel. In order to give an estimate of the bias associated with estimates of $\Delta\text{OA}/\Delta\text{CO}$ when different background levels of OA and CO are assumed, we have calculated the enhancement ratio assuming background levels from east of the Ship Channel (filled circles, also used in generating Figure 5b) and from west of the Houston urban center (open circles) in Figure S19. This comparison indicates that within the range of variability observed in the ratio from either method, conclusions regarding the evolution of OA in the plume are robust.

V) Comparison of two methods to determine the enhancement ratio of $\Delta\text{OA}/\Delta\text{CO}$

Enhancement ratios calculated as described in Section 3.1 are compared here with ratios determined from the slope of linear fits to scatter plots of OA vs. CO in each plume transect. In Figures S20-S21, the slope values are determined by Orthogonal Distance Regression (ODR) fits to the scatter plots of OA vs. CO in each plume transect. Precision of OA and CO measurements

were used as weighting functions in obtaining the fit. Total uncertainties in the slope values are then calculated using the uncertainty in the slope determined by ODR and the uncertainties in the OA and CO measurements. $\Delta OA/\Delta CO$ values presented are calculated as described in Section 3.1 and are the same as those estimates used in Figure 5. Data points are colored coded with the Pearson's r coefficient for each fit. A meaningful linear fit to points downwind of the Houston urban center could not be obtained on 27 Sept. since only a subset of points in the plume were unaffected by the Parish power plant plume, resulting in a small dynamic range in CO. The two compared methods provide equivalent estimates of the enhancement ratio within the range of uncertainties.

VI) Pseudo-steady-state approximation to calculate OH concentration

This approximation considers OH production via photolysis of formaldehyde and the reaction of $O^1(D)$, by-product of O_3 photolysis, with water molecules; it also considers removal rate of OH by reaction with NO_2 [Seinfeld and Pandis, 1998]:

The following equations are derived considering this approximation:

$$[OH]_{pssa} = \frac{2 \cdot j_{CH_2O \rightarrow HCO} \cdot [CH_2O] + 2 \cdot k_{O^1(D)+H_2O} \cdot [O^1(D)]_{pssa} \cdot [H_2O]}{k_{OH+NO_2} \cdot [NO_2]} \quad (1S)$$

$$[O^1(D)]_{pssa} = \frac{j_{O_3 \rightarrow O^1(D)} \cdot [O_3]}{k_{O^1(D)+H_2O} \cdot [H_2O] + k_{O^1(D)+M} \cdot [M]} \quad (2S)$$

The following is a list of the parameters used in this calculation:

$[OH]_{pssa}$: calculated pseudo-steady-state approximation concentration of OH (cm^{-3})

$[CH_2O]$: measured concentration of formaldehyde (cm^{-3})

$[O^1(D)]_{pssa}$: calculated pseudo-steady-state approximation concentration of $O^1(D)$ (cm^{-3})

$[H_2O]$: measured concentration of water vapor, based on the measured ambient relative humidity (cm^{-3})

[NO_2]: measured concentration of NO_2 molecules (cm^{-3})

[O_3]: measured concentration of O_3 molecules (cm^{-3})

[M]: calculated third body concentration, based on the measured ambient pressure and temperature (cm^{-3})

$j_{CH_2O, toHCO}$: calculated photolysis rate of formaldehyde (HCO radical formation channel), based on the measured actinic flux (s^{-1})

$k_{O^1(D)+H_2O}$: rate constant for $O^1(D)+H_2O$ reaction ($cm^3 s^{-1}$) [Sander *et al.*, 2006]

k_{OH+NO_2} : rate constant for $OH+NO_2$ reaction ($cm^3 s^{-1}$) [Sander *et al.*, 2006]

$j_{O_3, toO^1(D)}$: calculated photolysis rate of O_3 ($O^1(D)$ formation channel), based on the measured actinic flux (s^{-1})

$k_{O^1(D)+H_2O}$: rate constant for $O^1(D)+H_2O$ reaction ($cm^3 s^{-1}$) [Sander *et al.*, 2006]

$k_{O^1(D)+M}$: rate constant for third-body deactivation $O^1(D)$ ($cm^3 s^{-1}$) [Sander *et al.*, 2006]

VII) References

- Alfarra, M. R., et al. (2004), Characterization of urban and rural organic particulate in the Lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers, *Atmos. Environ.*, 38, 5745–5758, doi:10.1016/j.atmosenv.2004.01.054.
- Allan, J. D., J. L. Jimenez, P. I. Williams, M. R. Alfarra, K. N. Bower, J. T. Jayne, H. Coe, and D. R. Worsnop (2003), Quantitative sampling using an Aerodyne Aerosol Mass Spectrometer. Part 1: Techniques of data interpretation and error analysis, *J. Geophys. Res.*, 108(D3), 4090, doi:10.1029/2002JD002358.

Bahreini, R., E. J. Dunlea, B. M. Matthew, C. Simons, K. S. Docherty, P. F. DeCarlo, J. L.

Jimenez, C. A. Brock, and A. M. Middlebrook (2008), Design and Operation of a Pressure-Controlled Inlet for Airborne Sampling with an Aerodynamic Aerosol Lens, *Aerosol Sci. Technol.*, 42(6), 465–471, doi:10.1080/02786820802178514.

Brock, C. A., et al. (2008), Sources of Particulate Matter in the Northeastern United States in Summer: 2. Evolution of Chemical and Microphysical Properties, *J. Geophys. Res.*, 113, D08302, doi:10.1029/2007JD009241.

Canagaratna, M. R., et al. (2007), Chemical and Microphysical Characterization of Ambient Aerosols with the Aerodyne Aerosol Mass Spectrometer, *Mass Spectrom. Rev.*, 26, 185–222.

Jimenez, J. L., et al. (2003), Ambient aerosol sampling with an Aerosol Mass Spectrometer, *J. Geophys. Res.*, 108(D7), 8425, doi:10.1029/2001JD001213.

Matthew, B. M., A. M. Middlebrook, and T. B. Onasch (2008), Collection Efficiencies in an Aerodyne Aerosol Mass Spectrometer as a Function of Particle Phase for Laboratory Generated Aerosols, *Aerosol Sci. Technol.*, 42, 884–898, doi:10.1080/02786820802356797.

Quinn, P. K., et al. (2006), Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine, *J. Geophys. Res.*, 111, D23S36, doi:10.1029/2006JD007582.

Sander, S. P., et al. (2006), Chemical kinetics and photochemical data for use in atmospheric studies, *Evaluation 15*, JPL NASA.

Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric chemistry and physics: from air pollution to climate change*, John Wiley & Sons, Inc., New York.

B) Supplementary Table:

Table S1:

Date	Transect	OA		CO	
		East	West	East	West
Sep. 26	1 st	5.63 ± 0.73	6.04 ± 0.39	146 ± 7	142 ± 2
	2 nd	5.32 ± 0.46	5.83 ± 0.34	143 ± 4	152 ± 2
	3 rd	6.14 ± 0.79	6.20 ± 0.35	145 ± 6	146 ± 1
	4 th	6.23 ± 0.38	6.20 ± 0.35	140 ± 2	146 ± 1
	5 th	6.36 ± 0.25	6.05 ± 1.33	143 ± 1	149 ± 3
Sep. 27	1 st	5.49 ± 0.52	6.59 ± 0.29	135 ± 4	153 ± 2
	2 nd	5.81 ± 0.63	8.47 ± 0.39	139 ± 2	166 ± 2
	3 rd	5.63 ± 0.49	8.47 ± 0.39	136 ± 2	166 ± 2
	4 th	6.25 ± 0.37	7.59 ± 0.46	139 ± 2	163 ± 4
	5 th	6.25 ± 0.84	7.59 ± 0.46	146 ± 7	163 ± 4
	6 th	n/a	7.68 ± 0.41	n/a	159 ± 3
	7 th	5.74 ± 0.34	6.81 ± 0.53	146 ± 4	157 ± 2
	8 th	5.99 ± 0.31	6.81 ± 0.53	139 ± 3	157 ± 2
Oct. 5	1 st	5.84 ± 0.43	5.51 ± 0.70	141 ± 7	156 ± 7
	2 nd	5.98 ± 0.37	6.80 ± 0.66	154 ± 7	160 ± 4
	3 rd	5.24 ± 0.66	6.80 ± 0.66	154 ± 4	160 ± 4
	4 th	5.13 ± 0.54	5.33 ± 0.40	149 ± 4	150 ± 2
	5 th	n/a	5.52 ± 0.59	n/a	151 ± 1
Sep. 25	1 st	2.47 ± 0.14	2.70 ± 0.28	121 ± 3	118 ± 4

C) Supplementary Figure captions:

Figure S1. Histogram of the ratio of AMS mass to fine mass for all the data archived for the TexAQS-2006 study.

Figure S2. Scatter plot of AMS mass to fine mass for all the data archived for the TexAQS-2006 study.

Figure S3. Ratio of AMS mass to Fine mass as a function of age in the Dallas plume (25 Sept.)

Figure S4. Ratio of AMS mass to Fine mass as a function of age in the Houston plumes (26 Sept.)

Figure S5. Ratio of AMS mass to Fine mass as a function of age in the Houston plumes (27 Sept.)

Figure S6. Ratio of AMS mass to Fine mass as a function of age in the Houston plumes (5 Oct.)

Figure S7. Cumulative histogram of OA in the Houston plumes.

Figure S8. Cumulative histogram of SO_4^{2-} in the Houston plumes.

Figure S9. Cumulative histogram of NO_3^- in the Houston plumes.

Figure S10. Cumulative histogram of NH_4^+ in the Houston plumes.

Figure S11. Cumulative histogram of CO in the Houston plumes.

Figure S12. Cumulative histogram of benzene in the Houston plumes.

Figure S13. Cumulative histogram of SO_2 in the Houston plumes.

Figure S14. Cumulative histogram of NO in the Houston plumes.

Figure S15. Cumulative histogram of NO_2 in the Houston plumes.

Figure S16. Cumulative histogram of ambient relative humidity in the Houston plumes.

Figure S17. Cumulative histogram of ambient temperature in the Houston plumes.

Figure S18. Cumulative histogram of calculated OH in the Houston plumes.

Figure S19. Estimates of $\Delta\text{OA}/\Delta\text{CO}$ in urban-influenced plumes on 27 Sept. based on different background values.

Figure S20. Comparison of two methods for determining enhancement ratios of $\Delta\text{OA}/\Delta\text{CO}$ in urban plumes

Figure S21. Comparison of two methods for determining enhancement ratios of $\Delta\text{OA}/\Delta\text{CO}$ in Ship Channel plumes