

R. Moffet (Referee)

General:

This manuscript presents results from several measurements of aerosol chemistry and optical properties during an intensive sampling period in Shanghai. Overall the manuscript is well written and should be published with some improvements I mention below. The authors have done a nice job documenting the cluster analysis and particle types. There is also an excellent quantitative comparison between bulk  $\text{NH}_4$ ,  $\text{SO}_4$  and  $\text{NO}_3$  concentrations and ATOFMS peak area data. ATOFMS data has often been referred to as “non-quantitative”, but this paper clearly shows that there is utility in the ATOFMS peak areas. The one area that can be improved the most is the discussion on the chemical effect on optical properties. Much of the discussion is speculative and relies on empirical correlations – the strength of which may or may not depend on the reasons stated by the authors. The authors should have enough data to conclusively determine whether or not there is a chemical effect on optical properties through a closure study.

We thank the reviewer for the valuable comments on this manuscript. All the comments and suggestions raised by this reviewer are addressed below.

Detailed:

Abstract, Line 20: I suggest moving the sentence starting with “The comparison” after the sentence directly following it.

We accept this suggestion and shifted the two sentences in the revised manuscript.

Abstract, last sentence: It is stated that the mass extinction efficiency is controlled by the “chemical components”. This is a very general sentence that does not have very much impact because everything is composed of “chemical components”.

We delete “chemical components” from this sentence in the revised manuscript.

P. 31957, line 5: It is stated: “the radiative forcing of aerosols is largely determined by their chemical components...”. This sentence has two problems: 1) aerosols are not the ones being forced, so “forcing of aerosols” is awkward – I suggest using the term direct aerosol radiative forcing instead. 2) The direct effect is more strongly controlled by absolute particle concentration and size rather than particle chemical composition. Chemical composition plays a more secondary role due to modification of hygroscopic properties and refractive index (especially in the case of soot). I suggest the authors re-word their introduction to address these comments.

We rewrote this sentence in the revised manuscript as shown below:

“The direct aerosol radiative forcing is determined by the aerosol number concentration, size distribution and chemical composition (Seinfeld and Pandis, 2006). A high concentration of fine particles can lead to a significant impairment of visibility.”

P. 31961, line 11: Please describe the  $\text{NO}_x$  measurements in more detail. This measurement is

discussed briefly in Li et. al. 2011a, but I still think more detail regarding the NO<sub>2</sub> correction would improve the quality of the paper.

We add the following paragraph to describe the NO<sub>2</sub> correction in the aerosol optical measurement at the end of Section 2.3 in the revised manuscript:

“As the most important atmospheric gas phase absorber at 532 nm, NO<sub>2</sub> correction in the aerosol extinction coefficient measurement should be considered. NO<sub>2</sub> concentration (as shown in Fig. S1) was measured by a NO<sub>x</sub> analyzer (Model 42i, Thermo Scientific) through a separate inlet. The absorption cross-section of NO<sub>2</sub> at 1 atm and 298 K for 532 nm is given as 0.35 Mm<sup>-1</sup> ppb<sup>-1</sup> (1.45×10<sup>-19</sup> cm<sup>2</sup> molec<sup>-1</sup>) (Osthoff et al., 2006). During CRDS measurement, τ<sub>0</sub> was measured once per day using particle-free air. The NO<sub>2</sub> concentration at this time was converted to absorption coefficient and set as a reference for future NO<sub>2</sub> correction. The uncertainty of NO<sub>x</sub> concentration is ±0.4 ppb, equivalent to 0.14 Mm<sup>-1</sup> in the extinction coefficient uncertainty.”

P. 3165, line 11: Please clearly define “biomass burning”. Is it possible to distinguish residential/agricultural biomass burning from coal fly ash? There is a great deal of “biomass burning” particles contributing to the overall number concentrations, so I think this is an extremely important issue to discuss from an emissions standpoint.

We add the definition of biomass burning particle as below in the supplementary material:

“In China, most of the biomass burning particles come from crop residue burning. In this work, based on our laboratory research on the particles emitted from rice straw, wheat straw and corn stalk burning (paper in preparation), we set several criteria for identifying biomass burning particles: 1) There should be K-clusters such as <sup>113</sup>K<sub>2</sub>Cl<sup>+</sup> and <sup>213</sup>K<sub>3</sub>SO<sub>4</sub><sup>+</sup> in the positive MS. 2) <sup>26</sup>CN<sup>-</sup> should occur in the negative MS. 3) No <sup>7</sup>Li<sup>+</sup> should be observed (Liu et al., 2003; Spencer et al., 2008; Furutani et al., 2011).”

The identification of biomass burning particles is indeed a tough job for the ATOFMS because of the high LDI efficiency of K, while the <sup>39</sup>K<sup>+</sup> ion peak is usually a good marker of atmospheric aerosols with a biomass burning/biofuel burning origin. To our knowledge, particles that can be classified as coal fly ash should have an association of <sup>39</sup>K<sup>+</sup> and <sup>7</sup>Li<sup>+</sup> in the MS pattern (Liu et al., 2003; Spencer et al., 2008; Furutani et al., 2011). Moreover, potassium in coal combustion aerosol is not water soluble (Querol et al., 1996) while potassium in biomass burning aerosol (mostly KCl and K<sub>2</sub>SO<sub>4</sub>) has high water solubility (Gaudichet et al., 1995). To test our classification, the number concentration of the resulted biomass burning particles was further compared with the temporal profile of water soluble potassium obtained from MARGA (Section 3.2.2).

P. 31966, line 7: Suggest replacing the term “roller coaster” with a more formal term.

We replace “roller coaster” with “oscillating” in the revised manuscript.

P. 31966, line 17: Regarding the metal containing particles: I would think if it was a local point source, there would be spikes in the time series. Instead, I think the more constant concentration is

indicative of regional sources. To put it another way, it seems as if there is more than one source in the region leading to a constant baseline of these particles. Perhaps this is just a terminology issue and “regional source” is a better term. Also, the metal particles are representing an appreciable fraction of the total particles and it would be nice to see a bit more discussion/analysis on the possible sub-types making up this particle class.

We agree with this comment and rewrote this sentence as shown below:

“The temporal profile of Na-K-rich particle type presented no significant spikes during the whole sampling period, suggesting regional, rather than local, origins. Further discussion of the metal-containing particles is given in the supplementary materials.”

We added extra discussion about metal-containing particles in the supplementary materials:

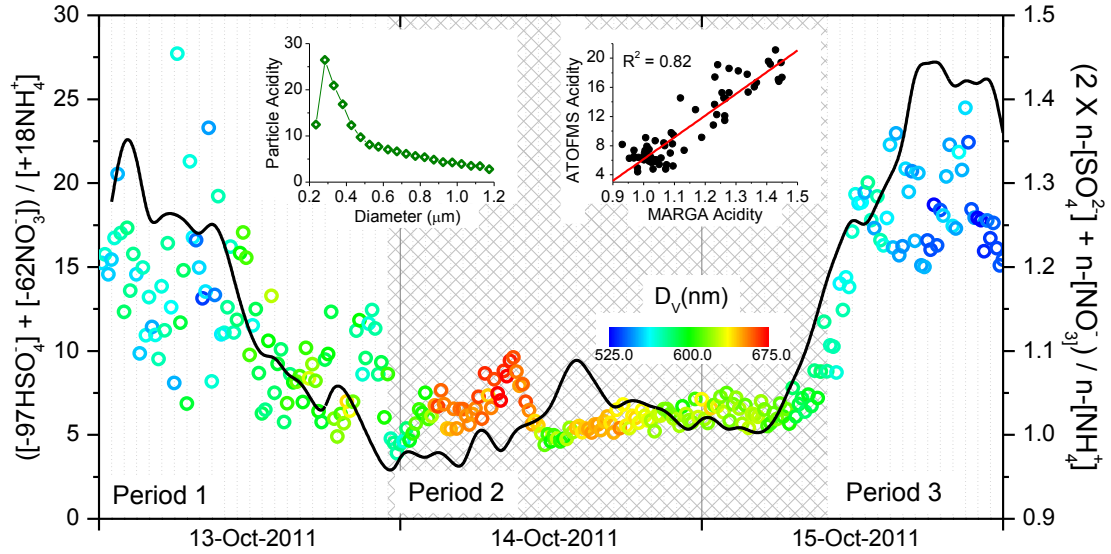
“Metal-containing particles consist of several sub-groups including Fe-, Na-Al-K-Mn-, V- and Pb-containing particles, accounting for 4.3%, 2.0%, 0.7% and 1.2% of total particles, respectively. The Fe-containing particles can be further divided into three sub-types as well (Na-K-Fe-, 0.9%; Fe-S-N-, 1.7%; Fe-N-, 1.7%), according to the mass spectra patterns and temporal variations. Pb- and Fe-S-N-containing particles had similar number fraction temporal variations (both having peaks during Period 2), indicating their sources from the northwest of Shanghai. V-containing particles occurred only when the wind blew from the east suggesting its source of ship emission (Ault et al., 2010). Fe-N- and Na-Al-K-Mn-containing particles performed nearly constant temporal number fraction, indicating regional sources. Na-K-Fe-containing particles only occurred in Oct 13 with two spikes at around 11:00 and 16:00, possibly originated from local plume.”

P. 31967, Line 13: What technique was used to correlate  $K^+$  with  $Cl^-$ ?

We used the method of least squares to correlate  $K^+$  with  $Cl^-$  concentrations measured by MARGA.

P. 31968, Line 22: The authors have shown an excellent correlation of particle acidity derived from bulk measurement with that derived from ATOFMS data. I think the authors should highlight this in the conclusions and abstract. It would be interesting to see if this correlation holds for different matrices. How strong is the correlation? It would be good if the authors could document the correlation by performing a sort of least squares fit and documenting the linear relationship.

We accept this suggestion and highlight this observation in the conclusions and abstract in the revised manuscript. We also follow the reviewer’s suggestion and modify Figure 4 to show how strong the correlation is using a least squares fit.



P. 31969, Line 22: What are the uncertainties on the SSA? I would expect they go up for low aerosol loadings. I suggest the authors add error bars to their optical property measurements. How did the authors correct for  $\text{NO}_2$  absorption? Please discuss the possible errors and QA procedures in the experimental section. So the reader can unequivocally rule out  $\text{NO}_2$  as a possible interference, please show the  $\text{NO}_2$  time series – this can be placed in the supplementary section.

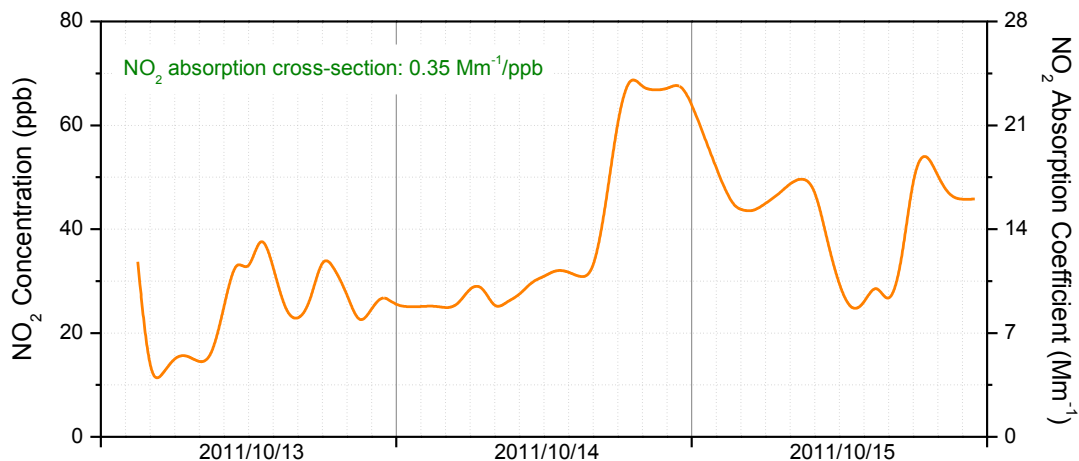
The SSA ( $\omega_0$ ) is defined as:

$$\omega_0 = \frac{\alpha_{scat}}{\alpha_{ext}}$$

The uncertainty of  $\omega_0$  is given by:

$$\frac{\Delta\omega_0}{\omega_0} = \sqrt{\left(\frac{\Delta\alpha_{scat}}{\alpha_{scat}}\right)^2 + \left(\frac{\Delta\alpha_{ext}}{\alpha_{ext}}\right)^2}$$

Li et al. (2011) suggested that in laboratory studies, the uncertainty of  $\alpha_{ext}$  is  $< 3\%$ , while under field conditions, given the varying air background and  $\text{NO}_2$  correction, the overall uncertainty of  $\alpha_{ext}$  is suggested to be smaller than  $5\%$ . When used in ambient measurement, the uncertainty of the integrating nephelometer (TSI 3563) is  $< 10\%$ . So the uncertainty of  $\omega_0$  will be no larger than  $12\%$ . Since the optical data is given in 5-min resolution in Figure 2, we think the addition of error bars will make the figure too busy. Instead, we add error bars in Figure 5a. The correction procedure of  $\text{NO}_2$  absorption is added at the end of Section 2.3, as shown above. We accepted the reviewer's suggestion and placed the temporal variation of  $\text{NO}_2$  concentration in the supplementary materials as below:



P. 31971, Line 12: The discussion of the effect aerosol chemical composition on optical properties is largely speculative. The best way to definitively conclude there is indeed a chemical effect is through a closure study whereby one calculates the absorption and scattering using measurements of aerosol size distributions and chemical composition and then comparing to the bulk optical measurements. The authors seem to have enough data to do this. Much of the discussion that follows does not decouple the interrelated effects of size, concentration and chemical composition on optical properties.

We agree that a closure study of size distribution and quantitative chemical analysis with the help of theoretical calculations will do a lot to definitively identify the chemical effect on optical properties. Unfortunately, we don't have enough data to do this. For example, we don't have size segregated quantitative chemical analysis of all the major aerosol components. MARGA only provided concentrations of water soluble inorganic ions in PM<sub>2.5</sub>. No quantitative measurement of BC and OC was done in this work. On the other hand, even with all of the bulk measurement data, the calculation will be based on an assumption that the particles are externally mixed without considering the internal mixing state at the single particle level, which adds nothing new to the literature. The best way to investigate the impact of mixing state on optical properties is to carry both chemical and optical measurements at the single particle level (Moffet and Prather, 2009). Without this kind of facility, our approach is: 1) Using mass extinction coefficient to characterize the aerosol's optical properties. 2) Using the available data to show that PM mass extinction efficiency is only valid while the particle mixing state remains stable. 3) With the help of the ATOFMS, we can identify time periods with constant chemical composition and mixing state of the particles and ensure more precise interpretations of aerosol optical properties.

P. 31972, Line 10: What values were measured by Chow et al.? These should be provided in the text to facilitate the discussion.

We add a few sentences to give the values in literatures:

“The observed mass extinction efficiencies are comparable with the literature data for urban areas. Mass scattering efficiencies for a variety of cities in North America were reported in the range of

1.7 - 5 m<sup>2</sup>g<sup>-1</sup> (PM<sub>2.5</sub>) by Chow et al. (2002). Bergin et al. (2001) reported mass scattering efficiencies between 2.3 and 3.6 m<sup>2</sup>g<sup>-1</sup> (PM<sub>10</sub>) in Beijing, China. Garland et al. (2008) reported mass scattering efficiencies of 3.60 - 4.13 m<sup>2</sup>g<sup>-1</sup> (PM<sub>1</sub>) and mass absorption efficiencies of 0.78 - 1.09 m<sup>2</sup>g<sup>-1</sup> (PM<sub>1</sub>) near Guangzhou, China.”

P. 31973, Line 13: What are the units and uncertainties associated with the scattering efficiencies quoted here? Was scattering efficiency properly defined in this paper?

The unit of mass scattering (absorption/extinction) efficiency here is m<sup>2</sup>g<sup>-1</sup>, referred to as the scattering (absorption/extinction) efficiency of unit PM<sub>1</sub> mass. In the revised manuscript, we added “mass” before scattering (absorption/extinction) efficiency. The uncertainties associated with the mass scattering/absorption efficiencies were added in the revised manuscript, Figure 5 and Table S1 in the supplementary materials.

Table 3: This table could be improved by including statistics of PM concentrations during the different periods rather than just correlation coefficients.

Since Part 3.3.1 provides few new findings (see the other reviewer’s comment), we decide to remove this part of the discussion including Table 3 and just left a few sentences to point out the inconsistency between PM<sub>1</sub> mass concentration and extinction coefficient. We added two more references here (Bergin et al., 2001; Garland et al., 2008) to support the statement that “In field studies, PM<sub>1</sub> has been reported to contribute over 80% of light extinction”.

Figure 1: it is not clear why there are three panels in this figure. Each panel should be labeled.

We used one panel of back trajectories for each day, combined with wind direction, to show the different air mass origins and their quick changes in these three days. In the revised Figure 1, we label each panel with date as below:

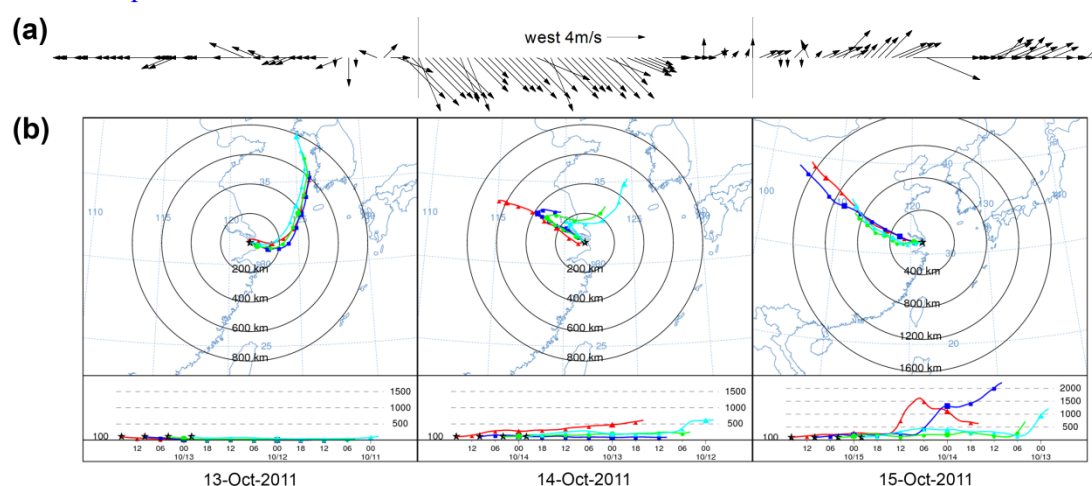
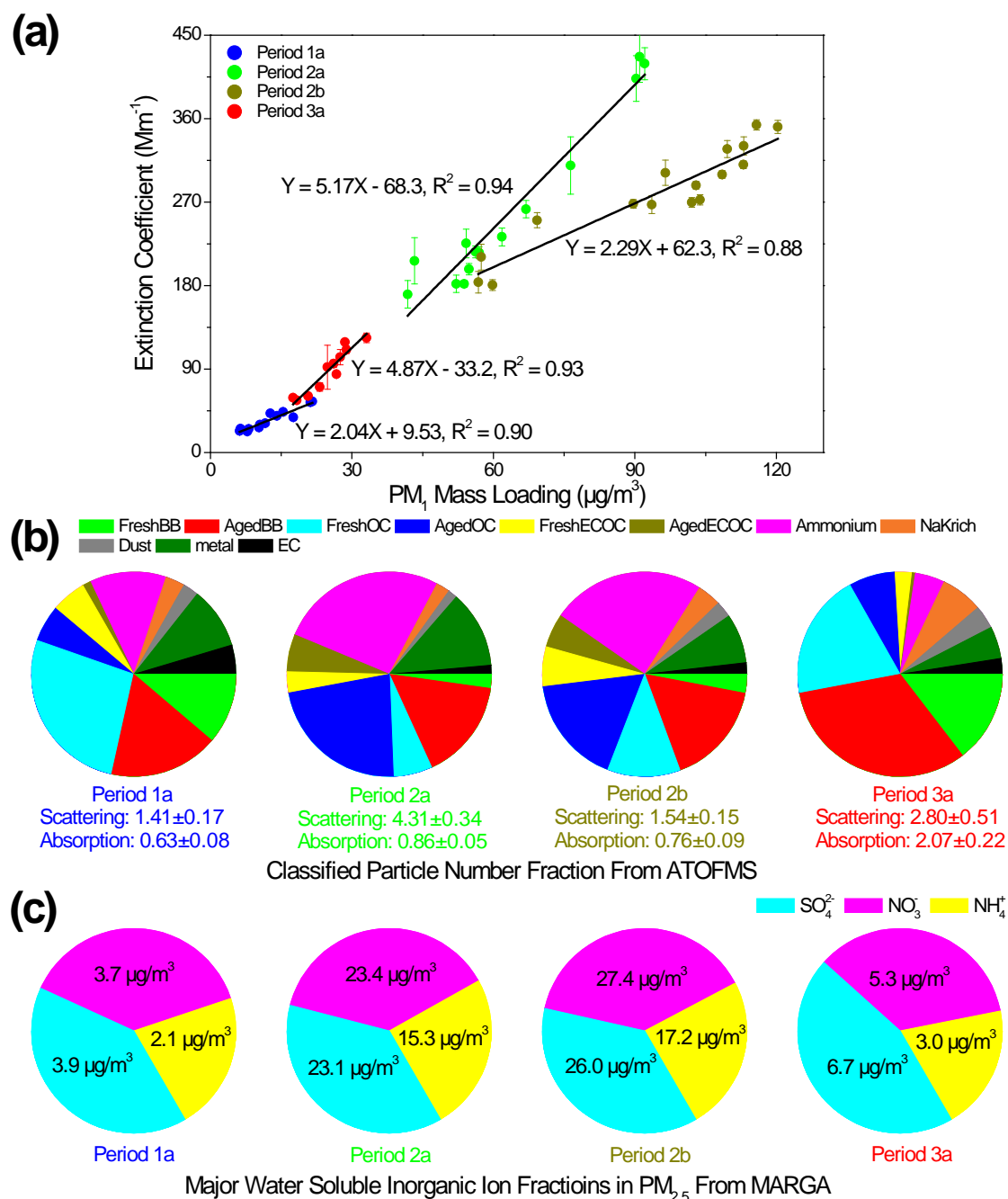


Figure 5. perhaps color code the text identifying the periods in panels b and c according to the dot color in panel a. This would greatly assist interpretation.

We accept this suggestion and revise Figure 5 accordingly. We also add error bars on the extinction coefficient in panel a and uncertainties on the scattering and absorption efficiencies in panel b in Figure 5 as below:



Reference:

- Ault, A. P., Gaston, C. J., Wang, Y., Dominguez, G., Thiemens, M. H., and Prather, K. A.: Characterization of the single particle mixing state of individual ship plume events measured at the port of Los Angeles, *Environ. Sci. Technol.*, 44, 1954-1961, doi:10.1021/es902985h, 2010.
- Bergin, M. H., Cass, G. R., Xu, J., Fang, C., Zeng, L. M., Yu, T., Salmon, L. G., Kiang, C. S., Tang, X. Y., Zhang, Y. H., and Chameides, W. L.: Aerosol radiative, physical, and chemical properties

- in Beijing during June 1999, *J. Geophys. Res.-Atmos.*, 106, 17969-17980, doi:10.1029/2001jd900073, 2001.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., and Richards, L. W.: Comparability between PM<sub>2.5</sub> and particle light scattering measurements, *Environ. Monit. Assess.*, 79, 29-45, doi:10.1023/a:1020047307117, 2002.
- Furutani, H., Jung, J., Miura, K., Takami, A., Kato, S., Kajii, Y., and Uematsu, M.: Single-particle chemical characterization and source apportionment of iron-containing atmospheric aerosols in Asian outflow, *J. Geophys. Res.*, 116, D18204, doi:10.1029/2011jd015867, 2011.
- Garland, R. M., Yang, H., Schmid, O., Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Takegawa, N., Kita, K., Miyazaki, Y., Kondo, Y., Hu, M., Sha, M., Zeng, L. M., Zhang, Y. H., Andreae, M. O., and Pöschl, U.: Aerosol optical properties in a rural environment near the mega-city Guangzhou, China: implications for regional air pollution, radiative forcing and remote sensing, *Atmos. Chem. Phys.*, 8, 5161-5186, doi:10.5194/acp-8-5161-2008, 2008.
- Gaudichet, A., Echalar, F., Chatenet, B., Quisefit, J. P., Malingre, G., Cachier, H., Buatmenard, P., Artaxo, P., and Maenhaut, W.: Trace elements in tropical African savanna biomass burning aerosols, *J. Atmos. Chem.*, 22, 19-39, doi:10.1007/bf00708179, 1995.
- Li, L., Chen, J. M., Chen, H., Yang, X., Tang, Y., and Zhang, R. Y.: Monitoring optical properties of aerosols with cavity ring-down spectroscopy, *J. Aerosol. Sci.*, 42, 277-284, doi:10.1016/j.jaerosci.2011.02.001, 2011.
- Liu, D. Y., Wenzel, R. J., and Prather, K. A.: Aerosol time-of-flight mass spectrometry during the Atlanta Supersite Experiment: 1. Measurements, *J. Geophys. Res.-Atmos.*, 108, 8426, doi:10.1029/2001jd001562, 2003.
- Moffet, R. C., and Prather, K. A.: In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, *Proc. Natl. Acad. Sci.*, 106, 11872-11877, doi:10.1073/pnas.0900040106, 2009.
- Osthoff, H. D., Brown, S. S., Ryerson, T. B., Fortin, T. J., Lerner, B. M., Williams, E. J., Pettersson, A., Baynard, T., Dube, W. P., Ciciora, S. J., and Ravishankara, A. R.: Measurement of atmospheric NO<sub>2</sub> by pulsed cavity ring-down spectroscopy, *J. Geophys. Res.-Atmos.*, 111, D12305, doi:10.1029/2005jd006942, 2006.
- Querol, X., Juan, R., LopezSoler, A., FernandezTuriel, J. L., and Ruiz, C. R.: Mobility of trace elements from coal and combustion wastes, *Fuel*, 75, 821-838, doi:10.1016/0016-2361(96)00027-0, 1996.
- Seinfeld, J. H., and Pandis, S. N.: *Atmospheric Chemistry and Physics: From air pollution to climate change*, 2nd ed. John Wiley & Sons, New York, 2006.
- Spencer, M. T., Holecek, J. C., Corrigan, C. E., Ramanathan, V., and Prather, K. A.: Size-resolved chemical composition of aerosol particles during a monsoonal transition period over the Indian Ocean, *J. Geophys. Res.-Atmos.*, 113, D16305, doi:10.1029/2007jd008657, 2008.