Atmos. Chem. Phys. Discuss., 11, C10304–C10359, 2011
www.atmos-chem-phys-discuss.net/11/C10304/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Typical types and formation mechanisms of haze in an eastern Asia megacity, Shanghai" *by* K. Huang et al.

K. Huang et al.

gzhuang@fudan.edu.cn

Received and published: 14 October 2011

Response to the comment by Anonymous Referee #1

In this study, Huang et al. presented measurements of aerosol and trace gases at a site in Shanghai, China from April to June 2009. Three major haze episodes having distinct characteristics were observed during the experiment, under different meteorological conditions. Using the correlation between gaseous pollutants (CO, SO2, and NOx) and PM2.5, chemical tracers of dust (Al) and biomass burning (K+ and OC, EC), as well as satellite and ground-based lidar data, the authors were able to attribute the three episodes to anthropogenic/industrial pollution, long-range transport of dust from Gobi, and agricultural ïňĄres in eastern China. Overall, the manuscript is based on a quite comprehensive, original data set collected from a megacity known to have severe air

quality issues. The topic is suitable for the special issue and should also be of interests to the wide science community. The results were presented in an organized fashion. On the other hand, this reviewer found the manuscript lacking quantitative, in-depth analysis, and missing some important details. Also the quality of the writing needs to be improved: there are numerous grammatical mistakes and typos in the manuscript (too many to list blow), making it difiňĄcult to follow at times. Major revisions are recommended before the manuscript can be accepted for publication in ACP.

We thank the reviewer for a thorough comment on this manuscript. In the revised manuscript, we made those corresponding corrections, following the comments point by point. In addition, we improved the quality of the writing and corrected those grammatical mistakes and typos. Below are the responses to all the comments one by one.

SpeciïňĄc Comments: In the manuscript, the authors focused on the impact of different sources on the three types of haze episodes. And this brings an interesting question: the sources and transport of dust and biomass burning emissions can well explain the episodic nature of episodes 2 and 3, then how about episode 1? The industrial and trafiňĄc emissions are not expected to change dramatically over two months, but why was episode 1 so much more polluted than the "normal period"? This is likely due to change in meteorological conditions, and the authors are encouraged to look into the meteorological mechanisms for the formation of major haze events.

Yes, thanks for the good suggestion of adding the meteorological parameters to look deeper into the formation of haze under different conditions. In the revised manuscript, we have added several meteorological parameters, i.e., wind speed and direction, relatively humidity (RH), dew point and the atmospheric pressure in Figure 1. During PE1, the local air was under a low pressure system turning from a high one several days ago as shown in Fig. 1a. Winds blew from various directions and the wind speeds were relatively low and even were stagnant sometimes, which were not favorable for the dispersion of pollution. There was an obvious decrease of relative humidity (RH) during PE1. Cold front from inland China probably contributed to the high pollution of

PE1 to some extent. The similar meteorological conditions were also observed during PE3. While during PE2, winds dominantly blew from northwest with high speeds, consistent with the backward trajectories in Fig. 3 in the manuscript. Due to the cold front from northern China, dew point and relative humidity both decreased a lot. During the normal days, i.e, the relatively clean periods, we could find that winds blew from the southeast at most times, i.e. from the East China Sea. Also, the wind speed in those normal days was usually higher than that in the haze events (except for PE2). Thus, we did find that the change of meteorological conditions could impact greatly on the formation of haze events as the reviewer suggested. Actually, we did mention the role of meteorological conditions on the haze formation in some parts of Section 3.1. For instance, the three days air mass backward trajectory computed by the HYSPLIT model in Fig. 3 showed the wind direction and speed, which was consistent with the surface meteorological measurements in Fig. 1a. Also, the height of PBL layer shown in Fig.3 was another important parameter for assessing the convection of air pollution. During PE1 and PE3, the average daily PBL height was around 500 meters. Thus, we think that the low PBL layer could also contribute to the haze formation. In the revised manuscript, Fig. 1 was revised, as shown above. Also, we added more detailed description of the possible role of meteorological conditions in the haze formation.

Section 2: a more detailed description should be given for the site – is it urban, suburban, or rural? Are there any major local emission sources (point sources, roads), and are they expected to have impact on the data set? And how is this mitigated? Is the site truly representative of a megacity? Also more detailed information is needed for gas analyzers – for example, what kind of calibration standard was used? Is zero check every week sufiňĄcient for the CO analyzer, among other instruments?

Yes, we have added the description of the observational site into Section 2.1 as follows: The observational site (31.3°N, 121.5°E) in this study is on the roof ($\sim$ 20 m high) of a teaching building on the campus of Fudan University in Yangpu district, Shanghai. Almost no high buildings are around this sampling site. This observational site is ap-

proximately 40 km inland from the East China Sea. The closest industrial sources are located approximately 10.5 km away and are primarily to the southeast and northwest (Li et al., 2011). About 1.3 million residents are living in this area (SMSB, 2011). This site could be regarded as a representative of the megacity Shanghai, standing for the mixing of residential, traffic, construction, and industrial sources (Wang et al., 2006).

The routine QA/QC procedures includes the daily zero/standard calibration, span and range check, station environmental control, staff certification, etc., according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai based on the national specification HJ/T193–2005, which was developed following the technical guidance established by the U.S. Environmental Protection Agency (U.S. EPA) [1998]. The multi-point calibrations were applied weekly upon initial installation of the instruments. At least five points were used for calibration, consist of three or more test concentrations, including zero concentration, a concentration between 80% and 90% of the full scale range of the analyzer, and some intermediate concentrations. If some instruments have malfunction, the multi-point calibrations are also used to verify the linearity of instruments. On a daily basis, a two-point calibration method was applied, which is easier and quicker. In the revised manuscript, we have added more detailed information about the QA/QC.

P21719, line 2, a ïňĄxed lidar ratio was used in spite of various aerosol types (industrial, dust, and biomass burning) observed at the site?

Yes, we admit that using a fixed lidar ratio under different types of haze is not very reasonable. Thus, in Section 3.4 of discussion about the aerosol vertical profile, we only quantitatively discussed the vertical profile of aerosol backscattering coefficient, while the vertical profile of aerosol extinction coefficient was only qualitatively discussed. We just want to state that a lidar ratio of 50sr was only applied to derive the extinction coefficient under normal times in Section 2.1.3,. While in some special haze events, i.e, dust and/or biomass burning, a different lidar ratio should be used. However, as the mixing proportion of dust, biomass burning aerosol, and secondary inorganic aerosol

is difficult to accurately determined, we didn't look very deep into the lidar ratio under different haze events.

P21721, line 18: why made the comparison between two stations that are 32 km apart?

At the observational site in this study there was no instrument directly measuring the visibility. For the purpose of evaluating the estimated visibility by using the formula shown in Section 3.1 (now move to Appendix A), we chose the available visibility data from the meteorological station at Pudong of the closest distance to our observational site. Although our site is 32 km away from this station, we think that this comparison is still reasonable, as the visibility within a narrow area should be relatively homogeneously distributed in the haze events. However, in the future study we will try to use the datasets at the same location for comparison or evaluation.

P21722, line 1: are the PM1, PM2.5 and PM10 mean concentrations given above the average of hourly or daily data? 24-h mean should be used to compare to the 24-h standard. P21722, line 15: air mass usually refers to large body of air of similar characteristics (e.g., Arctic air).

Yes, the PM1, PM2.5, and PM10 mean concentrations given are the average of 24-h concentrations. Yes, we have changed the term "air masses" into "air flows" here and elsewhere in the revised manuscript.

P21722, line 17 and Fig. 3: how was mixing height determined? Is it the mean along the trajectories? How does it compare to lidar data? Lower panel of Fig. 3b shows daily mixing height but the caption indicates it is 3-h average?

The mixing heights shown in Fig. 3 are computed from the NCEP Global Data Assimilation System (GDAS) model (http://ready.arl.noaa.gov/READYamet.php). The model outputs are 3-hr at the time resolution, thus the blue dots in Fig. 3 denoted the 3-h average mixing height. Also, we calculated the daily average mixing height as indicated by the pink horizontal step lines. In the revised manuscript, we have added the data

source of the mixing height.

The modeled PBL heights are overlaid with the aerosol vertical profile measured by lidar. As shown in the figures below, the temporal variations of modeled PBL heights (black dots) are relatively consistent with the PBL heights visualized from lidar at most times. This comparison suggests that both datasets are reliable.

P21723, line 18: April should be June?

Yes, this is typo. Thanks for pointing out this mistake. It was corrected in the new version.

P21724, line 11: the authors should not assume that the readers all have a good knowledge of the geography of China. Would recommend that the authors mark the important features/locations/regions on the map of Fig. 5.

Yes, thanks for the good suggestion of marking the major locations on the China map. However, we find it difficult to see clearly if too many descriptions are added on Fig. 5, as this figure is composed of various colors. Alternatively, we added the locations on Fig.4, as this figure has more blanks and it is easier to look at.

Section 3.2: overall, the analysis using satellite data is problematic. The authors should demonstrate that the Angstrom exponent from MODIS is a reliable product before using it to distinguish various aerosol types (refer to Levy et al., ACP 2010 for a recent validation study of the product). Otherwise, Angstrom exponent from ground-based sun photometers can be used. There seem to be artifacts in the processing of the satellite data, as Fig. 5a-d look odd with stripes and small data gaps. Also has OMI row anomaly been removed from the HCHO data shown in Fig. 5g?

Yes, we agree to what the reviewer said here. The satellite products usually have uncertainties due to the algorithm assumptions, different retrieve methods, and the interferences from clouds, precipitation, etc. As pointed out by Levy et al. (2010), the Angstrom exponent product has greater uncertainty than the other MODIS prod-

ucts. However, its values are still within reasonable range as compared to the ground-based AERONET products. As the reviewer suggested, Angstrom exponent from ground-based sun photometers should be better used for charactering the aerosol sizes. Unfortunately, in this study there was no AERONET data available in the region of the Yangtze River Delta. Even now there is no AERONET data available in the whole mainland China (refer to the global map of AERONENT sites distribution in http://aeronet.gsfc.nasa.gov/cgi-bin/type_piece_of_map_opera_v2_new). Thus, we have no choice but only are able to use the satellite data. Additionally, Angstrom exponent retrieved from satellite still has its advantage compared to the ground-based instrument, as it can provide a clearer picture of the regional distribution of aerosol optical properties. For instance, from Figure 5d we could confirm that the pollution during PE2 was caused by the large-scale dust storm but not local pollution such as construction works near the sampling site. Also, in the discussion of the Angstrom exponent in the manuscript, we didn't tend to quantitatively analyze it as we know that this parameter is highly uncertain. Instead, we focused on the qualitative analysis, e.g, the comparison between regional distribution of Angstrom exponent during PE1 and PE2, which gave a visualization of the different aerosol size. In the future study, we will try to use more ground-based techniques to accurately characterize the type of aerosols.

As for the stripes and small data gaps in the satellite image, it was due to that some grids have no data owing to the satellite scan gaps and relatively sparse pixels and bigger footprints at the marginal granule. Also, the interference of clouds and/or precipitation could also shield some information of aerosol. Thus, stripes and small data gaps should not be from the artifacts in processing the satellite data.

P21725, line 20: a more quantitative demonstration of the spatial correlation between CO and ïňĄre counts would be helpful. Similarly for HCHO and ïňĄre counts mentioned in line 11, P21726.

Yes, we have demonstrated the spatial correlation between CO, HCHO and fire counts as the reviewer suggested. All the data are grided with resolution of 0.5 $\times$ 0.5 degree

and then the linear regression was applied to all the data at the same grid. As shown in the figures above, CO and HCHO both had moderate correlation (R $\sim$ 0.49) with the numbers of fire spots, indicating the impact from biomass burning on the trace gases. However, the correlations were not very significant, as the effect of meteorological conditions were not considered. Overall, the linear correlations were still reasonable. In the revised manuscript, we have added more quantitative discussion of the correlation between CO and HCHO with fire spots.

P21726, line 21: why would sea breeze clean aerosol but not CO or HCHO?

Actually, we observed that the sea breezes tended to clean more aerosol (AOD) and HCHO than CO as shown in Fig. 5. We attribute the different behaviors to their different life times. Aerosol contains a considerable fraction of soluble species, i.e, sulfate, nitrate, ammonium salts, and soluble organic aerosol, which are easily subject to be scavenged by see breezes with rich moisture. For HCHO, it is highly water soluble. Also, HCHO is easy to be oxidized by some oxidants such as OH radical, O3, and etc. That's why we found that aerosol and HCHO were mostly scavenged over the East China Sea. For CO, its life time is much longer than aerosol or HCHO and it is relatively not easy to be oxidized. Thus, we could find that the transport distance of CO was longer than AOD and HCHO and the spatial distribution of CO is more dispersed.

P21728, line 28 and Fig. 6: this part is confusing. It appears that the Ca/Al ratio was also small for other days and is quite noisy – does not seem to be a good indicator for the dust source region.

The "noisy" Ca/Al ratios could be due to several causes. Shanghai is a fast developing city with frequent construction works almost all year around, such as housing demolition, municipal construction and road renovation. Enriched Ca content in aerosol in the urban cities mainly derived from the construction works (Wang et al., 2006; Yang et al., 2005). Also, the re-suspended dust lifted by the vehicles contained high-Ca aerosol. Compared to the Ca/Al ratio of 0.5 in the dust from the Gobi Desert, the Ca/Al ratios

during the normal times were usually around or above 1.0, due to the enrichment of Ca. The Ca/Al ratios during the study period seemed noisy because the intensity of construction works and traffic activities varied intensively daily. Thus, the fluctuation of Ca/Al ratios was expected and reasonable. There did have several low Ca/Al ratio case, i.e, on May 4 and 12. However, the mineral (Al) aerosol concentration was relatively low, indicating that these days were not influenced by the transport of dust and were relatively clean episodes from the local sources. We used the Ca/Al ratio as an indicator for the dust source region as it had a much lower value (0.5) in the Gobi Desert than in the local sources of Shanghai. When the local environment is influenced by the entrained dust, there would be an obvious decrease of the Ca/Al ratio. In this study, the Ca/Al ratio decreased to 0.75 when Al reached 13.7 μg m-3. However, this ratio was not close enough to the source region (i.e, 0.5) as the reviewer questioned that there were also other days with small Ca/Al ratios. That's because the dust event in this study was a weak event, the entrainment of dust couldn't dominate over the local dust. During a stronger dust event on April 2, 2007 in Shanghai, the daily TSP concentration reached 806.2 μg m-3, and the Ca/Al was lower with the value of 0.67 (Huang et al., 2010). Thus, the feasibility of using the Ca/Al tracer for the dust transport in downstream regions depended on the intensity of entrained dust and local anthropogenic dust. If the dust event is strong enough, we think it was a good choice to use the Ca/Al ratios to trace the dust source region.

P21729, line 29: what is the ratio between K+ and Cl-? Cl- can also be derived from coal burning.

In this study, the K+/Cl- ratio during biomass burning pollution was 2.09. Ryu et al. (2004) summarized the K+/Cl- ratios during biomass burning in various regions of the world, as shown in the table below (note that Cl-/K+ ratios are presented in the table). The K+/Cl- ratios ranged from 1.29 to 2.63 except the extremely low result in Africa savanna. Thus, the result of our study fell well into this range.

Cl- could be derived from coal burning as the reviewer said, because coal has always

contributed to the biggest share of the energy structure in Shanghai. The background (i.e, when fossil fuel combustion dominated) K+/Cl- ratio in Shanghai ranged from 0.10 to 0.46 based on a seasonal analysis (calculated from Table 3 in Wang et al. (2006)). During PE3 in this study, K+/Cl- ratio was much higher than its background ratio, indicating the dominance of biomass burning source. More detailed source profile is needed to quantitatively analyze the contribution from various sources. In the revised manuscript, we have added discussion on the possible source of Cl- from coal burning.

P21730, line 9-14: from the results of Yamaji et al. (cited above), the OC/EC ratio during MTX2006 was closer to 3 (Zhang et al., 2008) than to the results given here.

Yes, there seems inconsistence between this study and Yamaji et al. (2010) on the issue of OC/EC ratios from biomass burning. However, from the table above (Ryu et al., 2004), they did also observe higher OC/EC ratios during biomass burning in northeast Asia, which was consistent with our results. We thought that the relatively low OC/EC ratio in Yamaji et al. (2010) could be due to the mixing of local anthropogenic sources (e.g, industrial, traffic) with biomass burning. Shandong province, where the MTX 2006 campaign took place, is a big province of China with heavy anthropogenic emission. The background aerosol composition is high, which could probably shield the signature of biomass burning.

P21731, line 8-17: the enrichment of As in agricultural ïňĄre emissions is a very important result – any more data on As emissions from agricultural ïňĄres?

Yes, the enrichment of As in agricultural fire emissions is an important issue due to its adverse effects on human health and ecosystem. We do have multi-year aerosol As data at several sites of China, i.e, Eastern China, North China Plain and Western China. The next step of our study will be to gather more cases to investigate the relation between biomass burning and As enrichment in aerosol.

Section 3.4: from Fig. 6 one can tell that soil or dust was a sizable part of aerosols on April 6, however this was not reïňĆected in the lidar data?

Yes, dust was a significant part in the total suspended particles (TSP) on April 6. However, the secondary aerosol also presented the highest concentration on the same day as shown in Fig. 6. Thus, the abundant fine particles probably disguised the characteristics of coarse particles as coarse particles had much smaller backscattering efficiency than fine particles. As indicated from the depolarization ratio detected by the lidar, its values were almost lower than 5% on the whole day of April 6, indicating the dominance of spheric particles.

P21734, line 1, PE3 should be PE1?

Yes, this is a typo. We corrected "PE3" to be "PE1" in the new version.

P21735, line 5: recent studies show that SO2 emissions might have started decreasing in China (refer to Li et al., GRL, 2010 and Lu et al., ACP, 2010).

Yes, thanks for proving these two useful references. We have added into the discussion.

P21735, line 19: NO3-/SO42- not SO42-/NO3-?

Yes, it should be NO3-/SO42- , not SO42-/ NO3-. We did correct it in the new version. Thanks for pointing out this mistake.

P21737, line 10: there should be updated emission inventory for the region.

Yes, we replaced the original emission inventory with the latest INTEX-B emission inventory in Asia (Zhang et al., 2009) and re-calculated the results.

P21738, line 27: use of coal should be more or less correlated with utility generation and could be on the rise in China over the past decade or so.

Yes, we agree to what the reviewer said here. The emission from power plants are the main source of SO2 in China and the utility generation from coal usage has been increasing over the past decade. Based on the two reviewers' concern on Section 4, they both believe that this section seems not very closely linked to the main theme of

this paper. The authors decided to remove this section out in the new version to make the whole paper more focused on its main theme. Thanks for this reviewer's hard work on this section.

P21739, line 14: there are plenty of minerals as shown in this and previous studies, even if NH3 emissions are reduced.

Yes, we agree with the reviewer's statement. Minerals are also important for the formation of secondary aerosol as it can serve as alkaline surface for the heterogeneous reaction. In this study, most minerals accumulated in coarse particles. Minerals in fine particles (i.e, PM2.5) only accounted for about 11% in the total suspended particles (TSP). Thus, control of minerals should be beneficial for the mitigation of coarse particles. In those coastal urban cities in China, such as Shanghai, minerals mainly derive from the construction works and sometimes from the dust transport. Our recent results show that PM10 concentration during the 2010 Shanghai Expo had been significantly reduced due to the temporary shutdown of construction sites. However, to reduce the fine particle emission, control measures on the NH3 emission may be more efficient as sulfate ammonium and nitrate ammonium are mainly formed in fine particles, not in coarse particles. A very recent study applied the Response Surface Modeling (RSM) technique in the Community Multi-Scale Air Quality Model (CMAQ) to study the response of inorganic species to the change of anthropogenic emissions (i.e., NH3, SO2, NOx) (Wang et al., 2011). They found that in the most polluted areas in China such as NCP (North China Plain), and YRD (Yangtze River delta), NH3 was sufficiently abundant. The 90% increase of NH3 emissions during 1990 - 2005 resulted in $\sim$50-60% increases of NO3- and SO42- aerosol concentrations. It is suggested that the most effective pathway is to adopt a multi-pollutant strategy to control NH3 emissions in parallel with current SO2 and NOx controls in China.

Section 4: it would really be useful for the authors to give some statistics on different types of haze events: how many inorganic ones, how many biomass burning ones, and how many dust ones? That way, the quality of the paper will be much improved, and

the results would be more helpful for the policy makers.

Yes, thanks for the very good suggestion on summarizing the statistics on different types of haze events. At this stage, however it is difficult to finish this task during a very short time. In Shanghai, we started seasonal aerosol sampling from late 2004 till now. To analyze and differentiate from case to case of total 6 years' data will be a really big project in a limited time. In addition, the chemical analysis in laboratory is still ongoing for recent sampling periods (e.g, 2011). This paper could be regarded as a pilot study for the typical haze types in Eastern China. In the further study, as the reviewer suggested, a more comprehensive and long-term study of this issue will be conducted and the results will be expected to contribute to the community and be helpful for the policy makers.

P21741, line 1: a paper on the 2010 dust recently came out in Atmos. Environ. (Wang et al., First detailed observations of long-range transported dust over the northern South China Sea, 2011).

Yes, thanks for providing this reference.

Fig. 1b, may consider using different colors for PM2.5 and PM10. Also it would be helpful if the three episodes can be marked in the ïňĄgure.

Yes, we have used different colors for better visualization and the three episodes are marked in the revised figure.

Fig. 2, is gas concentration for standard temperature and pressure?

Yes, it is for standard temperature and pressure.

Fig. 7, the high EF of V for PE1 is interesting, and may deserve some discussion.

The EF of V during PE1 is about 11, indicating slight enrichment. It could be from the re-suspension of local soils and road pavement erosion (Amato et al., 2009).

Fig. 9, a and c are average proïňĄles for the entire day? Fig. 10, what do the error

bars stand for?

Fig. 9a and 9c represent average profiles of several hours on a certain day. We have added the detailed time information into the manuscript.

Error bars in Fig. 10 represent one standard deviation of the gaseous concentrations during different periods. We added the illustration of error bars in the caption of this figure.

Fig. 12. The CO/PM2.5 ratio seems to be higher in PE1 than in PE3, can you give more discussion on that?

The CO level was similar between PE1 and PE3 as shown in Fig. 10. However, the average PM2.5 concentration was 84.0$\pm$48.4 μg m-3 during PE3, higher than that of 63.6$\pm$16.4μg m-3 during PE1 as discussed in Section 3.1. Thus, the higher CO/PM2.5 ratio during PE1 was due to the higher PM2.5 concentrations during PE3. This probably meant that biomass burning could produce higher aerosol mass than the industrial/traffic emission as most of the biomass burning events are incomplete combustion, which couldn't effectively oxidize the hydrocarbon to CO2 or CO.

References: Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., and Moreno, T.: Spatial and chemical patterns of PM10 in road dust deposited in urban environment, Atmos. Environ., 43, 9, 1650-1659, 2009. Huang, K., Zhuang, G. S., Li, J. A., Wang, Q. Z., Sun, Y. L., Lin, Y. F., and Fu, J. S.: Mixing of Asian dust with pollution aerosol and the transformation of aerosol components during the dust storm over China in spring 2007, J. Geophys. Res., 115, D00K13, doi:10.1029/2009JD013145, 2010. Li, P. F., Li, X., Yang, C. Y., Wang, X. J., Chen, J. M., and Collett, J. L.: Fog water chemistry in Shanghai, Atmos. Environ., 45, 24, 4034-4041, 2011. Ryu, S. Y., Kim, J. E., Zhuanshi, H., Kim, Y. J., and Kang, G. U.: Chemical composition of post-harvest biomass burning aerosols in Gwangju, Korea, J. Air Waste Manage. Assoc., 54, 9, 1124-1137, 2004. SMSB: Shanghai Municipal Statistics Bureau, Shanghai sixth national census in 2010 Communiqué on Major Data (in Chinese), 2011. Wang, S. X., Xing, J., Jang, C., Zhu,

Y., Fu, J. S., and hao, J. M.: Impact Assessment of Ammonia Emissions on Inorganic Aerosols in East China Using Response Surface Modeling Technique, Environ. Sci. Technol., Accepted, 2011. Wang, Y., Zhuang, G. S., Zhang, X. Y., Huang, K., Xu, C., Tang, A. H., Chen, J. M., and An, Z. S.: The ion chemistry, seasonal cycle, and sources of PM2.5 and TSP aerosol in Shanghai, Atmos. Environ., 40, 16, 2935-2952, 2006. Yang, F. M., Ye, B. M., He, K. B., Ma, Y. L., Cadle, S. H., Chan, T., and Mulawa, P. A.: Characterization of atmospheric mineral components of PM2.5 in Beijing and Shanghai, China, Sci. Total Environ., 343, 1-3, 221-230, 2005. Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 14, 5131-5153, 2009.

Response to the comments from Anonymous Referee #2

The manuscript combined multiple-technique to study three types of haze pollution and the results are interesting and useful. This reviewer has only some minor comments for authors considering.

We thank the reviewer's hard work. We addressed the comments point by point as shown below.

Page21721, lines 1-19 could be moved to supporting information.

Yes, thanks for the suggestion. We removed this part to the appendix.

Page 21722, lines1-2 could be discarded since the two sentences are deviating from the main theme of discussion.

Yes, we have deleted these two sentences in the new version following the reviewer's suggestion.

Page 21722, lines 4-5, "The mass ratio of PM1/PM2.5 ranged from 0.90 to 0.99, indicating particles tended to accumulated in smaller sizes." The sentence needs to rewrite because the meaning is not clear to this reviewer.

Actually, we wanted to the emphasize that the aerosol mass accumulated in much smaller size, i.e, less than 1.0 um. As most of the published research results in Shanghai and other regions of China mainly focused on PM2.5 and/or PM10, the results of PM1 shown in this study could shed some light on the further study of smaller particles, as particles with smaller sizes probably had more negative health effects. In the revised manuscript, we have revised this sentence to be "The mass ratio of PM1/PM2.5 ranged from 0.90 to 0.99, suggesting that the mass of PM2.5 was mainly dominated by smaller particles, e.g, PM1.".

Page 21724, lines 1-4, the paragraph does not read well and the information presented is very negative. This reviewer believes that the authors are combining aerosol optical and chemical properties to support their classification later. This is fine, but it does not mean that the classification presented early is problematic. Rewrite.

Yes, we have revised the statement and make it more positive. This paragraph is rewritten to be "In the discussion above, the analysis of PM, pollutant gases and meteorological parameters had already shed some light on the pollution types of different episodes. And we will show more evidences of the optical and chemical properties in the discussions below."

Page 21724, lines 7-8, references are missing (e.g., Gao et al., 2011, AE, 45, 3069-3077).

Yes, we have added this reference into the revised manuscript.

Page 21725, lines3-5, here are too speculated and more evidences are needed.

Yes, we added more quantitative analysis in Section 3.3 to support our speculation as shown below. The mean Al concentration during PE1 was 5.48 $\pm$ 2.52 μg/m3, higher than the Al concentrations (2.51 $\pm$ 2.52 μg/m3) in the winter (Huang et al., 2011, manuscript in preparation) when dust transport was almost free. Also, the fraction of mineral aerosol in TSP during PE1 reached (40 $\pm$ 17)%, also higher than that ($\sim$

20%) in the non-dust days in Shanghai (Fu et al., 2010). This result combined with the regional distribution of Angstrom exponent probably indicated that PE1 could be influenced by the transport of dust aerosol to some extent.

Page 21725, line 8, not “ANYWAY”, should be “However”

Yes, we corrected it following the advice of the reviewer..

Page 21725, lines 13-14, this reviewer cannot follow the logic and the potential impact of dust storm should be elaborated.

In this paragraph, we want to confirm that PE2 was indeed caused by the long-range transport of dust from the view of remote sensing technique. We have revised these sentences in the new version to be “Thus, the remote sensing analysis confirmed that PE2 was impacted by the long-range transport of dust. The dust storm had spread over almost the whole Northern China Plain and Eastern China as shown in Fig. 5d.”.

Section 2.5 is informative, but does not focus. Suggest making some revisions.

Yes, we made some revisions to make this section more focused.

Page 21735, What is the role of “The problem for the present and future would be nitrogen oxides.’? Lines 6-19 are deviating from the main theme and need to be reorganized.

The role of this statement aims to make suggestion on the future control of NOx emission for the policy makers of local government. In the future, the major source of NOx would be from vehicle emission. As shown in Figure 1 below, the increase trend of the annual tropospheric NO2 in Beijing was consistent with the increase of vehicle numbers. In the eastern China, the annual tropospheric vertical columns concentration of NO2 has been significantly increasing in recent years as shown in Figure 2 (Zhang et al., 2007). The vehicle numbers in Shanghai increased from 1 million in 2000 to 2.5 million in 2008, thus, the NOx emission in the future in Shanghai would increase further, which had been discussed in Section 3.5. The positive effect of mitigating SO2

emission via the wide application of FGD in China would be probably offset due to the expansion of traffic system in the future. In the new version we make the statement of “The emission of nitrogen oxides would be the major pollutant to be concerned for the present and future” to emphasize the importance of mitigating the NOx emission, especially in the control of vehicle.

Lines 6-19 mainly focused on the comparison between the results of this study and some previous research, which gave a picture of the trends of NOx. We still think that this part is in the main scope of this paper as we found that nitrate played a more and more important role in the formation of inorganic secondary aerosol. In the new version, we reorganize some paragraphs to make them more closely linked to the main theme of this paper.

Page 21738,“In this study, although there was no OC data of high time resolution available due to restrictions of instruments, we believed that CO could be regarded as proxy of organic aerosol during the biomass burning events, which indirectly linked itself to the particle formation.” This reviewer still has concern on this statement. Please consider to revise.

Yes, we revised this sentence to be “Although there was no OC data of high time resolution available due to restrictions of instruments in this study, the exclusive correlation between CO and PM2.5 during the biomass burning events mirrored the dominance of organic aerosol in the particle formation. CO could be regarded as the proxy of organic aerosol when biomass burning dominated”.

Page 21738-21741, This reviewer cannot understand how Section 4 links to the main theme. Please clarify.

Yes, after we consider both of two reviewers’ opinions on this section, we decided to remove this section out in the new version of this paper and make the whole paper more linked to the main theme. Thanks a lot for the reviewer’s good suggestion.

References:

Fu, Q. Y., Zhuang, G. S., Li, J. A., Huang, K., Wang, Q. Z., Zhang, R., Fu, J., Lu, T., Chen, M., Wang, Q. A., Chen, Y., Xu, C., and Hou, B.: Source, long-range transport, and characteristics of a heavy dust pollution event in Shanghai, J. Geophys. Res., 115, D00K29, doi:10.1029/2009JD013208, 2010. Zhang, X. Y., Zhang, P., Zhang, Y., Li, X. J., and Qiu, H.: The trend, seasonal cycle, and sources of tropospheric NO2 over China during 1997-2006 based on satellite measurement, Sci. China. Ser. D, 50, 12, 1877-1884, 2007.

The revised version of the manuscript is shown as below:(Note: for the convenience of upload the file, all figures are posted in the part of supplement)

Typical types and formation mechanisms of haze in an eastern Asia megacity, Shanghai Kan Huang1,2, Guoshun Zhuang1ïĂł, Yanfen Lin1, Joshua S. Fu2*, Qiongzhen Wang1, Tingna Liu1, Rong Zhang1, Yilun Jiang1, Congrui Deng1, Qingyan Fu3, N. Christina Hsu4, and Benpei Cao1 1Center for Atmospheric Chemistry Study, Department of Environmental Science and Engineering, Fudan University, Shanghai, 200433, P. R. China 2Department of Civil and Environmental Engineering, The University of Tennessee, Knoxville, TN 37996, USA 3Shanghai Environmental Monitoring Center, Shanghai, 200030, China 4Goddard Space Flight Center, NASA, Greenbelt, Maryland, USA

Abstract An intensive aerosol and gases campaign has been performed at Shanghai in the Yangtze River Delta region over Eastern China from late March to early June, 2009. This study provided a complementary picture of typical haze types and formation mechanisms in megacities over China by using a synergy of ground-based monitoring, satellite observation and lidar inversion. During the whole study period, several extreme low visibility periods were observed with distinct characteristics, and three typical haze types were identified, i.e., secondary inorganic pollution, dust, and biomass burning. Sulfate, nitrate and ammonium accounted for a major part of PM2.5 mass during

the secondary inorganic pollution, and the good correlation between SO2/NOx/CO and PM2.5 indicated that coal burning and vehicle emission were the major sources. Large-scale regions with high AOD and low Ångström exponent were detected by remote-sensing observation during the dust pollution episode, and this episode corresponded to coarse particles rich in mineral components such as Al and Ca with mineral aerosol contributing 76.8% to TSP. The relatively low Ca/Al ratio of 0.75 combined with the air mass backward trajectory analysis suggested the dust source from Gobi Desert. Typical tracers for biomass burning from satellite observation (column CO and HCHO) and from ground measurement (CO, particulate K+, OC, and EC) were greatly enhanced during the biomass burning pollution episode. The exclusive linear correlation between CO and PM2.5 corroborated that organic aerosol dominated aerosol chemistry during biomass burning, and the high concentration and enrichment degree of arsenic (As) could be also partly derived from biomass burning. Aerosol optical profile observed by lidar demonstrated that aerosol was mainly constrained below the boundary layer and comprised of spheric aerosol (depolarization ratio < 5%) during the secondary inorganic and biomass burning episodes, while during the dust episode thick dust layer distributed at altitudes from near the ground to 1.4 km (average depolarization ratio = 0.122 ± 0.023) with dust accounting for 44-55% of the total aerosol extinction coefficient. This study had illustrated a good picture of the typical haze types and proposed that identification of the complicated emission sources was important for the air quality improvement in megacities in China.

1 Introduction China is now undergoing tremendous challenges of air quality impairment due to rapid industrial and transportation expansion, sharply increased demands of fossil fuel usage and increasing populations. Primary pollutant concentrations grow as a power-law function of population, and in China large emissions were concentrated in the mega-city clusters, such as Jing-Jin-Ji (Beijing-Tianjin-Hebei), the Pearl River Delta and Yangtze River Delta (YRD) regions (Parrish and Zhu, 2009). The YRD region, on which this study was focusing, included the biggest city in China, Shanghai, and Jiangsu and Zhejiang provinces. It has a population of over 80 million people and

occupied over 21% of China's total gross domestic product (GDP). Upon a globally decreasing trend of radiation, sunshine duration and sky visibility (Che et al., 2005; Kaiser and Qian, 2002; Wang et al., 2009), the YRD region had experienced substantially increasing haze days since 1990s (Chang et al., 2009; Che et al., 2007), which was attributed to the dimming effect of aerosol. Compared to Bejing and Guangzhou, the emissions of black carbon and NOx in Shanghai were 2∼3 times higher (2003∼2005) (Chan and Yao, 2008), and the emission of NOx was predicted to increase 60-70% by 2020 due to the expansion of transportation (Chen et al., 2006). Health effects, such as cardiorespiratory diseases and carcinogenesis were partially associated with air pollution (Kan et al., 2007; Ye et al., 2000; Zhao et al., 2003) and reductions of primary PM2.5 from industrial sector and mobile sources showed good health benefits in YRD (Zhou et al., 2010). It was estimated that the total economic cost of health impacts due to particulate air pollution in urban areas of Shanghai in 2001 was approximately 625.40 million US dollars, accounting for 1.03% of GDP of the city (Kan and Chen, 2004). In addition, the agriculture production was likely reduced by 2.5-9.2% due to exposure to ambient ozone (Liu et al., 2009). Some air quality research had been conducted in Shanghai and other areas in YRD. Investigation of major aerosol constituents were found to be sulfate, nitrate, ammonium (Wang et al., 2006; Yao et al., 2002; Ye et al., 2003) and organic aerosol (Feng et al., 2006; Feng et al., 2009; Yang et al., 2005a), concluding that fossil fuel combustion and vehicle emission were major sources of secondary components. Compared to Beijing, Shanghai had higher concentrations of black carbon (BC) and higher ratio of BC/CO, which were attributed to larger contribution from diesel burning (diesel powered vehicles and marine vessels) (Zhou et al., 2009). Ground based sunphotometer observation at various sites in YRD showed relatively high aerosol extinction to sunlight (AOD > 0.7) and high fraction of fine particles (Ångström exponent > 1.0) (Pan et al., 2010; Xia et al., 2007). Concentration and fraction of ultrafine (10-100 nm) particles in total particle counts at Taichang, YRD, were 2∼3 times higher than those reported in the urban/suburban areas in North America and Europe (Gao et al., 2009). And one research on the background site

Lin'an suggested that the aerosol properties were more close to urban areas rather than the suburban ones (Xu et al., 2002). Huang et al. (2008) found that there was a significantly decreasing trend of acid rain pH in Shanghai with 15-fold increased acidity during 1997-2005. However, the mechanism on the formation of haze was seldom discussed (Fu et al., 2008; Pathak et al., 2009; Zhou et al., 2009). Compared to some intensive field campaigns in the Pearl River Delta region and northeastern China, i.e., PRIDE-PRD2004, PRIDE-PRD2006 (Program of Regional Integrated Experiments on Air Quality over Pearl River Delta of China 2004 and 2006; Garland et al., 2008; Zhang et al., 2008), CAREBEIJING (Regional formation processes and controlling effects of air pollution before and during the Beijing Olympics: the results of CAREBEIJING; Wang et al., 2010), and EAST-AIRE (East Asian Studies of Tropospheric Aerosols: An International Regional Experiment; Li et al., 2007), no comprehensive initiatives have been carried out in YRD and especially, the source of haze, which was also referred to the atmospheric brown clouds (ABC), was not well disentangled due to the complicated aerosol sources in China currently. In this study, an intensive field experiment using various techniques was targeted to determine the typical pollution types that caused the frequent occurrence of haze in Eastern China. Aerosol chemical and optical experiments were combined with remote-sensing observation to distinguish and characterize different types of haze. Comments and discussions were made to emphasize the importance of aerosol source determination, which were beneficial for the local governments to improve air quality and mitigate climate effects.

2 Methodology 2.1 Field Observations 2.1.1 Observational Site The observational site (31.3°N, 121.5°E) in this study is on the roof (∼ 20 m high) of a teaching building on the campus of Fudan University in Yangpu district of Shanghai. Almost no high buildings are around this sampling site. This observational site is approximately 40 km inland from the East China Sea. The closest industrial sources are located approximately 10.5 km away and are primarily to the southeast and northwest (Li et al., 2011). About 1.3 million residents are living in this area (SMSB, 2011). This site could be regarded as a representative of the megacity Shanghai, standing for the mixing of residential,

traffic, construction, and industrial sources (Wang et al., 2006).

2.1.2 Automatic Aerosol and Gases Monitoring The Thermo Scientific TEOM 1405-D monitor simultaneously measured PM2.5, PM-Coarse (PM10-2.5) and PM10 mass concentration upon an oscillating balance. PM (particulate matter) accumulating on a filter mounted changes in the frequency of oscillation, which were related to the mass of material accumulating on the filter, were detected in quasi-real-time and converted by a microprocessor into an equivalent PM mass concentration every few seconds, as a 10 min running average. Sampler split a PM10 sample stream into its fine (PM2.5) and coarse (PM10-2.5) fractions using a USEPA-designed virtual impactor for the additional 2.5 μm cutpoint. The total flow rate operated at 16.67 l min-1, and two separate flow controllers maintained the coarse particle stream at 1.67 l min-1 and the fine particle stream at 3.0 l min-1. Besides, another Thermo Scientific TEOM 1405 monitor was set up to measure PM1 mass concentration operating at 3.0 l min-1 with a bypass flow rate of 13.67 l min-1. PM concentrations were averaged and used at intervals of 1hr in this study. Trace gases instruments included 43i SO2 analyzer, 42i NO-NO2-NOx analyzer, 49i O3 analyzer and 48i CO analyzer. The routine QA/QC procedures included the daily zero/standard calibration, span and range check, station environmental control, staff certification, etc., according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai based on the national specification HJ/T193–2005, which was developed following the technical guidance established by the U.S. Environmental Protection Agency (U.S. EPA, 1998). The multi-point calibrations were weekly applied upon initial installation of the instruments. And the two-point calibrations were applied on a daily basis.

2.1.3 Manual Sampling Aerosol samples of TSP and PM2.5 were collected on Whatman® 41 filters (Whatman Inc., Maidstone, UK) using medium-volume samplers manufactured by Beijing Geological Instrument-Dickel Co., Ltd. (model: TSP/PM10/PM2.5-2; flow rate: 77.59 l min-1). Aerosol samples of PM10 were collected on Whatman quartz microfiber filters (QM/A, 18.5cm$\times$23.7cm) using the high-

volume sampler (Thermo, flow rate: 1.00 m3 min-1). All the samplers were co-located with the online instruments on the roof ($\sim$30 m) of the 4th Teaching Building at Fudan University, Shanghai. The duration time of sampling was generally 24 hours. More samples with shorter duration time were collected during the heavy haze days. The filters before and after sampling were weighed using an analytical balance (Model: Sartorius 2004MP) with a reading precision 10 mg after stabilizing in constant temperature (20 $\pm$ 1°C) and humidity (40 $\pm$ 1%). All the procedures were strictly quality controlled to avoid the possible contamination of samples.

2.1.4 Lidar Observation A dual-wavelength depolarization lidar (Model: L2S-SM II) developed by the National Institute for Environmental Studies (NIES) was operated in this field campaign. The lidar could measure backscattering coefficients and the depolarization ratio at wavelength of 532 nm. The Lidar employed a flash lamp pumped Nd:YAG laser with a second harmonics generator. The laser beam was vertically oriented to the sky after collimated with a beam expander. Transmitted laser energy was typically 20 mJ per pulse at 1064 nm and 30 mJ per pulse at 532 nm. The pulse repetition rate was 10 Hz. The scattered light was received with a 20 cm Schmidt Cassegrain type telescope collimated and directed to the dichroic mirror. The polarization components were detected with two photomultiplier tubes (PMTs). Detected signals were recorded with a transient recorder (digital oscilloscope), averaged and transferred to the data acquisition computer for the web interface. The lidar continuously operated with 15 minutes intervals and 30 meters height resolution by setting a boundary condition at 3km. The Fernald inversion method (Fernald, 1984) was applied to deriving the extinction coefficient with lidar ratio (extinction-to-backscatter ratio) set to 50 sr (Liu et al., 2002) in inversion process.

2.2 Chemical Analysis 2.2.1 Ion Analysis One-fourth of each sample and blank filter was extracted ultrasonically by 10 mL deionized water (18MΩcm-1). Eleven inorganic ions (SO42-, NO3-, F-, Cl-, NO2-, PO43-, NH4+, Na+, K+, Ca2+, Mg2+) and four organic acids (formic, acetic, oxalic, and methylsulfonic acid (MSA)) were analyzed

by Ion Chromatography (ICS 3000, Dionex), which consisted of a separation column (Dionex Ionpac AS 11), a guard column (Dionex Ionpac AG 11), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50) and a gradient pump (Dionex Ionpac GP50). The detail procedures were given elsewhere (Yuan et al., 2003). 2.2.2 Element Analysis Half of each sample and blank filter was digested at 170°C for 4 h in high-pressure Teflon digestion vessel with 3ml concentrated HNO3, 1 ml concentrated HCl, and 1ml concentrated HF. After cooling, the solutions were dried, and then diluted to 10 ml with distilled deionized water. Total 24 elements (Al, Fe, Mn, Mg, Mo, Ti, Sc, Na, Ba, Sr, Sb, Ca, Co, Ni, Cu, Ge, Pb, P, K, Zn, Cd, V, S, and As) were measured by using an inductively coupled plasma atomic emission spectroscopy (ICP-OES; SPECTRO, Germany). The detailed analytical procedures were given elsewhere (Sun et al., 2004; Zhuang et al., 2001). 2.2.3 Carbonaceous Aerosol Analysis Quartz filters were pre-heated at 500âĎČ for 5h before using and the samples were analyzed for OC/EC using DRI Model 2001 (Thermal/Optical Carbon Analyzer). The IMPROVE thermal/optical reflectance (TOR) protocol (Chow and Watson, 2002) was used for the carbon analysis. The eight fractions (OC1, OC2, OC3, OC4 at 120, 250, 450 and 550°C, respectively in a helium atmosphere, EC1, EC2, EC3 at 550, 700 and 800°C, respectively, in the 98% helium/2% oxygen atmosphere) and OPC (optically detected pyrolized carbon) were measured separately. The IMPROVE protocol defined OC as OC1+ OC2+OC3+OC4+OPC and EC as EC1+EC2+EC3-OPC. 2.3 Satellite Observation In this study, a number of satellite sensors had been used to sense aerosol and trace gas information. The MODIS instrument (Moderate-resolution Imaging Spectroradiometer) provided a large regional view of aerosol distributions with a resolution of 10 $\times$ 10 km. Operational aerosol optical depths were reported at 0.55 μm by NASA (Chu et al., 2003; Kaufman et al., 1997). The total carbon monoxide column concentration retrieved from Atmospheric Infrared Sounder (AIRS) on board NASA's Aqua satellite were used to observe large scale transport from biomass burning sources (McMillan et al., 2005). Launched in 2004, the DutchâĂŘFinnish built Ozone Monitoring Instrument (OMI) aboard NASA's EOS Aura satellite provided daily global coverage

with a spatial resolution of 13 km $\times$ 24 km at nadir (Levelt et al., 2006), and the total formaldehyde column concentration had been used to study the signals of possible biomass burning source. Detailed description about the OMI instrument could be found elsewhere (Kurosu et al., 2004).

3. Results and Discussion 3.1. Identification of Three Pollution Episodes An intensive aerosol characterization campaign was carried out in Shanghai over the Yangtze River Delta region in 2009, which aimed to get insights into the formation mechanisms of haze in Eastern China. The study period had a coverage of 30 March $\sim$ 16 May and 28 May $\sim$ 3 June, and the absent intervals between the two time periods were due to malfunction and maintenance of some instruments. Haze was usually defined as an atmospheric phenomenon where dust, smoke and other pollutant particles reduced the visibility of the sky. Here we had calculated the visibility following the Koschmieder formula LV = 3.912/σext, where LV (km) was the visibility and the total extinction coefficient σext (km-1) was accounted by scattering and absorption from particles and gases. The method for calculating σext was described in Appendix A. Figure 1b shows the calculated hourly visibility and the recorded visibility at Pudong, which was about 32 km from the observational site in this study (An upper limit of LV = 10 km was recorded at the meteorological station of Pudong). As shown in the figure, the visibility measured by two different approaches had relatively good time-series consistency, especially during the low visibility periods, which suggested that visibilities estimated from aerosol extinction profile and pollutant gas were reasonable and could be used for further analysis. Figure 1c shows the temporal variation of PM mass concentration levels at three different sizes, i.e., PM1, PM2.5 and PM10. Based on the visibility, PM mass concentration levels and mass fraction of fine particles (PM2.5/PM10), we had sorted out three typical pollution episodes. The first pollution episode (PE1) occurred from 4-10 April, during which the mean visibility was as low as 3.5 km. The average concentrations of PM1, PM2.5, and PM10 were 60.9 $\pm$ 14.0, 63.6 $\pm$ 16.4, and 120.1 $\pm$ 40.7μg/m3, respectively. The average ratio of PM2.5/PM10 was 0.54 $\pm$ 0.09, indicating both fine and coarse particles could be important in the formation of pollution. The

mass ratio of PM1/PM2.5 ranged from 0.90 to 0.99, suggesting that the mass of PM2.5 was mainly dominated by smaller particles, e.g, PM1. Time series of pollutant gases, i.e., SO2, NOx and CO, showed their significant enhancements during this period (Figure 2), enhanced industrial and traffic emissions were probably responsible for this and the pollution during this period was probably caused by the local photochemical process. The detailed analysis on pollutant gases would be discussed in Section 3.5. Figure 1a shows the hourly surface meteorological parameters, including wind speed, wind direction, relatively humidity (RH), dew point and atmospheric pressure. During PE1, the local air was under a low pressure system turning from a high one several days ago. Winds blew from various directions and the wind speeds were relatively low and even stagnant sometimes, which were not favorable for the dispersion of pollution. There was an obvious decrease of relative humidity (RH) during PE1. Cold front from inland China probably contributed to the high pollution of PE1 to some extent. To study the aerosol transport characteristics, air mass backward trajectories were computed using the NOAA Hybrid Single-Particle Lagrangian Trajectory (HYSPLIT) model (R. Draxler and G. Rolph, HYSPLIT (HYbrid SingleâĂŘParticle Lagrangian Integrated Trajectory) Model, 2003, http://www.arl.noaa.gov/ready/hysplit4.html) with meteorological data provided by the Global Data Assimilation System (GDAS). Three-day backward trajectories at the end point of Shanghai during PE1 showed that air flows derived from various directions and traveled relatively short distances, consistent with the surface meteorological measurements. Additionally, the daily average mixing layer was almost below 500m (Figure 3a). This typical stagnant synoptic meteorological condition was especially unfavorable for the dispersion of particles and gases, and beneficial for the formation of haze pollution. The second pollution episode (PE2) occurred on 25 April and lasted a short duration. The daily concentrations of PM1, PM2.5, and PM10 were 26.3, 53.0, and 174.5μg/m3, respectively. And the ratio of PM2.5/PM10 reached the lowest value of 0.35 over the whole study period, indicating the characteristic of coarse particle pollution. Surface meteorology showed a dominant northwest wind (Fig. 1a) and air backward trajectories starting at various altitudes of 500, 1000 and 3000 me-

ters all flowed from northern China, which passed over the Gobi Desert in Mongolia and Inner-Mongolia (Figure 3b). The average wind speed reached as high as 7.5m/s in Shanghai with gust speeds over 10m/s. Relative humidity and dew points both had abrupt decreases, indicating the advent of cold front. Additionally, the intraday average mixing height was about 1000m, much more elevated than PE1. Thus, all the evidences above indicated that this coarse particle pollution was probably caused by the entrainment of dust aerosol from the desert in Mongolia and Inner-Mongolia via the long-range transport. Figure 4 depicts the regional distribution pattern of PM10 concentration during 24-26 April in northern and eastern China. On 24 April, high pollution (PM10 > 300μg/m3) occurred in the northern China, mainly in Inner-Mongolia and Shanxi province while the eastern and southern China was virtually dust-free (Figure 4a). On the next day, high level particles moved to major areas of central China and stretched to the eastern coastal regions (Figure 4b). As for Shanghai, our monitoring station observed that the dust entrainment actually had the most significant impacts on local air quality during two periods, i.e., from 0130 to 0800 LST and 1700 to 2300 LST (Local Standard Time). The average PM10 concentration reached 258 and 236μg/m3, respectively, while the concentrations of fine particles and pollutant gases stayed at low levels (Figure 1b & Figure 2), which was due to the dilution effect of dust on local pollutants. Till 26 April, the PM levels in northern China had sharply declined and the dust continued to travel southwestward along the east coast, which exerted a moderate influence on air quality of southern China (Figure 4c). In Shanghai, there was a significant decrease of PM10 concentration and an increase of PM2.5/PM10 ratio to over 0.50, indicating the re-dominance of fine particles after the pass of dust. The third pollution episode (PE3) occurred from 28 May to 3 June. The average concentrations of PM1, PM2.5, and PM10 were 67.8 $\pm$ 37.6, 84.0 $\pm$ 48.4 and 135.6 $\pm$ 71.4μg/m3, respectively, with the average PM2.5/PM10 ratio of 0.65 $\pm$ 0.04. Fine particle concentration levels and its mass contribution to the total particles were both the highest among all three pollution episodes. Notwithstanding, the concentration levels of pollutant gases were not as high as PE1 except for CO, SO2 was at a moderate level and

NOx was relatively low (Figure 2). Different from the high concentrations of pollutant gases during PE1, the formation mechanism of the PE3 pollution should be different from that of PE1. The meteorological conditions during this period were as similar as PE1, i.e., slow transport of air flows and relatively low mixing layer as shown in Figure 1a and Figure 3c, which also suggested the stagnant atmospheric condition during PE3. In the discussion above, the analysis of PM, pollutant gases and meteorological parameters had already shed some light on the pollution types of different episodes. And we will show more evidences of the aerosol optical and chemical properties in the discussions below.

3.2. Regional Characteristics and Possible Sources via Remote Sensing Observation The remote sensing analysis from satellite observation is a good way to indicate the spatial distribution, transport and possible source of airborne pollutants. Figure 5 shows the observed satellite signals during the three episodes, respectively. During PE1, zones of high aerosol optical depths (AOD) at the wavelength of 550 nm retrieved from MODIS were mainly concentrated in Jing-Jin-Ji (Beijing-Tianjin-Hebei), Shandong, Anhui, Henan, Hubei provinves, and the Yangtze River Delta region, including northern part of Zhejiang, Jiangsu provinces and Shanghai (Figure 5a). The average AOD value over Shanghai reached extremely high value of over 1.2, indicating strong aerosol extinction to sunlight in the atmosphere. Figure 5b shows the spatial distribution of Ångström exponent at the wavelength range from 470 to 670 nm. Ångström exponent was a good indicator of the aerosol size distribution, the larger this parameter, the smaller the particle size, and vice versa. The spatial pattern of Ångström exponent didn't resemble that of AOD. In some regions that the AOD values were moderate such as southern parts of Zhejiang province and major parts of central China, the Ångström exponents ranged from 1.3 to 1.5, indicating these regions were mainly dominated by fine particles. While in the high AOD regions that discussed above, the Ångström exponents were not correspondingly high and ranged from 0.8 to 1.2, which suggested there was non-negligible contribution of coarse particles during PE1. This was consistent with the moderate PM2.5/PM10 ratio that measured by our

ground monitoring as discussed in Section 3.1. As shown in Figure 5b, there was a belt of relatively low Ångström exponent extending from the Bohai Bay and the Shandong Peninsular to the Yangtze River Delta region along the east coast. The continuity of Ångström exponent probably indicated that the Yangtze River Delta could have been more or less influenced from the northern China. As PE1 was in the spring season when the occurrence of floating dust was frequent and ubiquitous, the downstream regions were probably influenced by the transport of dust aerosol to some extent. During PE2, high AOD values were observed in most parts of the study domain, which was as similar as PE1 to a certain extent, especially in the central and eastern parts of China with AOD exceeding 1.2 (Figure 5c). However, Ångström exponents were much lower than PE1. It ranged from 0.5 to 0.6 (Figure 5d), indicating considerable existence of coarse particles, which was consistent with ground measurements. And there were almost no regional gradients of the Ångström exponents, suggesting this episode was characteristic of large-scale influences. Thus, the remote sensing analysis confirmed that PE2 was impacted by the long-range transport of dust. The dust storm had spread over almost the whole Northern China Plain and Eastern China as shown in Fig. 5d. During PE3, large quantities of fire spots retrieved from MODIS were observed in the study domain (denoted by black dots in Figure 5e-5g), and they were mainly located in the conjunction of western Shanghai and southern Jiangsu province, major parts of Jiangsu, northern Zhejiang, northern Anhui province and eastern parts of Shandong province. The total column concentration of carbon monoxide (CO) retrieved from the Atmospheric Infrared Sounder (AIRS) showed very good spatial pattern with that of fire spots (Figure 5e). In the normal times, the major sources of CO were derived from anthropogenic sources, such as traffic and/or industrial emission. While it was a major product emitted from biomass burning along with many trace gases such as carbon dioxide (CO2), methane (CH4), nitrous oxides (NOx) and hydrocarbons (Crutzen and Andreae, 1990). Various studies had used CO as tracer for biomass burning in aircraft measurement (Boian and Kirchhoff, 2004), satellite observation (Choi and Chang, 2006; Mari et al., 2008) and other measurements (Kato et al., 1999; Kato et al., 2002).

The column concentration of CO over the intense burning areas reached 2.5 $\sim$ 3.0 $\times$ 1018 molecules/cm2 as shown in the figure, evidently distinguished from areas free of biomass burning and close to the levels when biomass burning occurred in northeastern China (Choi and Chang, 2006). Besides, the Ozone Monitoring Instrument (OMI) also detected high formaldehyde (HCHO) columns over the intense burning areas (Figure 5f). HCHO was a primary emission product from biomass burning, which was an intermediate product from the oxidation of hydrocarbons. And it was a good indicator of the local photochemical source as it only had a lifetime of a few hours. HCHO columns over the hotspot regions were greater than 3.0 $\times$ 1016 molecules/cm2, more than a factor of 2-4 larger than the areas free of fires. Spatial correlations between CO and HCHO with the numbers of fire spots showed moderate correlation (R $\sim$ 0.49) (not shown in figure). Thus, the enhancement of CO and HCHO in the accumulated fire spot regions indicated that the pollution during PE3 should be caused by biomass burning. The biomass emission resulted in high AOD values where large fire spots occurred, with the highest AOD up to about 2.0 in the Yangtze River Delta region. However, compared to the spatial distribution of CO and HCHO, the high AOD levels didn't always coincide with the fire regions. For example, there was no fire spots observed in Jiangxi province with low CO concentrations, but a high AOD region was found there. While as for Shandong province, the regions with great fire spots, high CO, and HCHO concentrations were at the relatively low AOD level. This suggested that CO and HCHO were more sensitive to biomass burning than AOD as AOD represented the overall extinction of various emission sources to light rather than the single source from biomass burning. The relatively low AOD over the Shandong Peninsula could have been due to the cleanup effect of the sea breezes as it was close to the sea. Anyway, the relatively good consistency between the observed satellite signals (e.g. carbon monoxide, formaldehyde and aerosol optical depth) over Eastern China and the fire hotspots clearly indicated that biomass burning should be the major cause of heavy haze during this period. Every year during May, June and October in Eastern China, crop residues after harvest were either directly returned to agriculture fields as

fertilizer, burned in the field, or used as biofuels. It has been previously reported that biomass burning usually occurred during the transition period from spring to summer (Wang et al., 2002) and in autumn (Xu et al., 2002), which was due to the burning of post-harvest straws by human activities. In this section, the remote sensing analysis had given us some highlights into the different characteristics of three pollution episodes, including possible sources and transport pathways and provided some consistent results to our ground measurements. However, there were large uncertainties due to satellite detection limit of the small fire size of the field crop residue burning that could be possibly missed by satellite observations (Chang and Song, 2010; Yan et al., 2006). And satellites could not capture all fire events occurring during this study period, because fires hidden under clouds could not be easily detected. Additionally, satellite overpass also brings about the missed detection of hotspots.

3.3. Aerosol Chemistry under Different Atmospheric Conditions In order to further identify the different types of hazes as envisioned by the discussion above, we have demonstrated the results of aerosol chemical measurements here. Figure 6 shows the temporal variations of some typical aerosol components during the whole study period. Time series of three major secondary inorganic species in PM2.5, i.e., SO42-, NO3-, and NH4+ were presented in Figure 6a. Obviously, the total concentrations of the three species above exhibited the highest levels during PE1 with average concentrations of 48.86 $\pm$ 5.01μg/m3, which accounted an average of 77% to PM2.5 mass. As precursors of sulfate and nitrate, SO2 and NOx also showed the highest levels during this episode which had been stated in Section 3.1. This suggested that the pollution during PE1 was dominated by the secondary inorganic aerosol. In addition, we found that during EP3, these species also exhibited a moderate concentration level with average values of 27.12 $\pm$ 7.37μg/m3, which probably indicated that biomass burning could also released considerable amounts of inorganic pollutants. For the other periods, the levels of theses species were much lower with values almost below 20μg/m3. The average sulfate level during the whole study period was 8.0 $\pm$ 5.8 μg/m3. Compared to the previous studies (Fu et al., 2008; Pathak et al., 2009; Wang et al., 2006; Yao et

al., 2002; Ye et al., 2003), sulfate was much lower in this study, indicating the effective policy controls on the SO2 emission. However, the average nitrate concentration reached 6.3 $\pm$ 5.7 μg/m3, comparable or even higher than those previous results. Additionally, the mass ratio of NO3-/SO42- of 0.75 $\pm$ 0.26 in this study had an increasing trend as compared to the values of 0.64 in 2006 (Wang et al., 2006), and 0.43 during 1999-2000 (Yao et al., 2002; Ye et al., 2003). The ratio of NO3-/SO42- could be used as an indicator of the relative importance of stationary vs. mobile sources (Arimoto et al., 1996) and the results indicated that the role of mobile emission had become more and more significant due to the rapid expansion of transportation. Figure 6b shows the temporal variation of elemental Al concentration, the ratio of Ca/Al, and the estimated mass fraction of mineral aerosol in the total suspended particles (TSP). Al was one of the inert and abundant elements in mineral aerosol and had been used as a good tracer for mineral aerosol in various studies (Huang et al., 2010; Wang et al., 2007; Zhang et al., 2010). As shown in the figure, the highest Al concentration occurred on 25 April, i.e, the second pollution episode (PE2). The daily Al concentration reached as high as 13.7μg/m3, almost 2$\sim$3 times that of the other periods. To quantify the mass concentration of mineral aerosol, it could be estimated by summing the major mineral elements with oxygen for their normal oxides, which was calculated using the formula: [Mineral concentration] = 2.2[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti] (Malm et al., 1994). According to this estimation, the percentage of mineral aerosol in TSP during PE2 was as high as 76.8%. Oppositely, the average concentration of sum of SO42-, NO3-, and NH4+ in PM2.5 was only 11.23 $\pm$ 5.25μg/m3, which was the lowest during the whole study period, indicating the dominance of non-anthropogenic sources and the prominent impact of dust entrainment on the local aerosol chemistry. To further characterize the origin of dust, the temporal variation of the elemental Ca/Al ratio was investigated as different dust regions in China were characterized of distinct Ca content and Ca/Al ratios in soils/particles (Zhang et al., 2003; Zhang et al., 1996). The Ca/Al ratio during PE3 reached a low value of 0.75, while in the other period it mainly ranged between 1.0 and 2.0. The relatively high Ca/Al ratios during the non-dust periods were

attributed to the frequent construction activities in recent years in Shanghai (Wang et al., 2006). The significant drop of Ca/Al ratio during PE2 confirmed that the local air quality must have been impacted by the outside sources. Elemental ratios of Ca/Al of dust aerosol in the three major dust source regions of China, i.,e., Gobi Desert, Loess Plateau, and Taklimakan Desert, were 0.52 $\pm$ 0.05, 1.09 $\pm$ 0.13, and 1.56 $\pm$ 0.14, respectively (Huang et al., 2010). Combined with the backward trajectory analysis in Section 3.1, we could confirm that the aerosol chemistry over Shanghai during PE2 was more close to that of the dust aerosol originating from Gobi Desert. During PE1, moderate Al concentrations (5.48 $\pm$ 2.52 μgm-3) were observed, indicating the influence from long transported dust aerosol to some extent. Figure 6c shows the temporal variation of particulate K+ concentration in PM2.5, which was a good indicator for tracing the biomass burning source (Andreae, 1983). Its highest level occurred just during PE3, with the average concentration of 2.84 μg/m3, elevated 5$\sim$10 times compared to the other days. As K+ could be also derived from soil and dust, we used the K/Fe ratio of 0.56 (Yang et al., 2005b) to exclude the contribution of mineral source. It was calculated that the biomass burning derived K+ could contribute about 80% of total K+, indicating the significant influence of biomass burning. The total potassium accounted for an average of 3.25% in PM2.5, also higher than that of 1.07% in the other times and close to that of 3.58% observed during the Mount Tai Experiment 2006 (MTX2006) which focused on biomass burning in Eastern China (Deng et al., 2010). Cl- and K+ were both important ions in particles from open burning of agricultural wastes (Li et al., 2007a). Individual particle analysis also found that large irregular shaped KCl particles existed in young smoke (Chakrabarty et al., 2006; Li et al., 2003). In this study, a very significant correlation between Cl- and K+ was observed with the correlation coefficient of 0.96. The K+/Cl- ratio during this episode was 2.09, much higher than its background ratio of 0.10 to 0.46 (Wang et al., 2006), indicating the dominance of biomass burning source. However, Cl- could be also derived from coal burning as coal had always contributed to the biggest share of the energy structure in Shanghai. Another significantly enhanced group of aerosol was the organic aerosol, including organic carbon

(OC) and element carbon (EC). OC and EC in PM10 averaged 35.8 $\pm$ 8.1 and 5.7 $\pm$ 1.3μg/m3 during PE3, and they were enhanced 30-100% compared to the other days. The concentration level of organic aerosol was comparable to the extensive burning biomass period during MTX2006 (EC: 7 μg/m3, OC: 24μg/m3) (Yamaji et al., 2010). If we applied an OM/OC ratio of 1.8 to estimate the mass of organic matter (OM) (Turpin and Lim, 2001), the average mass contribution of OM to PM10 would be as high as 50%. However, a higher factor (2.2 - 2.6) for aerosol heavily impacted by smoke was recommended (Turpin and Lim, 2001), thus it may result in an underestimated value for the faction of OM in this work. Compared to previous results of the mass percentage of organic aerosol of $\sim$30% over YRD in the non-biomass-burning times (Feng et al., 2009; Yang et al., 2005a), biomass burning evidently emitted much more hydrocarbons. The OC/EC ratio was commonly on the order of 3 in most urban cities of China (Zhang et al., 2008), where the major sources of OC and EC were dominated by fossil fuel combustions. High ratio of OC/EC (6.4) was observed during PE3, which indicated that biomass burning contributed far more organic carbon than fossil fuel combustion did (Yan et al., 2006). Field measurements also observed a high ratio of OC/EC (5) for the burning of wheat straw and an even higher ratio for maize stover (Li et al., 2007). Figure 7 shows the enrichment factors (EF) of major elements in PM2.5 during three episodes, respectively, which aimed to evaluate the enrichment extents of various elements in aerosol. Usually Al was used as the reference element as it was a relatively chemical inert element and almost had no anthropogenic sources. The calculation formula was EFx = (X/Al)aerosol / (X/Al)crust, of which X was the element of interest. Species with EFs less than 10 were usually considered to have a major natural source, which included Sc, Na, Ca, Co, Fe, Mn, Sr, Ba, P, K, Ni, Mn, Ti, and V. The EF of V was a little higher during PE1, which could be from the re-suspension of local soils and road pavement erosion (Amato et al., 2009). Species with higher EFs were contaminated by anthropogenic sources, which included Cu, Mo, As, Sb, Ge, Pb, Zn, Cd, S, and Se. As shown in the figure, the enrichment degrees of almost all the elements were the lowest during PE2. The dust aerosol originating from the Gobi Desert was relatively clean

(Huang et al., 2010), and its entrainment had a cleanup and dilution effect on the local pollution, which lowered the enrichment degrees of most pollution elements. Elements during PE1 were mostly enriched, especially for those elements, i.e, Pb, Zn, Cd, S, and Se, with EF values larger than 1000. Pb had the major source from traffic emission in early years, while coal combustion had dominated the lead pollution after the phasing out of leaded gasoline in 1997 in Shanghai (Chen et al., 2005; Tan et al., 2006; Zhang et al., 2009). Zn and Cd mainly derived from local industrial and traffic emission (Cao et al., 2008; Shi et al., 2008). As indicators for coal combustion (Nriagu, 1989), S and Se had the highest EFs among all the elements, indicating coal combustion was one of the major sources of air pollution in Shanghai. Most of the EFs of pollution elements during the biomass burning period, i.e., PE3, were higher than PE2 and lower than PE1. The only exception was arsenic (As), whose EF was comparable to that during PE1. The average As concentration during PE3 was 7.53 ng/m3, higher than that of 4.46 ng/m3 during PE1 and much higher than 2.02 ng/m3 in the normal periods. The high concentration and great enrichment of As should not be derived from its usual source such as coal burning, as no corresponding enrichment of the other pollution elements were found as in the PE1 case. High arsenic levels in groundwater in many areas over mainland China were observed (Mandal and Suzuki, 2002) and crop was most susceptible to As toxicity which sourced from the As-contaminated groundwater used for irrigation (Brammer and Ravenscroft, 2009). Thereby, the burning of agricultural residues would probably release considerable amounts of As, which resulted in the enrichment of As in particles.

3.4. Aerosol Vertical Profile Figure 8 shows the time-height cross-section of the lidar measured aerosol properties at the wavelength of 532nm during the three pollution periods, respectively. In this study, the total aerosol extinction coefficient was split to non-dust (spherical aerosols such as air pollution) and dust (nonspherical aerosol) fractions based on the aerosol depolarization ratio. Sugimoto et al.(2002) and Shimizu et al.(2004) described details of lidar observation and splitting method. Figure 8a presents the time-height cross-section of spheric aerosol extinction coefficient during

PE1. Lidar observation successfully captured several high extinction peaks, which was consistent with the ground observation (Figure 1b). Vertical distribution of aerosol extinction coefficient exhibited strong variations and showed obvious decreasing gradients from the ground to upper layers, which reflected that pollutants were mainly constrained near the surface ground. The height of the boundary layer could be visually assumed from the vertical profile of aerosol optical properties. The profile, where the extinction coefficient sharply decreased, could be determined as the top of planetary boundary layer (PBL) (Noh et al., 2007). During the daytime, the PBL height was relatively high, and sometimes it could reach up to 2km, which was due to the higher temperature and strong air convection. While during nighttime, it dropped to less than 0.5km due to the temperature inversion. We selected one typical day (1130 - 1500 LST, April 6) during PE1 to discuss its vertical profile (Figure 9a). The depolarization ratio at the wavelength of 532nm (δ532) from the ground to the upper layer ($\sim$1.5km) was less than 5%, indicating the aerosol was mainly composed of spheric particles. While at higher altitudes, the depolarization ratio increased a little bit, which could be due to the absence of spheric aerosol or the possible contamination of water clouds and ice clouds. The averaged profile of attenuated aerosol backscattering coefficient showed a steep decreased gradient from 0.037 km-1sr-1 near the ground to 0.0018-0.0030 km-1sr-1 around 1-1.5km. As for PE2, we presented the time-height cross-section of spheric aerosol extinction coefficient and depolarization ratio during 22-28, April (Figure 8b). The depolarization ratio showed high values on 25 April. The high depolarization ratio of aerosol was due to the nonsphericity (irregular shapes) and relatively large size of particles (Mcneil and Carswell, 1975) and we regarded this type of aerosol as mineral aerosol/dust aerosol for that dust was the most important component of nonspheric aerosols in East Asia. On April 25, two consecutive dust plumes were observed, which was consistent with the ground measurement. Before the dust event, the air quality was relatively good. The high extinction coefficients and low mixing layers (400-600m) on the whole day of April 24 were caused by the recorded rainfall. It should be emphasized that on the advent of the first dust plume

(0130-0800 LST), the extinction coefficients of spheric aerosol were still high, indicating the strong mixing of dust and pollutant aerosol. After the departure of dust, the values decreased, indicating the clear-out of pollutants. Until the advent of the second dust plume (13:00-21:45, LST), it increased again. We selected one dust plume (0130-0800 LST, 25 April) to discuss its vertical profile (Figure 9b). In addition to the profile of aerosol backscattering coefficient and total depolarization ratio, the fraction of dust aerosol extinction to the total aerosol extinction (fd) was also calculated based on the splitting method described by (Shimizu et al., 2004; Sugimoto et al., 2002). Compared to PE1, and PE3 that would be discussed below, PE2 showed evidently different profile. The backscattering coefficient sharply decreased from 0.04 km-1sr-1 near the surface to 0.01 km-1sr-1 at around 0.7 km. And then the coefficient almost stayed constant value of about 0.01 km-1sr-1 between 0.7 and 1.0 km, which indicated the transport of outside aerosol and this phenomena hadn't been observed in the other two episodes. Upwards, the backscattering coefficient started to sharply decrease again to low values. This type of vertical distribution of backscattering coefficient was closely related to the profile of depolarization ratio. As shown in the figure, there was an increase of δ532 from ground and peaked at around 1.0 km with value of 0.155. Correspondingly, the contribution of dust aerosol extinction to the total aerosol extinction peaked between 0.7 and 1.0 km with the values ranging from 51% to 57%. Thus, the relatively constant backscattering coefficient between altitudes of 0.7 and 1.0 km should be due to the increase of dust aerosol. Above this layer, fd was less than 10%, indicating the negligible existence of nonspheric aerosol in the upper layers. Using a threshold of δ532 = 0.06 to distinguish dust from other types of aerosol (Liu et al., 2008), the dust layer mainly distributed between ground and up to an altitude of around 1.4km. The average δ532 value of this layer was 0.122 $\pm$ 0.023, which was close to the dust observed in Korea that sourced from the same dust region (Kim et al., 2010). Above this layer, the δ532 values decreased to low values, indicating the transport of dust at relatively low altitudes. Actually, most of the dust plumes (approximately 70%) were observed near the ground (Kim et al., 2010). The contribution of dust aerosol extinction to the to-

tal aerosol extinction exhibited high values and relatively small vertical variations from near the ground to the upper layer of around 1km, ranging from 44% to 55%. If we applied the dust and soluble aerosol extinction efficiency (σep) of about 0.5 and 3 m2g-1, respectively (Lee et al., 2009), it could be estimated that the mass concentration of dust aerosol was almost 4$\sim$7 times that of spheric aerosol by using the formula, σep = βext/M, of which βext and M represented the extinction coefficient and mass concentration of dust/spheric aerosol. This was consistent with our ground measurement that dust aerosol contributed 76.8 % to the total aerosol mass as discussed in Section 3.3. Figure 8c shows the time-height cross-section of spheric aerosol extinction coefficient during PE3. As similar as PE1, high aerosol extinction coefficients and strong temporal variations were observed. Compared to PE1, the PBL height during this period was even lower. Figure 9c shows the vertical profile of backscattering coefficient and depolarization ratio on 1 June (1130 - 1530 LST). The depolarization ratio fluctuated within 0.05 in the whole layer, indicating the dominance of spheric particles. The backscattering coefficient was about 0.024 km-1sr-1 near the surface, much lower than PE1 and PE2. While the fine aerosol concentration during PE3 was the highest. The non-linearity between PM concentrations and optical properties should be due to the different chemical compositions among different periods. In biomass burning, organic aerosol dominated while sulfate ammonium, nitrate ammonium dominated during the secondary inorganic pollution episode. The mass scattering efficiency (m2g-1) of organics was about a factor of 2$\sim$3 lower than that of sulfate (Hasan and Dzubay, 1983; Ouimette and Flagan, 1982), thus this discrepancy resulted in the non-linearity between PM concentrations and optical properties.

3.5. Trace Gases Figure 10 compares the concentrations of trace gases among three pollution episodes and the normal period. The normal period was defined as the remaining days excluding the three pollution episodes. O3 during PE1 was the lowest with average concentration of 79 $\pm$ 63 μg/m3, and O3 and NOx were strongly anticorrelated, which was due to the titration effect of nitrogen oxides as the Yangtze River Delta was under a strong VOC-limited regime (Geng et al., 2009). O3 was highest

during PE3 with average concentration of 96 $\pm$ 63 μg/m3, which could be caused by the relatively high emission of hydrocarbons emitted from biomass burning and the relatively weak titration effect due to NOx. During PE1, the average concentrations of SO2, NOx and CO reached 54, 150, and 1334 μg/m3, respectively. Compared to the heaviest pollution recorded at Shanghai on 19 January in 2007, when the daily concentration of SO2 and NO2 reached 194 and 123 μg/m3, respectively (Fu et al., 2008), the concentration of SO2 in this study was obviously lower, which could be due to the energy policies in China that mitigated the SO2 emission, including desulfurization of coal-fired power plant plumes, decommissioning of coal-fired boilers in manufacturing facilities and small power plants, conversion of domestic coal use to cleaner fuels and etc. (Fang et al., 2009). The emission of SO2 almost remained constant during 1996-2005 (Chan and Yao, 2008) and recent studies show that SO2 emissions started decreasing in China after 2006 (Li et al., 2010; Lu et al., 2010). The emission of nitrogen oxides would be the major pollutant to be concerned for the present and future. The average concentration of NO2 and NOx during PE1 reached high levels of 109 and 150 μg/m3, respectively. Even during the normal period, their average concentration was 60 and 99 μg/m3, respectively, contrasting to 3-40ppbv NOx (1ppbv NOx equaled to about 1.9μg/m3) in 2007 (Geng et al., 2009) and 5-35μg/m3 NOx in 1999 (Wang et al., 2003). Satellite observation and model simulation both detected and predicted a strong increase of NO2 in Eastern China, especially after 2000 (He et al., 2007), and Shanghai had a significantly linear increase of NO2 column concentrations with about 20% per year during the period of 1996-2005 (van der A et al., 2006), which was the rapidest among all the mega-cities in China (Zhang et al., 2007). Due to the expansion of transportation system, NOx emissions were projected to increase by 60–70% by 2020 (Chen et al., 2006). Therefore, it could explain the relatively high concentration of particulate nitrate and increasing ratio of NO3-/SO42- as discussed in Section 3.3. Correspondingly, the effect of enormous vehicle emission had also been reflected in the carbon monoxide level. A significant correlation between CO and NOx during PE1 was observed with the correlation coefficient of 0.86, indicating their common sources. Av-

erage concentration of CO during PE1 reached 1334 $\pm$ 884 μg/m3, greatly enhanced as compared to the normal period of 884 $\pm$ 267 μg/m3, 500 - 900 μg/m3 in 1999 (Wang et al., 2003) and 654ppbv (1ppbv CO equaled to about 1.2 μg/m3) in 2005 (Zhou et al., 2009). Due to increases of vehicle population and mileages in China, the emissions of NOx and CO that apportioned to vehicular emission inventory had increased at an annual rate of 15% and 14% from 1980 to 2005, respectively. Especially, the Yangtze River Delta, which covered only 2.2% of the total territory of China, generated about 19% of total vehicular pollutants in 2005 (Cai and Xie, 2007). During the biomass burning period, the concentration levels of SO2 and NOx were much lower than during PE1 and close to the normal period. While CO was considerably enhanced with the average concentration of 1241 $\pm$ 352 μg/m3, which was close to PE1 and much higher than the other periods. This probably suggested that biomass burning could release large amounts of CO while contributed little to the SO2 and NOx emission. Laboratory and filed measurements of several types of crops in eastern China showed that the emission factor of SO2 (0.44 – 0.85 g kg-1) and NOx (1.12 – 4.3g kg-1) was far less than that of CO (53 – 141.2 g kg-1) and CO2 (791.3 – 1557.9 g kg-1) (Andreae and Merlet, 2001; Li et al., 2007a; Zhang et al., 2008), indicating SO2 and NOx were not the major gaseous pollutants emitted from biomass burning in this region. Figure 11 further compares the diurnal variations of CO and NOx between PE3 and the normal period, respectively. It was found that there was almost no difference for diurnal variation of NOx between the two periods, while great distinction existed for CO. During the normal period, usually two peaks would be observed at the morning (0600 – 0900 LST) and evening (1700 – 2000 LST) rush hours due to enhanced vehicular emission in big cities (Andreae et al., 2008; Tie et al., 2009). While during the biomass burning period, peaks evidently shifted to random times at around 0800 – 1000 and 1400 – 1600 LST, which could be controlled by the emission characteristics of local burning activities and transporting time from outside burning areas. The diurnal variation in this study was more or less similar as the profile based on fire observations from satellite over 15 tropical and subtropical regions (Giglio, 2007). Another distinct difference

between the two periods was that the hourly CO concentrations during PE3 were all higher than the normal period, while there was negligible difference for NOx, precluding the possible enhancement of vehicle emission to cause the increase of CO. The results above suggested that it might be possible to use the ratio of CO/NOx to distinguish between biomass burning from the other emission sources. Figure 10 shows the calculated average CO/NOx ratios during four periods. This ratio was close among NP, PE1, and PE2, which ranged between 9 and 10, while this ratio was much higher during PE3 with average value of 14. During the non-biomass-burning period, CO and NOx mainly derived from stationary (industry) and mobile (transportation) sources. No matter what type dominated the pollution, i.e., secondary inorganic aerosol, dust aerosol, or the normal period, the emission factors of fossil fuels wouldn't change much, thus the emission amounts of specific pollutants should almost be proportional regardless of the total emissions. That's why we could find that the CO/NOx ratio didn't vary much among NP, PE1, and PE2. As viewed from the emission inventory, it was calculated that the CO/NOx ratio of the INTEX-B non-biomass-burning inventory (i.e., sum of transportation, industry, domestic, large and small power plants emission inventory) (Zhang et al., 2009) was 7.4 for the grid cell of YRD , very close to the measurement results of this study. While the CO/NOx ratio of the biomass emission inventory was much higher of 24. By using a simple mixing model, in which the CO/NOx ratio in non-biomass-burning and in biomass burning period was assumed to be 7.4 and 24, respectively, we could roughly estimate that biomass burning accounted for a significant contribution of about 40% to the total CO emission in this study.

3.6. Formation Mechanisms of Different Types of Haze Correlation analysis could shed some light on the mechanisms of haze formation under different conditions. Figure 12 demonstrates the linear relationship between gaseous pollutants (SO2, NOx and CO) and particulate matters (PM2.5). During PE1, significant correlations were observed among all the three gaseous species and PM2.5 with correlation coefficients (R) larger than 0.70 (Figure 12a-c). As precursors of sulfate and nitrate, the good correlations between SO2/NOx and PM2.5 were predictable, which corroborated the results that sul-

fate and nitrate dominated the aerosol composition during PE1. Although CO couldn't act as precursor of secondary aerosol, we still found its good correlation with PM2.5 (R = 0.71). That's because CO was highly correlated with NOx as stated above, which indirectly linked itself to PM2.5. During PE2, there was only weak correlation between pollutant gases and aerosol (not shown in the figure), as the aerosol during this period was dominated by the minerals. Figure 12d-f show the different correlation pattern for PE3 compared to PE1. As indicated by the correlation coefficients, NOx had weak correlation with PM2.5 (R = 0.41) and SO2 even had no correlation with PM2.5 (R = 0.11), suggesting secondary inorganic aerosol contributed little to aerosol formation. The significant correlation was only found between CO and PM2.5 with high correlation coefficient of 0.80. Anyway, this correlation was different from PE1 and didn't mean vehicle or industry emission played a significant role in the aerosol formation as NOx was weakly correlated with PM2.5. In Section 3.3 & 3.5, we had demonstrated that organic aerosol accounted for a major fraction of particle mass, accompanied with high concentration of CO derived from biomass burning. Correlation between CO columns and AOD from many varied forest fire episodes overall the different time periods were found (Paton-Walsh et al., 2004). Sun et al. (2009) had ever observed that CO highly correlated with OA (organic aerosol) (R: 0.7$\sim$0.9) in several OA dominated events by using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Although there was no OC data of high time resolution available due to restrictions of instruments in this study, the exclusive correlation between CO and PM2.5 during the biomass burning events mirrored the dominance of organic aerosol in the particle formation. CO could be regarded as the proxy of organic aerosol when biomass burning dominated. As visualized in Fig. 12c and 12f, it could found that the CO/ PM2.5 slope was higher in PE1 than in PE3. The CO level was similar between PE1 and PE3 as shown in Fig. 10. Thus, the lower CO/ PM2.5 slope in PE3 was due to higher PM2.5 concentrations as discussed in Section 3.1. This probably meant that biomass burning could produce higher aerosol mass than the industrial/traffic emission as most of the biomass burning events were incomplete combustion, which couldn't effectively oxidize

the hydrocarbon to CO2 or CO.

4. Conclusions An intensive aerosol and trace gases campaign was carried out over the Yangtze River Delta region in Eastern China during April to June, 2009. Three pollution episodes were identified based on the atmospheric visibility, aerosol mass concentrations in different sizes, mass fraction of fine particles and modeled air trajectories. Distinct characteristics were observed among the three pollution episodes by using a synergy of ground-based measurement, satellite observation, and lidar inversion. Three typical types of air pollution for causing the haze weather in Eastern China were identified, i.e., secondary inorganic pollution, dust invasion and biomass burning. (1) During the secondary inorganic pollution episode, satellite inversion observed high AOD (>1.2) and relatively high Angstrom exponent (0.8$\sim$1.2) over the Eastern China region. The major components of PM2.5 were sulfate, nitrate and ammonium. The sum of these three species reached 48.86 $\pm$ 5.01μg/m3 and account for a dominant mass fraction of 77% in PM2.5. High concentrations of SO2, NOx and CO and good correlations between these trace gases and PM2.5 indicated that anthropogenic sources (coal burning, vehicle emission etc.) were the major cause. (2) During the dust pollution episode, high AOD (>1.2) and low Angstrom exponent (0.5$\sim$0.6) were observed in northern and eastern China, indicating the existence of considerable coarse particles. Mineral aerosol accounted for 76.8% of the total suspended particles (TSP) and the Ca/Al elemental ratio dropped to a relatively low value of 0.75, which indicated its dust source region in Gobi Desert. (3) The biomass burning pollution episode was characteristic of high column concentrations of CO, HCHO and AOD, which were relatively consistent with regions of dense fire spots. Particulate components such as K+, OC and EC were greatly enhanced as well as the ratio of OC/EC. The organic aerosol was estimated to account for over 50% to PM10, and the significant correlation between CO and PM2.5 while the weak correlations between SO2, NOx and PM2.5 corroborated that organic aerosol was the major species during biomass burning. (4) The enrichment factor analysis demonstrated that elements during dust pollution were least enriched while the enrichment degrees were highest during the inorganic sec-

ondary pollution. The concentration level and enrichment degree of arsenic (As) was highest during the biomass burning period. We speculated that it could be more from the biomass burning emission source other than its usual source from coal burning as the water for irrigating the crops in East Asia had been probably contaminated by arsenic pollution. (5) Lidar measurement revealed that aerosol were mainly composed of spheric particles (deplorization ratio δ532 < 5%) during the secondary inorganic pollution and biomass burning episodes, and vertical profile of backscattering coefficient had a sharp decrease with altitudes. While the average δ532 value of the boundary layer was 0.122 $\pm$ 0.023 during the dust period, indicating existence of considerable coarse particles. The dust period had a different profile from the other two periods that the dust layer contributed about 51 – 57% to the total aerosol extinction at the altitude of 0.7 – 1.0 km, which compensated the decrease of spheric aerosol extinction.

Appendix A In order to compare with the recorded visibility data, we calculated the near-surface extinction coefficient caused by aerosol (σep) by averaging the lidar measured aerosol extinction coefficient from the ground to an altitude of 300m. Absorption of visible light by gases was considered to be essentially due to NO2 and the absorption coefficient (σag) could be estimated using the formula σag = 0.33 $\times$ [NO2] (Groblicki et al., 1981). Here, NO2 was in units of $\times$10-9V/V. Rayleigh scattering coefficient (σsg) was assumed to be a constant of 0.013km-1 at sea level (Chan et al., 1999; Peundorf, 1957)). The scattering coefficient of light due to moisture in the air (bsw) could be neglected when relatively humidity (RH) was lower than 70% (Cass, 1979; Chan et al., 1999). In this study, the average relative humidity was about 60%. Consequently, the total light extinction by particles and gases (σext = σep + σag + σsg) was calculated and the visibility could be estimated.

Acknowledgments Many thanks to the MODIS, OMI and AIRS data processing team members. We thank Prof. Sugimoto Nobuo and Shimizu Atsushi of National Institute for Environmental Studies, Japan for the lidar setup and data inversion. This work was supported by the great international collaboration project of MOST,

China (2010DFA92230), National Natural Science Foundation of China (Grant Nos. 41128005 (fund for collaboration with oversea scholars), 20877020, 20977017), and Shanghai environmental protection science developing funding (No.2010-003).

References Amato, F., Pandolfi, M., Viana, M., Querol, X., Alastuey, A., and Moreno, T.: Spatial and chemical patterns of PM10 in road dust deposited in urban environment, Atmos. Environ., 43, 9, 1650-1659, 2009. Andreae, M. O.: Soot Carbon and Excess Fine Potassium - Long-Range Transport of Combustion-Derived Aerosols, Science, 220, 4602, 1148-1151, 1983. Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cycles, 15, 4, 955-966, 2001. Andreae, M. O., Schmid, O., Yang, H., Chand, D., Yu, J. Z., Zeng, L. M., and Zhang, Y. H.: Optical properties and chemical composition of the atmospheric aerosol in urban Guangzhou, China, Atmos. Environ., 42, 25, 6335-6350, 2008. Arimoto, R., Duce, R. A., Savoie, D. L., Prospero, J. M., Talbot, R., Cullen, J. D., Tomza, U., Lewis, N. F., and Jay, B. J.: Relationships among aerosol constituents from Asia and the North Pacific during PEM-West A, J. Geophys. Res., 101, D1, 2011-2023, 1996. Boian, C., and Kirchhoff, V. W. J. H.: Measurements of CO in an aircraft experiment and their correlation with biomass burning and air mass origin in South America, Atmos. Environ., 38, 37, 6337-6347, 2004. Brammer, H., and Ravenscroft, P.: Arsenic in groundwater: A threat to sustainable agriculture in South and South-east Asia, Environ. Int., 35, 3, 647-654, 2009. Cai, H., and Xie, S. D.: Estimation of vehicular emission inventories in China from 1980 to 2005, Atmos. Environ., 41, 39, 8963-8979, 2007. Cao, T., An, L., Wang, M., Lou, Y. X., Yu, Y. H., Wu, J. M., Zhu, Z. R., Qing, Y. K., and Glime, J.: Spatial and temporal changes of heavy metal concentrations in mosses and its indication to the environments in the past 40 years in the city of Shanghai, China, Atmos. Environ., 42, 21, 5390-5402, 2008. Cass, G. R.: On the relationship between sulfate air quality and visibility with examples in los angeles, Atmospheric Environment, 13, 8, 1069-1084, 1979. Chakrabarty, R. K., Moosmuller, H., Garro, M. A., Arnott, W. P., Walker, J., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle

morphology and size, J. Geophys. Res., 111, D7, doi:10.1029/2005JD006659, 2006. Chan, C. K., and Yao, X.: Air pollution in mega cities in China, Atmos. Environ., 42, 1, 1-42, 2008. Chan, Y. C., Simpson, R. W., McTainsh, G. H., Vowles, P. D., Cohen, D. D., and Bailey, G. M.: Source apportionment of visibility degradation problems in Brisbane (Australia) using the multiple linear regression techniques, Atmospheric Environment, 33, 19, 3237-3250, 1999. Chang, D., and Song, Y.: Estimates of biomass burning emissions in tropical Asia based on satellite-derived data, Atmos. Chem. Phys., 10, 5, 2335-2351, 2010. Chang, D., Song, Y., and Liu, B.: Visibility trends in six megacities in China 1973-2007, Atmos. Res., 94, 2, 161-167, 2009. Che, H. Z., Shi, G. Y., Zhang, X. Y., Arimoto, R., Zhao, J. Q., Xu, L., Wang, B., and Chen, Z. H.: Analysis of 40 years of solar radiation data from China, 1961-2000, Geophys. Res. Lett., 32, L06803, doi:10.1029/2004GL022322, 2005. Che, H. Z., Zhang, X. Y., Li, Y., Zhou, Z. J., and Qu, J. J.: Horizontal visibility trends in China 1981-2005, Geophys. Res. Lett., 34, L24706, doi:10.1029/2007GL031450, 2007. Chen, C. H., Wang, B. Y., Fu, Q. Y., Green, C., and Streets, D. G.: Reductions in emissions of local air pollutants and co-benefits of Chinese energy policy: a Shanghai case study, Energy Policy, 34, 6, 754-762, 2006. Chen, J. M., Tan, M. G., Li, Y. L., Zhang, Y. M., Lu, W. W., Tong, Y. P., Zhang, G. L., and Li, Y.: A lead isotope record of shanghai atmospheric lead emissions in total suspended particles during the period of phasing out of leaded gasoline, Atmos. Environ., 39, 7, 1245-1253, 2005. Choi, S. D., and Chang, Y. S.: Carbon monoxide monitoring in Northeast Asia using MOPITT: Effects of biomass burning and regional pollution in April 2000, Atmos. Environ., 40, 4, 686-697, 2006. Chow, J. C., and Watson, J. G.: PM2.5 carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites, J. Geophys. Res., 107, D21, doi:10.1029/2001JD000574, 2002. Chu, D. A., Kaufman, Y. J., Zibordi, G., Chern, J. D., Mao, J., Li, C. C., and Holben, B. N.: Global monitoring of air pollution over land from the Earth Observing System-Terra Moderate Resolution Imaging Spectroradiometer (MODIS), J. Geophys. Res., 108, D21, doi:10.1029/2002JD003179, 2003. Crutzen, P. J., and Andreae, M. O.: Biomass Burning in the Tropics - Impact on

Atmospheric Chemistry and Biogeochemical Cycles, Science, 250, 4988, 1669-1678, 1990. Deng, C. R., Zhuang, G. S., Huang, K., Li, J., Zhang, R., Wang, Q. Z., Sun, Y. L., Guo, Z. G., and Wang, Z. F.: Chemical characterization of aerosols at the summit of Mountain Tai in the middle of central east China, Atmos. Chem. Phys. Discuss., 10, 1-47, doi:10.5194/acpd-5110-5191-2010, 2010. Fang, M., Chan, C. K., and Yao, X. H.: Managing air quality in a rapidly developing nation: China, Atmos. Environ., 43, 1, 79-86, 2009. Feng, J. L., Hu, M., Chan, C. K., Lau, P. S., Fang, M., He, L. Y., and Tang, X. Y.: A comparative study of the organic matter in PM2.5 from three Chinese megacities in three different climatic zones, Atmos. Environ., 40, 21, 3983-3994, 2006. Feng, Y. L., Chen, Y. J., Guo, H., Zhi, G. R., Xiong, S. C., Li, J., Sheng, G. Y., and Fu, J. M.: Characteristics of organic and elemental carbon in PM2.5 samples in Shanghai, China, Atmos. Res., 92, 4, 434-442, 2009. Fernald, F. G.: Analysis of Atmospheric Lidar Observations - Some Comments, Appl. Opt., 23, 5, 652-653, 1984. Fu, Q. Y., Zhuang, G. S., Wang, J., Xu, C., Huang, K., Li, J., Hou, B., Lu, T., and Streets, D. G.: Mechanism of formation of the heaviest pollution episode ever recorded in the Yangtze River Delta, China, Atmos. Environ., 42, 9, 2023-2036, 2008. Gao, J., Wang, T., Zhou, X. H., Wu, W. S., and Wang, W. X.: Measurement of aerosol number size distributions in the Yangtze River delta in China: Formation and growth of particles under polluted conditions, Atmos. Environ., 43, 4, 829-836, 2009. 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 Poschl, 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, 17, 5161-5186, 2008. Geng, F. H., Zhang, Q., Tie, X. X., Huang, M. Y., Ma, X. C., Deng, Z. Z., Yu, Q., Quan, J. N., and Zhao, C. S.: Aircraft measurements of O-3, NOx, CO, VOCs, and SO2 in the Yangtze River Delta region, Atmos. Environ., 43, 3, 584-593, 2009. Giglio, L.: Characterization of the tropical diurnal fire cycle using VIRS and MODIS observations, Remote Sensing of Environment, 108, 4, 407-421, 2007. Groblicki, P. J., Wolff, G.

T., and Countess, R. J.: Visibility-Reducing Species in the Denver Brown Cloud .1. Relationships between Extinction and Chemical-Composition, Atmos. Environ., 15, 12, 2473-2484, 1981. Hasan, H., and Dzubay, T. G.: Apportioning Light Extinction Coefficients to Chemical-Species in Atmospheric Aerosol, Atmos. Environ., 17, 8, 1573-1581, 1983. He, Y., Uno, I., Wang, Z., Ohara, T., Sugirnoto, N., Shimizu, A., Richter, A., and Burrows, J. P.: Variations of the increasing trend of tropospheric NO2 over central east China during the past decade, Atmos. Environ., 41, 23, 4865-4876, 2007. Huang, K., Zhuang, G. S., Li, J. A., Wang, Q. Z., Sun, Y. L., Lin, Y. F., and Fu, J. S.: Mixing of Asian dust with pollution aerosol and the transformation of aerosol components during the dust storm over China in spring 2007, J. Geophys. Res., 115, D00K13, doi:10.1029/2009JD013145, 2010. Huang, K., Zhuang, G. S., Xu, C., Wang, Y., and Tang, A. H.: The chemistry of the severe acidic precipitation in Shanghai, China, Atmos. Res., 89, 1-2, 149-160, 2008. Kaiser, D. P., and Qian, Y.: Decreasing trends in sunshine duration over China for 1954-1998: Indication of increased haze pollution?, Geophys. Res. Lett., 29(21), 2042, doi:10.1029/2002GL016057, 2002. Kan, H. D., and Chen, B. H.: Particulate air pollution in urban areas of Shanghai, China: health-based economic assessment, Sci. Total Environ., 322, 1-3, 71-79, 2004. Kan, H. D., London, S. J., Chen, G. H., Zhang, Y. H., Song, G. X., Zhao, N. Q., Jiang, L. L., and Chen, B. H.: Differentiating the effects of fine and coarse particles on daily mortality in Shanghai, China, Environ. Int., 33, 3, 376-384, 2007. Kato, S., Akimoto, H., Rockmann, T., Braunlich, M., and Brenninkmeijer, C. A. M.: Stable isotopic compositions of carbon monoxide from biomass burning experiments, Atmos. Environ., 33, 27, 4357-4362, 1999. Kato, S., Pochanart, P., Hlrokawa, J., Kajii, Y., Akimoto, H., Ozaki, Y., Obi, K., Katsuno, T., Streets, D. G., and Minko, N. P.: The influence of Siberian forest fires on carbon monoxide concentrations at Happo, Japan, Atmos. Environ., 36, 2, 385-390, 2002. Kaufman, Y. J., Wald, A. E., Remer, L. A., Gao, B. C., Li, R. R., and Flynn, L.: The MODIS 2.1-mu m channel - Correlation with visible reflectance for use in remote sensing of aerosol, Ieee Transactions on Geoscience and Remote Sensing, 35, 5, 1286-1298, 1997. Kim, S. W., Yoon, S. C., Kim, J., Kang, J. Y.,

and Sugimoto, N.: Asian dust event observed in Seoul, Korea, during 29-31 May 2008: Analysis of transport and vertical distribution of dust particles from lidar and surface measurements, Sci. Total Environ., 408, 7, 1707-1718, 2010. Kurosu, T. P., Chance, K., and Sioris, C. E.: Preliminary Results for HCHO and BrO from the EOS-Aura Ozone Monitoring Instrument, Proc. of SPIE Vol. 5652, Passive Optical Remote Sensing of the Atmosphere and Clouds IV, edited by Si Chee Tsay, Tatsuya Yokota, Myoung-Hwan Ahn, 2004. Lee, S., Ghim, Y. S., Kim, S. W., and Yoon, S. C.: Seasonal characteristics of chemically apportioned aerosol optical properties at Seoul and Gosan, Korea, Atmos. Environ., 43, 6, 1320-1328, 2009. Levelt, P. F., Van den Oord, G. H. J., Dobber, M. R., Malkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J. O. V., and Saari, H.: The Ozone Monitoring Instrument, Ieee Transactions on Geoscience and Remote Sensing, 44, 5, 1093-1101, 2006. Li, C., Zhang, Q., Krotkov, N. A., Streets, D. G., He, K. B., Tsay, S. C., and Gleason, J. F.: Recent large reduction in sulfur dioxide emissions from Chinese power plants observed by the Ozone Monitoring Instrument, Geophys. Res. Lett., 37, L08807, doi:10.1029/2010GL042594, 2010. Li, J., Posfai, M., Hobbs, P. V., and Buseck, P. R.: Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles, J. Geophys. Res., 108, D13, doi:10.1029/2002JD002310, 2003. Li, P. F., Li, X., Yang, C. Y., Wang, X. J., Chen, J. M., and Collett, J. L.: Fog water chemistry in Shanghai, Atmos. Environ., 45, 24, 4034-4041, 2011. Li, X. G., Wang, S. X., Duan, L., Hao, J., Li, C., Chen, Y. S., and Yang, L.: Particulate and trace gas emissions from open burning of wheat straw and corn stover in China, Environ. Sci. Technol., 41, 17, 6052-6058, 2007. Lu, Z., Streets, D. G., Zhang, Q., Wang, S., Carmichael, G. R., Cheng, Y. F., Wei, C., Chin, M., Diehl, T., and Tan, Q.: Sulfur dioxide emissions in China and sulfur trends in East Asia since 2000, Atmos. Chem. Phys., 10, 13, 6311-6331, 2010. Li, Z. Q., Chen, H., Cribb, M., Dickerson, R., Holben, B., Li, C., Lu, D., Luo, Y., Maring, H., Shi, G., Tsay, S. C., Wang, P., Wang, Y., Xia, X., Zheng, Y., Yuan, T., and Zhao, F.: Preface to special section on east Asian studies of tropospheric aerosols: An international regional experiment (EAST-AIRE), J. Geophys. Res., 112,

D22S00, doi:10.1029/2007JD008853, 2007. Liu, F., Wang, X. K., and Zhu, Y. G.: Assessing current and future ozone-induced yield reductions for rice and winter wheat in Chongqing and the Yangtze River Delta of China, Environ. Pollut., 157, 2, 707-709, 2009. Liu, Z., Liu, D., Huang, J., Vaughan, M., Uno, I., Sugimoto, N., Kittaka, C., Trepte, C., Wang, Z., Hostetler, C., and Winker, D.: Airborne dust distributions over the Tibetan Plateau and surrounding areas derived from the first year of CALIPSO lidar observations, Atmos. Chem. Phys., 8, 16, 5045-5060, 2008. Liu, Z. Y., Sugimoto, N., and Murayama, T.: Extinction-to-backscatter ratio of Asian dust observed with high-spectral-resolution lidar and Raman lidar, Appl. Opt., 41, 15, 2760-2767, 2002. Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., and Cahill, T. A.: Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United-States, Journal of Geophysical Research-Atmospheres, 99, D1, 1347-1370, 1994. Mandal, B. K., and Suzuki, K. T.: Arsenic round the world: a review, Talanta, 58, 1, 201-235, 2002. Mari, C. H., Cailley, G., Corre, L., Saunois, M., Attie, J. L., Thouret, V., and Stohl, A.: Tracing biomass burning plumes from the Southern Hemisphere during the AMMA 2006 wet season experiment, Atmos. Chem. Phys., 8, 14, 3951-3961, 2008. McMillan, W. W., Barnet, C., Strow, L., Chahine, M. T., McCourt, M. L., Warner, J. X., Novelli, P. C., Korontzi, S., Maddy, E. S., and Datta, S.: Daily global maps of carbon monoxide from NASA's Atmospheric Infrared Sounder, Geophys. Res. Lett., 32, L11801, doi:10.1029/2004GL021821, 2005. Mcneil, W. R., and Carswell, A. I.: Lidar Polarization Studies of Troposphere, Appl. Opt., 14, 9, 2158-2168, 1975. Noh, Y. M., Kim, Y. J., Choi, B. C., and Murayama, T.: Aerosol lidar ratio characteristics measured by a multi-wavelength Raman lidar system at Anmyeon Island, Korea, Atmos. Res., 86, 1, 76-87, 2007. Nriagu, J. O.: A Global Assessment of Natural Sources of Atmospheric Trace-Metals, Nature, 338, 6210, 47-49, 1989. Ouimette, J. R., and Flagan, R. C.: The Extinction Coefficient of Multicomponent Aerosols, Atmos. Environ., 16, 10, 2405-2419, 1982. Pan, L. A., Che, H. Z., Geng, F. H., Xia, X. G., Wang, Y. Q., Zhu, C. Z., Chen, M., Gao, W., and Guo, J. P.: Aerosol optical properties based on ground measurements over the Chinese Yangtze Delta Region, Atmos. Environ., 44, 21-22,

2587-2596, 2010. Parrish, D. D., and Zhu, T.: Clean Air for Megacities, Science, 326, 5953, 674-675, 2009. Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM2.5 ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, Atmos. Chem. Phys., 9, 5, 1711-1722, 2009. Paton-Walsh, C., Jones, N., Wilson, S., Meier, A., Deutscher, N., Griffith, D., Mitchell, R., and Campbell, S.: Trace gas emissions from biomass burning inferred from aerosol optical depth, Geophys. Res. Lett., 31, L05116, doi:10.1029/2003GL018973, 2004. Peundorf, R.: Tables of the refractive index for standard and the Rayleigh scattering coefficient for the spectral region between 0.2 and 20.0 microns and their application to atmospheric optics, Journal of the Optical Society of America, 47, 176-182, 1957. Shi, G. T., Chen, Z. L., Xu, S. Y., Zhang, J., Wang, L., Bi, C. J., and Teng, J. Y.: Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China, Environ. Pollut., 156, 2, 251-260, 2008. Shimizu, A., Sugimoto, N., Matsui, I., Arao, K., Uno, I., Murayama, T., Kagawa, N., Aoki, K., Uchiyama, A., and Yamazaki, A.: Continuous observations of Asian dust and other aerosols by polarization lidars in China and Japan during ACE-Asia, J. Geophys. Res., 109, D19S17, doi:10.1029/2002JD003253, 2004. SMSB: Shanghai Municipal Statistics Bureau, Shanghai sixth national census in 2010 Communiqué on Major Data (in Chinese), 2011. Sugimoto, N., Matsui, I., Shimizu, A., Uno, I., Asai, K., Endoh, T., and Nakajima, T.: Observation of dust and anthropogenic aerosol plumes in the Northwest Pacific with a two-wavelength polarization lidar on board the research vessel Mirai, Geophys. Res. Lett., 29, 19, doi:10.1029/2002GL015112, 2002. Sun, Y., Zhang, Q., Macdonald, A. M., Hayden, K., Li, S. M., Liggio, J., Liu, P. S. K., Anlauf, K. G., Leaitch, W. R., Steffen, A., Cubison, M., Worsnop, D. R., van Donkelaar, A., and Martin, R. V.: Size-resolved aerosol chemistry on Whistler Mountain, Canada with a high-resolution aerosol mass spectrometer during INTEX-B, Atmos. Chem. Phys., 9, 9, 3095-3111, 2009. Sun, Y. L., Zhuang, G. S., Ying, W., Han, L. H., Guo, J. H., Mo, D., Zhang, W. J., Wang, Z. F., and Hao, Z. P.: The air-borne particulate pollution in Beijing - concentration, composition, distribution and sources, Atmospheric Environment, 38, 35, 5991-6004, 2004. Tan, M. G., Zhang,

G. L., Li, X. L., Zhang, Y. X., Yue, W. S., Chen, J. M., Wang, Y. S., Li, A. G., Li, Y., Zhang, Y. M., and Shan, Z. C.: Comprehensive study of lead pollution in Shanghai by multiple techniques, Anal. Chem., 78, 23, 8044-8050, 2006. Tie, X. X., Geng, F. H., Peng, L., Gao, W., and Zhao, C. S.: Measurement and modeling of O-3 variability in Shanghai, China: Application of the WRF-Chem model, Atmos. Environ., 43, 28, 4289-4302, 2009. Turpin, B. J., and Lim, H. J.: Species contributions to PM2.5 mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 1, 602-610, 2001. U.S. Environmental Protection Agency (U.S. EPA) (1998), Quality assurance handbook for air pollution measurement systems, EPAâĂŘ454/RâĂŘ98–004, Research Triangle Park, N. C. van der A, R. J., Peters, D. H. M. U., Eskes, H., Boersma, K. F., Van Roozendael, M., De Smedt, I., and Kelder, H. M.: Detection of the trend and seasonal variation in tropospheric NO2 over China, J. Geophys. Res., 111, D12317, doi:10.1029/2005JD006594, 2006. Wang, H. X., Tang, X. Y., Wang, M. L., Yan, P., Wang, T., Shao, K. S., Zeng, L. M., Du, H. F., and Chen, L. M.: Characteristics of observed trace gaseous pollutants in the Yangtze Delta, Sci. China. Ser. D, 46, 4, 397-404, 2003. Wang, K. C., Dickinson, R. E., and Liang, S. L.: Clear Sky Visibility Has Decreased over Land Globally from 1973 to 2007, Science, 323, 5920, 1468-1470, 2009. Wang, T., Cheung, T. F., Li, Y. S., Yu, X. M., and Blake, D. R.: Emission characteristics of CO, NOx, SO2 and indications of biomass burning observed at a rural site in eastern China, J. Geophys. Res., 107, D12, 10.1029/2001JD000724, 2002. Wang, T., Nie, W., Gao, J., Xue, L. K., Gao, X. M., Wang, X. F., Qiu, J., Poon, C. N., Meinardi, S., Blake, D., Wang, S. L., Ding, A. J., Chai, F. H., Zhang, Q. Z., and Wang, W. X.: Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, Atmos. Chem. Phys., 10, 16, 7603-7615, 2010. Wang, Y., Zhuang, G. S., Tang, A. H., Zhang, W. J., Sun, Y. L., Wang, Z. F., and An, Z. S.: The evolution of chemical components of aerosols at five monitoring sites of China during dust storms, Atmos. Environ., 41, 5, 1091-1106, 2007. Wang, Y., Zhuang, G. S., Zhang, X. Y., Huang, K., Xu, C., Tang, A. H., Chen, J. M., and An, Z. S.: The ion chemistry, seasonal cycle, and sources of PM2.5 and TSP

aerosol in Shanghai, Atmos. Environ., 40, 16, 2935-2952, 2006. Xia, X. G., Li, Z. Q., Holben, B., Wang, P., Eck, T., Chen, H. B., Cribb, M., and Zhao, Y. X.: Aerosol optical properties and radiative effects in the Yangtze Delta region of China, J. Geophys. Res., 112, D22S12, doi:10.1029/2007JD008859 2007. Xu, J., Bergin, M. H., Yu, X., Liu, G., Zhao, J., Carrico, C. M., and Baumann, K.: Measurement of aerosol chemical, physical and radiative properties in the Yangtze delta region of China, Atmos. Environ., 36, 2, 161-173, 2002. Yamaji, K., Li, J., Uno, I., Kanaya, Y., Irie, H., Takigawa, M., Komazaki, Y., Pochanart, P., Liu, Y., Tanimoto, H., Ohara, T., Yan, X., Wang, Z., and Akimoto, H.: Impact of open crop residual burning on air quality over Central Eastern China during the Mount Tai Experiment 2006 (MTX2006), Atmos. Chem. Phys., 10, 15, 7353-7368, 2010. Yan, X. Y., Ohara, T., and Akimoto, H.: Bottom-up estimate of biomass burning in mainland China, Atmos. Environ., 40, 27, 5262-5273, 2006. Yang, F., He, K., Ye, B., Chen, X., Cha, L., Cadle, S. H., Chan, T., and Mulawa, P. A.: One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai, Atmos. Chem. Phys., 5, 1449-1457, 2005a. Yang, F. M., Ye, B. M., He, K. B., Ma, Y. L., Cadle, S. H., Chan, T., and Mulawa, P. A.: Characterization of atmospheric mineral components of PM2.5 in Beijing and Shanghai, China, Science of the Total Environment, 343, 1-3, 221-230, 2005b. Yao, X. H., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K. B., and Ye, B. M.: The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China, Atmos. Environ., 36, 26, 4223-4234, 2002. Ye, B. M., Ji, X. L., Yang, H. Z., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., and Mulawa, P. A.: Concentration and chemical composition of PM2.5 in Shanghai for a 1-year period, Atmos. Environ., 37, 4, 499-510, 2003. Ye, S. H., Zhou, W., Song, J., Peng, B. C., Yuan, D., Lu, Y. M., and Qi, P. P.: Toxicity and health effects of vehicle emissions in Shanghai, Atmos. Environ., 34, 3, 419-429, 2000. Yuan, H., Wang, Y., and Zhuang, G. S.: Simultaneous determination of organic acids, methanesulfonic acid and inorganic anions in aerosol and precipitation samples by ion chromatography, Journal of Instrumental Analysis, 22, 11-44, 2003. Zhang, H. F., Ye, X. N., Cheng, T. T., Chen, J. M., Yang, X., Wang, L., and Zhang, R. Y.: A laboratory study of agricultural

crop residue combustion in China: Emission factors and emission inventory, Atmos. Environ., 42, 36, 8432-8441, 2008. Zhang, Q., Streets, D. G., Carmichael, G. R., He, K. B., Huo, H., Kannari, A., Klimont, Z., Park, I. S., Reddy, S., Fu, J. S., Chen, D., Duan, L., Lei, Y., Wang, L. T., and Yao, Z. L.: Asian emissions in 2006 for the NASA INTEX-B mission, Atmos. Chem. Phys., 9, 14, 5131-5153, 2009. Zhang, W. J., Zhuang, G. S., Huang, K., Li, J. A., Zhang, R., Wang, Q. Z., Sun, Y. L., Fu, J. S., Chen, Y., Xu, D. Q., and Wang, W.: Mixing and transformation of Asian dust with pollution in the two dust storms over the northern China in 2006, Atmos. Environ., 44, 28, 3394-3403, 2010. Zhang, X. Y., Gong, S. L., Shen, Z. X., Mei, F. M., Xi, X. X., Liu, L. C., Zhou, Z. J., Wang, D., Wang, Y. Q., and Cheng, Y.: Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 1. Network observations, Journal of Geophysical Research-Atmospheres, 108, D9, doi:10.1029/2002JD002632, 2003. Zhang, X. Y., Wang, Y. Q., Zhang, X. C., Guo, W., and Gong, S. L.: Carbonaceous aerosol composition over various regions of China during 2006, J. Geophys. Res., 113, D14, doi:10.1029/2007JD009525, 2008. Zhang, X. Y., Zhang, P., Zhang, Y., Li, X. J., and Qiu, H.: The trend, seasonal cycle, and sources of tropospheric NO2 over China during 1997-2006 based on satellite measurement, Sci. China. Ser. D, 50, 12, 1877-1884, 2007. Zhang, X. Y., Zhuang, G. Y., Zhu, G. H., Zhang, D., An, Z. S., Chen, T., and Huang, X. P.: Element tracers for Chinese source dust, Science in China (Series D), 39, 5, 512-521, 1996. Zhang, Y. H., Hu, M., Zhong, L. J., Wiedensohler, A., Liu, S. C., Andreae, M. O., Wang, W., and Fan, S. J.: Regional Integrated Experiments on Air Quality over Pearl River Delta 2004 (PRIDE-PRD2004): Overview, Atmos. Environ., 42, 25, 6157-6173, 2008. Zhang, Y. P., Wang, X. F., Chen, H., Yang, X., Chen, J. M., and Allen, J. O.: Source apportionment of lead-containing aerosol particles in Shanghai using single particle mass spectrometry, Chemosphere, 74, 4, 501-507, 2009. Zhao, X. S., Wan, Z., Zhu, H. G., and Chen, R. P.: The carcinogenic potential of extractable organic matter from urban airborne particles in Shanghai, China, Mutation Research-Genetic Toxicology and Environmental Mutagenesis, 540, 1, 107-117, 2003. Zhou, X. H., Cao, J., Wang,

T., Wu, W. S., and Wang, W. X.: Measurement of black carbon aerosols near two Chinese megacities and the implications for improving emission inventories, Atmos. Environ., 43, 25, 3918-3924, 2009. Zhou, Y., Fu, J. S., Zhuang, G. S., and Levy, J. I.: Risk-Based Prioritization among Air Pollution Control Strategies in the Yangtze River Delta, China, Environ. Health Perspect., 118, 9, 1204-1210, 2010. Zhuang, G. S., Guo, J. H., Yuan, H., and Zhao, C. Y.: The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment, Chinese Science Bulletin, 46, 11, 895-901, 2001.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C10304/2011/acpd-11-C10304-2011-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21713, 2011.