Response to Reviewers' Comments (#1)

Review comments on "How to improve the air quality over mega-cities in China? – Pollution characterization and source analysis in Shanghai before, during, and after the 2010 World Expo" by Huang et al.

This manuscript provides an important study on the PM2.5 pollution in Shanghai before, during, and after the 2010 World Expo. The topic is applicable for Atmospheric Chemistry and Physics; however several concerns have been identified. Major revisions as indicated in the comments and remarks below are needed before consideration of publication in ACP.

We appreciate the reviewer for a very thorough comment on this manuscript and we do find it useful for the improvement of this manuscript. In the responses below, we have made the corresponding corrections following the comments point by point. Below are the responses to all the comments one by one. Also, in the revised manuscript, we have highlighted the changes with red color.

This manuscript claimed that the enhanced human activities increased PM2.5 concentrations especially the nitrate concentration during the World Expo, which is based on in-situ measurements at Fudan University. However, there are some important issues needed to be clarified. First, because only one site is used to in this study, can the Fudan site reflect influences from Expo activities? More information is needed here, like what is the distance between the Fudan site and the Wolrd Expo campus? What is the prevalent wind direction before, during and after the World Expo? Shanghai is a large city, so the enhanced human activities should be located near the Expo field and other areas in Shanghai should be considered as 'business as usual'. One site might only present the environment nearby, thus the authors should make sure the Fudan site can sample the influences from the Expo.

Thanks for the comments. To clarify the reviewer's concerns of whether the monitoring site at Fudan University could reflect the air quality on the Expo campus, we get the monitoring data at one site (Name: Weifang) in the Pudong District from Shanghai

Environment Monitoring Center (SEMC). Figure R1 shows the locations of Fudan and Weifang monitoring sites, which are located in the Yangpu and Pudong District (the administrative districts of Shanghai are denoted in the figure), respectively. The figure also shows the area of the Expo campus (denoted by the red polygon). It was partly built on the Pudong District and partly on the Yangpu District, which was separated by the Huangpu River. As shown in the figure, the Fudan monitoring site is located to the north of the Expo campus and the distance from the Fudan site to the Expo campus is around 8 – 11 km.

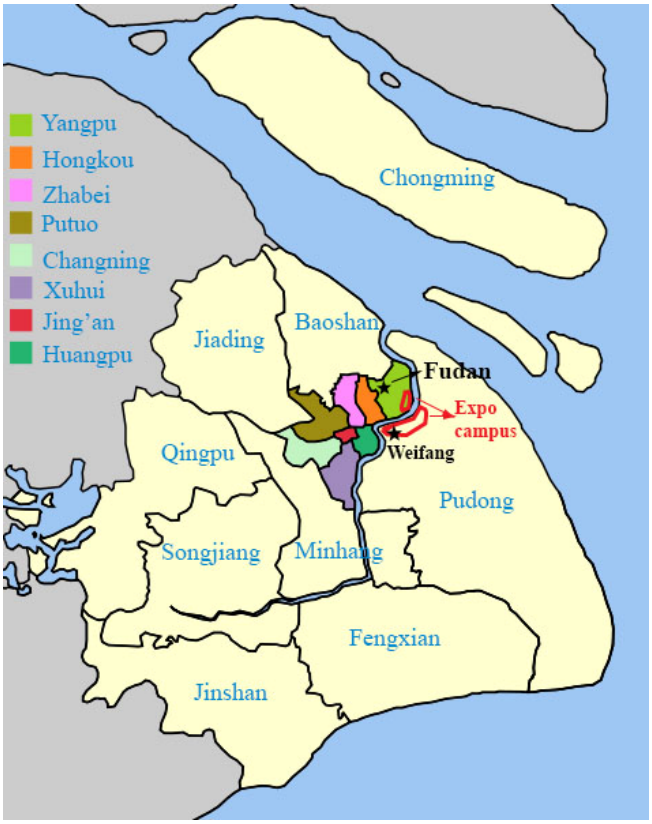


Fig. R1. Map of Shanghai with district borders. The area of the Expo campus is shown by the red polygon, and the monitoring sites at Fudan and Weifang are denoted by the black stars.

The Weifang monitoring site is located inside the Expo campus and it could be used to represent the air quality around the Expo area. Figure R2a shows the hourly PM_{10} concentrations measured at Fudan and Weifang during the Expo period. The data before and after the Expo in Weifang is not shown as SEMC only provided data during the Expo. As shown in the figure, the time-series of PM_{10} concentrations at these two sites co-

varied very consistently with each other. Figure R2b shows the linear correlation of the hourly PM_{10} concentrations between the two sites, with a significant correlation coefficient of 0.83. The slope of the regression equation reaches 0.97, very close to 1.00. Thus, this indicates the Fudan site could indeed represent the air quality of the Expo campus.

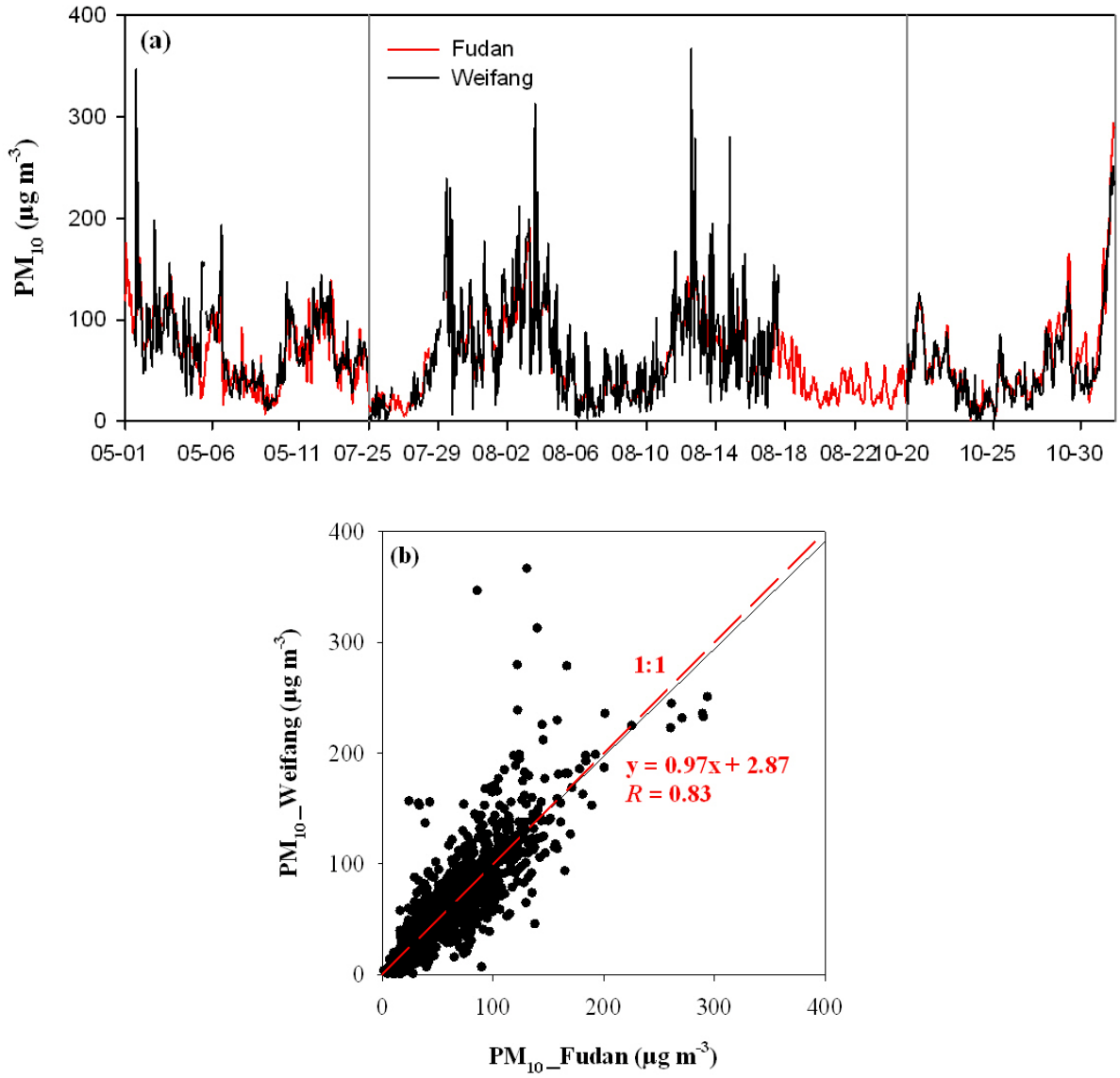
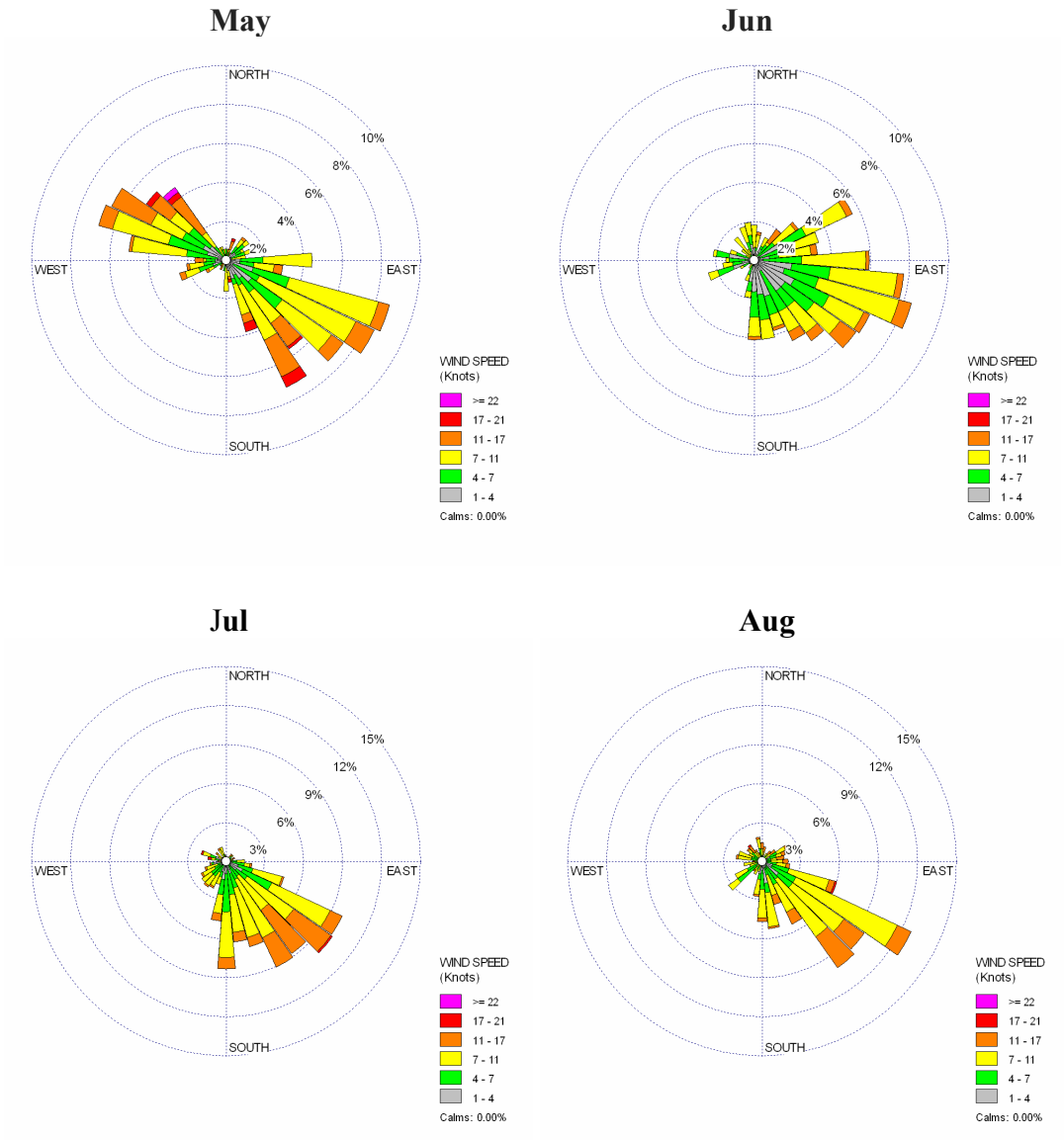


Fig. R2. (a) Time-series of PM_{10} concentrations at Fudan and Weifang (b) The linear correlation between PM_{10} concentrations at Fudan and Weifang. The red dashed line represents the 1:1 fit line, and the regression equation is shown in the figure.

Figure R3 shows the monthly wind rose at Fudan from May to October in 2010. As shown in the figure, southeast winds dominated during the whole study period. The Fudan site is located to the northwest of the Expo campus as shown in Figure R1. Thus, it is evident that our monitoring site would be significantly impacted by the upstream emission from the Expo campus.



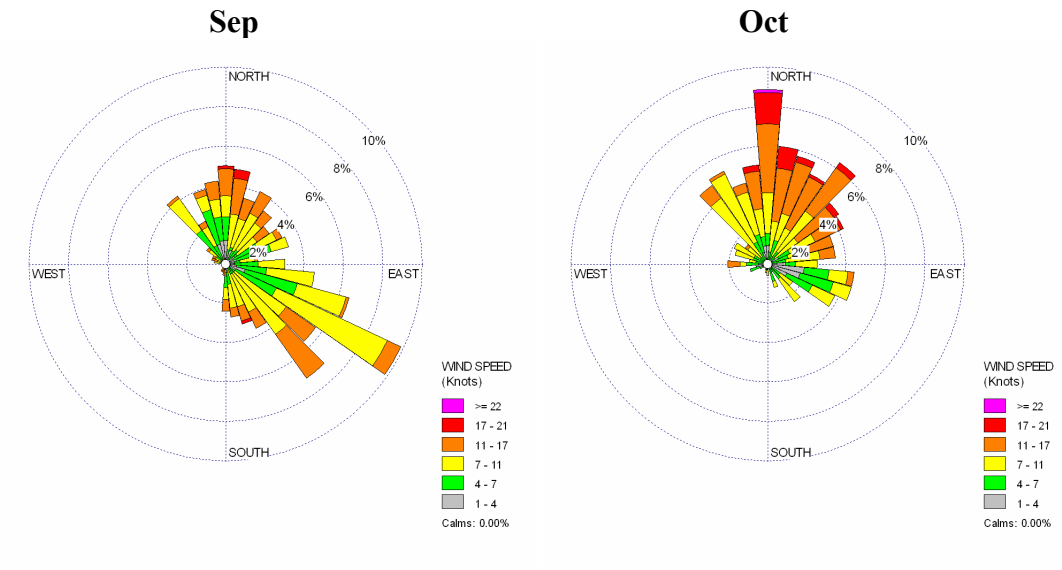


Fig. R3. Monthly wind rose plots at Fudan during the Expo. Each circle represents the percentage of the winds from a particular direction and various wind speed range is marked by different colors.

In the revised manuscript, we have added the information above into Section 2.1.1. Please refer to Line 100 – 119 for the changes.

Second, this manuscript also discussed enhanced human activities during the Expo. However, as showed in Figure S3, the number of Expo visitors is around 200,000 per day in May. Compared with 20 million residents in Shanghai, this number is trivial (only ~ 1%), and we should also keep in mind that some of these visitors could be Shanghai residents. On the other hand, Shanghai Expo made effort to reduce emissions, for instance, using electric buses. It was expected that the Expo was 'green' and environment friendly. So, the authors should provide details to support the statement that the influences from Expo activities can be identified from the background. In summary, to support the authors' argument that 'enhanced Expo activities increase the PM2.5 and nitrate concentrations', two more statements are needed: 1) the observations can reflect the influences from Expo; 2) the Expo activities can be identified from normal activities in Shanghai.

Thanks for the comments. As for the concern from the reviewer that "the observations can reflect the influences from Expo", we have thoroughly evaluated the representative of

our observation site on reflecting the influences from Expo in the response to the first comment above.

The total Expo visitors reached 73.08 million in 184 days over the Expo campus which occupied an area of 5.28 km^2. Please imagine the average daily people density of more than 75,000 per km^2 compared to the population density of 3631 per km^2 of Shanghai, which already has the largest population density in China. We agree with the reviewer's saying that some of the Expo visitors are the local residents. However, they still needed to use the transportation tools to get to the Expo campus as Shanghai is a big city, and many people may get there in their own cars.

The number of Expo visitors we used in this study could be regarded as an index for representing the relative strength of human activities between day and day, but not means that the perturbation of emission is only caused by the visitors to the Expo pavilions. For example, a lot of people coming from other provinces and cities would like to spend several days on traveling inside the city and visiting some other landscapes in Shanghai besides the Expo and this number could be enormous. In addition, most of the Expo visitors also tended to visit some famous resorts close to Shanghai, such as the West Lake in Hangzhou and the Suzhou Gardens in Suzhou after or before they visited the Expo. Owing to this, several Shanghai long-distance transportation companies had changed the frequency of buses from normally 1 per hour to 1 per half hour or even 1 per fifteen minutes during the Expo period. For security reasons, passengers who took the road transportation were required to step down their cars or buses for a routine check before they entered the city border of Shanghai. During the check, most cars were idling, which could also cause more vehicular emission.

Overall, the Shanghai Expo is not an independent event that could be separated from other human activities, it brought chain effects on various aspects of the city, such as the transportation system, electricity power grid, the tourism of both Shanghai and other nearby cities in the Yangtze River Delta and etc. Thus, all these factors impelled the local government to make great effort on reducing the anthropogenic emission, e.g. using electric buses as the reviewer mentioned. However, the results of our study still showed higher nitrate concentrations in some periods of the Expo, especially in autumn, which

indicated the enhanced human activities offset the control efforts in reducing the transportation emission.

Data presented in this manuscript definitely showed changes of PM2.5 pollution in 2010, compared with 2009. Meteorological parameters such as wind speed, wind direction, pressure, relative humidity, and dew point are presented as well. The authors claimed that the changes are caused by control measures. However, to the PM2.5 pollution especially nitrate aerosols, the most important meteorological variables are precipitation and temperature. The precipitation controls the lifetime of PM2.5 through wet deposition. The formation of nitrate aerosols are sensitivity to the ambient temperature, i.e., in a thermodynamic equilibrium. Therefore, more data are needed to support the statement that the PM2.5 pollution in 2010 (influenced by Expo control measures) is different from the observations in 2009. For instance, precipitation data are necessary to elaborate that compared to 2009, 2010 is not an atypical wet year; the 2010 summer, i.e., ambient temperature, is not significantly hotter (high temperature doesn't favor the formation of nitrate aerosols, so if the temperature was significantly higher, less nitrate aerosols would be formed and nitrogen compounds would exist in form of nitric acid. To summarize, the author should explain that year 2009 and 2010 don't have significant differences in climate.

Thanks for the suggestion on comparing the difference of climate between years. Now we have provided the information as shown below. Figure R4 shows the monthly mean values of the major meteorological parameters, i.e. temperature, dew point, wind speed, atmospheric pressure and monthly accumulated precipitation amount between 2009 and 2010. As shown in the figure, there were small differences between the two years for the first four parameters. As for temperature, the monthly difference (2010 minus 2009) during the Expo was -1.4, -1.8, -0.1, 2.5, 0.6, and -1.4 °C from May to October. Thus, 2010 is not a significant hotter year. As for dew point, wind speed and atmospheric pressure, the monthly difference was within the range of -1.7 ~ 1.8 °C, -0.5 ~ 0.5 ms^{-1}, and -1.2 ~ 2.2 mb, respectively. Compared to their absolute values, these differences could be considered as trivial. Although monthly precipitation had larger divergence compared to the other meteorological parameters between the two years due to its high

variability in both spatial and temporal scales, the difference of the total rainfall amount was still relatively small of 14% between 2009 (828.8 mm) and 2010 (709.2 mm) during the Expo. Also, 2010 was not a typical wet year compared to 2009.

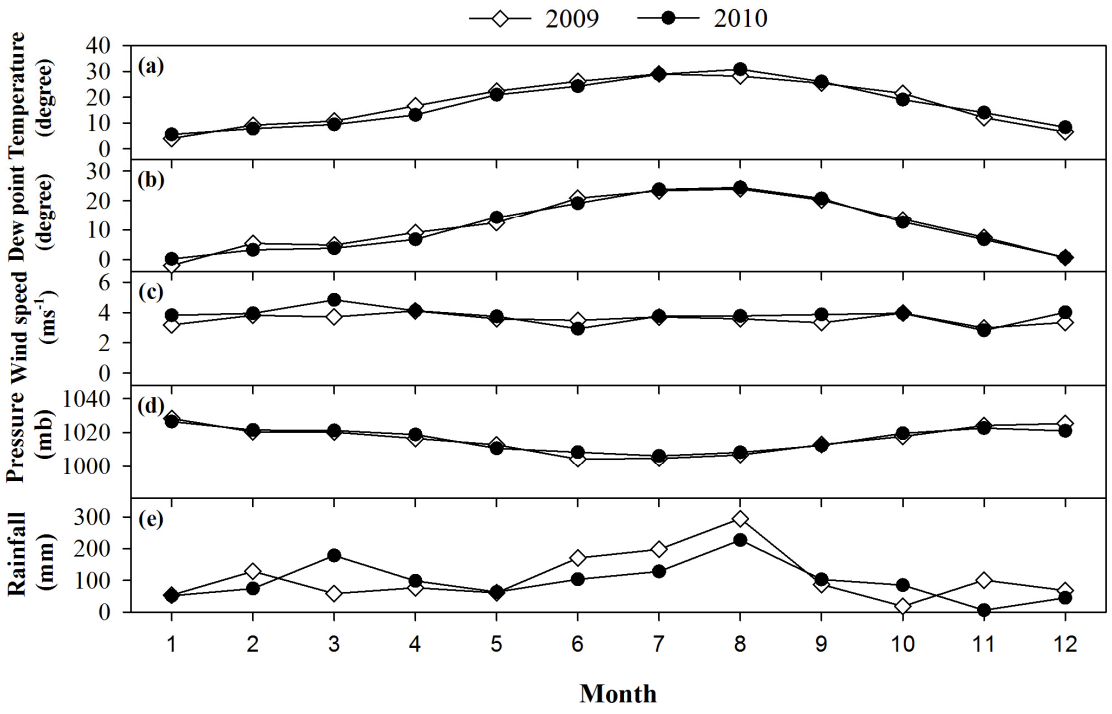


Figure R4. The monthly mean values of the major meteorological parameters, i.e. temperature, dew point, wind speed, atmospheric pressure and monthly accumulated precipitation amount between 2009 and 2010.

Overall, there were not significant differences of the major meteorological conditions between 2009 and 2010. Hence, in regard of a long-term period (e.g. on a monthly or seasonal basis), the air quality should be mainly determined by the emission. However, in regard of a short period, e.g. daily or a short episode, the role of meteorological conditions on air quality could be very important as the reviewer raised.

In the revised manuscript, we have added an overview of meteorological conditions between 2010 and 2009 into Section 3.4.1. Please refer to Line 464 - 476 for the changes.

Remarks/Suggestions for Revision

Page 3380 Line 12-13: As discussed above, ambient temperature data are needed to support this statement. If spring and summer of 2010 are significantly cooler than

2009, the low temperature favors the formation of nitrates but prevents oxidation of SO2 to sulfates.

As discussed above, the temperature differences between 2010 and 2009 in the spring and summer were not very significant. And the small differences of temperature between the two years were supposed to have insignificant effect on the sulfate and nitrate formation. In the revised manuscript, we have added an overview of meteorological conditions between 2010 and 2009 into Section 3.4.1. Please refer to Line 464 - 476 for the changes.

Page 3382 Line 11: Human activities could be influenced by weather as well. Under rainy weather, less visitors would attend the Expo, which is mostly outdoor. For instance, only 70,000 visitors attended the Expo on May 5 (Figure S3) due to the rain, and the rain could reduce the PM2.5 pollution. How to identify the weather-related human activities is important in this study to support the statement.

We agree with the reviewer. In the revised manuscript we added the precipitation data into Figure 3 (labeled as Figure 4 in the revised manuscript) and we did find there were rain events on May 5 and 6, when the Expo visitor number was at a relatively low level. The number of Expo visitors was probably influenced by those rain events.
In the revised manuscript, we have changed Line 20 – 23 in Page 3389 as "Afterwards, the daily visitor numbers from May 3 to 7 decreased about 40 %. It was found that several rainfall events occurred on May 5 and 6, and this probably partly accounted for the less attendance number. Both reduced Expo visitors and the occurrences of precipitation were beneficial for the reduction of air pollution, which was reflected in the decrease of PM concentrations (Fig. 2) and also the SNA concentrations (Fig. 4c).". Please refer to Line 271 - 275 for the changes.

Line 19: no 'Huang et al. 2012' in the referene

This reference is "Huang, X.-F., He, L.-Y., Xue, L., Sun, T.-L., Zeng, L.-W., Gong, Z.-H., Hu, M., and Zhu, T.: Highly time-resolved chemical characterization of atmospheric fine

particles during 2010 Shanghai World Expo, Atmos. Chem. Phys., 12, 4897–4907, doi:10.5194/acp-12-4897-2012, 2012." as listed in the reference.

Page 3383 Line 6: Details like distance between the Fudan site and Expo fields are needed.

Yes, in the revised manuscript we added this information into Section 2.1.1 as indicated in the response to the first comment.

Line 15 to 19: This sentence is hard to understand. Revision is suggested.

Yes, in the revised manuscript we have rephrased this sentence to make it more clearly as shown in Line 123 - 126:
PM (particulate matter) accumulated on a mounted filter. The accumulation of the PM mass caused the changes of the frequency of oscillation. And this frequency was detected in quasi-real-time and then converted by a microprocessor into an equivalent PM mass concentration at the time resolution of every few seconds and recorded in the running average of 10 min.

Line 21: Define USEPA when it is first mentioned.

Yes, in the revised manuscript we have added the full name of USEPA (U.S. Environmental Protection Agency).

Page 3384 Line 2: Add 'TECO' before '43 i: : :'

Yes, in the revised manuscript we have added this term.

Line 5: details or references are needed to explain how to eliminate the potential intereferences of NOy on NO2

Yes, in the revised manuscript we have added more information as shown in Line 136 - 138.

Line 136 - 138: A Teflon filter was placed in front of the Mo Catalytic converter that connected to the gas sampler. The Teflon filter had a retention rate of over 99.7% for particles (e.g. particulate HNO_3) larger than 0.3 μm.

Line 10: Define 'USEPA' in Page 3383 Line 21.

Yes, in the revised manuscript we have defined this term at where it first appears.

Page 3389 Line 17-18: As discussed above, the variation of SIA could be associated with the weather changes (temperature and precipitation), which also influence the number of attendants. Data are needed to support this statement.

Yes, in the revised manuscript we have added the time-series of temperature and precipitation data (shown below and Figure 4 in the revised figures) for more explicit analysis of the temporal variation of SIA. As shown in the figure below, the majority of precipitation events during the 2010 spring study period occurred before April 22. Most precipitation events were associated with relatively low SIA concentrations, e.g. on April 11, 13-14, and 20-21, indicating the important role of wet scavenging on reducing the particulate pollution. Since April 22, rare precipitation events occurred, thus the role of wet scavenging on cleansing the air pollutants was negligible. Temperature had a gradually increasing trend from April 22 to May 2 as shown in the figure. Although higher temperature didn't favor the accumulation of nitrate and ammonium in the particulate phase, the temporal variation of SIA presented an evidently increasing trend from April 20 to May 2 in 2010. Especially, Nitrate had the most significant increase, probably indicating the enhanced traffic emission due to the increasing visitor numbers.

Since the opening of the Expo, rare precipitation events occurred. On May 1 and 2, visitor numbers both exceeded 200,000, which were at high levels in this study period and could explain the high SIA level on these two days. Afterwards, the daily visitor numbers from 3 to 7 May decreased about 40 %. It was found that several rainfall events

occurred on May 5 and 6, and this probably partly accounted for the less attendance number. Both reduced Expo visitors and the occurrences of precipitation were beneficial for the reduction of air pollution, which was reflected in the decrease of PM concentrations (Fig. 2) and also the SIA concentrations (Fig. 4).".

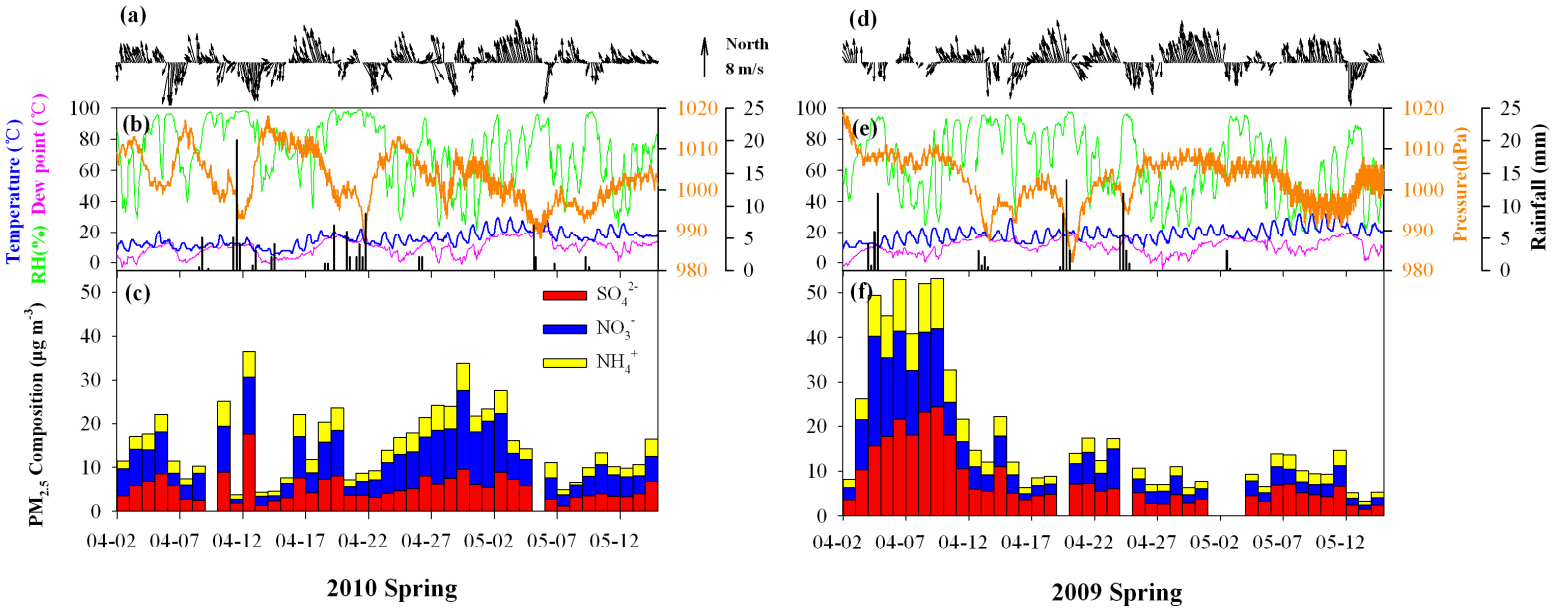


Figure R5. Temperature and precipitation data are added into the figure. Temperature is plotted as blue line in the left Y-axis. Precipitation is plotted as black bars in the right Y-axis.

In the revised manuscript, we have made changes in Line 244 - 255 and Line 271 - 275.

Page 3390 Line 5-6: Weather data, especially precipitation, are needed to discuss the fluctuation of particle concentrations.

Yes, in the revised manuscript we have added more description about the meteorological conditions as shown in Line 282 – 288 in the revised manuscript.

Line 282 – 288: During the summer study period, the major meteorological conditions fluctuated insignificantly. For example, the standard deviation of temperature, dew point, RH, and atmospheric pressure was 3.1 °C, 1.2 °C, 10.7%, and 3.9 mb, respectively, as compared to their average values of 31.1 °C, 26.1 °C, 75.8%, and 994.0 mb. Winds dominantly blew from the southeast as shown in Fig. 5a. Precipitation events occurred

mainly on four days, i.e. on August 2, 4, 15, and 18, respectively. The wet scavenging would generally reduce the aerosol concentrations, especially the heavy rain on August 18 caused a significant decrease of SIA level as shown in Fig. 5c.

Page 3392 Line 26-29: incomplete combustion like biomass burning can produce CO and NOx and the same time. So discussion and/or more data are needed to support this statement.

Thanks for the suggestion. We have double checked if there were any biomass burning events on October 31 and November 1. As shown in the figure below, the fire spots from MODIS (Moderate Resolution Imaging Spectroradiometer) on Aqua and Terra are plotted for these two days. Almost no or very few fire spots were observed in Shanghai and areas adjacent to Shanghai. Thus, we can preclude the impact of biomass burning emission on the extremely high CO and NOx concentrations on October 31 and November 1.

In the revised manuscript, we have added the information in Line 376 – 380.

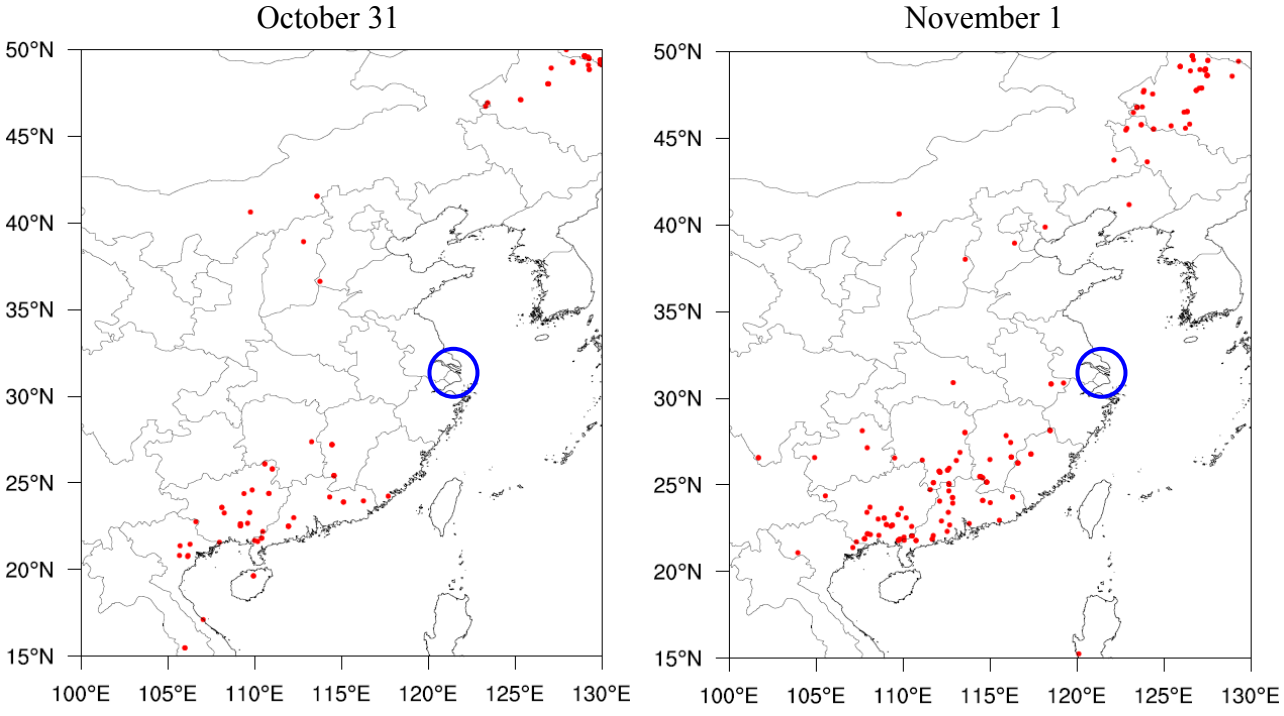


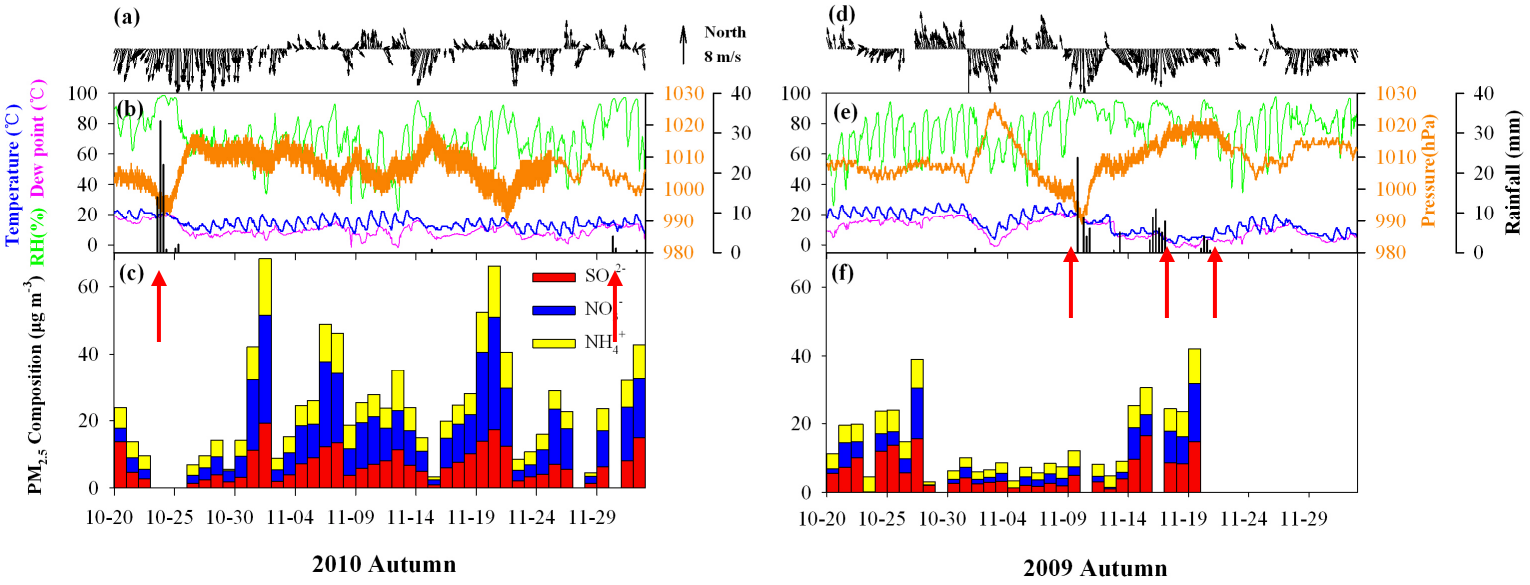
Figure R6. Fire spots (red dots in the figure) detected from MODIS (Moderate Resolution Imaging Spectroradiometer) on Aqua and Terra on October 31 and November 1, respectively.

Page 3394 Line 7: should ‘southeast’ be ‘northeast’?

Yes, in the revised manuscript we have corrected this.

Line 21-22: Does it mean that the strict control measures were implemented in Fall 2009? Any supporting document? Or more precipitation in Fall 2009 reduce the PM2.5 pollution significantly?

We have investigated that there weren’t any special strict control measures implemented in the fall of 2009 as no mega-events took place in Shanghai at that time.



The figure showing the comparison between the fall in 2010 and 2009 with added precipitation data is shown above. As indicated by the red arrows in the figure, no aerosol samples were taken during almost all the precipitation events. For example, no aerosol samples were taken (indicated by the blank bar in the figure) on October 23 – 25, November 30 in 2010, when there were precipitation. Similarly, no aerosol samples were taken on November 10, 16, and 20 in 2010, when there were precipitation. To protect the sampler from malfunction in the rainy events and to prevent the contamination of the

aerosol samples from the raindrop, we usually didn't take aerosol samples during rainy days (especially heavy rain events). Thus, the statement "Over 100% increase of SIA in 2010 than 2009 during the post-Expo period clearly suggested lifting of control measures was the main cause for the frequent occurrences of pollution episodes and poor air quality." in Line 21-22 of Page 3394 was based on the fact that the impact of precipitation events on SIA levels was minimized as no aerosol samples were taken during rainy days.

Page 3396 Line 15-25: As presented in the manuscript, several dust events are observed. Should these pollution episodes included in the calculations? The author should also evaluate the contribution from these episodic events to the statistics analysis.

Thanks for pointing out this issue. We didn't include the dust events in the statistical comparison between 2010 and 2009. The reason is that dust event is an unusual phenomenon of high pollution with low frequency of occurrence in areas far away from the desert (e.g. Shanghai in this study). The extremely high aerosol concentration caused by the intrusion of dust would shield some information if those episodes are included in the statistical analysis. For example, when we compared the average $Ca_{anthropogenic}$ concentration between the Expo and post-Expo (Line 2 – 4 in Page 3396), the dust events had to be excluded because dust is rich in mineral aerosol such Ca. The major goal of this paper is to evaluate the impact of human activities on air quality in an urban area, thus we think it is better to exclude the unexpected pollution events (e.g. dust) during the process of the statistical analysis.

Page 3397 Line 21-22: High temperature also doesn't favor formation of nitrates.

Yes, we agree with the reviewer. In the revised manuscript, we have revised this sentence as "Higher temperature did not favor the formation of ammonium salts (e.g. NH_4NO_3 and $(NH_4)_2SO_4$) in the particulate phase and probably resulted in stronger depletion of NH_4^+."

Page 3399 Line 25: Again. Please make sure it is not caused by the difference of temperature in 2009 and 2010.

Yes, in the response to the reviewer comment # 4, we have compared the difference of temperature in 2009 and 2010. We think the insignificant difference of temperature shouldn't be the major cause for the significant change of the concentrations of aerosol chemical composition.

Page 3400 Line 17: should be 'CaSO4' and 'Ca(NO3)2'

Thanks for pointing out this mistake. We have corrected this in the revised manuscript.

Page 3408 Table 1: Ye et al. (2003), Huang et al. (2012), and Li et al. (2011) are missing.

Thanks for pointing out the missing of these references. We have added those references in the revised manuscript as shown below.

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, 499 – 510, 2003.

Huang, K., Zhuang, G., Lin, Y., Fu, 5 J. S., Wang, Q., Liu, T., Zhang, R., Jiang, Y., Deng, C., Fu, Q., Hsu, N. C., and Cao, B.: Typical types and formation mechanisms of haze in an Eastern Asia megacity, Shanghai, Atmos. Chem. Phys., 12, 105–124, doi:10.5194/acp-12-105-2012, 2012a.

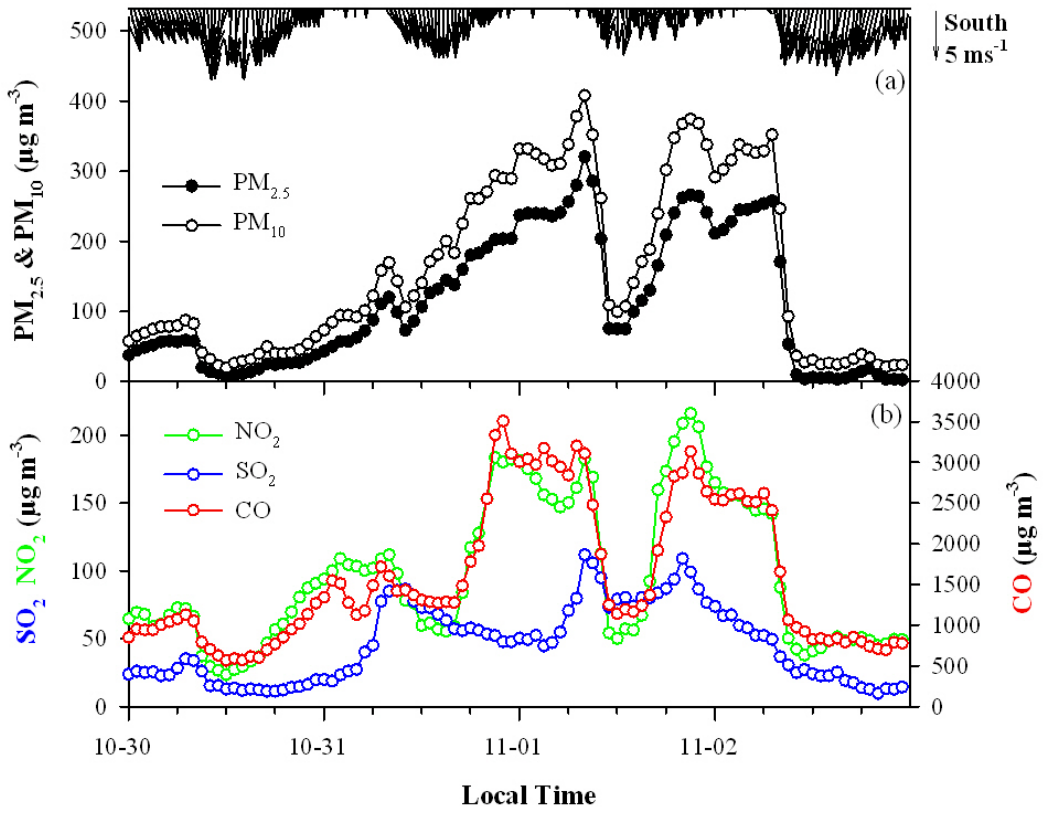
Li, P. F., Li, X., Yang, C. Y., Wang, X. J., Chen, J. M., and Collett, J: Fog water chemistry in Shanghai, Atmos. Environ., 45, 4034 – 4041.

Page 3411 Figure 3: units are needed for wind speed and direction. Precipitation and temperature data are suggested for Figure 3, as well as Figure 4, and Figure 7.

Thanks for the suggestion. In the revised manuscript we have added the units and direction of wind, precipitation and temperature data for all the figures. Please refer to the revised figures (Figure 4, Figure 5, and Figure 8 in the revised manuscript) for those changes.

Page 3414 Figure 6: Does precipitation plays the role at 12:00 on 01 Nov.? Impacts from meteorology should be thoroughly discussed.

We didn't find any precipitation events on Nov 1 as shown in the revised Figure 8. However, we found other factors that could explain the diurnal variation of aerosol concentrations as shown in the revised Figure 7 below. Around the noon time on Nov. 1, winds dominantly came from the northeast and the north. Compared to the stagnant atmosphere a few hours ago, increased wind speeds quickly cleaned the accumulated pollutants. In addition, the possible elevated mixing layer at noon due to higher temperature could also dilute the emission. Similar phenomena occurred after 8:00 AM on Nov. 2, when the northeast and north winds persistently blew from the ocean to cleanse the air pollutants.



In the revised manuscript, we have thoroughly discussed the role of meteorology on this pollution episode. Please refer to Line 341 - 366 for the changes.

Page 3415 Figure 8: Hard to read the 2009 and 2010 data. Separating them into a) 2009 and b) 2010 is suggested.

Thanks for the suggestion. In the revised manuscript, we have separated the original figure to two figures. Please refer to the revised figure (Figure 9 in the revised manuscript) for the changes.