



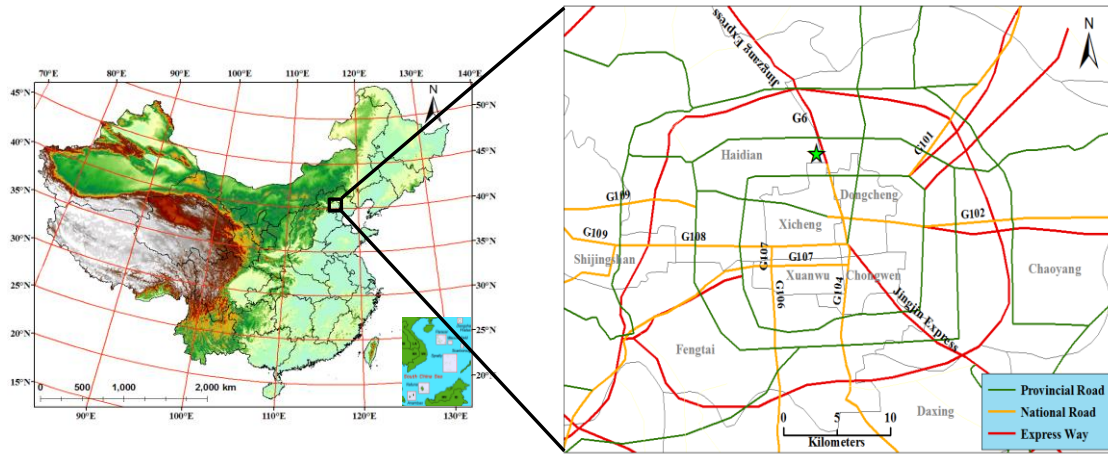
*Supplement of*

## **New characteristics of submicron aerosols and factor analysis of combined organic and inorganic aerosol mass spectra during winter in Beijing**

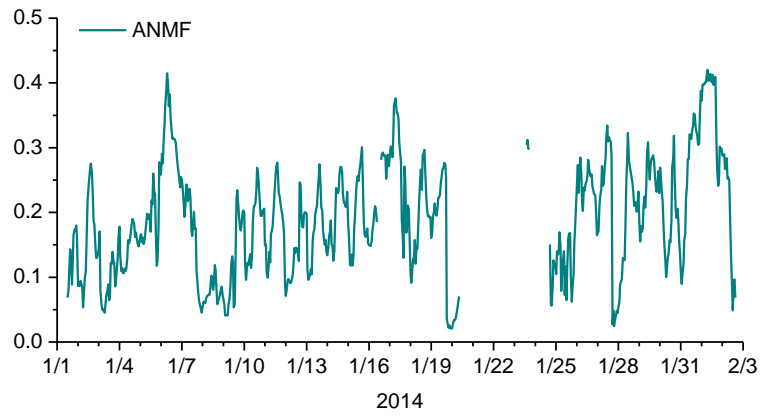
**J. K. Zhang et al.**

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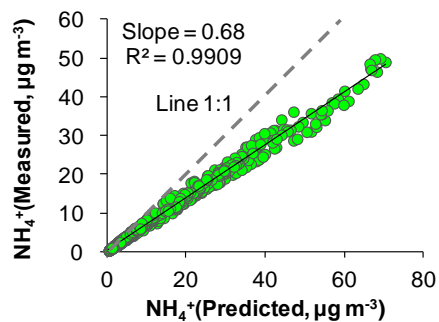
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**Figure S1.** Map of the study area in Beijing. The green star symbol denotes the sampling site.



**Figure S2.** Time series of ammonium nitrate mass fraction (ANMF) ( $\text{ANMF} = (80/62 \times \text{NO}_3) / (\text{NH}_4 + \text{SO}_4 + \text{NO}_3 + \text{Chl} + \text{Org})$ ) (Middlebrook et al., 2012).



**Figure S3.** Scatter plot diagram comparing the predicted  $\text{NH}_4^+$  with the measured  $\text{NH}_4^+$ . The predicted  $\text{NH}_4^+$  was calculated on the basis of the sulfate, nitrate, and chloride concentrations measured by the aerosol mass spectrometer (AMS) assuming they were fully neutralized by  $\text{NH}_4^+$  (Predicted  $\text{NH}_4^+ = 18 \times (2 \times \text{SO}_4^{2-}/96 + \text{NO}_3^-/62 + \text{Cl}^-/35.5)$ ) (Zhang et al., 2007).

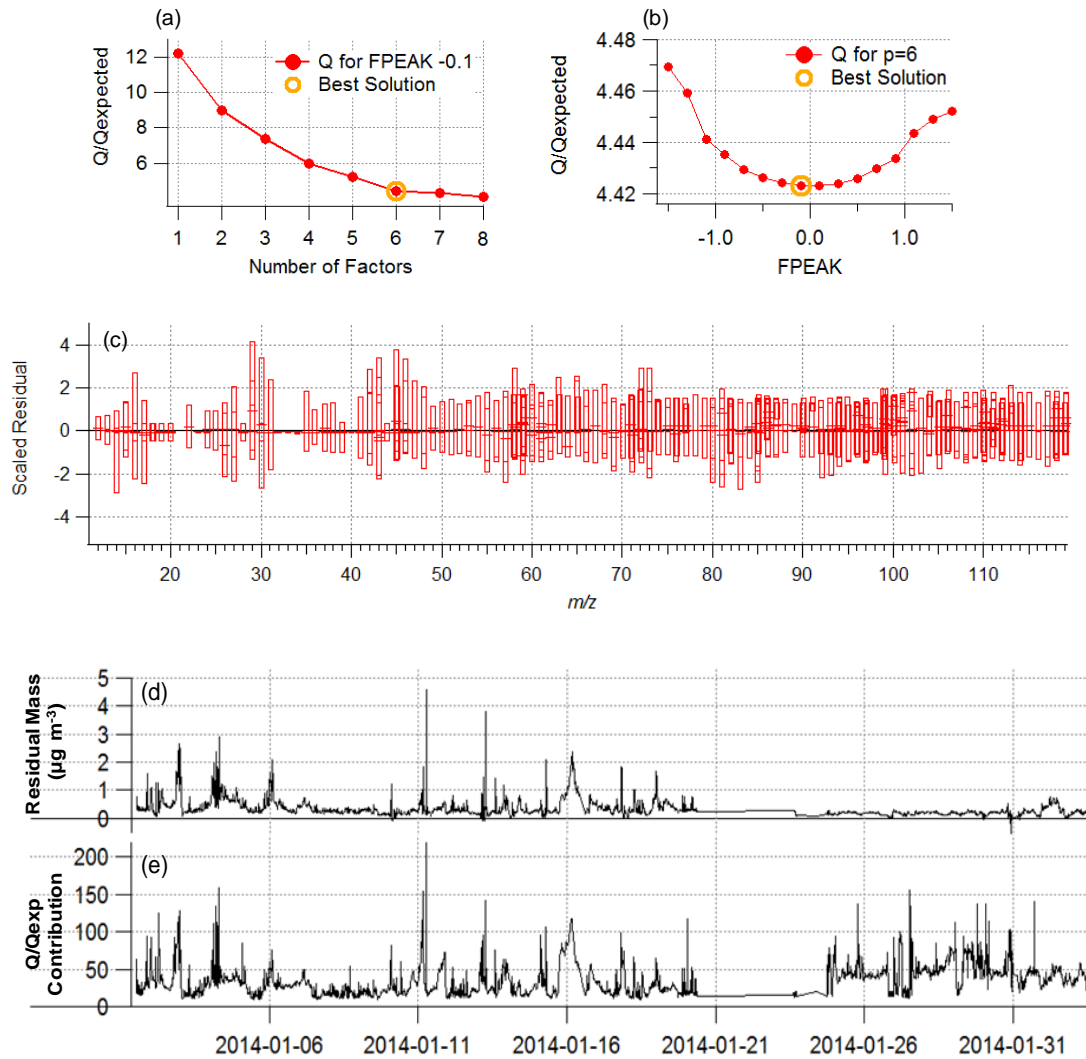
### **Discussion S1:** Selection of the optimal PMF solution

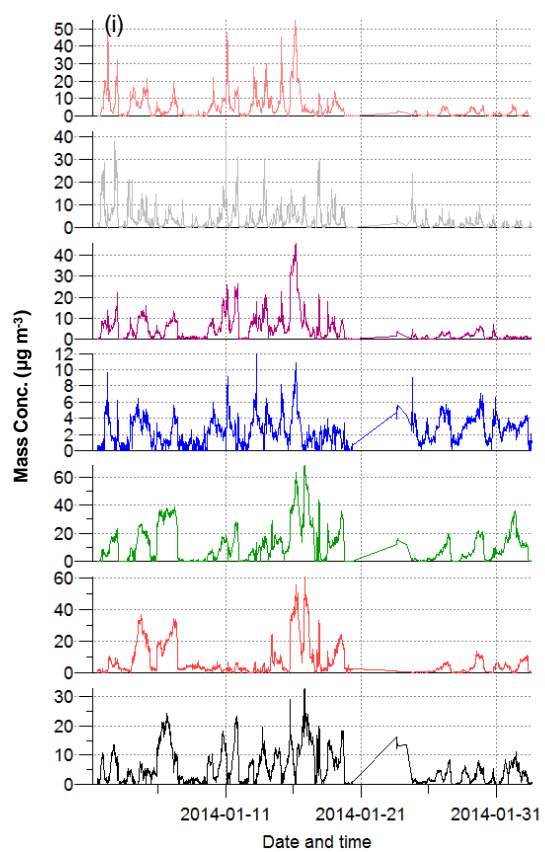
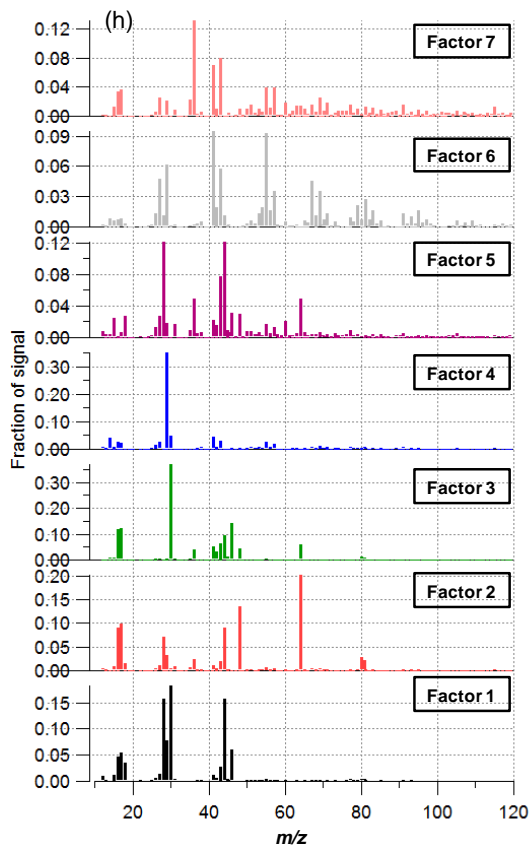
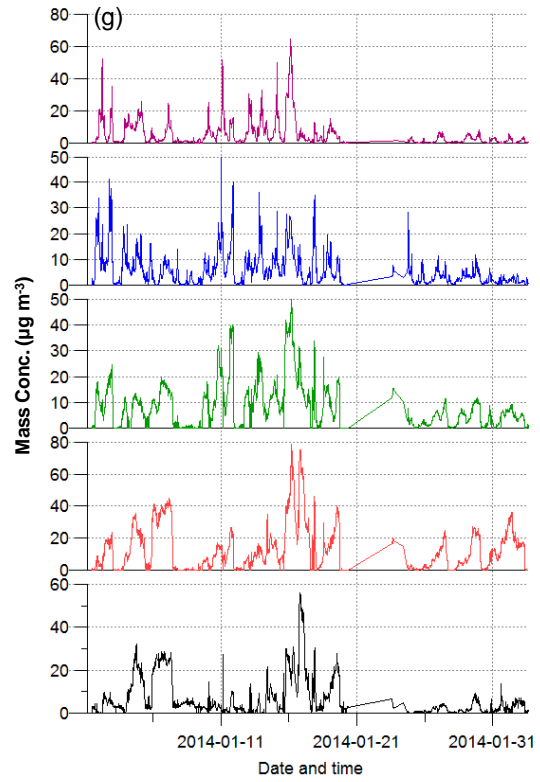
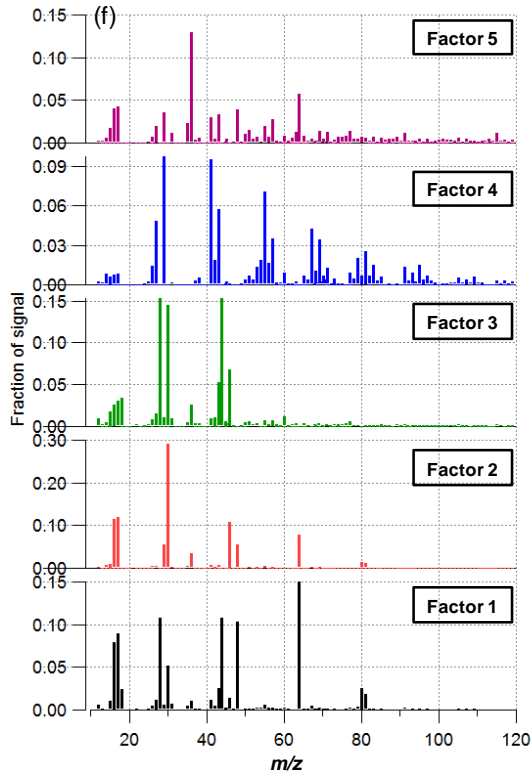
The PMF analysis was performed for 1 to 8 factors, based on the HRMS dataset observed in the campaign. In the PMF analysis, the  $Q/Q_{exp}$  values represented the ratios between the actual sum of the squares of the scaled residuals ( $Q$ ) obtained from the PMF least squares fit and the ideal  $Q$  ( $Q_{exp}$ ), which was obtained if the fit residuals at each point were equal to the noise specified for each data point. Values of  $Q/Q_{exp}$  that exceeded the ideal value of 1 were indicative of the fact that the input noise values underestimated the true noise because they did not include errors associated with the high-resolution peak fitting process (He et al., 2011). When the number of factors was between 1 and 4, the residuals at the key  $m/z$ 's and time periods were too large. The  $Q/Q_{exp}$  values given were too high; they were 12.2, 9.0, 7.4 and 6.0 respectively (Fig. S4a). We also found some key  $m/z$  were appeared in one factor; the inorganic fragment ions were mixed together and could not be distinguished. In the 5-factor solution, the  $Q/Q_{exp}$  decreased (5.2) and the separation remained poor (Fig. S4f). We can easily found that a large number of fragments of sulfate ( $m/z$  48, 64), nitrate ( $m/z$  30) and ammonium ( $m/z$  15, 16, 17) appeared in factor 1. The  $m/z$  60 was also distributed in three factors (factors 3, 4 5), which are very difficult to explain. Therefore, the 5-factor solution was considered inappropriate. In the 6-factor solution, there was a clear decrease of  $Q/Q_{exp}$  value to 4.4. Two  $NO_3$ -OA factors were then indentified, each showing a different oxidation state and diurnal variation. The factor 3 contained a large number of sulfate and  $C_xH_yO_z^+$  fragment ions and showed the highest oxidation. The  $m/z$  60 mainly appeared in factor 6, which also contained a large number of the chloride fragment ions. [This factor therefore showed characteristics associated with biomass and coal combustion. In present](#)

study, we thought that it is more appropriate to identify this factor as coal combustion OA (CCOA). This is because: (1) in general, the biomass burning is concentrated in June, September and October in North China (Zhu et al., 2005), and it is much weak in winter. However, the coal consumption will increase significantly in winter due to the city heating; (2) many previous studies also identified this type of factor as CCOA. For example, Sun et al. (2013) found that CCOA is the most important primary source during winter in Beijing, on average accounting for 33% of OA and 17% of NR-PM<sub>1</sub>, which is almost equivalent to the sum of HOA and COA. Meanwhile, CCOA contributes a considerable fraction of OA and NR-PM<sub>1</sub> throughout the day, ranging from 26–37% and 12–22 %, respectively, indicating a sustained impact of coal combustion on PM pollution throughout the whole day. The other two factors could be identified as HOA (hydrocarbon-like OA) and COA (cooking OA). Furthermore, the diurnal cycles of the six components were distinctive and their element ratios were in a reasonable range compared with that in other studies. Most importantly, the 6-factor solution was in agreement with the actual situation in Beijing. When the number of factors changed from 7 to 8, there was no clear decrease in the Q/Q<sub>exp</sub> value (Fig. S4a), and some of the split factors had time series and MS that appeared mixed (Fig. S4h). The 6-factor solution was therefore chosen as the optimal solution. The sensitivity of the 6-factor solution to rotation and starting values was explored by varying the FPEAK and seed parameters. Lower Q/Q<sub>exp</sub> values can indicate a better fit to the data set and can therefore be used as a criterion for the choice of a suitable solution (Ulbrich et al., 2009). With the FPEAK varying from -1.5 to 1.5 in increments of 0.2 (seed = 0), the lowest Q/Q<sub>exp</sub> value was obtained at approximately -0.1 (Fig. S4b). Therefore, FPEAK = -0.1 was chosen as the

optimal solution. With a seed value varying from 0 to 250 in increments of 10 ( $FPEAK = 0$ ), the  $Q/Q_{exp}$  value showed almost no change. Based on all of these tests, the 6-factor,  $FPEAK = -0.1$ , seed = 0 solution was selected as the optimal solution for this analysis.

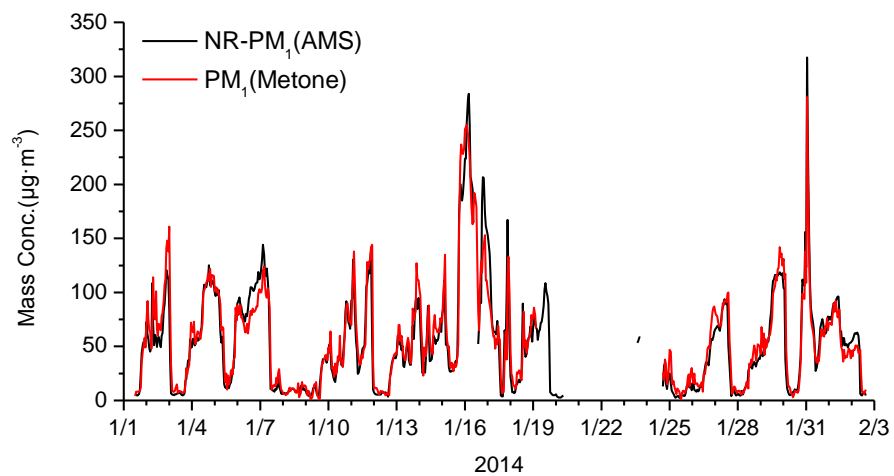
For more details on PMF and the interpretation of these plots see Ulbrich et al. (2009).



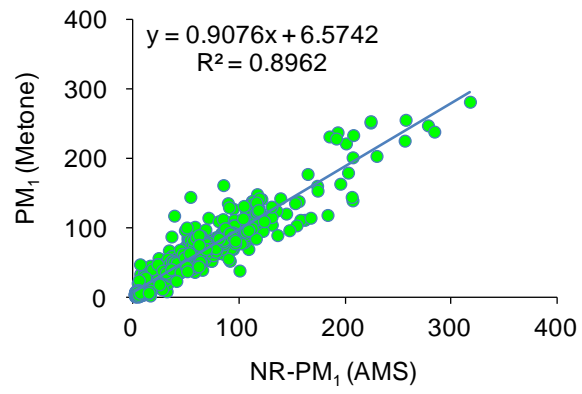




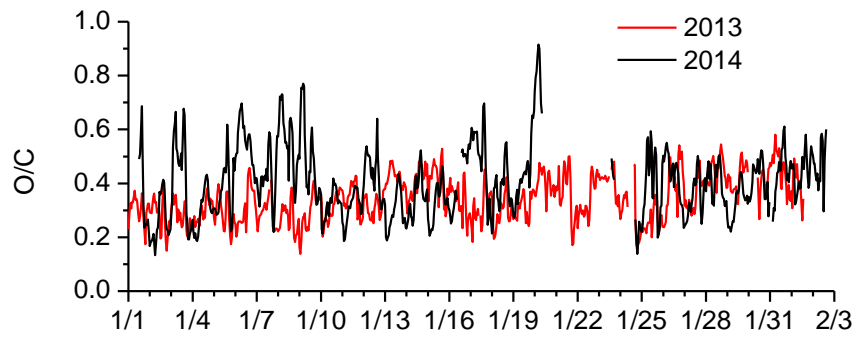
**Figure S4.** PMF diagnostic plots: (a) Q/Q expected (Q = the sum of squared scaled residuals over the whole dataset) plotted versus the number of factors used in the PMF solution; (b) Q/Q expected plotted versus the rotational forcing parameter (FPEAK) for solutions with 6 factors; (c) Median (line within the boxes) and lower/upper quartiles (boxes) of the scaled residuals per m/z; (d,e) time series of the total residual and Q/Q expected contribution for every point in time during the study; (f) 5-factor profiles (mass spectra); and (g) time series for the 5-factor solution (with FPEAK = -0.1); (h) 7-factor profiles and (i) time series for the 7-factor solution (with FPEAK = -0.1);



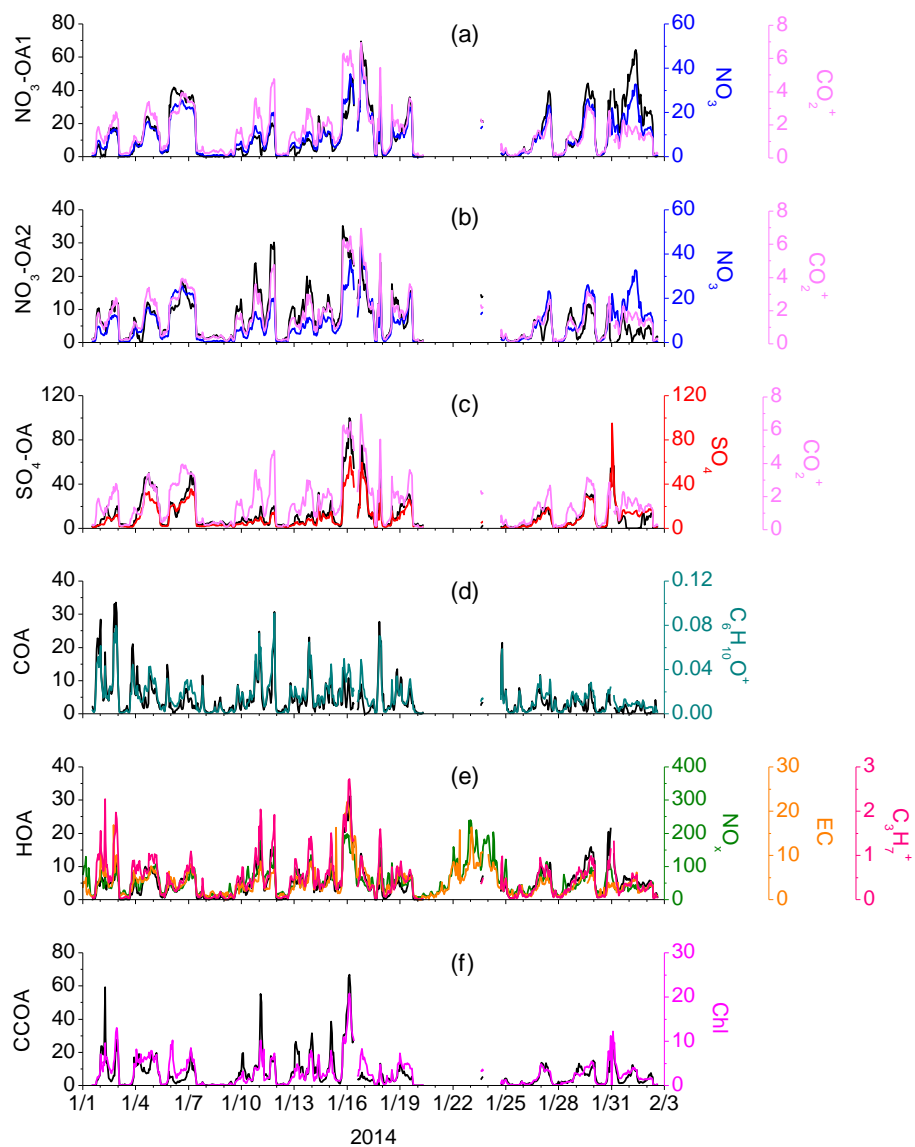
**Figure S5.** NR-PM<sub>1</sub> and PM<sub>1</sub> mass concentrations measured by AMS and MET ONE BAM-1020 in January 2014, respectively.



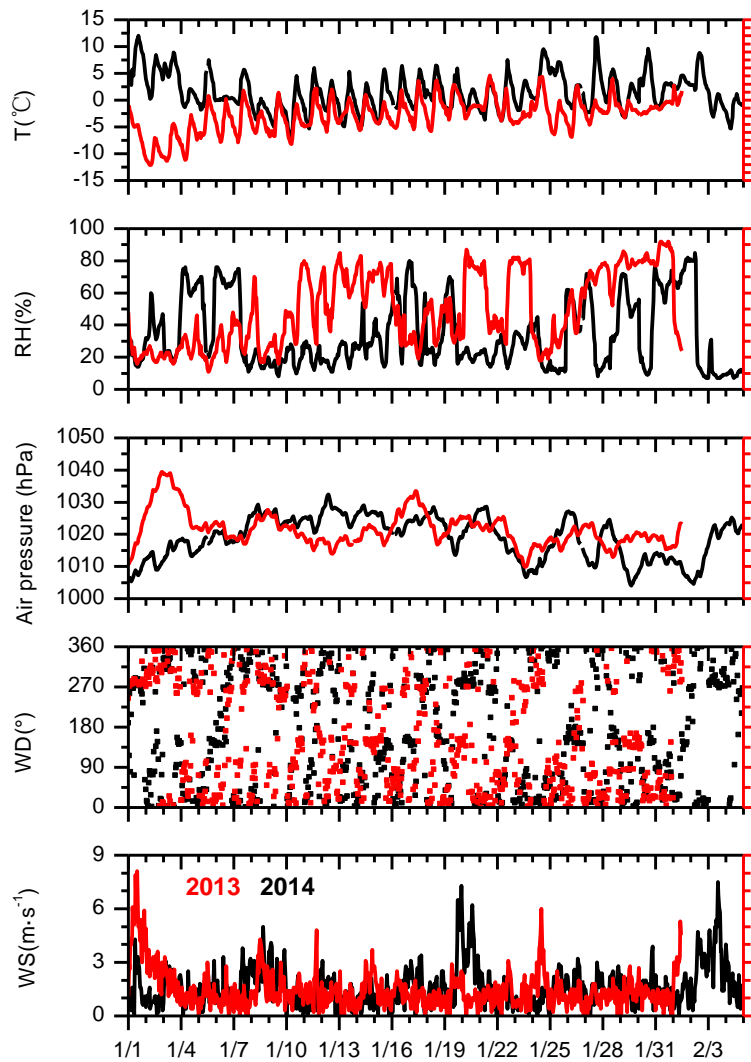
**Figure S6.** Scatter plot that compares NR-PM<sub>1</sub> and PM<sub>1</sub> mass concentrations measured by AMS and MET ONE BAM-1020, respectively



**Figure S7.** Time series of O/C ratio in January 2013 and 2014.



**Figure S8.** Time series of PMF factors and relevant tracers. The units of  $\text{NO}_x$  is ppbv, while the units of other species are  $\mu\text{g m}^{-3}$ .



**Figure S9.** Ambient meteorological parameters in January 2013 and 2014. (The red curve or dot represent the observation results in 2013, while the black curve or dot represent the observation results in 2014).

## References

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