Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1142-AC2, 2020 © Author(s) 2020. This work is distributed under the Creative Commons Attribution 4.0 License.



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Interactive comment

# Interactive comment on "Elucidating the pollution characteristics of nitrate, sulfate and ammonium in $PM_{2.5}$ in Chengdu, southwest China based on long-term observations" by Liuwei Kong et al.

Liuwei Kong et al.

lxgstar@126.com

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Response to Reviewer Comments

Dear Reviewer,

We would like to thank you for your great effort and detailed work on this manuscript. We have revised the manuscript and responded to each of the comments from the reviewers. In our response, your questions are shown in italics, and the responses are shown in standard text. For the ACP discussion, our research team also performed further analysis of the research results and made minor modifications to this manuscript.

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We appreciate your help and time.

Sincerely yours, Xingang Liu and coauthors. School of Environment Beijing Normal University 100875 Beijing China E-mail: liuxingang@bnu.edu.cn; lxgstar@126.com Tel: +86-13810193569

Referee This paper presented an overview of air pollution in Chengdu, southwest China based on study, a three-year observations of gas and particulate pollutants. Probably due to the special topography, the data from this site shows special characteristics of pollutants, different from most other polluted regions in China, e.g., North China plain and Pearl River Delta etc. Thermodynamic models and trajectory analysis have also been applied to analyze aerosol pH, partitioning of inorganic semi-volatile species and the contribution of potential source regions. Overall, I think that the datasets are very interesting and valuable, and authors have tried to give a comprehensive overview and analysis of the mechanisms beyond. However, there is still much room for improvement. I would suggest the authors to carefully consider my comments/suggestions in their revision before its final publication in ACP. Response: We appreciate your comments and have revised the manuscript accordingly. We firmly believe that your guidance is of great significance for improving our research.

concern: 1. Meteorological parameters and PM compositions show distinct diurnal variations compared to other regions such as NCP, PRD and YRD. Though chemistry is in this game, I guess that the special topography may play a dominant role in these features, which is missing from this submission. I'd suggest the authors to add these discussions. Response: We appreciate your comments and have revised the text. We also noticed that during the data analysis, the pollutant concentration in the daytime

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was higher, which was obviously different from that in NCP, PRD and YRD. We also collated the relevant research results in NCP, PRD and YRD and found that they were consistent with the questions you raised. Therefore, according to your guesses and prompts, we conducted an in-depth analysis. The unique topographic structural features did have an important impact on the diurnal variation of meteorological factors in the Sichuan Basin, which may also be an important factor that causes the daily changes in air pollutants with unique characteristics. We also supplement and discuss the corresponding parts of the manuscript. Now, the text reads as follows: In previous studies in Beijing-Tianjin-Hebei and the Pearl River Delta, the concentration of pollutants was affected by meteorological factors, and it was usually lower in the daytime than at night. In the Yangtze River Delta, the peak usually occurs in the morning, but in our study, the concentration was higher in the daytime than at night (Peng et al., 2011; Wang et al., 2018; Guo et al., 2017b). In addition to the diurnal variations in WS and atmospheric humidity, some studies have shown that due to the unique topographical structure of the Sichuan Basin, the atmospheric circulation between the Qinghai-Tibet Plateau, Yunnan-Guizhou Plateau and Sichuan Basin and the meteorological conditions of the Chengdu region are affected, such as the characteristics of air mass transport and typical "night rain" (more precipitation at night than in the day) under the influence of atmospheric circulation (Zhang et al., 2019b; Zhang et al., 2019a). Reference: Guo, J., Xia, F., Zhang, Y., Liu, H., Li, J., Lou, M., He, J., Yan, Y., Wang, F., Min, M., and Zhai, P.: Impact of diurnal variability and meteorological factors on the PM2.5 - AOD relationship: Implications for PM2.5 remote sensing, Environmental pollution, 221, 94-104, 10.1016/j.envpol.2016.11.043, 2017b. Peng, G., Wang, X., Wu, Z., Wang, Z., Yang, L., Zhong, L., and Chen, D.: Characteristics of particulate matter pollution in the Pearl River Delta region, China: an observational-based analysis of two monitoring sites, Journal of Environmental Monitoring, 13, 1927-1934, 10.1039/c0em00776e, 2011. Wang, L., Li, W., Sun, Y., Tao, M., Xin, J., Song, T., Li, X., Zhang, N., Ying, K., and Wang, Y.: PM2.5 Charac-

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Discussion paper



teristics and Regional Transport Contribution in Five Cities in Southern North China

Plain, During 2013–2015, Atmosphere, 9, 157, 10.3390/atmos9040157, 2018. Zhang, L., Guo, X., Zhao, T., Gong, S., Xu, X., Li, Y., Luo, L., Gui, K., Wang, H., Zheng, Y., and Yin, X.: A modelling study of the terrain effects on haze pollution in the Sichuan Basin, Atmospheric Environment, 196, 77-85, 10.1016/j.atmosenv.2018.10.007, 2019a. Zhang, Y., Xue, M., Zhu, K., and Zhou, B.: What Is the Main Cause of Diurnal Variation and Nocturnal Peak of Summer Precipitation in Sichuan Basin, China? The Key Role of Boundary Layer LowâĂŘLevel Jet Inertial Oscillations, Journal of Geophysical Research: Atmospheres, 124, 2643-2664, 10.1029/2018jd029834, 2019b.

-- 2. QA/QC. Quality assurance and control is essential for multi-year analysis. Maybe I overlooked it and I didn't find a description to assure the data quality. QA/QC would give the readers more confidence in your data and analysis, e.g., the extremely high NH3 in the winter of 2017. Response: We appreciate your comments and apologize for our unprofessional description. We agree with you very much because the instruments involved in this study are online monitoring equipment and have high time resolution (1 hour), so data quality assurance and control are the keys to determining the accuracy and scientific nature of this study. Therefore, we added this information to the supplementary materials. Now, it reads as follows: Data quality control and assurance are important components of atmospheric comprehensive observation experiments. In addition to regular inspection and correction of the equipment through professional operation and maintenance to ensure the accuracy of experimental data, the quality control and processing of monitoring data, such as excluding outliers and data beyond the detection limit, are also an important. As shown in Figs. S1-4, the time sequence of monitoring data and the red part in the figure indicate that the data are missing and that the overall data integrity is good. The missing rates of PM10, PM2.5 and PM1 data in Fig. S1 are 5.0, 6.8 and 6.1%, respectively. The missing rates of NO3-, SO42-, NH4+, OC and EC data in Fig. S2 are 18.3, 17.1, 20.9, 15.2 and 19.6%, respectively. In Fig. S3, the gaseous pollution of NO data is missing 18.2%, NH3 is missing 11.3%, and other gases are missing 9%. The quality of meteorological data is good (Fig. S4).

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and the overall missing rate is 3.1% or less. On the whole, the observation data are good and do not affect the continuity of the data as a whole. The Cl-, Na+, K+, Mg2+ and Ca2+ data are significantly missing, and this study only involved in analysis of the ISORROPIA-II thermodynamic equilibrium model. To ensure that each sample data point can be input into the model completely, 618 sample input models are selected according to the data quality control to eliminate the impact of missing ion data to ensure that the model analysis results are effective.

Fig. S1. PM10, PM2.5 and PM1 data quality assurance and control

Fig. S2. NO3-, SO42-, NH4+, OC (organic carbon) and EC (element carbon) data quality assurance and control

Fig. S3. NOx, SO2, NO2, NO, CO and NH3 data quality assurance and control

-- Line 27 "Seasonal and diurnal variations have obvious

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characteristics, winter still has a high NSA concentration and emission intensity, and the concentration during the day was higher than that at night. "This is unusual; is it because of the valley topography Response: We appreciate your comments and apologize for our unprofessional description. As you commented in "Major concern: 1", we have performed a comparative study of other regions of China, Beijing-Tianjin-Hebei, the Yangtze River Delta and the Pearl River Delta, and found that, as you believe, the diurnal variation of air pollutants in Sichuan Basin is indeed different from that in other regions. Based on related research results, the unique topographical structure of Sichuan Basin will indeed affect the meteorological conditions of Sichuan Basin by affecting the atmospheric circulation (interaction of the Qinghai Tibet Plateau, Yunnan Guizhou Plateau and Sichuan Basin). Therefore, the daily variation characteristics of pollutants may be significantly affected by meteorological conditions. In response

to "Major concern: 1", we have made corresponding modifications in the manuscript.

Line

34 "The ammonia-rich environment became increasingly obvious in the atmosphere of Chengdu" It is not clear what you want to say. Do you mean that you see an increase in NH3 concentration or partition rate? Response: We appreciate your comments and apologize for our unprofessional description. We have reconsidered our research purpose and found that the expression of the "ammonia-rich" environment is not accurate. Therefore, we revised the expression based on our current research results. In section 3.4.3 of the manuscript, the ratio of NH4+ to NO3- and SO42- was analysed and found to increase from 2015 to 2017. The results may be attributed to the fact that the concentration of PM2.5 gradually decreased under the implementation of relevant air pollution control measures, and its chemical composition also changed significantly; for example, the SO42- concentration decreased more. Therefore, in the corresponding position of the manuscript, we corrected the expression "ammonia-rich environment" and revised the relevant contents.

\_\_\_\_\_\_ Page 3 line 69

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<sup>&</sup>quot;For example, photochemistry may affect the formation of NSA at high solar radiation,

and the homogeneous reaction may dominate the formation of NSA in high relative humidity" I think you mean "heterogeneous" instead of homogeneous? Response: We appreciate your comments and apologize for our unprofessional description. Our purpose is to express the complex characteristics of NSA chemical conversions. According to previous studies, both homogeneous and heterogeneous reactions have chemical conversion processes of secondary inorganic aerosols, such as photochemical reactions, aerosol liquid-phase oxidation environments, and mineral dust catalysis. Therefore, we rewrote this sentence. Now, it reads as follows: In addition, the chemical conversion of NO2, SO2 and NH3 to form NSA is still very complex, and both homogeneous and heterogeneous reactions involve the chemical conversion of secondary inorganic aerosols, such as photochemical reactions, aqueous phase oxidation environments of aerosols and catalysis of mineral dust.

line 123, Sect 2.1 According to the high NO concentrations, the site could be quite close to adjacent sources. This should be mentioned in the site description. Response: We appreciate your comments and apologize for our unprofessional description. As you believe, our observation station is located in the central area of the city, and the contribution of vehicle emissions may also be prominent, so we revised the description of the observation station. Now, it reads as follows: Comprehensive observations were carried out at the Chengdu comprehensive observation station of atmospheric

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combined pollution (30.63°N, 104.08°E). The observation equipment was placed on the top of a building, approximately 25 m from the ground, and there was no obvious pollution source within approximately 200 m. The site is located in south section 1 of Yihuan Road, Wuhou District, Chengdu (Fig. 1), and traffic emission sources may be the main pollution emission source around the observation station. This is a typical residential, traffic and commercial mixed area that represents the characteristics of the urban atmospheric environment.

-- Page 7 line 154 "Temperature (T), relative humidity (RH) and the total concentrations (i.e., gas + aerosol) of Na+, SO42-, NH3, NO3-, Cl-, 155 Ca2+, K+ and Mg2+ were input into the ISORROPIA-II thermodynamic mode" Do you have HCI, and HNO3 measured? I don't see it in your instrument list. You may need to do a back calculation to check the modelled value and see if you may retrieve these information iterative model calculations. You may need to calculate the uncertainties or bias due to these missing data in your model input. Response: We appreciate your comments and apologize for our unprofessional description. Your comment was very helpful for us in improving this research, and it also reminded us to pay attention to the key points when entering data in the ISORROPIA-II thermodynamic model. Therefore, we re-simulated and analysed the the model. In our observation experiment, HCl and HNO3 were not measured, so the data of these two species could not be obtained. Therefore, in our data input, CI- and NO3- are entered, and NH3 is the total ammonium (NH3+NH4+) of gas and aerosol inputs. We used this model to analyse the observation and simulation data of NSA in metastable and stable state conditions in forward mode. We used NH3 model simulation data and observation data to perform linear regression fitting to verify the model run effect, and the fitting slope of linear regression is 0.96 (R2=0.98), which shows that the model effect is also good, and it can reflect the state of chemical components in aerosols. To reduce the uncertainties or bias caused by missing data, through strict data quality control during data input, we ensured the integrity and validity of each sample data, 618 samples were simulated, and the content of this model in the current manuscript

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was also re-described.

-- Page 7 line 159 "The simulated data and observed data were compared and analysed. Simultaneously, the aerosol water content (AWC) and pH of aerosols were calculated. The sensitivity of the interaction between aerosol chemical components (NSA) was analysed (Ding et al., 161 2019; Fountoukis et al., 2009). Could you show a comparison between the modelled and measured gas phase NH3, HCl and HNO3? This result can be used to check the reliability and performance of thermodynamic models. Response: We appreciate your comments and apologize for our unprofessional description. Through data quality assurance and control, combined with our research purpose, the usage of thermodynamic balance in this manuscript is modified. We agree that it is necessary to analyse the reliability and performance of the output results of the model. Therefore, we performed a comparative analysis of the output data and the observation data. Considering that the observation experiment did not measure HCl and HNO3, we only analysed the observation and simulation data of NH3 and compared the observation and simulation data of NSA. In addition, in section 2.4 of the manuscript, we also give an accurate description of the model and the methods used in this study. In response to the current comment, we made the following revision in section 2.4: The simulated data and observed data were compared and analysed, and the observation data of NH3 were consistent with the input data of the model. The linear regression fitting slope of NH3 was 0.96 (R2=0.98), which showed that the run result of the model had good reliability and performance.

Page 8 line 178 "the conditional probability function (CPF) was introduced the R Programming Language." Complete the sentence. Response: We appreciate your comments and apologize for our unprofessional description. Now, the text reads as follows: We used the conditional probability function (CPF) to analyse the characteristics of pollutants under the influence of wind direction (WD) and wind speed (WS). The analysis results using CPF were obtained using the R programming language, named openair.

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observation research carried out in Beijing (Ji et al., 2019). Reference: Geng, G., Xiao, Q., Zheng, Y., Tong, D., Zhang, Y., Zhang, X., Zhang, Q., He, K., and Liu, Y.: Impact of China's Air Pollution Prevention and Control Action Plan on PM2.5 chemical composition over eastern China, Science China Earth Sciences, 62, 1872-1884, 10.1007/s11430-018-9353-x, 2019. Ji, D., Gao, W., Maenhaut, W., He, J., Wang, Z., Li, J., Du, W., Wang, L., Sun, Y., Xin, J., Hu, B., and Wang, Y.: Impact of air pollution control measures and regional transport on carbonaceous aerosols in fine particulate matter in urban Beijing, China: insights gained from long-term measurement, Atmospheric Chemistry and Physics, 19, 8569-8590, 10.5194/acp-19-8569-2019, 2019. Wang, Y., Li, W., Gao, W., Liu, Z., Tian, S., Shen, R., Ji, D., Wang, S., Wang, L., Tang, G., Song, T., Cheng, M., Wang, G., Gong, Z., Hao, J., and Zhang, Y.: Trends in particulate matter and its chemical compositions in China from 2013-2017, Science China Earth Sciences, 62, 1857-1871, 10.1007/s11430-018-9373-1, 2019.

- Page 9 line 216 "The annual average mass concentration of NSA also changed significantly. and the difference was large. The Mann-Whitney U test showed that the variation in NO3 - was nonsignificant (p > 0.05), and SO4 2- and NH4 + had obvious significance from 2015 to 2017 (p < 0.05), indicating that NO3 - had not decreased significantly, and there was an increase in 2017 compared to 2015." Here, you could further discuss the reasons why the concentration SO2 and sulfate decease more than that of NOx and nitrate. Response: We appreciate your comments and apologize for our unprofessional description. This similar problem has also been raised by Anonymous Reveiwer #1. We believe that the current greater emission reduction efforts are due to the implementation of the Air Pollution Prevention and Control Action Plan, and a series of pollution control measures have been implemented. Therefore, we have added in the manuscript the emission reduction and control measures taken by Sichuan Province in recent years to control air pollution. The concentrations of SO2 and SO42- decease more than those of NOx and NO3-, indicating that it is necessary to strengthen the air treatment for NOx emissions. We have made corresponding

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-- Page 12, line 283 "This also shows that the implementation of air pollution reduction measures should increase the emission reduction intensity in terms of NOx and NH3 emissions, especially the implementation of autumn and winter air pollution prevention and control action." You were talking about high NH3 in 2017 and then taking to NOx? I am missing a link here. Also I'd like to see an explanation about the high NH3 concentration up to 60 ppb. This is very high for a monthly average. What's the pH under this condition? Response: We appreciate your comments and apologize for our unprofessional description. We are here to make a brief summary of the monthly change trend of gaseous pollution; because we have revised a mistake in expression that caused ambiguity. We also noticed that in the second half of 2017, there was a higher NH3 emission intensity, especially in winter. In combination with Section 3.5, we also found that there will be a higher concentration of pollutants at lower wind speeds (CPF analysis). There may be an emission source in the nearby area that played a more significant role in 2017. In addition, the PSCF analysis also has an obvious regional transport source in the northeast direction. The contribution in this direction is significantly higher than that in 2015 and 2016. Therefore, we believe that the higher NH3 emissions in 2017 are affected by local emissions and regional transport. Since chemical transport models were not available in this study to quantitatively analyse the contribution of local emissions and regional transport, it is necessary for us to conduct in-depth research in this area in the future. We recalculated and analysed the ISORROPIA-II thermodynamic equilibrium model through data quality assurance and control. Because the data were not suitable for annual change analysis, the pH value of aerosols at higher NH3 concentrations in 2017 was not analysed.

Page 13 line 293 "Sulfate has a significant downward trend in all seasons from 2015 to 2017, especially in winter. This downward trend was due to implementation of the Air Pollution 294 Prevention and Control Action Plan" Such discussion should be put in Sect 3.1. Response: We appreciate your comments and

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apologize for our unprofessional description. We have adjusted the position of this discussion and revised the manuscript.

-- Page 15 line 325 "As shown in Fig. S4, from 9:00 to 11:00 a.m., the concentrations of SO2, NOx, NH3, CO and other gases increased significantly, indicating that the primary emission of pollutants was relatively strong. At this time, higher RH (Fig S5) also provides favourable conditions for the formation of secondary aerosols and promotes the accumulation of NSA" But the RH in Fig. S5 is decreasing in contrast to an increase in aerosol concentrations? Response: We appreciate your comments and apologize for our unprofessional description. As you have noticed, RH is indeed decreasing from 9:00 to 11:00. In our analysis, despite the decrease, RH was still relatively high (approximately 65%). Therefore, we have revised and supplemented this description. Now, it reads as follows: As shown in Fig. S7, from 9:00 to 11:00 a.m., the concentrations of SO2, NOx, NH3 and CO increased significantly, indicating that the primary emission of pollutants was relatively strong. At this time, although RH is in a declining stage, it still has a relatively high atmospheric humidity (approximately 65%), and O3 and NO2/NO also occasionally show an increasing trend, indicating that the atmospheric oxidizability has also increased (Figs. S7 and S8). This situation also provides favourable conditions for the formation of secondary aerosols and promotes the accumulation of NSA. Sect.

3.4.1 In general, it is true that the emissions of multi-pollutant may come from the same kinds of sources. But you cannot draw such a conclusion based on correlation studies. Because the variation of most pollutants, especially those of long-lifetime, is strongly influenced by the boundary layer developments, and may show a similar diurnal variation in spite of different origins (sources). Response: We appreciate your comments and apologize for our unprofessional description. We agree with you. During the ACP discussion stage of the manuscript, our research team also carefully reviewed this text and found that the current analysis is not appropriate and may affect the integrity of the manuscript. Therefore, we decided to delete this section.

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20 Line 430 "Figure 7 shows the variation characteristics of NSA chemical conversions and meteorological conditions with increasing RH. SOR and NOR increased with increasing RH, suggesting that SO2 and NO2 were more likely to produce sulfate and nitrate under higher RH conditions. In Fig. 7, how did you do the calculation, classifying the data according to RH or you keep all input the same but change RH only? In the former case, the apparent correlation with RH may not represent the real causation as chemical compositions and other parameters may change also change. Response: We appreciate your comments and apologize for our unprofessional description. We have revised this text. In response to your concerns, we classified and statistically analysed the variation characteristics of NOR and SOR under different RH conditions according to RH observation data. Regarding the latter comment you raised, we also very much agree with you. The correlation is not enough to explain the relationship between chemical components and other parameters. Therefore, we combined the phase state of the chemical components analysed by the ISORROPIA-II thermodynamic equilibrium model to supplement the analysis. Sect

3.5.2 I understand that the authors adopted this approach based on a published study. This approach, however, is subject to several problems, e.g., neglecting the dilution of pollution in the course of transport which may overestimate the contribution of distant sources, or the endpoint is not necessary at the ground level, or why 24 hour (aerosols have a longer lifetime) etc. If you still want to keep this part, please explicitly include these caveats in the text to avoid misinterpretation of this result. Response: We appreciate your comments and apologize for our unprofessional description. As you pointed out, aerosols do influence of emissions, diffusion, chemical conversions and deposition in the process of regional transport. In our study, PSCF is a kind of conditional probability function relationship. Using Meteorological data from the National Oceanic and Atmospheric Administration (NOAA) to analyse the potential sources of pollution is helpful for explaining the importance of regional joint prevention

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D. R., Robarge, W., and Paerl, H. W.: Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density, Atmospheric Environment, 38, 1235-1246, 10.1016/j.atmosenv.2003.11.027, 2004.

Please also note the supplement to this comment: https://www.atmos-chem-phys-discuss.net/acp-2019-1142/acp-2019-1142-AC2-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1142, 2020.

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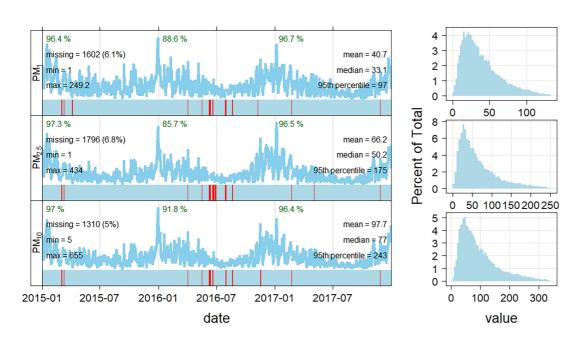
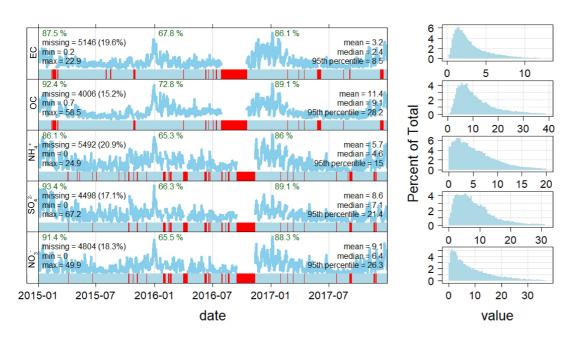


Fig. 1. Fig. S1. PM10, PM2.5 and PM1 data quality assurance and control.

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**Fig. 2.** Fig. S2. NO3-, SO42-, NH4+, OC (organic carbon) and EC (element carbon) data quality assurance and control.

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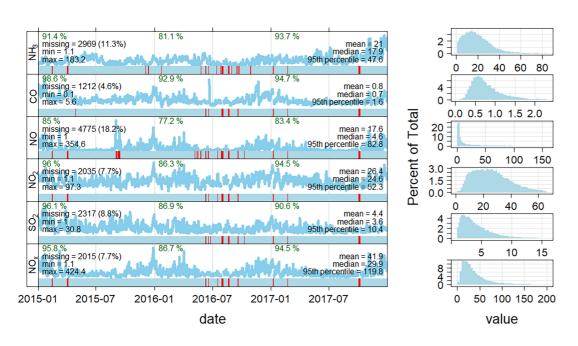
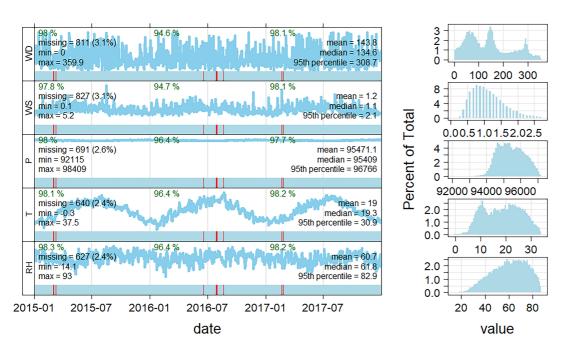


Fig. 3. Fig. S3. NOx, SO2, NO2, NO, CO and NH3 data quality assurance and control.

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**Fig. 4.** Fig. S4. Relative humidity (RH), temperature (T), atmospheric pressure (P), wind speed (WS) and wind direction (WD) data quality assurance and control.

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