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.

We appreciate your help and time.

Sincerely yours,

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Title: Elucidating the pollution characteristics of nitrate, sulfate and ammonium in $PM_{2.5}$ in Chengdu, southwest China, based on three-year measurements

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Response to Anonymous Referee

This study provided a good data basis for explaining the pollution characteristics of secondary inorganic aerosols in PM2.5 through a long-term atmospheric observation experiment. The formation mechanism and role of secondary inorganic aerosols during the formation of haze are still a research hot issue. The author not only explained the pollution characteristics of nitrate, sulfate and ammonium in Chengdu, but also analyzed its formation mechanism through observation data and ISORROPIA-II thermodynamic model simulation. Finally, the author also analyzed the distribution characteristics of pollution emissions and potential sources in Chengdu. At present, China is strengthening the control and treatment of air pollution, a long-term atmospheric observation experiment has a high research value for the analysis of the formation of air pollution and the implementation of haze abatement measures. However, there are some writing, grammatical and technical errors in the paper, and it is suggested that the author carefully revise and organize the presentation of the paper.

Response:

We appreciate your comments and have revised the full text; we also regret each error and have discussed and corrected them.

Line. 53-54, PM2.5 interpretation is inaccurate. "PM2.5(aerodynamic diameter less than 2.5 μm)"

Response:

We appreciate your comments and apologize for our unprofessional description. Now, it reads as follows:

particles with aerodynamic equivalent diameter ≤ 2.5 μm in ambient air ($PM_{2.5}$, also known as fine particles)

Line. 58-61, "NSA" is the abbreviation of nitrate, sulfate and ammonium in the paper? please rewrite this sentence.

Response:

We appreciate your comments and apologize for our unprofessional description. Now, it reads as follows:

Nitrate, sulfate, ammonium, organic matter and elemental carbon are the main components of $PM_{2.5}$, among which nitrate, sulfate, and ammonium (NSA) are the main secondary inorganic aerosols in $PM_{2.5}$.

Line. 77-78, suggest reinterpreting this sentence, how to understand the "regional transport"

Response:

We appreciate your comments and apologize for our unprofessional description. Now, it reads as follows:

In addition to the air pollution caused by the local emission of pollutants, the regional transportation of pollutants from its surrounding cities also has an important impact on the urban air quality.

Line. 82-83, if the author defines an abbreviation at the beginning of the paper, it is recommended to use the abbreviation below. Please use "NSA" abbreviations instead of nitrates, sulfates and ammonium.

Response:

We appreciate your comments and have revised the manuscript. Now, it reads as follows:

Higher concentrations of NSA in $PM_{2.5}$ were also found in regions with more serious air pollution in China, such as Beijing-Tianjin-Hebei, the Yangtze River Delta, the Pearl River Delta, the Fenwei Plain, and the Chengdu-Chongqing region.

Line. 87, please correct this writing, "(2013-207)"

Response:

We appreciate your comments and have revised the text. Now, it reads as follows:

In response to this situation, the Chinese government issued an Air Pollution Prevention and Control Action Plan (2013-2017) in 2013 to reduce pollutant emissions and improve air quality.

Line. 106-109, "high time resolution", what's the meaning of this?

Response:

We appreciate your comments and apologize for our unprofessional description. We mean that the time interval for gathering observation data is relatively small, at 1 hour. Compared with the daily average data of manual operation sampling, the time resolution is higher; we have revised and polished this sentence. Now, it reads as follows:

However, these analyses may be affected by the experimental equipment, observation stations and other conditions, and the time span of these atmospheric observations usually includes several pollution processes or lasts for weeks or months. Thus, it is difficult to analyse the long-term variations in characteristics of air pollution through comprehensive observation. In particular, there are few high-time-resolution (1 hour) observation experiments carried out with online automatic observation systems.

Line. 141, in Table 1, parameters not covered in this paper can be removed, such as PM1 and H2S

Response:

We appreciate your comments and have revised it. Now, it reads as follows:

Table 1. The experimental instruments used in this study

Instruments	Parameters	Manufacturer/Country
URG-9000	$NO_3^-/SO_4^{2-}/NH_4^+/Na^+/Mg^{2+}/Ca^{2+}/Cl^-/K^+$	Thermo Fisher Scientific/USA
SHARP 5030	$PM_{2.5}$	Thermo Fisher Scientific/USA
RT-4	OC/EC	Sunset Laboratory/USA
Xact-625	Metal elements	Cooper Environmental Services /USA
17i/450i/48i/49i	$NOx/NO_2/NO/NH_3/SO_2/CO/O_3$	Thermo Fisher Scientific/USA
WXT520	Meteorological parameters	VAISALA/Germany

OC: organic carbon; EC: element carbon

Line. 185-186, percentile (e.g. 0-25, 25-50, 50-75 and 75-100), please confirm it is consistent with the title of Fig. 13-15 (0-25%, 25-50%, 50-75%, and 75-100%.) in Supplementary materials.

Response:

We appreciate your comments and have revised the text in the Supplementary Materials. We have made the writing consistent throughout the manuscript and adopted percentiles (e.g., 0-25, 25-50, 50-75 and 75-100), and the "%" in the figure title was deleted.

Line. 185-186, it is suggested that the author briefly describe what measures should be taken.

Response:

We appreciate your comments. There is no description of "measures" in line 185, and we presume that the reviewer refers to the description in lines 228-230 about the measures taken in the Air Pollution Prevention and Control Action Plan. We also describe this part in detail. Now, it reads as follows:

From 2015 to 2017, the measures taken by Sichuan Province in the coordinated reduction of multiple pollutants have been continuously strengthened, and the scope of management and control has been continuously expanded, for example, in the improvement of desulfurization, denitrification and dust removal technologies in key industries, from accelerated improvement in 2015 to deeper improvement in 2017. The

process of eliminating small coal-fired boilers began in 2015 and was completed in 2017, when the ultra-low-emission coal-fired power plant transformation was promoted. In terms of vehicle emission control, we accelerated the elimination of "yellow label" vehicles (general term for gasoline vehicles with emission levels lower than the national I emission standard and diesel vehicles with emission levels lower than the national III emission standard when new vehicles are finalized) and “old vehicles” (the emission level does not meet the national stage IV emission standard) in 2015 and basically completed the elimination of yellow standard vehicles in 2017. The quality supervision of oil products has also been improved, and non-road mobile machinery pollution control requirements were proposed in the 2017 plan (ThePeople'sGovernmentofSichuanProvince, 2015, 2016, 2017).

References:

The People's Government of Sichuan Province. Detailed rules for the implementation of the action plan for the prevention and control of air pollution in Sichuan Province 2015 annual implementation plan. Website：http://www.sc.gov.cn/10462/10883/11066/2015/4/22/10333390.shtml，last access: June 17 2020.

The People's Government of Sichuan Province. Detailed rules for the implementation of the action plan for the prevention and control of air pollution in Sichuan Province 2016 annual implementation plan. Website：http://www.sc.gov.cn/zcwj/xxgk/NewT.aspx?i=20160401095908-612769-00-000，last access: June 17 2020.

The People's Government of Sichuan Province. Detailed rules for the implementation of the action plan for the prevention and control of air pollution in Sichuan Province 2017 annual implementation plan. Website：http://www.sc.gov.cn/zcwj/xxgk/NewT.aspx?i=20170527091543-450025-00-000，last access: June 17 2020.

Line. 263, “These variations have similar trends due to meteorological factors”, what do you mean?

Response:

We appreciate your comments and apologize for our unprofessional description. What we want to say is that the meteorological conditions also have obvious monthly variation characteristics, which may have some influence on the variation characteristics of NSA. Now, the text reads as follows:

The monthly variation characteristics of NSA from 2015 to 2017 are shown in Fig. 3. At the beginning and end of each year, the pollutant concentration is relatively high and relatively low in the middle of each year. The meteorological conditions also have obvious monthly variation characteristics (Fig. S5 a and b); from April to August, they have higher WS and lower RH, which is not only conducive to the dilution and diffusion of pollutants but also reduces the chemical conversions of pollutants by aqueous phase and influences the formation of secondary inorganic aerosols.

Line. 306, the legend in Fig. 3 is suggested to be modified, with one reserved, and also pay attention to modify other pictures, such as Fig.S2 and S8.

Response:

We appreciate your comments and apologize for our unprofessional description. We reviewed similar problems in the other figures and have corrected them.

Line. 309, replace "daily changes" with "diurnal variation".

Response:

We appreciate your comments and have revised the text.

Line. 400, please explain what "r" in Fig. 5 means?

Response:

We appreciate your comments and apologize for our unprofessional description. This text has been revised in the manuscript, and this error will not appear in the new manuscript.

Line. 452, in Fig.7h, "SO42- gas-particle phase partitioning"? inconsistent with the

NH4+ in the picture.

Response:

We appreciate your comments and apologize for our unprofessional description. The analysis content has been modified in this section, and the comments made by you in the manuscript have also been resolved.

Line. 470, please explain what "k" in Fig. 8 means?

Response:

We appreciate your comments and apologize for our unprofessional description. Now, the text reads as follows:

Fig. 8. Molar ratio analysis of NSA (nitrate, sulfate and ammonium). (a) Interannual variation in the molar ratio of SO_4^{2-} and NH_4^+. (b) Interannual variation in the molar ratio of NO_3^- and NH_4^+. (c) Seasonal variation in the molar ratio of SO_4^{2-} and NH_4^+. (d) Seasonal variation in the molar ratio of NO_3^- and NH_4^+. k: Fitting slope of linear regression.

In Section 3.5.2, authors are advised to supplement PSCF analysis of NO2 and NO.

Response:

We appreciate your comments and have revised the text.

Line. 470, modify the Fig.9, remove the repeat "PSCF" in the picture

Response:

We appreciate your comments and apologize for our unprofessional description. This issue is also associated with the previous issue, and we have solved the problem.

Line. 521-525, the description is too simple, please rewrite the research results.

Response:

We appreciate your comments and apologize for our unprofessional description. Now, the text reads as follows:

The results of using the ISORROPIA-II thermodynamic equilibrium model to simulate

NO_3^-, SO_4^{2-} and TNH_3 emission reduction control effects of 5%, 10%, 15% and 20%, respectively, are shown in Table S3, showing that controlling the concentration of NO_3^- and SO_4^{2-} is also helpful to reduce the concentration of NH_4^+ and indicating that controlling its precursor NOx and SO_2 is of great significance to reduce the secondary inorganic aerosol in $PM_{2.5}$ (the detailed results are described in the supplementary materials).

supplementary materials

Through observation data quality control, we screened 618 sample input ISORROPIA-II thermodynamic equilibrium models to ensure the integrity of the samples and the effectiveness of the data. The control variable method was used to explore the impact of a concentration reduction for other species. For example, to explore the impact of NO_3^- concentration reduction for SO_4^{2-} and NH_4^+, the NO_3^- data were calculated based on the 5, 10, 15 and 20% emission reduction ratio, and other parameters were input into the model using the observation data to explore the relative variable of SO_4^{2-} and NH_4^+ concentration. The simulation results are shown in Table S3. When only NO_3^- and SO_4^{2-} were reduced, NH_4^+ was significantly reduced, but the changes in SO_4^{2-} and NO_3^- were not obvious, and the relative variables of approximately 12% and 7% may be mainly affected by the change in phase state. When only TNH_3 was controlled, the relative variable of SO_4^{2-} was not obvious, and the concentrations of NO_3^- and NH_4^+ decreased, but the relative variable was not large. NSA has a good reduction effect under synergistic emission reduction control. The results show that reducing the amount of NO_3^- and SO_4^{2-} can not only reduce their concentrations but also help to reduce the concentration of NH_4^+. It also suggests that controlling the gaseous precursors NOx and SO_2 is of great significance to reduce the amount of secondary inorganic aerosol in $PM_{2.5}$. Studies in Mexico City have also shown that reducing total sulfates and total nitrates rather than total ammonium helps reduce $PM_{2.5}$ concentrations in an ammonium-rich environment (Fountoukis et al., 2009).

Table S3. Simulation of NO_3^-, SO_4^{2-} and TNH_3 emission reduction control effect (%) and its influence on pH based on the ISORROPIA-II thermodynamic model.

Reduction	Only NO_3^- Reduction				Only SO_4^{2-} Reduction			
	NO_3^-	SO_4^{2-*}	NH_4^+	pH*	NO_3^-	SO_4^{2-*}	NH_4^+	pH
5%	11.92	12.25914	8.33	4.0495	7.19	17.1088	9.77	4.08
10%	16.58	12.25911	11.13	4.0519	7.09	21.9593	13.65	4.13
15%	21.23	12.25909	13.91	4.0546	7.00	26.8093	17.50	4.19
20%	25.88	12.25906	16.69	4.0547	6.91	31.6596	21.58	4.25
	Only TNH_3 Reduction				Synergistic **			
	NO_3^-	SO_4^{2-*}	NH_4^+	pH	NO_3^-	SO_4^{2-*}	NH_4^+	pH
5%	7.51	12.25938	5.85	4.02	12.08	17.1090	12.86	4.07
10%	7.79	12.25965	6.20	3.99	16.85	21.9596	19.80	4.09
15%	8.10	12.25998	6.59	3.95	21.64	26.8097	26.17	4.11
20%	8.45	12.26040	7.03	3.91	26.37	31.6601	33.29	4.16

Notes: NO_3^-, SO_4^{2-} and TNH_3 are the concentration variables relative to the observation data;

pH is the average; TNH_3: $NH_3 + NH_4^+$;

*: In order to display the data difference, the number of digits after the decimal point was increased

**: NO_3^-, SO_4^{2-} and TNH_3 decreased in the same proportion

Reference:

Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., Van Reken, T., Fischer, M., Matias, E., Moya, M., Farmer, D., and Cohen, R. C.: Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006, Atmospheric Chemistry and Physics, 9, 2141-2156, 10.5194/acp-9-2141-2009, 2009.

Authors are requested to write rules uniformly. It is not recommended to use abbreviations in the title of the figures, such as NSA, AWC, SOR, NOR PSCF. In addition, there are "(a)", "(b)" and "(c)" in the picture, please explain what it means in the title.

Response:

We appreciate your comments and apologize for our unprofessional description. We have checked and corrected the abbreviations for consistency throughout the

manuscript.

In Fig. 5 and Fig. S4, please confirm the carbon monoxide (CO) unit, "ppb" and "ppm"?

Response:

We appreciate your comments and apologize for our unprofessional description. The unit of carbon monoxide (CO) is ppm, and we have revised it.

In Supplementary materials, Line. 90 and 96, pay attention to writing, it shouldn't be "2107"

Response:

We appreciate your comments and have revised it.
