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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect assessment of NO_x and SO_2 control policies on acid species in precipitation from 2005 to 2016 in China based on satellite monitoring" *by* Xiuying Zhang et al.

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1. The authors begin with a thorough description of emissions policies in China over the last two decades.

Response: We highly appreciate the reviewer's comments. This study aims to detect the trend of the contribution of SO42- and NO3- on precipitation acidity, which is greatly influenced by the policies enacted in China to improve air quality. Therefore, we gave the background in the Introduction. In this version, we have shifted the focus from discussing the effect of the air quality polices to the trends of wet SO42- -S and NO3- -N depositions across China as the reviewer suggested.

2. The methods rely heavily on assertions from linear correlations.

Response: In order to make our manuscript better fit the scope of ACP, we have made significant changes on data and analysis of our study. In this round of revision, we have collected the ground measurements on SO42- and NO3- concentrations in precipitations from 2005 to 2016 at 60 sites across China. We used the ground measurements to construct the model to estimate wet SO42- -S and NO3- -N depositions, based on the SO2 and NO2 columns in atmospheric boundary layer (ABL). The rationale behind this is that NO2 reacts with O3 to form NO3− and then highly soluble N2O5 (NO2 + NO3 → N2O5, N2O5+H2O→2 HNO3), thus most of the bulk NO3−-N in precipitation originates from HNO3 and aerosol nitrate (NO3−) (Barrie, 1985;Liu et al., 2017). Similarly, the rationale of using SO2 columns to estimate wet S deposition is based on the relationship between SO2 and SO42-. At the gas phase, SO2 is oxidized by reaction with the hydroxyl radical via an intermolecular reaction (SO2 + OHâĂć → HOSO2âĂć), which is followed by (HOSO2âĂć + SO2 → HO2âĂć + SO3); in the presence of water, sulfur trioxide (SO3) is converted rapidly to sulfuric acid (SO3 (g) + H2O (l) → H2SO4). Furthermore, the wet deposition flux (F) could be estimated by F=W×P×C, where W is scavenging ratios, P is precipitation amount, and C indicates SO2 or NO2 concentrations in atmosphere (Barrie, 1985;Sakata et al., 2006). We used the ground on SO42- or NO3- concentrations and the ABL SO2 or NO2 to estimate the scavenging ratios.

The results showed that SO2 and NO2 columns in ABL have potential to estimate wet SO42- -S and NO3- -N depositions ($R = 0.883$, intercept = 0.903, $P < 0.05$ for SO42–S estimations; and $R = 0.893$, intercept = 0.755, $P < 0.05$ for NO3–N estimations).

Therefore, although the core model to estimate the wet SO42- -S and NO3- -N depositions in this study is a statistical model, it has rationale behind. We resolved the problem of wet deposition from another view point apart from the atmospheric chemical transport (ACT) theory, and the key point is that we gained a reliable result.

3. The data the authors analyze is not well documented. Some of the data, including

the measured sulfate and nitrate (Section 2.1.3) are referenced to other published papers but without a brief characterization of the nature of the data collection or extent spatially or temporally of the dataset.

Response: In this revision, we have used the ground measurements on SO42- and NO3- concentrations in precipitations to replace the data collected from published papers. The precipitation samples at 60 sites are collected based on the routine procedure on acid precipitation monitoring technology (HJ/T165ïij■2004). Precipitation amount is measured immediately after every precipitation event finished, and the concentrations of $SO4^{2-}$ and NO3- are measured using ion chromatography. The quality of monitoring data is evaluated and supervised by China National Accreditation Board for Laboratories according to international requirements. The detailed information on the locations of sites, number of the collected precipitation events and spanned time is listed in Table S1.

4. Other key parameters in the statistical models are not described, such as the atmospheric boundary layer SO2 term. Evidence of the quality of the models (eq. 5) essential to calculating the OMI-derived S/N metric is not presented. Although the model for nitrogen deposition was recently published in another journal, the model for sulfate deposition, from which the important correlation coefficient arises for the S/N metric, has not yet been peer reviewed.

Response: Please refer to our detailed response for #2.

5. The explanations of data included or excluded in figures (e.g., very small number of observations in Fig 5c) is neglected as are the sources of the emissions. Throughout the manuscript, the quality of the statistical analysis, representations of error, and propensity to neglect outliers without physical reason calls into question the quality of these underlying statistical models, which are not evaluated in this manuscript.

Response: In this version, the analysis on Fig. 5 has been removed. And we have tried to correct the questions mentioned above.

6. Furthermore, the authors seek to explain an outlier in the SO2 downward trend by acknowledging that 2011 had the least precipitation on record for the last 50 years.

Response: In fact, SO2 columns showed a downward from 2005 to 2016, except for the year of 2011. Since SO2 emissions did not high in this year, the low removal by dry and wet depositions and the long-range transport might be the reasons. Therefore, our analysis in the previous version does not fully consider all of the factors. In this version, the analysis on the peak of SO2 in 2011 has been removed, since the related contents have been removed.

7. The authors do not take this opportunity to acknowledge the inherent difficulty in using a gas phase satellite based observation of precipitable species to explain wet deposition nor do they explain how the linear models that are the basis for the S/N metric account for the way that rain depletes the nitrate and sulfate concentrations in the atmosphere.

Response: Please refer to our detailed response for #2.

8. Finally, the authors do not make a case for using a satellite-based metric for estimating the ratio of wet-deposited sulfate to nitrate when measurements of the ions in rain water are already being conducted across China. Because of the poor evaluation of the statistical models underlying the conclusions, the absence of documentation of datasets, the inherent difficulty in the approach attempted, and the lack of purpose for the results, I cannot recommend this manuscript for publication in Atmospheric Chemistry and Physics.

Response: Although the acid rain pollution across China has been monitored, not all of the chemical compositions in precipitations have been measured. Furthermore, the report on the spatial distribution of the wet SO42- -S and NO3- -N depositions based on ground measurements has not been reported yet. The key contributions of this study are that we estimate the long-term trend of wet SO42- -S and NO3- -N depositions with high spatial resolutions across China, compare the contributions of H2SO4 and

HNO3 on precipitation acidity, and detect the trend in their combining acidity. The trend of acid species in precipitations would help understand the acid pollution in China and thus make efficient way to control acid pollutions. We believe the results in this study will provide the scientific information to the experts in global change studies and the policy makers.

Reference:

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