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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

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Abstract

The effects of NO_x and SO_2 policies on acid species in precipitation was assessed in China from 2005 to 2016, based on the OMI measured SO_2 and NO_2 columns. The results showed that the SO_2 and NO_2 columns in the atmospheric boundary layer (ABL) could be used to indicate the variations of S / N in precipitations ($R = 0.90$, incept = 0.97, $P < 0.05$). The spatial distribution of S / N was lower in eastern China than the west, which had a negative logarithmic relationship with population densities ($R = 0.78$, $P < 0.05$). The OMI-derived S / N decreased significantly from 2005 to 2016 (17.21 and 10.70 in 2005 and 2016, respectively), mainly due to the controlling S and N policies enacted at different times. The ABL SO_2 columns showed a decreasing trend from 2005 to 2016, while NO_2 presented an increasing tendency from 2005 to 2011 then decreasing until 2016. The temporal variations of SO_2 and NO_2 were not only determined by their emissions but also affected by precipitation amount, which induced the highest SO_2 and NO_2 concentrations in 2011 during the study time. With the combined acidification

effects of S and N, the acidity had increased from 2005 to 2011, then decreased until 2016. The acidity in 2016 has declined 11.0% and 25.4%, respectively, compared with those in 2005 and 2011, indicating the policies on joint controlling SO_2 and NO_2 have gained effects.

Keywords: Acid species, precipitation, policies, China, remote sensing, OMI

1. Introduction

The economic growth in recent 30 years in China has been accompanied by increased energy demand and massive emissions of pollutants (Kuribayashi et al., 2012). Among them, sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are important precursors of acid rain. After released into the atmosphere, SO_2 and NO_2 can be transformed into nitrate (NO_3^-) and sulfate (SO_4^{2-}) through complex physical and chemical processes (Yu et al., 2016), and then diluted with precipitation. Increased acid deposition and the followed decreased pH of precipitation, directly and indirectly, influence the eco-environments (Charlson and Rodhe, 1982;Li et al., 2017;Larssen and Carmichael, 2000). Currently, China is becoming one of the highest acid deposition areas on a global scale (Vet et al., 2014), which has been drawing serious concerns from the public and policy makers in China due to the adverse impacts of acid rain on the ecological environment.

To control acid rain pollution, the Chinese government has implemented a series of policies from the 9th to 12th Five-Year Plans (1996-2015). “Decision of the State Council on Several Issues Concerning Environmental Protection” was issued in 1996, in which “15 major categories of small pollutant enterprises” related to pollutant emissions should be closed ([1996]31). In 1998, the Chinese government adopted national legislation, known as the “two control zones (TCZs) plan”, to limit ambient SO_2 pollution and halt the increase of acid rain. During the 11th Five-year Plan, a clear aim was announced that national wide SO_2 emission in 2010 should be reduced by 10% of that in 2005, and the

increasing tendency of NO_x should be controlled. Under such strict policies, small power generating units and inefficient industrial facilities were closed, and 82.6% of the thermal power plants were equipped with flue gas desulfurization (FGD) in 2010 (China Environmental Bulletin 2010). However, the ground measurements of precipitation pH indicated that the control policies had not been successful in reducing acid rains (China Environmental Bulletin 2010). Thus several studies have argued whether it is enough to control acid rain pollutions through only controlling SO_2 emissions (Zhao et al., 2009;Fang et al., 2013).

To further improve the air quality and control acid rains, the Chinese government issued “Twelfth Five-Year Plan for National Environment Protection” in 2011, and set a goal to reduce the emissions of NO_x by 10% and SO_2 by 8% in 2015. Additionally, the Ministry of Environmental Protection, National Development and Reform Commission, and Ministry of Finance jointly issued "12^{th} Five-Year Plan on air pollution prevention and control in Key regions" in 2012, which aims to reduce the emissions of SO_2 and NO_x by 12% and 13%, and the concentrations of SO_2 and NO_2 by 10% and 7% in the key regions in 2015. Selective catalytic reduction (SCR) equipment was recommended to install in this period and the SCR equipment number grew from a percentage of about 18% in 2011 to 86% in 2015 (Liu et al., 2016a). Moreover, several new national emission standards for cars have been implemented to reduce the NO_x emissions generated by traffics (Wu et al., 2017).

Several studies have discussed the effect of environmental protection policies on the emissions, concentrations, and depositions of S and N in China, based on the ground measurements or satellite monitoring information (Kuribayashi et al., 2012;Krotkov et al., 2016;Zhao et al., 2013;Ronald et al., 2017;de Foy et al., 2016). It was found that SO_2 emissions in China increased continuously before 2006, and declined after 2006 due to wide application of flue-gas desulfurization (FGD) in power units since

2005 (Fang et al., 2013;Duan et al., 2016). NO_x emission was also found to have a rapid increase from 1990 to 2011 and decreased from 2012 because of the broad applications of SCR in coal-fired power plants (Wang et al., 2014). The remotely sensed SO_2 and NO_2 columns also showed that FGD had a significant effect when a much stricter control of the actual use of the installations began in the years of 2008-2009 (Ronald et al., 2017). The remotely sensed NO_2 columns reached the peak in 2011 and then decreased from 2012 in China (Chen et al., 2017). But the emission peak years for NO_2 varied from province to province (Ronald et al., 2017). Although the peak years for SO_2 and NO_2 varied in different studies, these studies confirmed that atmospheric S and N increased first due to the economic development, and then decreased because of the enacted policies.

The different changing steps of S and N in the atmosphere, including the different increasing / decreasing rates and peak years, directly influence the S and N depositions through precipitation (Huang et al., 2009;Liu et al., 2016d;Liu et al., 2016c). According to a review on chemical compositions precipitation in recent years, the pollution in precipitation is still dominated by sulfur type with a trend to sulfuric-nitrous mixed type in China (Wang and Xu, 2009). The declined ratio of SO_4^{2-} to NO_3^- concentration has been observed in northern China (Wang et al., 2012;Pu et al., 2017), southeast China (Huang et al., 2008;Fang et al., 2013), and southwest China (Liu et al., 2016b), indicating the proportion of NO_3^- concentration on precipitation acidity has been increased in recent years. Combining the acidification effects of S and N, the benefits of SO_2 reductions during 2005−2010 might be largely offset by increases of N emissions (Zhao et al., 2009). However, the change of the contributions of SO_4^{2-} and NO_3^- on precipitation acidity has not been evaluated, particularly on a national scale.

Compared with the ground measurements, the remote sensing technique provides a new means to

89 monitor the concentrations of SO_2 and NO_2 in the atmosphere, with the advantages of extensive spatial
90 details and continuous temporal coverage (Zyrichidou et al., 2013). At present, the Global Ozone
91 Monitoring Experiment (GOME2A, 2007-; GOME2B, 2013-), Scanning Imaging Absorption
92 Spectrometer for Atmospheric Cartography (SCIAMACHY, 2002-2012), and the Ozone Monitoring
93 Instrument (OMI, 2004-) on the Aura satellite provide both of the SO_2 and NO_2 column products.
94 Among them OMI provides the smallest instantaneous ground pixel resolution (13×24 km^2 at nadir)
95 and its products have been widely used for studying the spatial and temporal variations of SO_2 and NO_2
96 concentrations in the atmosphere and evaluating the effects of policies (Ronald et al., 2017;Chen et al.,
97 2017;Krotkov et al., 2016;Song and Yang, 2014;de Foy et al., 2016;Lamsal et al., 2015). However, few
98 studies have used the remotely sensed SO_2 and NO_2 columns data to indicate the variations of acid
99 components in precipitation (Liu et al., 2017;Zhang et al., 2012).
100 Remotely sensed SO_2 and NO_2 columns have been used to study the effect of precipitation variation on
101 severe acid rains in southern China (Xie et al., 2009), and evaluate the influence of SO_2 and NO_2
102 columns on precipitation pH in Anhui and Liaoning Provinces (Shi et al., 2010;Zhang et al., 2012).
103 More particularly, Liu et al. estimated monthly NO_3^{-1} deposition through precipitation using the OMI
104 NO_2 columns and precipitation amount (Liu et al., 2017). In their work, the atmospheric boundary layer
105 (ABL) NO_2 columns below the precipitation height instead of the tropospheric NO_2 columns were used
106 to construct the statistical model to estimate NO_3^{-1} depositions, since the scavenging effect on N
107 compounds is from the top precipitation height rather than the top troposphere height (Racette et al.,
108 1996). Therefore, the ABL SO_2 and NO_2 columns should be better than tropospheric columns when
109 indicating the acid components deposited.
110 Based on the ABL SO_2 and NO_2 columns, this study aims to evaluate the trends of the contributions of

111 the sulfate and nitrate ions on the acidity of precipitation from 2005 to 2016, under the policies enacted
112 and economic development in China. First, the remotely sensed indicator of S / N to the ratio of sulfate
113 and nitrate ions in rainwater is constructed based on ABL SO_2 and NO_2 columns; second, the spatial
114 variations and the trends of the S / N in rainwater are detected; finally, the spatial and temporal
115 variations of the potential acidification by sulfate and nitrate ions are evaluated.

116 **2. Materials and methods**

117 **2.1. Materials used in this study**

118 **2.1.1. Tropospheric NO_2 and ABL SO_2 columns from OMI**

119 The OMI satellite instrument is a nadir-looking UV-visible spectrometer on the Aura satellite (Levelt et
120 al., 2006). Aura was launched on 15 July 2004 and flies in a sun-synchronous polar orbit with a local
121 equatorial overpass time of 13:40 on the ascending node. The NO_2 columns are provided in the publicly
122 released level 2.0 (DOMINO 2.0) (http://www.temis.nl/), which has greatly improved the accuracy of
123 the tropical NO_2 columns of the version 1.0 (Boersma et al., 2011). A new data set of ABL SO_2
124 columns from OMI is available, which agree on average within 12% with ground observations,
125 strongly improved on earlier SO_2 data sets from satellites (Theys et al., 2015).

126 In this study, the monthly tropospheric NO_2 columns from Jan 2005 to Dec 2016 over China are used.
127 The missing data is interpolated using IDW (Inverse Distance Weight) method, and then the unit of DU
128 (Dobson unit) for SO_2 column is transformed to molec. cm^{-2} by multiplying 2.6875×10^{16} molec. cm^{-2}
129 (1DU = 2.6875×10^{16} molec. cm^{-2}) (Lee et al., 2011). Finally, the monthly mean SO_2 columns are
130 averaged from the daily data.

131 **2.1.2. NO_2 profiles simulated from MOZART-4**

132 The 56 levels of NO_2 concentrations in the atmosphere along altitudes from 2005 to 2016 have been

simulated from MOZART-4, a global chemical transport model. This model is driven by NCEP/NCAR reanalysis meteorology and uses emissions based on POET (Precursors of Ozone and their Effects in the Troposphere), REAS (Regional Emission inventory for Asia) and GFED2 (Global Fire Emissions Database, version 2). Evaluation with several sets of observations shows that MOZAR-4 can reproduce tropospheric chemical composition with an acceptable accuracy (Emmons et al., 2010). The output data used in the current work are temporally varying six hours every day, which are upon request by Louisa Emmons at National Center for Atmospheric Research (NCAR) (http://www.acom.ucar.edu/wrf-chem/mozart.shtml).

2.1.3. Concentrations of SO_4^{2-} and NO_3^- in precipitation during 2005 - 2016 collected from the published papers

To test whether OMI-derived S/N could be used to indicate SO_4^{2-} / NO_3^- in precipitation, the SO_4^{2-} and NO_3^- concentrations in precipitation during 2005-2016 in China from the published studies were collected. The detailed information on searching the relevant papers has been detailed described in those studies (Liu et al., 2016c;Liu et al., 2016d). Since the mentioned two studies collected the data from 2000-2013, we removed the data from 2000 to 2004 and added the SO_4^{2-} and NO_3^- data published during 2014-2016 in this study. In total, 168 records on annual SO_4^{2-} and NO_3^- concentrations in precipitation have been selected.

2.1.4 Spatial distribution of population density

The spatial distribution of population density in 2010 in China is used to study the relationship between the S / N and population density. The spatial resolution is 1 km × 1 km. This data set was produced by integrating the physical geography factors and the statistical data on population in 2010, which is freely downloaded from http://www.geodoi.ac.cn/doi.aspx?doi= 10.3974/geodb.2014.01.06.v1.

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155 **2.2. Methods**

156 **2.2.1. Calculation of ABL NO_2 columns**

157 The MOZART-4 output of NO_2 concentrations includes 56 vertical levels from the ground to the top of

158 the troposphere. To simulate the profile of NO_2, a Gauss function is used:

159 $f(C_h^M) = \sum_{r=2}^{n} a^r exp\left(\frac{-(h-b_r)^2}{c_r^2}\right)$ (1)

160 where C_h^M is the NO_2 concentrations at the atmospheric height h; a refers to the amplitude, b is the

161 centroid (location), c refers to the peak width, n is the number of peaks to fit. In this study, the models

162 with n from 2 to 6 are simulated, among which the model with the lowest RMSE (Root Mean Square

163 Error) and the highest R^2 is selected.

164 The tropospheric and ABL NO_2 columns $\left(\Omega_{trop}^M, \Omega_{ABL}^M\right)$ simulated from MOZART-4 are simulated by

165 an integration method:

166 $\Omega_{trop}^M = \int_0^{trop} f(C_h^M)$ (2)

167 $\Omega_{ABL}^M = \int_0^{ABL} f(C_h^M)$ (3)

168 Then the OMI-derived ABL NO_2 column (Ω_{ABL}^O) is calculated as:

169 $\Omega_{ABL}^O = \Omega_{trop}^O \times \frac{\Omega_{ABL}^M}{\Omega_{trop}^M}$ (4)

170 Where Ω_{trop}^O is the NO_2 columns retrieved from OMI.

171 **2.2.2. Calculation of the OMI-derived S / N to indicate the SO_4^{2-} / NO_3^- in precipitation**

172 In the study of Liu et al. (2017b), the NO_3^- deposition in precipitation ($D_{NO_3^-}$) could be estimated by the

173 following equation:

174 $D_{NO_3^-} = \alpha + \beta(\Omega_{ABL,N}^O \times P - \varepsilon)$ (5)

175 Where α and β are the intercept and the slope of the constructed model, ε is the site bias, P is the

176 precipitation amount, and $\Omega_{ABL,N}^O$ is an indicator of N compounds in the atmosphere. Here, $\Omega_{ABL,N}^O$

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refers to the ABL NO_2 columns.

Similarly, the SO_4^{2-} deposition in precipitation could be estimated by the similar equation format as Eq. (5)[1]. Here, we directly use the coefficients of β for N and S in the two studies to indicate the dilution rates on N and S by precipitation, in which β for N and S was 9.33 and 7.10, respectively (Liu et al., 2017).

Thus the OMI-derived S / N is calculated by :

$$S / N = \frac{\beta_S \times \Omega^O_{ABL,S}}{\beta_N \times \Omega^O_{ABL,N}} \quad (6)$$

The correlation coefficient between the OMI-derived S / N and the collected data of *SO42- / NO3-* in precipitation is calculated to determine the degree to which the two data sets are associated. Other parameters of relative error (*RE*) and absolute error (*AE*) are used to assess the accuracy of the estimated NO_2 by the following function:

2.2.3. Potential acidity induced by H_2SO_4 and HNO_3

Generally, the precipitation acidity is due to H_2SO_4 and HNO_3, whereas HCl, HF, and other organic acids are considered as negligible acidity contributors compared to H_2SO_4 and HNO_3 (He et al., 2010;Khwaja and Husain, 1990). If all of the non-seasalt sulfate and NO_3^- presented in free acid forms, the potential acidity could be estimated using the sum of nss-SO_4^{2-} and NO_3^- in precipitation (Rodhe et al., 2002). Since the method and the simulated result on $D_{NO_3^-}$ have been well evaluated by Liu (Liu et al., 2017), here we directly use the format of the equation to estimate the concentration in H^+.

Since H_2SO_4 has two H^+ while HNO_3 has one, the latent acidification effects could be calculated as follows:

$$PA = \beta_N \times \Omega^O_{ABL,N} + 2\beta_S \times \Omega^O_{ABL,S} \quad (7)$$

[1] This study has not been published yet.

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Here PA is not an actual value of the concentration of H^+ induced by H_2SO_4 and HNO_3, since equation (7) does not calculate the S and N deposition through H_2SO_4 and HNO_3. The PA is used here to indicate the variation of H^+ induced by H_2SO_4 and HNO_3 for a long-term study.

3. Results and discussions

3.1. Validation of the OMI-derived S / N on SO_4^{2-} / NO_3^- in precipitation

The scatter plots of the OMI-derived S / N and SO_4^{2-} / NO_3^- is illustrated in Fig. 1(a). The OMI-derived S / N has achieved a reasonably high predictive power on the ratio of SO_4^{2-} to NO_3^- in precipitation, with a slope of 0.97 and R of 0.90. From Fig. 1(a), four points appatently deviated from the main trend were located in Xizang, Yunnan, Guizhou, and Hainan provinces (Red circle in Fig 1(b)). If these points were removed, the R would be increased from 0.90 to 0.94. This confirmed that the OMI derived S / N could be used to indicate the variations of SO_4^{2-} / NO_3^- in precipitation across China.

The spatial distribution of the relative errors between the collected SO_4^{2-} / NO_3^- and OMI-derived S / N components is shown in Fig.1 (b). The relative errors ranged from -56.2% to 210.4%, indicating the ability of OMI-derived indicator on SO_4^{2-} / NO_3^- varied greatly across China. The average of the *RE* and *AE* was -11.8 % and 22.0 % for the 168 data records, which denoted that the OMI-derived S / N had underestimated the ratio of SO_4^{2-} / NO_3^-- in precipitation. About 134 data records had the *RE* within -30% to 30%, indicating 80% of the OMI-derived S / N at the collected sample locations could be used to indicate the SO_4^{2-} / NO_3^- in precipitation. Eighteen and three data records had the *RE* between -45% - -30% and 30% -45%, respectively. While six data records had very high *RE* values, particularly for the sites in Southwestern China, which might be caused by the errors of the NO_2 and SO_2 columns derived from OMI in these areas.

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3.2. Spatial distribution of OMI-derived S / N in China

The spatial distribution of OMI-derived S / N in 2016 is illustrated in Fig. 2. The ratio ranged from 0.49 to 71.73, with an average of 10.70, which was much higher than the average of SO_4^{2-} / NO_3^- in precipitation (2.59) from 474 stations by ground measurements (China Environmental Bulletin 2016). The big gap was mainly due to that 10.70 was the average of S / N for the whole China, while 2.59 was calculated from the 474 measuring sites, most of which were located in urban areas. The average of OMI-derived S / N at the 474 points was 2.78, which was very close to that SO_4^{2-} / NO_3^- in precipitation in 2016.

According to the classification standard on acid rain types (Cheng and Huang, 1998), 17.3% of the total areas of China in 2016 had the acid rains of sulfuric-nitrous mixed types ($0.50 < S / N < 3$). The rest 82.7% had sulfuric acid rains ($S / N > 3$), among which 49.1% were contributed by the areas with S / N values higher than 10. Since only several pixels had the S / N values lower than 0.50 (the minimum of 0.49 very close to 0.50), which have been neglected in this study. Thus, the precipitation acidity in China is still mainly from the contribution of sulfuric species at present.

The large range of S / N indicated that a high variation of sulfate to nitrate components in precipitation existed across China. The S / N values lower than 3 covered large areas from the northeast China to the south China, including the whole province of Shandong, Jiangsu, Anhui, and Henan, and partly provinces of Liaoning, Hebei, Shanxi, Shaanxi, Hubei, Hunan and Zhejiang. Also, in some local areas around Urumqi, Lanzhou, Yinchuan in northeast China, Chengdu and Chongqing in Central China, Nanning, Guangzhou and Taiwan in South China, Changchun and Harbin in Northeast China, the S / N also presented low. Particularly, some areas around Beijing-Tianjin-Hebei, Shandong, Shanghai-Jiangsu-Zhejiang, Guangdong, Hubei, Shaanxi, and Chongqing-Sichuan, had the S / N less

than 1, indicating the dominant acid component has changed from sulfate to nitrate. While in the Qinghai-Xizang areas, the northern part of Inner Mongolia, and the south of Yunnan Province, the ratio showed relative high.

The ratio of S / N was mainly determined by the different sources of SO_2 and NO_x. In fact, SO_2 and NO_x are released by more or less the same anthropogenic sources, i. e. the burning of coal or oil, volcanic activity, burning biomass. The main difference to SO_2 is that traffic is a much more important source for NO_x (Ronald et al., 2017). The highly developed traffics in the densely populated areas, and the more widespread application of the FGD than SCR in power units might be the main reasons for the low values of S / N in the mentioned regions (Duan et al., 2016;Wang et al., 2014;Fang et al., 2013).

The spatial pattern of S / N is highly negatively correlated to that of population densities (Fig. 2b). To illustrate the relationship between the population density and the ratio of S to N, the zonal means of S / N were calculated by the different grades of population density (< 100, 100-200, 200-300, 300-400, 400-500, 500-1000, 1000-5000, 5000-10000 people/km^2). It was found that the population density had a significantly negative logarithmic relationship on S / N (Fig. 3). With the population density increases, the S / N decreased. The population might not directly influence on the S / N, while it indirectly effects on the emission source of S and N through human activities.

3.3. Long-term trends of the S / N from 2005 to 2016

The averages of the OMI-derived S / N, SO_2, NO_2 columns are shown in Fig. 4. In China, SO_2 concentrations in the atmosphere increased first from 2005 to 2007 and then declined with a little fluctuation from 2008 to 2016. This trend of SO_2 columns is greatly influenced by the variations of SO_2 emissions, since SO_2 emissions also showed an increasing trend from 2005 to 2006, and then decreasing until 2016. The consistency of the trends of SO_2 emissions and concentrations was

263 interrupted in 2011 when the SO_2 concentration reached the highest while the SO_2 emission did not.
264 This inconsistency is mainly because the atmospheric conditions also influence SO_2 concentrations in
265 the atmosphere through changing the chemical reactions with other components and the vertical and
266 horizontal transportations (Uno et al., 2007;Emmons et al., 2010;Schaub et al., 2007). Among the
267 climatic factors, precipitation amount might be a dominant one since it can scavenge the relevant
268 S-related components in the atmosphere. This study also confirmed that the precipitation amount has an
269 obvious negative correlation coefficient (-0.69, $P < 0.05$) with SO_2 concentrations (Fig. 5a). In 2011,
270 the average precipitation amount was only 556.8 mm in China, which was the lowest in the recent 50
271 years (China Climate Bulletin 2011). The lowest dilution effect on ions of precipitation in 2011 might
272 contributed a strong influence on the highest concentrations of SO_2 in the atmosphere. If the year of
273 2011 was excluded, the correlation coefficient between SO_2 emissions and concentrations in the
274 atmosphere would have increased to 0.95 from 0.73 ($P < 0.05$) (Fig. 5b).
275 The ABL NO_2 columns showed a steadily increasing from 2005 to 2011 and then decreasing until to
276 2016 (Fig. 3c). Also, NO_x emissions showed declining from 2011 (China Climate Bulletin 2011, 2012,
277 2013, 2014, 2015, and 2016), which was highly consistent with the trend of NO_2 concentrations (Fig.
278 5d). However, although precipitation had the similar effect on NO_2 in the atmosphere with that on SO_2,
279 precipitation amount did not show a statistically significant negative effect on NO_2 concentrations (Fig.
280 5c). This might mean that the variations of NO_2 concentrations were mainly determined by the
281 emissions in China. The maximum of ABL NO_2 columns also occurred in 2011, which might be caused
282 by both the highest NO_x emissions and the lowest precipitation amounts.
283 The possible reasons for the trends of SO_2 and NO_2 concentrations and emissions have been widely
284 described previously (Ronald et al., 2017;Krotkov et al., 2016), including the economic development

and the implements of a series of policies on atmospheric environmental protection. The trends on SO_2 and NO_2 directly influenced the variations of acid species in precipitation. The OMI-derived S / N showed a significant decline (17.21 and 10.70 in 2005 and 2016, respectively), indicating the contribution of the sulfate on the precipitation pH has decreased while nitrate contribution is increasing. From 2005 to 2010, the decreasing trend of S / N was due to the slightly decreased SO_2 and rapidly increased NO_2. In 2010, SO_2 decreased by only 1.0% compared with that in 2005, but decreased by 10.5% compared with the highest SO_2 concentration in 2007. During the same period, NO_2 increased by 36.9% in 2010. From 2011 to 2016, both of SO_2 and NO_2 declined, but SO_2 had a higher decreasing rate than NO_2 (43.77 molec. cm^{-2} yr^{-1} for SO_2 and 11.39 molec. cm^{-2} yr^{-1} for NO_2). The different decreasing rates induced the further decline of S / N. In 2016, S / N decreased about 37.9% compared with that in 2005.

The decreasing trend of SO_4^{2-} / NO_3^- in precipitation was also observed from the ground measurements of the national monitoring on acid rains (China Climate Bulletin 2011, 2012, 2013, 2014, 2015, and 2016), which showed that the ratio has decreased from 3.80 in 2011 to 2.59 in 2016 (3.49, 3.50, 3.18, 2.90 in 2012, 2013, 2014, and 2015, respectively. In some areas of China, such as Jinyunshan, Beijing, Guangzhou, ground measurements also showed that the SO_4^{2-} / NO_3^- in precipitation decreased in recent years (Pu et al., 2017;Liu et al., 2016b;Fang et al., 2013).

Considering the classification standard of acid types on precipitation (Cheng and Huang, 1998), the precipitation acidity is still dominated by the sulfuric species. The percentages of the areas with sulfuric-nitrous mixed precipitations showed an increasing trend from 9.0% in 2005 to 17.3% in 2016, while the percentages of the areas with sulfuric rains accordingly has decreased. Particularly, the percentage of the areas with S / N > 10 showed a much obvious decreasing trend. The average

decreasing rate for the areas with S / N greater than 10 was 1.76 % per year, while the increasing rate for the areas with S / N less 3 was 0.92% yr^{-1} (Fig. 6). This meant that not only the areas with the sulfuric-nitrous mixed precipitations sprawled, but also the areas with high S / N values shrank with a higher decreasing rate. The whole situation confirmed that the contribution of sulfuric species is getting lower for precipitation acidity in China.

Figure 7 shows the trend of S / N for those grid cells that have a statistically significant trend. A large negative trend is visible in China, while only several pixels had a positive trend in Taiwan. This is mainly due to that the environmental regulations on reducing SO_2 emissions were implemented earlier than those on NO_x in China (Ronald et al., 2017). The steadily decreasing trend for SO_2 and the first increasing then decreasing trend for NO_2 resulted in the decrease of S / N in most areas, particularly in east China. The decreasing rate of S / N was within 0-0.25 per year. We should notice that in western China and the north part of Inner Mongolia, the decreasing rates of S / N were relatively higher than those in eastern China. This might not be due to the policies on controlling SO_2 and NO_x emissions, but the rapid increased NO_2 emissions caused by significant socio-economic changes following the National Western Development Strategies (The "Go West" movement) (Cui et al., 2016). NO_x might be getting higher than SO_2 due to their different sources, which decreased the S / N rapidly.

3.4. Long-term trends of the potential acidity in precipitation

It has confirmed that the SO_2 emissions and concentrations in the atmosphere have decreased since 2007. However, the situation of acid rains has not been obviously alleviated since then. According to the statistic, the ratio of cities with occurring acid rains kept relatively stable around 50% from 2005 to 2014, but rapidly decreased to about 20% in 2015 and 2016 (Fig. S1). The potential acidity (PA) curve increased first and then decreased (Fig. 8), close to the trend of the ratio of cities with acid rains (R =

0.86, $P < 0.05$). Even with the year of 2011 not included, this trend did not change but with different simulated peak years (2008 for 2011 included or 2009 for 2011 excluded). Compared with the highest PA in 2011, 25.5% of acidic ions have been reduced in 2016. If compared with that in 2005, about 11.7% of acidic ions have been reduced in 2016, indicating that some successes on the recovery of acid rain had been achieved.

The spatial distribution of potential acidity in 2005, 2010, and 2016 are described in Fig. 9. From the map in 2005, the hotspots occurred in north China extending from the northeast China to the Yangtze delta areas, the highly populated Sichuan Basin, the megacity clusters around Shanghai and Guangzhou. While in 2010, these regions with high potential acidity still existed. Particularly the areas with relatively high potential acidity ranged from 10,001 to 15,000 have obviously expanded around Urumqi in Northwest China. The regions in Xizang and the west Sichuan and Yunnan Province with the potential acidity lower than 5,000 showed an obvious decrease, indicating the PA had increased. Combing the decreased ratio of S / N in western China, the acidic ability should be contributed more by the NO_3^-. This is confirmed in the study of NO_x trends in western China (Cui et al., 2016). The contrary phenomenon was found in Pear River Delta. The potential acidity obviously decreased around the areas of Guangzhou, which was confirmed by the regional monitoring network data in PRD due to the deceased SO_2 emissions (Wang et al., 2013;Fang et al., 2013).

Although spatial heterogeneities existed between potential values induced by H_2SO_4 and HNO_3 in 2005 and 2010, the PA in 2010 increased by 2.4% compared with that in 2005. Combing the change of S /N from 2005 to 2010, the very close PA values in the two years confirmed that the policy only controlling SO_2 emissions had not an obvious effect on alleviating acid rain pollution. A similar conclusion was obtained through MODELS-3/Community Multiscale Air Quality system (V4.4), in which they

concluded that the benefits of SO_2 reductions during 2005-2010 might be negated by increased N emissions (Zhao et al., 2009).

On the map of potential acidity in 2016, the spatial pattern has changed greatly from those in 2005 and 2010. The hotspots with PA higher than 40,000 are very few, and were mainly located in the northern China. The big hotspot areas in 2010 occured in Sichuan, Guizhou, and Guangdong Provinces were gone in 2016, and some small hotspot areas in Ningxia, Hubei, Guangxi, Guangdong were also lost, meaning that the PA has significantly decreased in these areas. The heavily acid regions extending from the northeast to the Yangtze areas in 2010 have obviously decreased in 2016. While in the western China, the PA increased around the Urumqi and in Yunnan, Sichuan and Xizang. If the PA increased further in the coming years, the acid pollution might be higher in these regions although PA is still low at present. The increased PA in Western China should be paid attention by the government or the policy makers.

It should be noted here that the spatial pattern of PA is not consistent with that of the precipitation pH (Fig S2). The reason for the acidity of precipitation are complex, and many of the primary influencing factors such as sulfide emissions caused by fossil fuel consumption, atmospheric diffusion capacity, and the neutralization capability of atmospheric aerosol have strong regional variations in China (Li, 1998). Although the spatial pattern of PA and precipitation pH were different, both of them showed the acid pollution had decreased in 2016 even compared with 2005 and 2010.

3.5 Uncertainties

Since the ABL SO_2 and NO_2 could indicate the variations of SO_4^{2-} and NO_3^- in precipitation, the uncertainty induced by OMI NO_2 columns should be considered in this study. The uncertainty in satellite-based vertical columns is dominated by air mass factors, which have been discussed in detail

in a number of previous studies (Boersma et al., 2004;Nowlan et al., 2014;Zyrichidou et al., 2013). Especially in the western China where the values of SO_2 and NO_2 were relative low, errors of the ABL SO_2 and NO_2 columns might be high.

This study only considered the potential acidity induced by the SO_4^{2-} and NO_3^- the organic acid was not involved. Although the contribution of organic acids to precipitation pH was minor, it could not be neglected, particularly in forest and suburban areas (Stavrakou et al., 2012;Willey et al., 2011). In these areas, the contribution of organic acids on precipitation pH was much higher than in urban areas.

This study mainly discussed the change of acidic species in precipitations, but the neutralization should be fully considered when the precipitation pH is studied. The implementation of particulate matter reduction policy has not only resulted in the decreasing trend of the acid-related compound, but also the decrease of alkaline species in precipitation (Zhao et al., 2009;Wang et al., 2012;Tang et al., 2010). However, the neutralizing is not considered in this study.

4. Conclusions

The effect of national NO_x and SO_2 policies on acid components in precipitation was assessed in China, based on the OMI ABL SO_2 and NO2 columns. The OMI information on S and N obtained a reliable indicator on the variations of SO_4^{2-} / NO_3^- in precipitation. The long-term trend of S / N in precipitation significantly decreased from 2005 to 2016 in China, which meant the contribution of nitrates getting higher on precipitation pH. This decline of S / N in precipitation was mainly due to the national NO_x and SO_2 policies enacted at different times. Under such policies, SO_2 showed a decreasing trend while NO_2 showed the increasing first then decreasing trend from 2005 to 2016. The ABL SO_2 and NO_2 columns had a good consistency with those of emissions, but they were also greatly influenced by the precipitation amounts. Particularly for the year of 2011, SO_2 and NO_2 got their peaks, respectively,

mainly due to the joint contribution from the lowest precipitation amounts and high emissions in 2011. The spatial distribution of S / N in precipitation showed considerable regional variations in China. The low values were mainly located in East China, and the areas around Urumqi in Northwest China, which is close to the spatial distribution of population densities. The highly developed traffics in the densely populated areas, and the more widespread application of the FGD than SCR in power units might be the main reasons for the low S / N in the mentioned regions.

The potential acidity of S and N in precipitation increased first from 2005 to 2011 and then decreased from 2011 to 2016. The increased PA indicated that the benefits of SO_2 reductions during 2005-2010 might be offset by increased N emissions obtained by the previous studies, while the decreased PA from 2011 to 2016 indicated that the national NO_x and SO_2 policies issued in 12^{th} Five Plan are in effect.

Author contribution

Xiuying Zhang conceived and designed the methodology and wrote the paper with Dongmei Chen. Lei Liu, Limin Zhao, and Wuting Zhang help to process the data sets.

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Competing interests

The authors declare that they have no conflict of interest.

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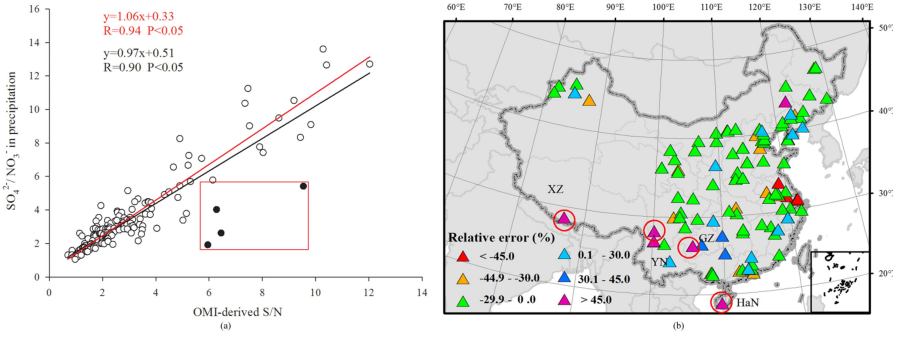

Fig. 1. (a) Scatter plots of the OMI-derived S / N and the collected SO_4^{2-} / NO_3^- in precipitation; (b) spatial distribution of the relative errors between the OMI-derived S / N and the collected ratio of SO_4^{2-} / NO_3^- in precipitation

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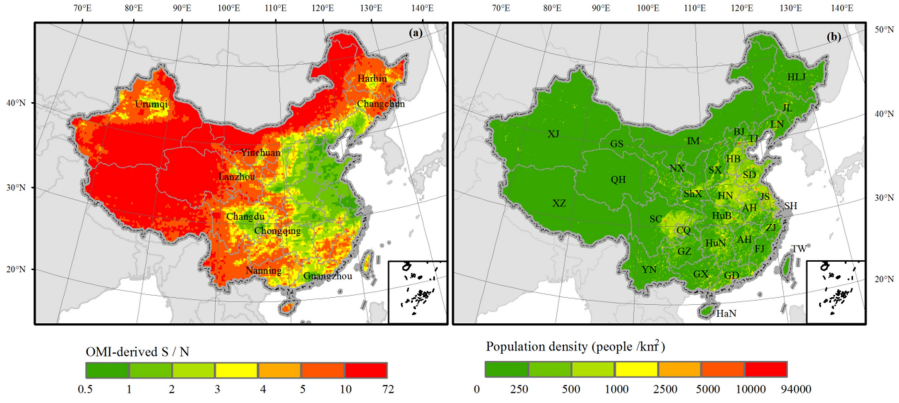

Fig. 2. Spatial distribution of (a) OMI-derived S / N in 2016 and (b) the population density in China. The successfully full provincial names are Beijing (BJ), Tianjin (TJ), Hebei (HeB), Shandong (SD), Shanxi (SX), Henan (HeN), Shaanxi (SaX), Liaoning (LN), Jilin (JL), Heilongjiang (HLJ), Neimenggu (NMG), Gansu (GS), Ningxia (NX), Xinjiang (XJ), Shanghai (SH), Jiangsu (JS), Zhejiang (ZJ), Anhui (AH), Hubei (HuB), Hunan (HuN), Jiangxi (JX), Fujian (FJ), Guangdong (GD), Hainan (HaN), Yunnan (YN), Guizhou (GZ), Chongqing (CQ), Sichuan (SC), Guangxi (GX), Xizang (XZ), Qinghai (QH), and Taiwan (TW).

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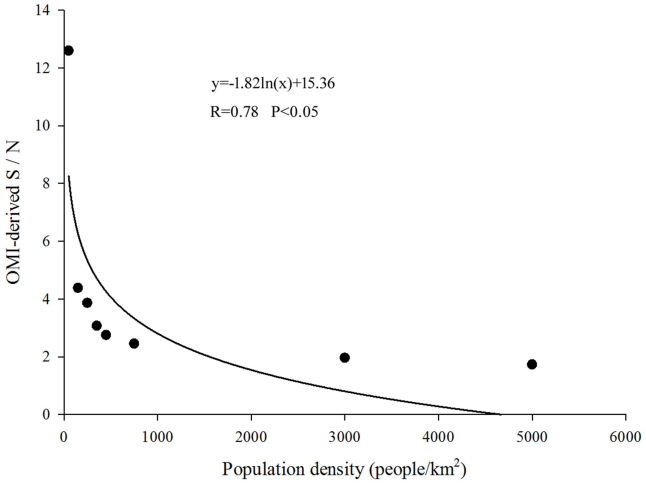

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Fig. 3. Relationship between Omi-derived S / N and population density

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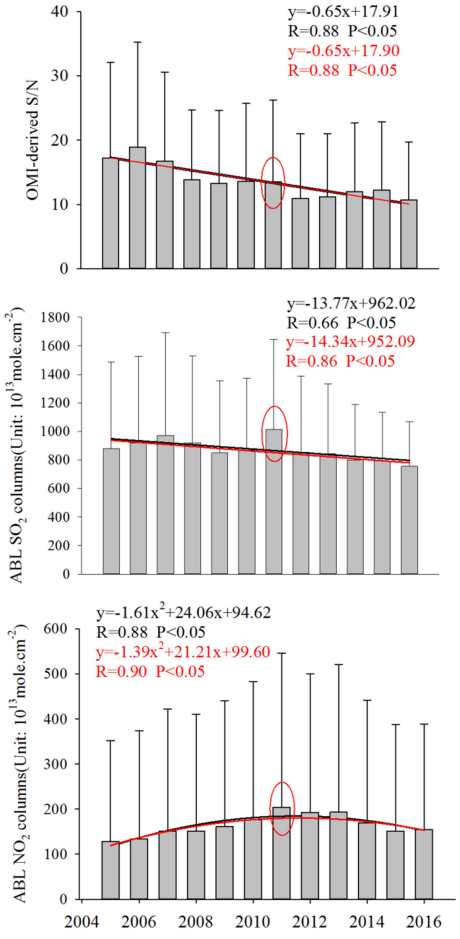

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591 **Fig. 4.** Long-term trends of OMI-derived S / N, ABL SO_2 columns, ABL NO_2 columns from 2005 to 2016 in China

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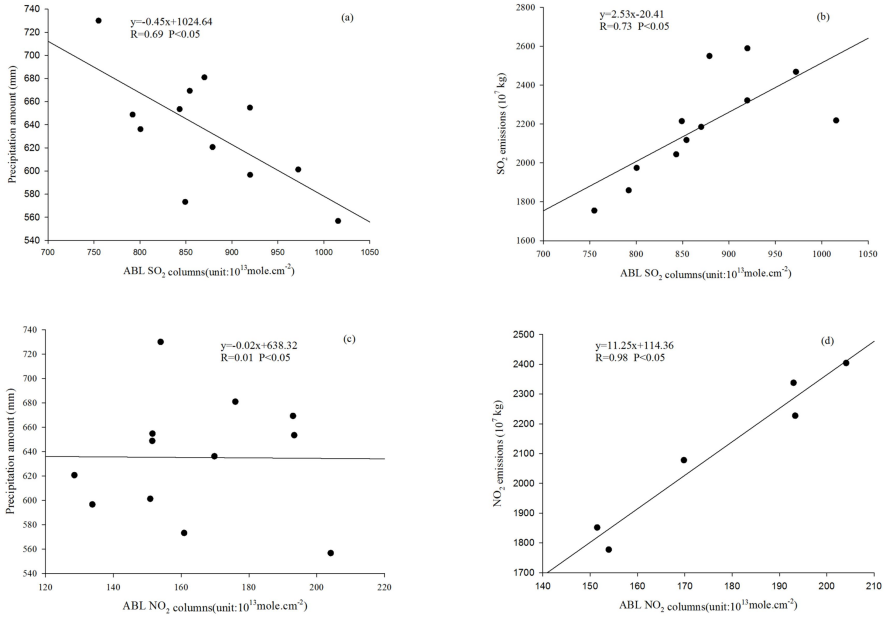

Fig. 5. Relationship between the (a) ABL SO_2 columns and precipitation amounts, (b) ABL SO_2 columns and SO_2 emissions, (c) ABL NO_2 columns and precipitation amounts, (b) ABL NO_2 columns and NOx emissions

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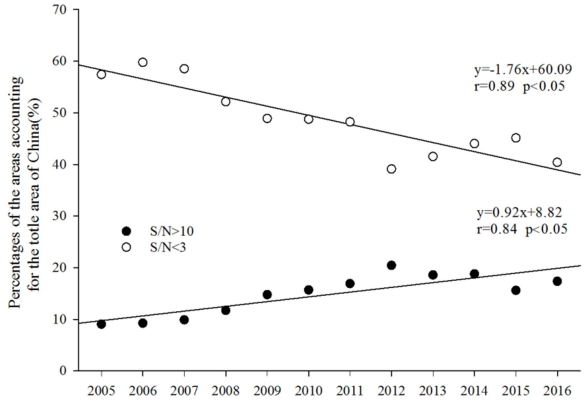

596

597 **Fig.6.** Percentages of the areas with mixed acidic precipitation types from 2005 to 2016

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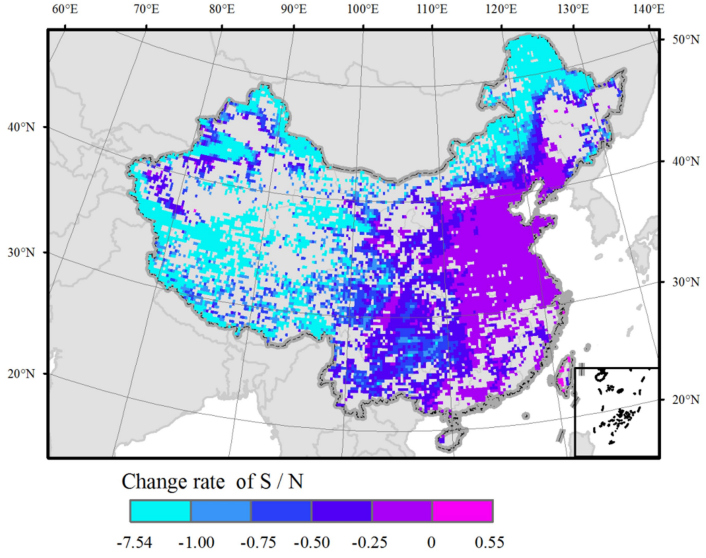

598
599 **Fig.7.** Linear trend per year for the ratio of OMI-derived S/ N in from 2005 to 2016 derived from OMI. For the light grey areas
600 no significant trend has been found in the time series.

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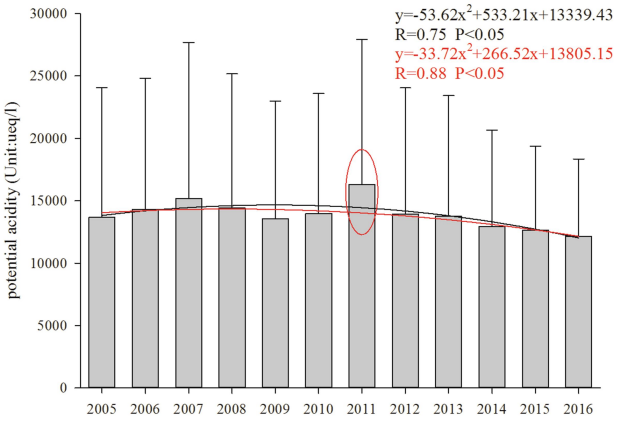

601
602
603 **Fig. 8.** Trends of potential acidity induced by SO_4^{2-} and NO_3^- from 2005 to 2016 in China
604

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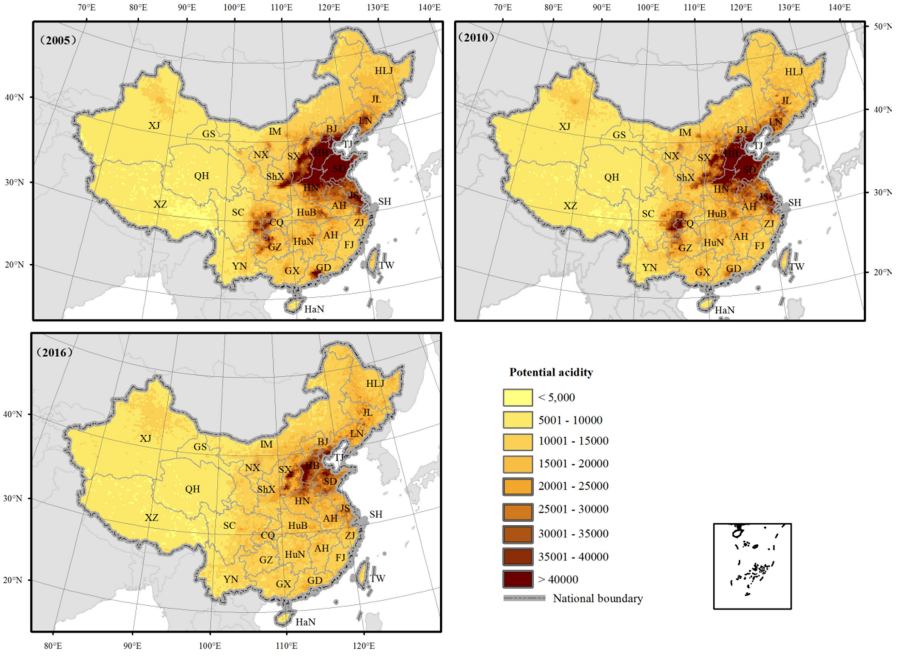

605
606 **Fig. 9**. Spatial distributions of potential acidity in 2005, 2010, and 2016 in China. The successfully full provincial names are the
607 same with **Fig. 2**.
608
609