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1   **Increased inorganic aerosol fraction contributes to air pollution and**

2   **haze in China**

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Abstract

23   The detailed formation mechanism of increased number of haze events in China is

24   still not very clear. Here, we found that reduced surface visibility and an increase in

25   satellite derived columnar concentration of inorganic precursor concentrations are

26   connected with each other. Typically higher inorganic mass fractions lead to increased

27   aerosol water uptake and light scattering ability in elevated relative humidity. Satellite

28   observation of aerosol precursors of NO_2 and SO_2 showed increased concentrations

29   during study period. Our in-situ measurement of aerosol chemical composition in

30   Beijing also confirmed increased contribution of inorganic aerosol fraction as a function

31   of increased particle pollution level. Our investigations demonstrate that the increased

32   inorganic fraction in the aerosol particles is a key component in the frequently occurring

33   haze days during studying period, and particularly the reduction of nitrate, sulfate and

34   their precursor gases would contribute towards better air quality in China.

Introduction

36   As one of the most heavily polluted regions in the world, China has suffered from

37   air pollution for decades (Hao et al., 2007; Zhang et al., 2015). Aerosol particles, as

38   major air pollutant, have significant effects on human health (Lelieveld et al., 2015).

39   The general public and the central government in China have realized the severe

40   situation and have taken some measures to improve the air quality nationwide in the

41   recent years. For example, the state council published a plan for air pollution control,

42   in September of 2013, aim to reduce $PM_{2.5}$ concentrations by 10%~25% in different

43   regions of China. The successful implementation requires a sufficient knowledge of

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44   haze formation mechanism (Kulmala, 2015) and comprehensive observation network

45   (Kulmala, 2018). Our understanding on haze events with high $PM_{2.5}$ concentrations in

46   China is still limited due to the spatial-temporal variation of aerosol properties and

47   limited observation information (Wang et al., 2016). Recent studies found that

48   secondary aerosol components are important during the intense haze events in Beijing,

49   Xi'an, Chengdu and Guangzhou during January of 2013, and the reduction of aerosol

50   precursors is a key step to reduce particle pollution (Guo et al., 2014; Huang et al.,

51   2014). The analysis of longer time series data from Nanjing shows that secondary

52   particles are typically dominating even the number concentrations in polluted

53   conditions (Kulmala M., 2016). The most abundant mass fractions of atmospheric

54   aerosol are inorganic and organic components, which have large spatio-temporal

55   variation (Jimenez et al., 2009). Identifying the most abundant as well as critical aerosol

56   species that contribute to the haze formation in a longtime perspective is important to

57   draw up effective plans for the air pollution control.

58   Here, we used comprehensive data sets to reveal that an increasing trend of

59   inorganic components in atmospheric aerosol may be a pivotal factor, at least, which

60   leads to frequently occurred haze events in China from 1980-2010. As a result, the

61   controlling of inorganic aerosol components of nitrate, sulfate and their precursors

62   should be of a high priority.

2.Methodology

64   The daily averaged visibility and relative humidity data in 262 sites of China are

65   obtained from the Integrated Surface Dataset (ISD) from National Oceanic and

66   Atmospheric Administration National Climate Data Center of the USA

67   (https://www.ncdc.noaa.gov/isd). The visibility observations were made three times a

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68   day at 8-hour intervals begins at 00:00 by well trained technicians. They measured

69   visual range using distinctive markers, such as tall buildings, mountains and towers,

70   to which the distance from the meteorological monitoring stations are known. First,

71   we quantified the importance of relative humidity to visibility as the hygroscopic

72   inorganic compounds typically grow in size in high humidity(Swietlicki et al., 2008).

73   In this study, for a given site and given year, we used the observed annual visibility

74   (V) as a ratio (R_i) between visibility values from the surface observation stations,

75   when the daily average RH was below 40% for more than 20 days. In the

76   corresponding high-humidity cases daily RH was between 80%~90% for more than

77   20 days each year at a given observation site:

78

79   $$R_i = \frac{V_{dry}}{V_{wet}}.$$

80   We use this ratio to infer long trend of aerosol hygroscopicity information. In

81   addition, we calculate anomaly (A) from the ratio for a given year i as a difference from

82   the 30-year (R_{30y}) from 1980 to 2010:

83   $$A = R_i - R_{30y}.$$

84   Our spatial focus is placed on North China Plain, Yangtze River Plain and Sichuan

85   Basin due to frequent haze events (Zhang et al., 2012). The stations in Pearl River delta

86   region and other Southern China stations were not included due to limited days with

87   the daily average RH below 40%.

88   The atmospheric column amount of NO_2 and SO_2 data are obtained from

89   SCIAMACHY (Scanning Imaging Absorption spectrometer for Atmospheric

90   CHartographY) satellite products. Modeled aerosol chemical composition from GEOS

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91   (Goddard Earth Observing System) - Chem chemical transport model in China during

92   1998-2012 is used. The model utilizes assimilated meteorology data and regional

93   emission inventories with a horizontal resolution of 2°×2° with 47 vertical levels from

94   surface to 80 km. The detailed information about the model can be found in (Boys et

95   al., 2014). Aerosol chemical composition of organic, sulfate, nitrate, ammonium and

96   chloride were measured with a high-resolution-time of flight-aerosol mass

97   spectrometers (DeCarlo et al., 2006). Detailed information of data analysis, collection

98   efficiencies (CE) and relative ionization efficiencies are presented in Zhang et al. (2014).

99   **3. Results and discussion**

100   **3.1 Decreasing trend in visibility in high relative humidity conditions**

101   According to the geographical division, our study sites are mainly in North China

102   Plain (NCP), Sichuan Basin (SCB) and Yangtze River Plain (YRP) as showed in Figure

103   1. Looking at the time series as a whole, the visibility in dry (RH <40%) condition did

104   not have a clear trend in Yangze River Plain and Sichuan Bsain region, whereas

105   visibility in high RH (80%~90%) conditions showed a decreasing trend. The average

106   ratio of visibility in low RH to that in high RH from 1980-2010 is presented in Figure

107   1. The maximum ratios were identified in eastern China and in some western Chinese

108   cities. Overall, the enhancement factor due to hygroscopicity is within expected values

109   both from modeling and observation results (van Donkelaar et al., 2010; Xin et al.,

110   2015). The higher ratios occurred in more severe air pollution areas, like North China

111   Plain, Sichuan Basin and the city of Urumqi, where the contribution of hygroscopic

112   aerosol is more pronounced in comparison with non-hygroscopic dust particles. Long

113   time trends of this ratio in a specific site can reveal the variation of aerosol inorganic

114   fraction and organic fraction due to their different hygroscopicity and water uptake

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115   capacity and associated light extinction ability. That is, the mass fractions and

116   concentrations of sulfate, nitrate and ammonium may have increased over study period

117   as they dominate water uptake ability compared with other components (e.g., organic,

118   black carbon, dust and metal elements) in the atmospheric aerosol (Wang et al., 2015).

119   For the selected regions, we have calculated the anomaly as a regional average as shown

120   in Figure 2. The ratio showed increasing trends over three regions of China and the

121   maximum trends occurred in North China Plain with the value of 0.0168 per year,

122   which indicate an increase of hygroscopic aerosol in these regions during the 30-year

123   observation period.

124   To corroborate our results, Yang et al. (2011) showed an increasing fraction of

125   inorganic components by 20% in Beijing from 1998 to 2008, especially in summer,

126   while the fractions of hydrophobic components such as organic and black carbon

127   decreased in the aerosol phase. A recent study by Boys et al. (2014) revealed that

128   increasing fraction of secondary inorganic aerosol is dominated in the increased mass

129   concentration of $PM_{2.5}$ in China from 1998-2012. Due to the increase in hygroscopic

130   inorganic aerosol composition, the number of haze days have significantly increased in

131   the past three decades over North China Plain (Fu et al., 2014).

132   **3.2 Enhanced emissions of inorganic aerosol precursors**

133   The longterm trends of aerosol precursors and their spatial variability can improve

134   our understanding of the trends in aerosol chemical composition. Figure 3 and Figure

135   4 show atmospheric column trends of NO_2 and SO_2 observed from SCIAMACHY. The

136   column NO_2 level can be a good proxy for vehicle and coal burning emission associated

137   with oil and coal consumption (Richter et al., 2005). The column amount of NO_2

138   showed pronounced increasing trends in three regions of China, particularly in Northern

139 China with the value of 0.14 $\times 10^{15}$ molecule/cm^2/year from 2002 to 2011. This is

140 probably associated with the increase in power plant and on-road vehicle emissions

141 (Wu et al., 2012). The average NO$_2$ concentration in Northern China increased by more

142 than two-fold, while in the Yangze River Plain region experienced a considerable

143 smaller trend in NO$_2$, with the value of 9.7 $\times 10^{15}$ molecule/cm^2 in 2010 and 6.4 $\times 10^{15}$

144 molecule/cm^2 in 2002. As a whole, the column NO$_2$ concentration in China doubled

145 from 2002 to 2010, with the values of 1.4$\times 10^{15}$ molecule/cm^2 in 2002 and 2.8 $\times 10^{15}$

146 molecule/cm^2 in 2010, respectively.

147 Figure 4 depicts trend in SO$_2$ concentration in four regions of China from 2004 to

148 2010. The SO$_2$ concentration showed and increasing trends in North China Plain,

149 Sichuan Basin and Yangze River Plain, but nearly a constant trend in China as a whole.

150 A decreasing trend was observed during the year of 2008 and 2009, especially in

151 Northern China Plain. This may be due to a combination of Chinese economic

152 downturn and emission reduction during the Olympic games (Lin and McElroy, 2011)

153 (Wang et al., 2010). Anyway, the aerosol precursor of NO$_2$ showed the most increasing

154 trend in China, consistent with the trend of increased aerosol concentration (Xing et al.,

155 2015) . Figure S1 shows the annual trends of aerosol inorganic fraction in PM$_{2.5}$ mass

156 concentration from 1998-2012 with GEOS-Chem model in China. The results indicate

157 that North China Plain area suffered the most from heavily pollution, consistent with

158 our surface observations as well as earlier work (Xin et al., 2015). Aerosol concentrations

159 have increased considereably from 1980 to 2010. The modeling results show that concurrently

160 the fraction of inorganic fractio`n has increased more rapidly. Consequently the water uptake

161 of the aerosol have increased leading to reduced visibility, which is consistent with our ground-

162 based observations.

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163 3.3 Validation of increased inorganic aerosol components with elevated air

164 pollution level with in-situ measurement

165   To validate our hypothesis that the increased inorganic components contribute to

166 visibility degradation, we used four months of aerosol chemical composition and

167 visibility data from urban Beijing from November of 2010 to February of 2011. As

168 shown in Figure 5, we divided the visibility values into four bins, which corresponds to

169 clean time to heavy pollution time and to conditions in between. The inorganic aerosol

170 precursors of SO_2 and NO_x doubled as the visibility decreased from more than 10 km

171 (clean time) to less than 2 km (heavily polluted time). At the same time, the mass

172 concentration of nitrate, sulfate and ammonium components increased to 13.5 μg m^{-3},

173 15.5 μg m^{-3} and 10.6 μg m^{-3}, respectively. Meanwhile, the mass fraction of these

174 inorganics increased from 11% to 13%, from 14% to 21% and from 10% to 14%,

175 respectively. At the same time, the mass concentration and fraction of organic

176 components decreased from12.2 μg m^{-3} to 33.4 μg m^{-3} and 60% to 46%, respectively.

177 This direct observation shows that the contribution of inorganic components increased

178 during this campaign. It is plausible that the increased concentration of SO_2 and NO_x

179 are highly associated with this giving rise to the long-term trends observed in Figure 2

180 (Pan et al., 2016; Wang et al., 2014).

181

182 4. Conclusion and implication for atmospheric air pollution control

183   Atmospheric pollution and associated haze events has a dramatic effect on climate

184 change, human health and visibility degradation (Ding et al., 2013; Petäjä et al., 2016;

185 Wang et al., 2015; Zhang et al., 2015). Here, longterm visibility measurements

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186   combined with satellite data sets, in-situ measurements and model results revealed that

187   increased fractions of inorganic aerosol components in the particle matter are crucial in

188   contributing to more haze events.   In this way, aerosol hygroscopic growth has

189   occurred in lower relative humidity conditions than before due to more ammonium

190   nitrate aerosol, and the light scattering ability of atmospheric aerosol enhanced as

191   shown in Figure 6. Another mechanism is that high concentration of NO_x can promote

192   the conversion of SO_2 to form sulfate aerosol via aqueous phase oxidation during

193   intensive pollution periods (He et al., 2014; Wang et al., 2016). Considering the vast

194   energy consumption in the future decades and the sources of inorganic components in

195   atmospheric aerosol, we denmonstrate that the reduction nitrate, sulfate, ammonium

196   and their precursors maybe more critical in China.

197

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205

206   **Competing financial interests**

207   The authors declare no competing financial interests.

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Author contributions

208

209   Y.H.W had the original idea. L.L.W and C.S.G provided and processed satellite and

210   visibility data. Y.S.W provided measurements of aerosol chemical composition

211   data.Y.H.W, Y.S.W, L.L.W, T.P and M.K interpreted the data and write the paper.

212   All the authors commented on the paper.

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288   Figure caption
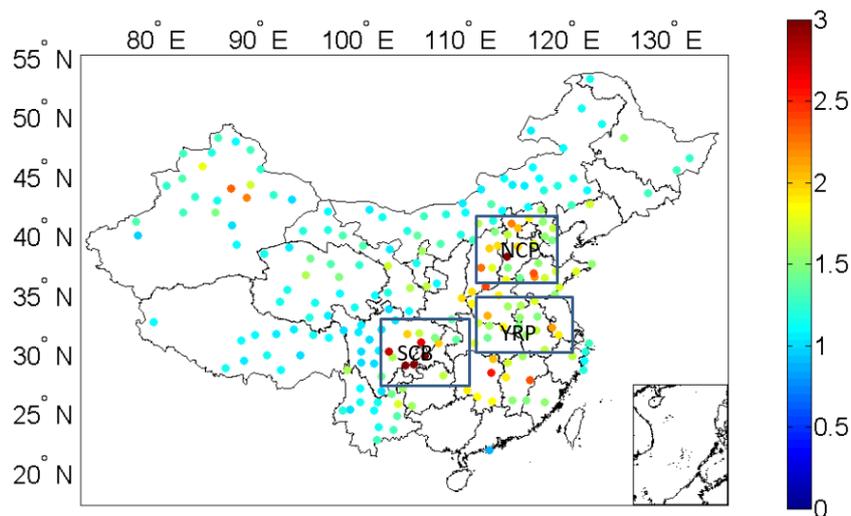
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290   **Figure 1.** The distribution of the average surface visibility ratio in dry and wet

291   conditions based on observations at 262 surface observation sites in China. The

292   aerosol in the industrialized regions of China in the East are more hygroscopic than

293   aerosol particles in the west of China.
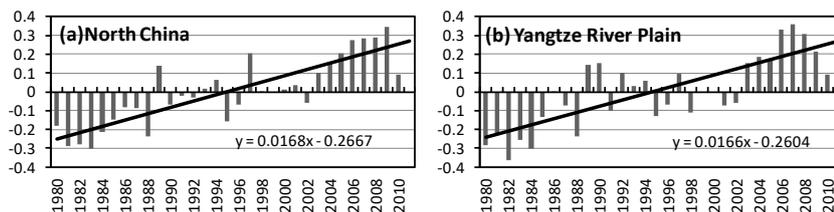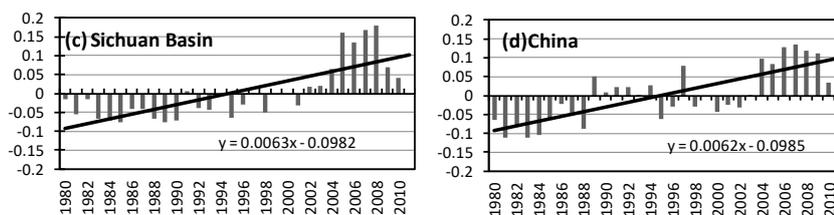
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Figure 2. Anomalies and trends of ratio of visibility in North China Plain, Yangtze

Plain, Sichuan Basin and in China as a whole. The relative contribution of

hygroscopic aerosols to the visibility reduction has increased from 1980 to 2010 in

China.

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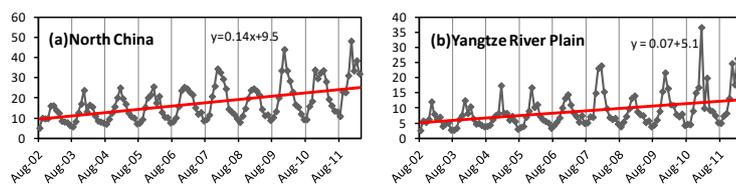
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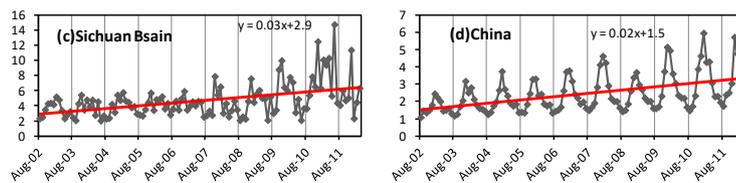
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318   Figure 3. Trends of NO$_2$ concentration over china from SCIAMACHY from the year
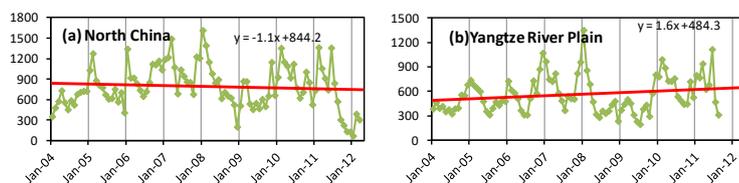
319   2002 to 2012 (10^{15} mol/cm^2)

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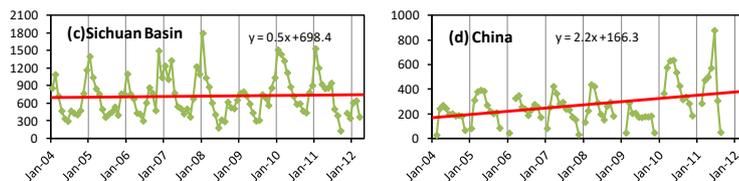
Figure 4. Trends of SO_2 concentration over china from SCIAMACHY from the year of
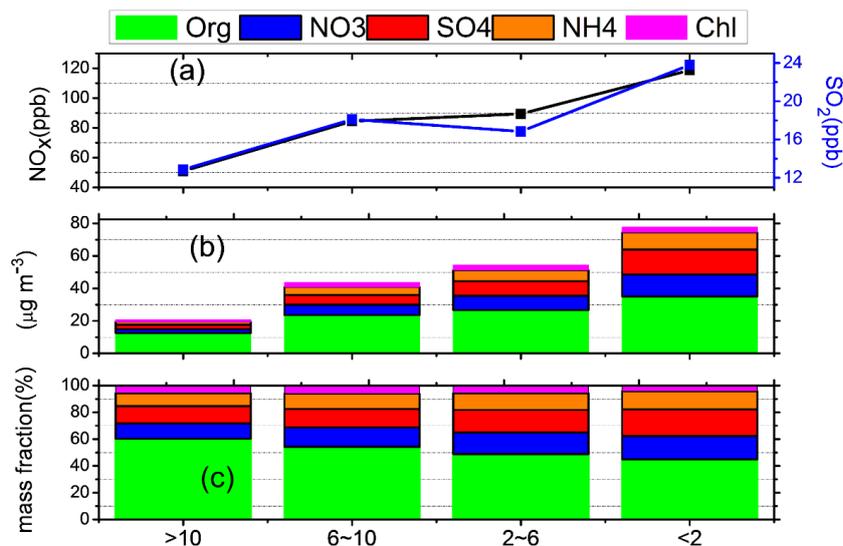
2004 to 2012 (1000DU)
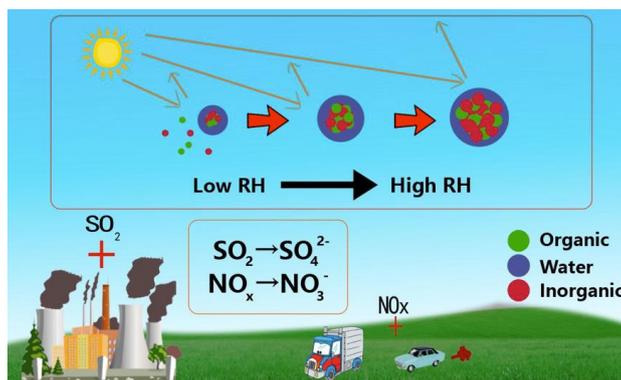
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Figure 5: Variation of (a) NO_x, SO_2, (b) chemical composition (c) mass fraction of

organic, nitrate, sulfate, ammonium and chloride with decreased visibility during the

intensive campaign in Beijing.

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352   Figure 6. A schematic picture illustrating the process of enhanced emission of

353   aerosol inorganic precusors and formation of aerosol inorganic components leading to

354   increased hygroscopicity and aerosol water uptake ability leading to considerable

355   visibility degradation in China. The plus symbols represents the strengthening of a

356   specific process.

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