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Increasing Ammonia Concentrations Reduce the Effectiveness of Particle Pollution Control Achieved via SO_2 and NO_X Emissions Reduction in East China

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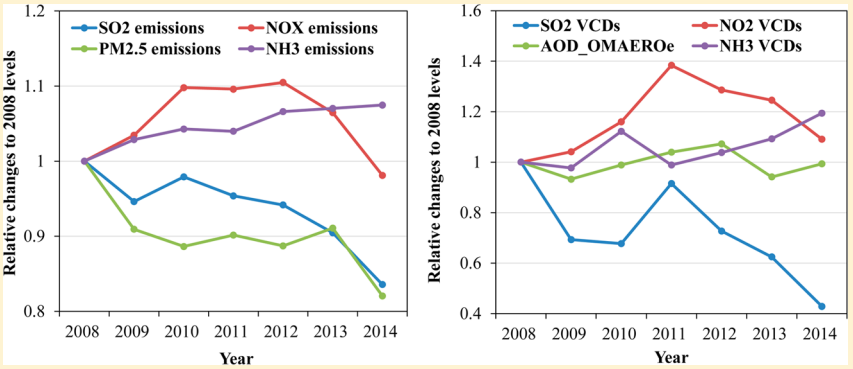
Supporting Information



ABSTRACT: Atmospheric ammonia (NH_3) plays a crucial role in the formation of secondary inorganic aerosols (SIAs). Although China produces a large amount of NH_3 emissions, it has not yet taken any measures to control NH_3 emissions. Satellite retrievals show that NH_3 vertical column densities (VCDs) have obviously increased in recent years, by approximately 20% from 2011 to 2014, in contrast to the decreases seen for SO_2 and NO_X VCDs. Evidence of the ground-based observations and satellite retrievals indicates that the increases in NH_3 concentrations have weakened the benefits of the reduction in SIA concentrations (especially for nitrate) from SO_2 and NO_X emissions control. Results from model simulations suggest that the simultaneous control of NH_3 emissions in conjunction with SO_2 and NO_X emissions is more effective in reducing particulate matter (PM) pollution than the process without NH_3 emissions control is. Our findings indicate that the continual increases in free NH_3 concentrations can result in a lower sensitivity of PM reduction to NH_3 emissions control in the future, and reducing NH_3 emissions is urgently required for the effective control of PM pollution in China.

1. INTRODUCTION

NH_3, which is one of the important atmospheric components and the major form of reactive nitrogen, can affect atmospheric nitrogen chemistry and particle formation. Recent studies have suggested that increases in NH_3 emissions are responsible for soil acidification, water eutrophication, biodiversity loss, and perturbation of ecosystems.[1,2] As the most abundant alkaline gas in the atmosphere, NH_3 plays a key role in the formation of secondary aerosols, which account for a large fraction of the total fine particles in China.[3,4] NH_3 can react with sulfuric and nitric acid to generate ammonium sulfate, ammonium bisulfate, or ammonium nitrate, thereby increasing secondary inorganic aerosol (SIA) concentrations. Additionally, NH_3 can enhance the yield of secondary organic aerosols (SOAs) through aqueous chemistry.[5] Therefore, NH_3 is a key component for particle pollution.

Major sources of NH_3 are agricultural activities, including livestock and fertilizer use.[6,7] As China is one of the largest agricultural and meat producers in the world, the increasing demands for grain and meat may increase NH_3 emissions in China. Meanwhile, NH_3 emissions can also increase because of global warming.[8] In addition to agricultural sources, some researchers[9,10] mentioned the importance of nonagricultural

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sources (e.g., vehicles, coal combustion, etc.), especially in urban areas.

Since 2005, China has taken effective measures to control the emissions of primary particles SO_2 and NO_X.[11] Satellite observations indicated that SO_2 and NO_2 concentrations declined, especially during the 12th Five-Year Plan period (2011−2015).[12] However, until now, NH_3 has not attracted much attention. There is a lack of knowledge about the historical trends of NH_3 concentration levels and the effects of NH_3 on PM pollution in China.

In this study, satellite and ground observations were used to investigate the historical trends of atmospheric NH_3 concentrations in Eastern China from 2008 to 2014. Possible causes of historical changes in NH_3 concentrations and their effects on PM pollution were also explored to provide useful insights for policy-making in improving air quality in China.

2. MATERIALS AND METHODS

2.1. Satellite Observations. Satellite observations can provide information about the spatial and temporal patterns of NH_3 on a larger and longer scale. In this study, we analyzed seven years (2008−2014) of NH_3 vertical column density (VCD) measurements from the infrared atmospheric sounding interferometer (IASI)/MetOp-A instrument[13] to investigate recent changes in the spatial and temporal patterns of NH_3 over China. The data were derived from level 2 retrieval products based on a flexible and robust NH_3 retrieval algorithm described in ref 14. The validation of IASI/MetOp-A NH_3 measurements has been discussed by Van Damme at al.[15] and Whitburn et al.[14] The IASI/MetOp-A instrument crosses the equator twice a day at 9:30 a.m. and 9:30 p.m. local time. In this study, we only used the data measured in the morning because the signal is more sensitive to NH_3 due to a favorable thermal contrast, resulting in smaller errors.[16] A weighted averaging method based on relative errors was used to process IASI observations, as described by Van Damme at al.[16] As shown in Figure S1, regional annual average relative errors in East China were 44−55%. Spatially, relative errors in the north part were lower (approximately 20−60%) than those in the south part with low NH_3 VCDs.

Historical trends of SO_2 VCDs, NO_2 VCDs, and atmospheric optical depth (AOD) were investigated for the same periods as NH_3 VCDs were. The satellite measurements from the ozone monitoring instrument (OMI) were used. For NO_2, monthly data retrieved by the Royal Netherlands Meteorological Institute (KNMI)[17] were adopted. Lin et al.[18] evaluated this data set and found NO_2 VCDs were consistent with ground observations. The OMI SO_2 data were derived from the daily level 3 data set OMSO2e released by the NASA Goddard Earth Sciences Data and Information Services Center.[19] Lee et al.[20] reported that the total errors of the SO_2 data were 44−80% for China. For AOD, we used the daily level 3 data set OMAEROe,[21] which was retrieved using the multiwavelength algorithm. The evaluation of the OMAEROe product has been discussed by Lin et al.[22] In this study, AODs at 342.5 nm were used. Additionally, AODs at 550 nm derived from the moderate-resolution imaging spectroradiometer (MODIS) onboard the Terra satellite were also used.

2.2. Ground Observations. In addition to NH_3 VCDs observed via satellite, we collected ground observations of NH_3 concentrations for four years (2011−2014) at four sites in the North China Plain,[23] including the China Agriculture University site in Beijing (urban; 40.02°N, 116.28°E), the Shangzhuang site (suburban; 40.11°N, 116.20°E), the Zhengzhou site (urban; 34.75°N, 113.63°E), and the Quzhou site (rural; 36.78°N, 114.94°E).

In China, the long-term observation data of SIA are very limited and not publicly available. In this study, we collected the annual average concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ for seven years (2008−2014) at three CAWNET (China Atmosphere Watch Network) sites,[24] including the Gucheng site (39.13°N, 115.80°E) in the Jing-Jin-Ji (JJJ) region, the Linan site (30.30°N, 119.73°E) in the Yangtze River Delta (YRD) region, and the Panyu site (23.00°N, 113.35°E) in the Pearl River Delta (PRD) region, as shown in Figure 1.

2.3. NH_3 Emission Inventory. To explore the effects of NH_3 emissions on NH_3 concentration variations, we estimated NH_3 emissions in China from 2008 to 2014 based on the emission factor method. Emission sectors include livestock, fertilizer application, chemical industry, biomass burning, human excrement, vehicles, coal combustion, and ammonia slip from selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR) systems. Activity data were collected at the provincial level on the basis of statistical yearbooks. Emission factors were extracted from the previous studies of NH_3 emissions.[25−28] Results showed that agricultural sources, including livestock and fertilizer application, were the most important emission sectors, accounting for 51.6 and 38.7% of total NH_3 emissions during 2008−2014, respectively. Human excrement, chemical industry, and other sources accounted for 5.2, 2.9, and 1.6% of total NH_3 emissions, respectively. Monte Carlo simulations[6,29,30] were conducted to estimate the uncertainties of the NH_3 emission inventories. The uncertainties were −38 to 59%, −38 to 62%, and −39 to 64% for 2008, 2011, and 2014, respectively.

2.4. Meteorological Data. Temperature is important for the partitioning of NH_3 to the aerosol phase, especially for ammonium nitrate (NH_4NO_3). To explore the effects of temperature changes on NH_3 concentration variations, we extracted 2 m temperatures from the European Centre for Medium-Range Weather Forecasts ERA-Interim reanalysis data.[31] This data set provides global meteorological assimilation data from 1979 to the present. Previous studies[32−35] have evaluated the reliability of these data over China.

3. RESULTS AND DISCUSSION

3.1. Trends in Atmospheric NH_3. Figure 2 shows the 12 month moving averages of tropospheric SO_2, NO_X, and NH_3 VCDs observed via satellite as well as AODs normalized to the levels of June 2008 for Eastern China between 2008 and 2014. NH_3 VCDs increased by approximately 20% from 2008 to 2014. In particular, from 2011, NH_3 VCDs showed a continuously increasing trend ($p < 0.05$). Surface observations[23] demonstrated that NH_3 concentrations at the four sites have increased by 15−95% from 2011 to 2014.

We further investigated the trends in three key regions with the most developed economy and highest population densities in China (Figure 1): (1) the Jing-Jin-Ji (JJJ) region, including Beijing, Tianjin, and Hebei; (2) the Yangtze River Delta (YRD) region, including Jiangsu, Zhejiang, and Shanghai; and (3) the Pearl River Delta (PRD) region, here referring to the entirety of Guangdong province. As shown in Figure 3 and Table 1, during 2008−2011, NH_3 VCDs in the YRD and PRD regions increased by 6.5% ($p < 0.05$) and 11.7% ($p < 0.15$), respectively, but NH_3 VCDs in the JJJ region decreased by approximately 22.7% ($p < 0.05$). During 2011−2014, NH_3 VCDs in all the three regions exhibited increasing trends ($p < 0.05$). In the JJJ and PRD

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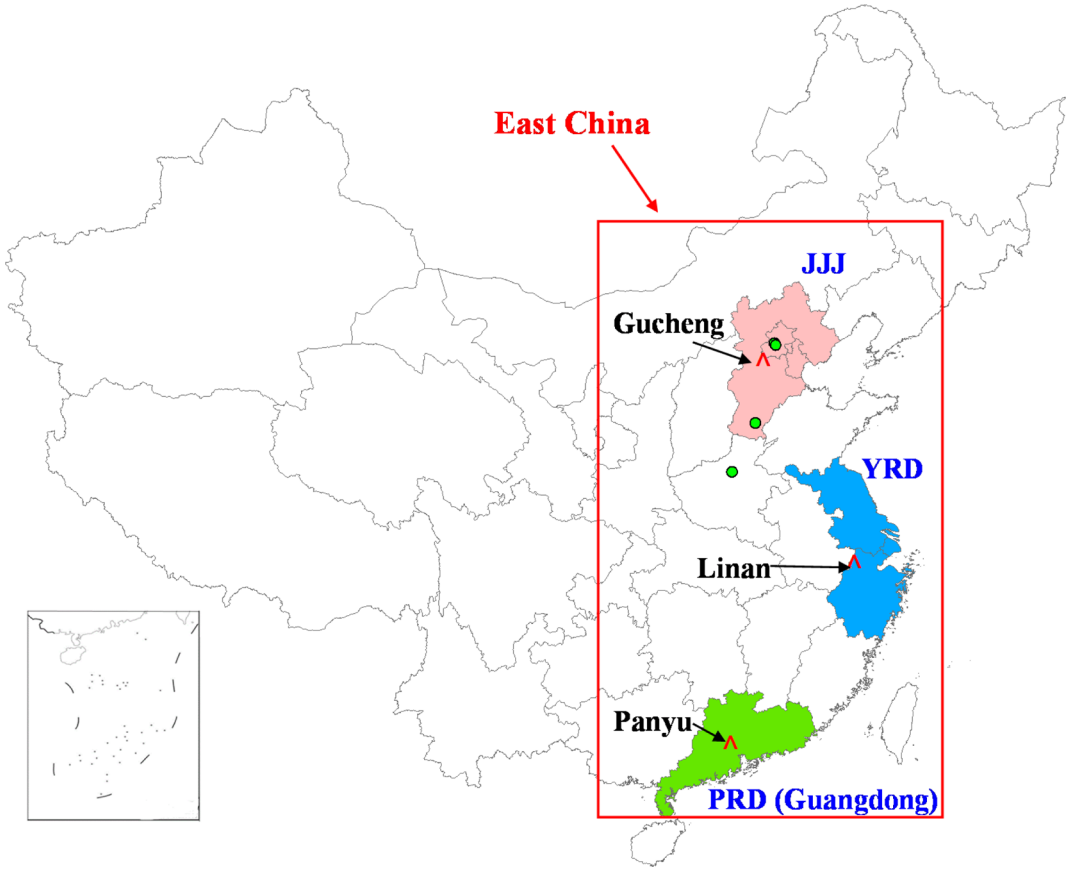

Figure 1. Target regions: East China, Jing-Jin-Ji (JJJ), Yangtze River Delta (YRD), and Pearl River Delta (PRD). The red symbols represent the three observation sites for SIA concentrations, and the green symbols represent the four surface NH_3 monitoring sites.

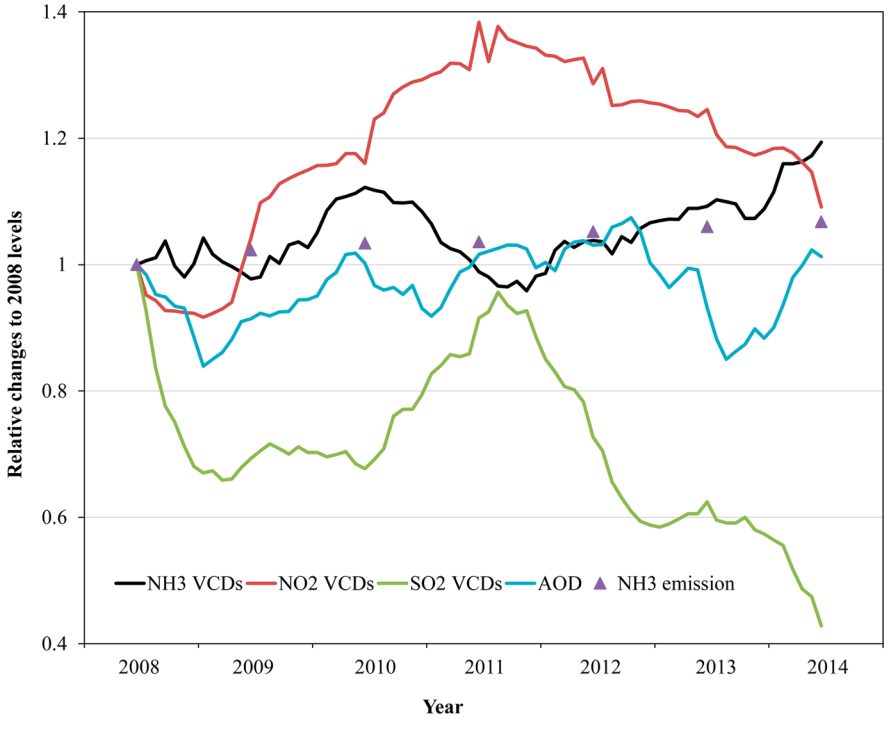

Figure 2. Interannual trends in SO_2 VCDs, NO_2 VCDs, NH_3 VCDs, AOD_ OMAEROe, and NH_3 emissions over East China from 2008 to 2014. All the years are normalized to the year 2008.

regions, the increasing percentages were higher (approximately 29.6 and 19.6%, respectively). In the YRD region, the increasing percentage was relatively lower (~5.7%) because NH_3 VCDs in Zhejiang province has declined by −15.7%.

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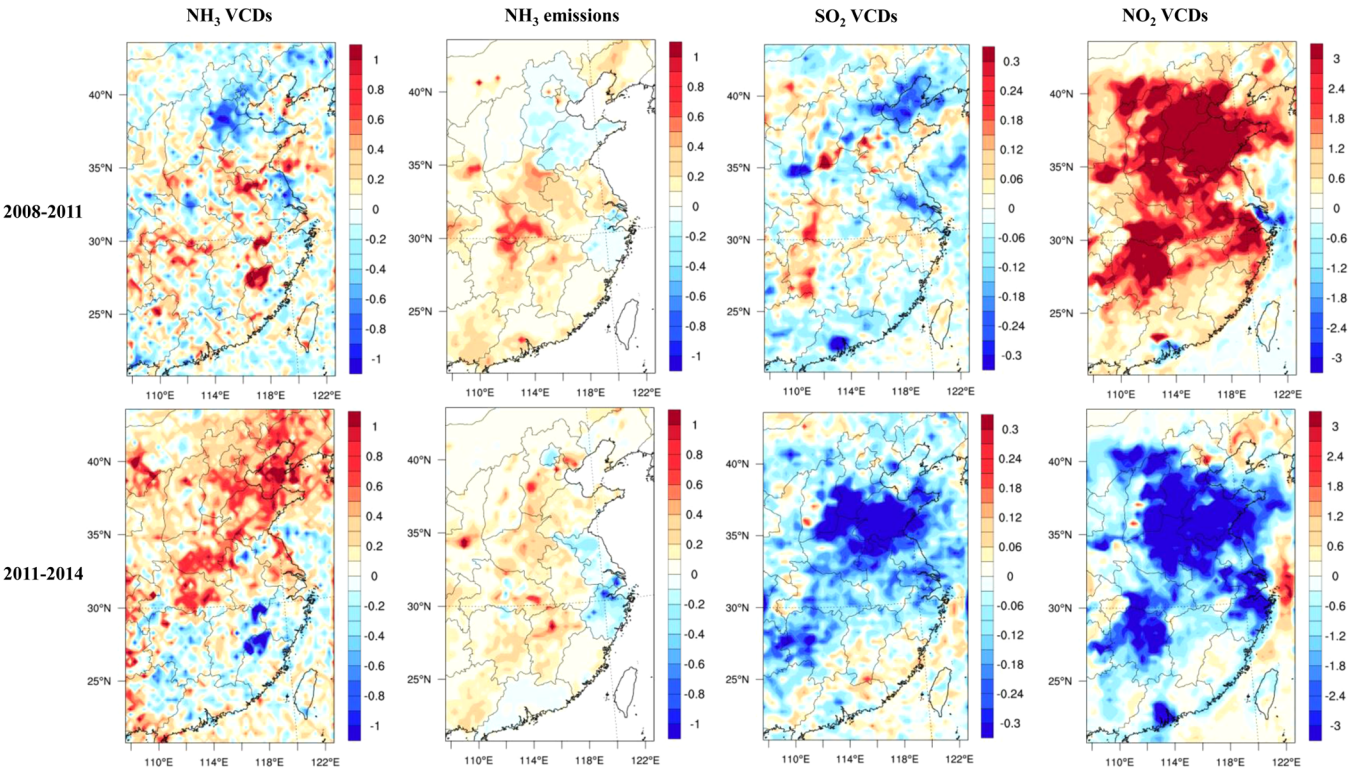

Figure 3. Spatial distribution of changes for SO_2 VCDs (unit, Dobson units), NO_2 VCDs (unit, 10^{15} molecules per square centimeter), NH_3 VCDs (unit, 10^{16} molecules per square centimeter), and annual NH_3 emissions (unit, kilotons) from 2008 to 2011 and from 2011 to 2014.

Table 1. Changes in NH_3 VCDs, NH_3 Emissions, SO_2 VCDs, NO_2 VCDs, and AODs for East China, in the JJJ, YRD, and PRD Regions from 2008 to 2011 and from 2011 to 2014[a]

		2011−2008				2014−2011			
		East China	JJJ	YRD	PRD	East China	JJJ	YRD	PRD
NH_3 VCDs	%	−1.1	−22.7	6.5	**11.7**	20.7	29.6	5.7	19.6
	p value	<0.05	<0.05	<0.05	**<0.15**	<0.05	<0.05	<0.05	<0.05
NH_3 emissions	%	**4.0**	−0.5	0.9	**4.5**	**3.4**	3.8	**-4.4**	0.1
	p value	**<0.15**	—	—	**<0.1**	**<0.15**	<0.05	**<0.1**	—
SO_2 VCDs	%	−8.5	−13.1	−15.6	−74.0	−53.2	−36.8	−68.9	−52.8
	p value	—	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_2 VCDs	%	38.4	40.3	19.8	7.1	−21.1	−17.0	−20.2	−16.5
	p value	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
AOD_ OMAEROe	%	4.0	−6.7	6.7	4.5	−4.4	2.2	−6.8	8.0
	p value	<0.05	<0.05	<0.05	<0.05	<0.05	—	<0.05	—
AOD_ MODIS	%	4.8	−0.2	2.0	4.8	−8.4	−2.6	−3.4	0.2
	p value	<0.05	—	<0.05	<0.05	<0.05	<0.05	<0.05	—

[a]The changes noted in bold are not statistically significant at the 95% confidence level but are statistically significant at the 85 or 90% confidence level. No values when $p > 0.15$.

NH_3 concentrations can be affected by NH_3 emissions and the partitioning of NH_3 to NH_4^+. As important precursors of $(NH_4)_2SO_4$ and NH_4NO_3, fewer SO_2 and NO_X emissions can lead to more NH_X staying in the gas phase. Additionally, temperature can affect the thermodynamic equilibrium of NH_4NO_3 with NH_3 and HNO_3. Higher temperatures favor more NH_X staying in the gas phase. In the next two sections, we analyzed the effects of NH_3 emissions and the partitioning of NH_3 to NH_4^+ on NH_3 concentrations.

3.2. Effects of NH_3 Emissions on NH_3 Concentrations. NH_3 concentrations can be affected considerably by local emissions. China is a large agricultural and meat producer, but control measures have not been taken for NH_3 emissions. As seen in Figure 2, NH_3 emissions in East China increased by 7.5% from 2008 to 2014. The increasing percentages were 4.0 and 3.4% from 2008 to 2011 and from 2011 to 2014, respectively, which are significant at the 85% confidence level. This growth occurred mainly because of the increasing emissions from livestock, with a growth percentage of 13.9% from 2008 to 2014. However, as another important NH_3 emission source, NH_3 emissions from fertilizer application decreased by 1.3% from 2008 to 2014, because of reductions in the extent of application of nitrogen fertilizers with high emissions factors (e.g., ammonium bicarbonate), as shown in Figure S2.

Regionally (Table 1), NH_3 emissions in the JJJ region exhibited no significant trend from 2008 to 2011 and increased

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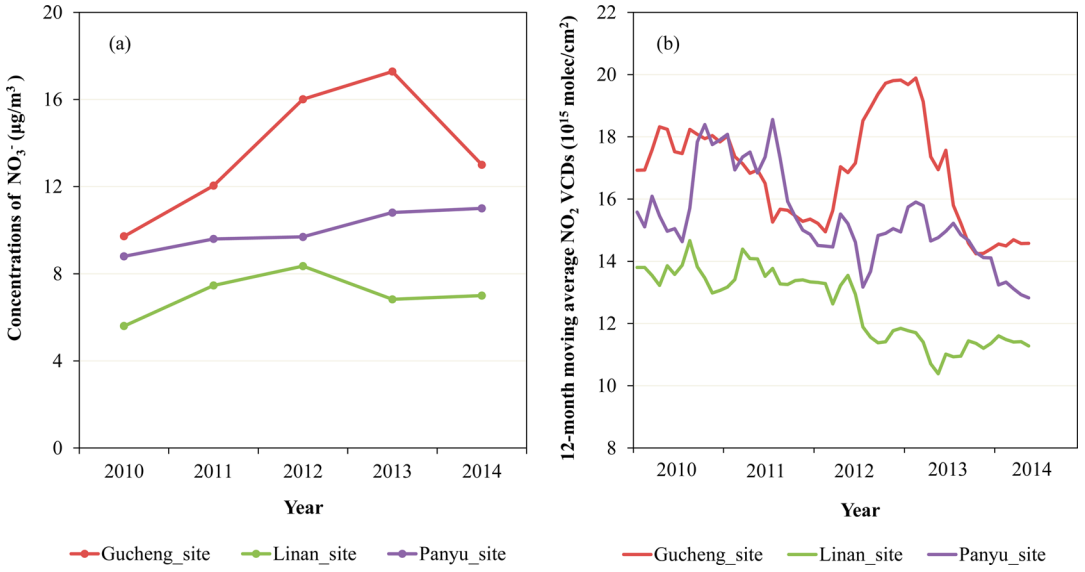

Figure 4. Interannual trends in (a) annual average NO_3^- concentrations and (b) 12 month moving average NO_2 VCDs.

by 3.8% ($p < 0.05$) from 2011 to 2014. The emission changes can partly explain the changes in the NH_3 VCDs, although the variation percentages of NH_3 VCDs were much larger. From 2008 to 2011, NH_3 emissions in the PRD region increased by 4.5% ($p < 0.1$), which was consistent with the variation trends of NH_3 VCDs. However, NH_3 emissions in the YRD region decreased from 2011 to 2014, which was in contrast with the increasing trend of NH_3 VCDs.

In general, the increased NH_3 emissions contributed to the variation in NH_3 VCDs but cannot completely explain the full increases in NH_3 VCDs over time, and another important impact factor exists, which is discussed below.

3.3. Effects of the Partitioning of NH_3 to NH_4^+ on NH_3 Concentrations. *3.3.1. Effects of SO_2 and NO_X Emissions Control.* To improve air quality, the Chinese government undertook a series of measures to control SO_2 emissions in the 11th Five-Year Plan period (2006−2010), resulting in the SO_2 VCDs in East China decreasing by 8.5% from 2008 to 2011. However, over the same period, NO_2 VCDs in East China significantly increased by 38.4% ($p < 0.05$) because of the lack of control measures, which led to a 1.1% reduction of NH_3 VCDs in East China, notwithstanding the increasing NH_3 emissions and decreasing SO_2 emissions. The increasing NO_X emissions have neutralized the increased rate of conversion of NH_3 into the particle phase. During the 12th Five-Year Plan period (2011−2015), NO_2 emissions control measures were implemented and more effective regulations were simultaneously enforced for SO_2 emissions control, which led to a 21.1% ($p < 0.05$) reduction in NO_2 VCDs and 53.2% ($p < 0.05$) reduction in SO_2 VCDs from 2011 to 2014. As shown in Figure 2, the continuous growth of 12 month moving averages for NH_3 VCDs from 2011 was in good agreement with the decreasing trends of SO_2 and NO_2 VCDs, and the correlation coefficients (R) are 0.92. This implied that SO_2 and NO_2 emissions control was an important factors affecting the significant enhancement of NH_3 VCDs in East China during 2011−2014. The decrease in SO_2 and NO_2 emissions led to more NH_X remaining as free NH_3. In three key regions, the large increase in NO_2 emissions in the JJJ region enhanced the decline of NH_3 VCDs from 2008 to 2011. In the PRD region, highly effective SO_2 emissions control led to a continuous increase in NH_3 VCDs from 2008 to 2014.

Judging from ground observations (Figure S3), obvious positive correlations existed between NH_4^+ molar concentrations and $2SO_4^{2-} + NO_3^-$ molar concentrations. The correlation coefficient (R) values were 0.6, 0.8, and 0.9 for the Gucheng, Linan, and Panyu sites, respectively. As presented in Figure S3b, in the Linan and Panyu sites, $2SO_4^{2-} + NO_3^-$ molar concentrations exhibited decreasing trends from 2008 to 2014 (p values of 0.28 and 0.07, respectively), leading to more NH_X (NH_3 and NH_4^+) remaining in the gas phase (NH_3). At the Gucheng site, the $2SO_4^{2-} + NO_3^-$ molar concentrations presented no trends, because of the increase in the NH_4NO_3 concentrations offsetting the decrease in $(NH_4)_2SO_4$ concentrations.

3.3.2. Effects of Temperature. The annual average temperatures in 2011 decreased by 0.40, 0.38, 0.29, and 0.24 K compared to those in 2008, over East China and the JJJ, YRD, and PRD regions, respectively. The annual average temperatures in 2014 increased by 0.86, 1.16, 0.38, and 0.69 K compared to those in 2011, over these four regions, respectively. On the basis of the SORROPIA II thermodynamic theory,[36] we estimated the effects of temperature changes on NH_3 concentrations. From 2008 to 2011, the decreases in temperature favored the partitioning of NH_3 into the aerosol phase, which reduced NH_3 concentrations by 5.3, 5.2, 3.8, and 3.1% over East China and the JJJ, YRD, and PRD regions, respectively. From 2011 to 2014, the increases in temperatures were in favor of the partitioning of NH_3 into the gas phase, which increased NH_3 concentrations by 12.3, 17.6, 5.3, and 9.3% over East China and the JJJ, YRD, and PRD regions, respectively. It can be seen that changes in temperature had an important impact on NH_3 concentrations. NH_3 concentrations would be higher if the climate were to become warmer in the future.

3.4. Effects of Atmospheric Ammonia on PM Pollution Control. NH_3 is an important precursor for SIAs that are the predominant components of fine particles in China. The increases in NH_3 concentrations can reduce the effectiveness of PM pollution control by reducing SO_2 and NO_X emissions. As shown in Figure 2 and Table 1, since 2011, SO_2 and NO_2 VCDs in East China have decreased by 53.2 and 21.1%, respectively. Simultaneously, $PM_{2.5}$ emissions in East China have decreased by 12.4% during 2011−2014.[37] However, the AOD in East China has decreased by only <10%. In three other regions, the AOD exhibited no trend or a slightly decreasing trend.

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Ground observations of SIA concentrations (Figure 4) also suggested that, despite the observed NO_2 VCDs presenting significant declining trends since 2010 ($p < 0.05$ for all three sites), no decreasing trends could be found for nitrate concentrations. At the Panyu site, nitrate concentrations even exhibited a significant increasing trend ($p < 0.05$). This may be largely attributable to the increases in NH_3 concentrations.

As discussed above, to control PM pollution and reduce SIAs, more attention should be paid to the reduction of NH_3 emissions. The Community Multiscale Air Quality (CMAQ)[38] modeling system was applied to evaluate the effects of NH_3 emissions control. The model configurations and inputs for baseline simulation were the same as those described by Fu et al.[39] Additionally, three sensitivity simulations were conducted. In simulation I, the reduction percentage of SO_2 and NO_X emissions was estimated to be 55% over the next 15−20 years under the energy-saving policies and progressive end-of-pipe control strategies (PC[1] in ref 37), and NH_3 emissions were set to be the same as those at present. In simulation II, the changes in SO_2 and NO_X emissions were the same as those in simulation I, and the NH_3 emissions were reduced by 30% with effective control measures.[40] In simulation III, NH_3 emissions were reduced by 30%, and SO_2 and NO_X emissions remained the same as those at present. Simulations were performed for January, April, July, and October as representatives of the four seasons. By comparing the results of simulations I and II, we found that NH_3 emissions control resulted in an additional 10% reduction in SIA concentrations (from 13% in simulation I to 23% in simulation II), an additional 22% reduction in nitrate concentrations (from 8% in simulation I to 30% in simulation II) in particular. PM pollution control can be more effectively achieved through enforcing NH_3 emissions control in conjunction with SO_2 and NO_X emissions control. The differences in simulated concentrations between simulation III and the baseline simulation represented the sensitivities to NH_3 emissions reduction at present, whereas the differences between simulation II and simulation I were considered to be the sensitivities to NH_3 emissions reduction in the future when SO_2 and NO_X emissions will be reduced. The results suggest that the effect of 30% NH_3 emissions reduction on nitrate concentrations reduction was decreased from 31% at present to 28% in the future when SO_2 and NO_x emissions were reduced, because of more free NH_3 caused by less sulfate and nitrate. Therefore, it is more effective to enforce NH_3 emissions control now than later.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00143.

Relative errors of IASI NH_3 VCDs in East China (Figure S1), amounts of nitrogen fertilizer used in China from 2008 to 2014 (Figure S2), correlation between $2SO_4^{2-} + NO_3^-$ and NH_4^+ molar concentrations at three observation sites and interannual variations in $2SO_4^{2-} + NO_3^-$ molar concentrations, which are normalized to the year 2008 (Figure S3), and percentage changes in SIA concentrations for each sensitivity simulation compared to the baseline simulation (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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