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Atmospheric Nitrogen Emission, Deposition, and Air Quality Impacts in China: an Overview

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Abstract Atmospheric reactive nitrogen (N) has induced large impacts on air pollution and ecosystem health worldwide. Atmospheric reactive N emission and deposition have largely increased in China since 1980 due to rapid agricultural, industrial, and urban development. But scientific gaps still remain in the regional and temporal variability in atmospheric N emissions and deposition. Meanwhile, the environmental impacts of N pollution and deposition are of great concern in China. This paper overviews the status of anthropogenic N emissions and deposition and their linkages to air pollution in China. The major findings include two aspects: (1) anthropogenic reactive N (e.g., NH_3 and NO_x) emissions contribute greatly to secondary inorganic aerosol formation and haze pollution and (2) dry N deposition is comparable in importance to wet N deposition, suggesting that both dry and wet deposition should be quantified simultaneously. Future research challenges on atmospheric N emission and deposition are discussed as well. China needs to (1) reduce the uncertainties of national emission inventory of various N species, especially organic N compounds; (2) establish national networks for atmospheric N concentration and deposition monitoring; and (3) evaluate ecological and environmental impacts of N pollution and deposition in typical ecosystems. Last but not least, N deposition modeling tools should be improved based on localized parameters and further used in future N regulation.

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Introduction

Atmospheric nitrogen (N) deposition is not only an important component in the human-accelerated global N cycle [1] but also an indicator of atmospheric N pollution [2••]. Excess N deposition has aroused ecological concerns about negative impacts on ecosystem health and services such as loss of biodiversity, forest soil acidification, and increased greenhouse gas emission [3•, 4, 5]. Rates of N deposition, especially oxidized N deposition, have leveled off or decreased in Europe and the USA since the 1980s or early 1990s with the implementation of stricter legislation to limit atmospheric pollution [6–8]. In contrast, emissions of both NH_3 and NO_x in China have been increasing continuously since the 1980s mainly due to growing agricultural and industrial activities [2••]. These increased reactive N emissions to the atmosphere have aroused widespread concerns on air pollution and their relationship with atmospheric N deposition in China [9, 10]. Wet/bulk and dry N deposition monitoring programs have been conducted since the 2000s [11•, 12, 13]. The impacts of N deposition on terrestrial ecosystems have been previously overviewed globally [3•, 14] and in China [15]. Also, latest modeling results have shown the spatial distribution of N deposition and N critical load exceedance in China based on eutrophication [16]. There are, however, still large gaps in knowledge of the magnitude of N deposition fluxes and impacts of atmospheric N on air pollution [2••, 17].

In this review, we summarize recent (especially after 2010) progress on N deposition studies in order to identify: (1) the spatio-temporal variability of N deposition fluxes, (2) the major impacts of atmospheric N on air quality, and (3) some future research recommendations and regulatory strategies for mitigation of atmospheric N pollution in China.

Atmospheric Reactive N Emissions

NH_3 Emission

NH_3 is certainly among the most important pollutants in terms of contributing to N deposition and particulate matter (PM) formation [2••, 18]. As one of the world's most populated countries, China's national NH_3 emissions have surged from 5 to 7 Tg $year^{-1}$ in the late 1970s to 10–16 Tg $year^{-1}$ in 2000s, accounting for 30–55% of total Asia emissions [19]. Such large quantity of NH_3 released into the atmosphere have enhanced ambient NH_3 concentrations over China, as confirmed by a number of field measurements [11•, 15] as well as satellite observations [20•, 21]. Meanwhile, modeling studies reveal that NH_3 emission control is the most cost-effective strategy to reduce N deposition and PM pollution [17, 22]. Unlike SO_2 and NO_x, NH_3 emissions have not been regulated in China.

Agricultural activities dominate China's NH_3 emissions despite the highly variable emission factors adopted in different studies [23–25]. This is particularly true in intensive agricultural areas of the North China Plain (NCP) [26], Sichuan Basin [27], and Guanzhong Plain [28]. Agricultural NH_3 emissions in NCP were estimated to be 3.1 Tg N $year^{-1}$ in 2004; 54% of them were derived from fertilizer application, followed by emissions from livestock operations involving pigs (27%), cattle (7%), sheep/goats (7%), and poultry (5%) [26]. Recent work indicates that NH_3 emissions in China have decreased due to a phenomenal shrinkage of livestock production since 2007 [23]. Using the heat balance method, Xu et al. [24] also reported an annual emission factor of 1.4 kg NH_3 pig^{-1} $year^{-1}$ from a typical pig farm in China, only half of that in northern Europe [29]. But whether or not China has experienced a turning point of NH_3 emissions is still an open question to date [30].

Although the overall magnitude of non-agricultural sources of NH_3 might be thought to be small in China, gathering evidence reveals that non-agricultural NH_3 emissions accumulating in urban SO_2- and NO_x-rich atmospheres will contribute disproportionately to city-scale NH_3 budget and subsequent haze pollution caused by fine particle formation [31, 32]. Therefore, there is an on-going hot debate regarding the origins of ambient NH_3 in Chinese megacities like Shanghai and Beijing. Recent research on stable N isotope measurements has helped quantify sources of NH_3/NH_4^+ in China [33–35]. Controversy remains and further research is greatly needed, but there is growing evidence that on-road traffic is also an important source of NH_3 in urban areas [32, 36, 37].

NO_x Emission

Derived mainly from fossil fuel combustion processes including power plants, transportation, and industrial activities [38•], anthropogenic NO_x emissions in China have increased from 1.3 Tg N $year^{-1}$ in 1980 to more than 6.0 Tg N $year^{-1}$ in 2010 [2••]. The contribution of nitric acid to acid rain is thus growing in importance due to the stricter control of SO_2 emissions, similar to the trend observed in Europe and the USA in the early 1980s [39]. The government recently set goals to reduce NO_x emissions by 10% in 2015 relative to 2010 levels (12th Five-year Plan) (http://news.xinhuanet.com/politics/2011-03/16/c_121193916.htm). As evidenced by a decline of nitrate deposition [7, 40, 41], NO_x emissions in Europe and the USA have been reduced substantially during past decades. These successful implementations of the NO_x emission regulations provide insight into potential strategies and technologies for China, which is currently an enormous NO_x emitter. In the

near future, NO_x emissions in China are expected to be progressively curbed by stricter national ambient air quality standards (http://bz.mep.gov.cn/), following the trend in Europe and the USA.

Organic N Emission

As indicated by global and regional assessments based on limited monitoring results [42•, 43, 44], organic N contributes substantially to the atmospheric N cycling. Jickells et al. [42•] suggested that on a global basis, dissolved organic N (DON) deposition accounts for approximately 25% of total N deposition. Similarly, Zhang et al. [43] and Du and Liu [44] estimated that DON is approximately 25% of bulk deposition in China. Atmospheric N has been supposed to be resulted from direct emissions, adsorption of gases to pre-existing aerosol particles, and the formation of new particles within the atmosphere [42•]. The evaluation of the diverse sources of atmospheric organic N (including urea, peroxyacyl nitrates (PAN), amino acids, etc.) is challenging. Kanakidou et al. [45] have adapted an organic carbon model to create the first global model of atmospheric organic N. According to their model, in spite of uncertainties, the total emission of organic N (including that formed indirectly in the atmosphere) is 27.4 Tg N $year^{-1}$, with major contribution from combustion sources (45%), primary biogenic particles (32%), and ocean particulate emissions (20%). However, there is still a lack of national emission inventory of organic N species in China. The research gaps of organic N emissions require further research efforts.

Monitoring Networks for Atmospheric Reactive N

Ground-Level Monitoring Networks

Measurements of N deposition in China have been conducted since the early 1980s when the Chinese National Environment Bureau organized a nationwide campaign for acid rain measurement [46]. Currently, the Chinese Ministry of Environmental Protection and the National Meteorological Bureau have been running two independent precipitation chemistry (also covering ammonium and nitrate) monitoring networks since the late 1990s [47, 48]. Moreover, four Chinese cities (Xi'an, Xiamen, Chongqing, and Zhuhai) have joined the Acid Deposition Network in East Asia (EANET) (http://www.eanet.asia/site/index.html). Since 2004, China Agricultural University has organized a Nationwide Nitrogen Deposition Monitoring Network (NNDMN) [11•, 15]. The Chinese Ecosystem Research Network (CERN) has also included measurements of wet N deposition [12]. Both networks contain more than 40 monitoring sites across China, covering forest, grassland, desert, lake, cropland, and urban ecosystems. However, most existing monitoring networks measure only bulk or wet deposition, leaving large gaps in the estimate of dry deposition in China. The NNDMN has recently started to include estimation of dry N deposition based on measured atmospheric N concentrations and simulated deposition velocities (V_d) [11•].

Satellite Monitoring Networks

The ground-based measurements can accurately grasp changes of NO_x and NH_3, while the in situ observation is largely constrained by the limited number and uneven spatial distribution of measurement sites. Satellite products facilitate the acquisition of continuous NO_2 and NH_3 concentrations in the atmosphere from regional to global coverage.

At present, column NO_2 concentrations are measured by multiple space-based instruments, including the Global Ozone Monitoring Experiment (GOME), SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY), Ozone Monitoring Instrument (OMI), and Global Ozone Monitoring Experiment-2 (GOME-2) [49, 50]. These space-borne sensors provide a long period (from 1996 to present) of column NO_2 concentrations on a global scale, with high spatial and temporal resolutions (Table 1). In recent years, the NO_2 columns also have been used to estimate the total N deposition based on statistical models [51, 52] and gaseous NO_2 deposition from an inferred model [53]. However, there were still gaps in estimating N deposition with a high prediction accuracy based on a statistical method.

Compared with NO_2 measurements (since 1996), satellite NH_3 measurements have been conducted much later by the Atmospheric Infrared Sounder (AIRS, 2002-, resolution 13.5 × 13.5 km^2), the Infrared Atmospheric Sounding Interferometer (IASI, 2008-, resolution 12 × 12 km^2), and the Tropospheric Emissions Spectrometer (TES, 2004-, resolution 5 × 8 km^2) [54]. The IASI NH_3 product has been widely validated by ground-based measurements [20•], while the AIRS datasets were first reported by Warner et al. [55] and need to be validated by more measurements in the future. Van Damme et al. [21] provided a comprehensive work on the validation of the IASI NH_3 measurements. In their work, the IASI NH_3 columns have been converted to surface concentrations by using model profiles. Over China, the analysis between the monthly NH_3 concentrations from IASI and those in NNDMN gave a Pearson's correlation coefficient of 0.39 and a slope of the regression of 0.21 (n = 1149) [21], suggesting further investigation is needed to consider the performance of IASI NH_3 measurements, especially as translated to surface concentration estimates. When the satellite NH_3 and NO_2 columns are converted to surface concentrations, dry deposition fluxes of NH_3 and NO_2 can be estimated according to atmospheric concentrations and simulated V_d of both N species.

Table 1 The satellite instruments monitoring column NH_3 and NO_2 concentrations

Sensor	Satellite	Period	Temporal coverage (days)	Overpass time	Geometric resolution (km^2)	NO_2	NH_3
GOME	ERS-2	1996–2003	3	10:30	320 × 40	✓	
SCIAMACHY	Aqua	2002–2012	6	10:00	60 × 30	✓	
OMI	Aqua	2004-	1	13:45	24 × 13	✓	
GOME-2	Metop-A	2007-	1	9:30	80 × 40	✓	
GOME-2	Metop-B	2013-	1	9:30	80 × 40	✓	
IASI	Metop-A	2008-	0.5	9:30 and 21:30	12 × 12		✓
IASI	Metop-B	2013-	0.5	9:30 and 21:30	12 × 12		✓
AIRS	Aqua	2002-	0.5	13:30	13.5 × 13.5		✓

Uncertainty Analysis of Various Monitoring Approaches

To generate a total N deposition flux, one must keep in mind that atmospheric N is deposited via precipitation (wet deposition) and as gases and particles (dry deposition). Besides the pathways, it is critically important to consider various N species (NO_y and NH_x). Therefore, it is important to quantify both wet and dry deposition of NO_y and NH_x; otherwise, an extrapolation of total N deposition flux could yield a high underestimation [56].

The clarification of the terminology for N deposition, especially for wet deposition, bulk deposition, dry deposition, or total deposition of inorganic and organic N, is therefore crucial, when investigating and estimating the effects of N deposition on ecosystems [57]. Especially, we must clarify two concepts about wet and bulk deposition. The former refers strictly to wet-only deposition collected only during rainfall and snowfall events. The latter refers to rainfall and snowfall samples collected using traditional rain gauges which are open permanently. This gives bulk deposition containing wet plus unquantifiable dry deposition of gases and particles and therefore it should be higher than wet deposition but much lower than total deposition.

For example, wet deposition only contributed 40% (28–57%) to total inorganic N deposition in northern China [17]. Annual difference between bulk and wet deposition was 1.3–9.6 kg N ha^{-1} in northern Chinese agroecosystems, equivalent to 5–32% of bulk deposition [58]. This contribution increased to 39% in urban regions [59]. Total N deposition to ecosystems will often be several times larger than bulk deposition data. We therefore suggest the clarification of the terminology regarding N deposition, especially for wet deposition, bulk deposition, gaseous and particulate dry deposition, or total deposition when investigating the ecological impacts of N deposition.

Quantification of Atmospheric N Deposition

Inorganic N Deposition

Due to the difficulty in measuring dry N deposition, earlier studies focus on wet or bulk N deposition, calculated as a product of precipitation-weighted mean N concentration and annual precipitation [60, 61]. Based on the NNDMN and published data, Liu et al. [2••] showed annual bulk N deposition in China increased from 13.2 kg N ha^{-1} in the 1980s to 21.1 kg N ha^{-1} in the 2000s, with an annual increase of approx. 0.4 kg N ha^{-1}. Jia et al. [62] and Lü and Tian [63•] reported a similar increasing trend in N deposition in China. Different from Europe and the USA [6, 8], China's wet/bulk N deposition was still at high level and showed increasing trend [2••, 30]. Compared with NO_3^--N, NH_4^+-N was the dominant form in most reported wet/bulk deposition results in China [2••, 7•, 12], although the ratio of NH_4^+-N/NO_3^--N in precipitation decreased since the 1980s [2••]. The main reasons for the enhanced wet/bulk deposition are the increased energy consumption and N fertilizer use [2••, 30, 62]. Although the methods for estimation of the relevant deposition are different to some extent among the above mentioned studies, their results are highly comparable, and thus can represent the magnitudes of current wet/bulk deposition in China.

Dry N deposition can be measured directly using micrometeorological methods [64] or estimated by employing inferential models that require measurements of deposition velocity (V_d, from standard surface meteorological and biological parameters) and ambient concentrations of gaseous- or aerosol-N compounds [65•]. However, the application of micrometeorological techniques to flux measurements of N species are limited to short-term or a few species [66, 67], and thus are hard to give reliable annual dry N deposition fluxes. For these reasons, the most extensively used method worldwide remains the inferential method, albeit with considerable uncertainty [65•].

Over the last decade, many studies have successfully quantified dry N deposition at a local scale [68, 69], or at a regional scale [12, 70] in China using the inferential method. More recently, Xu et al. [11•] systematically reported average wet/bulk and dry N deposition to be 19.3 and 20.6 kg N ha^{-1} $year^{-1}$ respectively from 43 in situ monitoring sites in the NNDMN during 2010–2014. The spatial variability of wet and dry N deposition by regions showed: North China>Southern China>Northeast China>Northwest China>the Tibetan Plateau (Fig. 1), consistent with the national atmospheric N emission

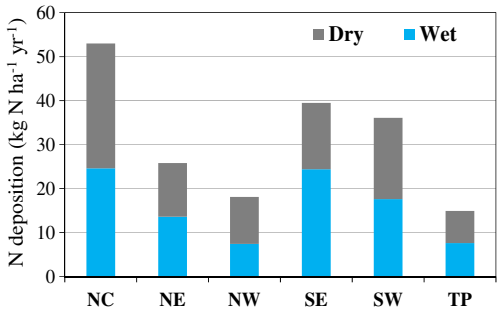

Fig. 1 Spatial patterns of dry and wet N deposition in China (northern China consists of North China (NC), Northeast China (NE), and Northwest China (NW); Southern China consists of Southeast China (SE) and Southwest China (SW); *TP* the Tibetan Plateau. Data shown in the figure are cited from Xu et al. [11•]

intensities [23] as well as the differences in N fertilizer use and energy consumption [12, 30]. A similar study by Jia et al. [13] showed that dry N deposition averaged 7.5 Tg N $year^{-1}$ during 2005–2014 in China and exhibited an increasing trend. It seems clear that dry N deposition (comparable to wet deposition) contributes to a significant fraction of total N deposition and thus should be considered when assessing N deposition-induced ecological risks. However, there are still some unresolved issues, especially related to quantification of NH_3 bi-directional exchange between atmosphere and biosphere [71, 72]. Incorporation of bi-directional exchange into NH_3 dry deposition modeling frameworks typically reduces net deposition to the surface.

Organic N Deposition

Organic N deposition, which accounted for about 20–30% of total N compounds in wet and dry deposition [73], has received much less attention than inorganic N compounds due to in part to the more critical requirements of sampling, storage, transport, and analysis [42•]. Early research mostly concentrated on wet deposition in remote marine and coastal areas [74•], while recent research has expanded to different ecosystems including organic N not only from precipitation but also from aerosols [75, 76].

Concentrations of DON concentrations in precipitation in China ranged from 13.2 to 190.3 μmol L^{-1}, with averaged value of 70.5 μmol L^{-1}, while DON concentrations in other regions ranged from 0.01 to 69.3 μmol L^{-1}, with average value of 15.6 μmol L^{-1} (Fig. 2a). Fractions of DON in total dissolved N (TDN) (DON/TDN value) from precipitation in China ranged 0.07 to 0.67, with an average value of 0.28, while DON/TDN values in other regions ranged from 0.02 to 0.58, with an average value of 0.19 (Fig. 2b). DON concentrations from aerosols were also measured worldwide, with higher concentrations (65 to 204 nmol m^{-3}) in China [77] than in other regions (1.3 to 15.8 nmol m^{-3}) in other regions [78, 79]. Although available data of DON deposition in China were mainly collected in agricultural ecosystems (only few data from other ecosystems) [43, 80], they were substantially higher than the values in other regions [42•], which could be explained by the widespread heavy nitrogenous species emission and deposition over China [2••, 15]. DON/TDN values from precipitations in China were also significantly higher than that in other regions, but both the two group values were located in reasonable range [81], and the relationship between higher DON concentration and higher DON/TDN was poorly understood. Taking the annual precipitation amount into account, organic N from wet deposition in China averaged 7 kg N ha^{-1} $year^{-1}$ [43].

Source Analysis of N Deposition

The analysis of N sources in deposition has long been critical for constructing emission-deposition relationships. Compared with modeling methods, stable isotopes of reactive N in deposition can provide fingerprint information on major sources and transportation of different N species in deposition [82]. Particularly, new methods such as the conversion of nitrate to nitrous oxide for N and oxygen isotope analysis [83] have greatly improved the sample stability and reduced the requirements of sample sizes. Based on the sensitive denitrifier methods, the $\delta^{15}N$ techniques were developed for source analysis on NH_4^+, NO_3^-, and DON in wet deposition [84, 85]. However, it remains challenging to achieve accurate and quantitative apportionment of N deposition only by the $\delta^{15}N$ technique.

Atmospheric $\delta^{15}N$ studies in China have mostly concentrated on NH_4^+ and NO_3^- in precipitation [86, 87], with very few studies on aerosols [34•] and gaseous N species [88]. Due to the difficulties in direct $\delta^{15}N$ analysis of DON [89], its origins remain very uncertain, although the variable $\delta^{15}N$ values reported for marine-to-terrestrial precipitation DON suggested the potential of $\delta^{15}N$ in DON source differentiation [90•]. Moreover, complex N emissions and gas-to-particulate transformation or precipitation washout may produce more variable and overlapped $\delta^{15}N$ values in N deposition, which requires more lab and field evidence on isotopic fractionations of N before deposition because substantial isotope effects could confound $\delta^{15}N$ signals between dry and wet deposition [91], between terrestrial and marine N sources [92]. Future efforts on these questions would allow us to better quantify contributions from multiple sources and to achieve regional $\delta^{15}N$ observations of N deposition in China.

Modeling Wet and Dry N Deposition

Recent Development of Atmospheric Deposition Simulation

Global and regional chemical transport models (CTMs), which are capable of modeling the physical and chemical processes of atmospheric N pollution, have been applied to

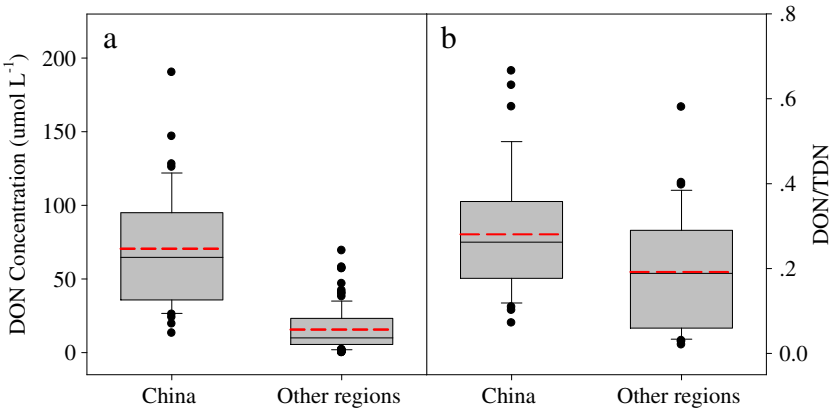

Fig. 2 Distribution of DON concentration (*a*) and DON/TDN ratio (*b*) from precipitation in China and other regions (both the DON concentrations ($p < 0.001$) and DON/TDN ratios ($p < 0.01$)) in China were significantly higher than those in other regions. The *solid and dash lines in the boxes* represent the median and average values, respectively. Data in this figure for China are sourced from recent publications [43, 74•, 76, 80, 81]

simulate the dry and wet N deposition over China [93, 94]. Simple statistical models (e.g., Gu et al. [95]) are also established to calculate N deposition as a function of energy consumption, fertilizer use, and precipitation amount, although they may be subject to great uncertainties by not considering various N emission sources and atmospheric processes. CTMs generally parameterize wet deposition as a function of precipitation activity and scavenging efficiency for different air pollutant species, and deploy the Wesley standard resistance-in-serious scheme [96] to derive V_d for gaseous pollutants. Wu et al. [97] developed a new gaseous dry deposition parameterization, namely Naoh-GEM, and showed that Naoh-GEM model calculated V_d for ozone, PAN, and NO_y agreed well with the field measurements [98].

Modeling N Deposition in China

Simulations of N deposition at the global scale indicated that China has become one of the hotspots of N deposition in the world [99]. Regional CTMs at higher resolutions (5–36 km) now better characterize the spatial and temporal patterns and the budgets of N deposition in China [93, 94]. Zheng et al. [93] modeled the N deposition in China for the year of 2010 using the WRF/CMAQ modeling system. Their modeling results showed that national averaged total N deposition flux was estimated to be only 7.9 kg N ha^{-1} $year^{-1}$, with the higher deposition occurring in the east region than the west. Dry deposition (mainly via NH_3 and HNO_3) was the dominant form, contributing 62% to the total deposition. The reduced N deposition was about twice of the oxidized N deposition. Combining site-level monitoring gridded precipitation data and atmospheric transport modeling results, Lu and Tian [63•] reported China's bulk N deposition increased from 12.64 kg N ha^{-1} $year^{-1}$ in the 1960s, to 15.89 kg N ha^{-1} $year^{-1}$ in the 1980s and further to 20.07 kg N ha^{-1} $year^{-1}$ in the 2000s, similar to summarized monitoring results across China [2••]. More recently, total inorganic N deposition fluxes were simulated to be 16.4 kg N ha^{-1} $year^{-1}$ on average of 2008–2012 over China, with 62% (10.2 Tg N $year^{-1}$) from reduced N (NH_x) and 38% (6.2 Tg N $year^{-1}$) from oxidized N (NO_y) [16]. The modeled N deposition results showed substantially higher in intensively agricultural or economically developed areas than in the national average. For example, the regional averaged deposition was estimated to be 47 kg N ha^{-1} $year^{-1}$ in the NCP in 2008 by [100] and 31 kg N ha^{-1} $year^{-1}$ in the Pearl River Delta (PRD) region of Southern China in 2006 by Huang et al. [94]. In both NCP and PRD, reduced N compounds were the major deposited N components, comprising 63 and 77% of the total N deposition, respectively [94, 100]. Zhao et al. [101] found that N deposition will increase across most of China from 2005 to 2020, with more than 40% rise in south-central and eastern China under the projection of a business-as-usual scenario.

The increasing N deposition input to the marginal seas nearby the mainland of China has also been paid much attention recently [102]. Using the GEOS-Chem nested model over Asia, Zhao et al. [103] showed that atmospheric N deposition to the Yellow Sea and the South China Sea ranged from 0.8–20 kg N ha^{-1} $year^{-1}$, which declines quickly downwind of the Asian continent. Present atmospheric N deposition is comparable to riverine N inputs, and thus has become an important contributor to the total N inputs to the marginal seas of China [104]. Total deposited N over the eastern China seas, including the Bohai Sea, Yellow Sea, and East China Sea, corresponds to about 3% of the N emission in China and would result in up to 4% increase of new productivity over that sea area [105]. The source attribution analysis using an adjoint model indicated that N emission over mainland China contributed about 90 and 70% of N deposition to the Yellow Sea and South China Sea, respectively [103].

Contribution of Atmospheric Reactive N to Air Pollution

Contribution to $PM_{2.5}$ Pollution

NO_x and NH_3 are important precursors for the formation fine particles in the atmosphere. As a dominant alkaline gas, ammonia (NH_3) can react with acidic compounds such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3) to form particulate ammonium (NH_4^+) [106]. Due to the high emission intensities of NO_x and NH_3 in China [2••], the emissions of NO_x and NH_3 have been found to contribute to the formation of a large quantity of secondary inorganic aerosols (SIA, such as NH_4NO_3, NH_4HSO_4, and $(NH_4)_2SO_4$), which account for ~20–60% of $PM_{2.5}$ mass concentration [107]. For example, Huang et al. [108••] found that total mass concentrations of SIA during the high pollution events in Beijing, Shanghai, Guangzhou, and Xi'an ranged from 28.5 to 66.9 μg m^{-3}, which accounted for 19.4–41.3% of the total $PM_{2.5}$ mass concentration. Xu et al. [37] also found high annual mean concentrations of SIA (35.9 to 49.6 μg m^{-3}) in $PM_{2.5}$ at four rural and urban sites in the North China Plain, accounting for 29–39% of the total $PM_{2.5}$ mass concentration.

In many urban areas of China, such as Beijing, a higher proportion of SIA relative to SOA (secondary organic aerosols) has been observed during haze episodes, suggesting a greater importance of SIA in haze pollution chemistry [36]. From an extreme haze pollution event during early 2013, NH_4^+ and related SIA (including NO_3^-) contributed 7.2 and 22.2% of $PM_{2.5}$ on clean days. These numbers increased to 10.4 and 36.2% at heavy polluted days [109]. On an annual basis, NH_4^+ and SIA contributed 9.2 and 35.0% of $PM_{2.5}$, respectively. The percentages of NH_4^+ in $PM_{2.5}$ mass ranged from 7.4–12.4%, with highest values in spring and the lowest in autumn. Contributions of SIA to $PM_{2.5}$ mass decreased as follows: spring (42.6%) > winter (33.7%) > autumn (32.8%) > summer (31.1%) [110]. On the national scale, the percentages of NH_4^+ and SIA in $PM_{2.5}$ mass ranged from 1.1–10.6% and 7.1–57%, respectively. At both urban and rural sites in the eastern region, the NH_4^+ and SIA typically constituted much higher fractions (6.5–10.6% and 40–57%) of $PM_{2.5}$ mass, indicating more local formation/production and regional transport of SIA [110, 111].

Field and laboratory studies have shown that NO_x acts as a catalyst and can promote the conversion of SO_2 to sulfate on the surfaces of mineral oxides [112, 113]. Moreover, the formed nitrate species can enhance the hygroscopicity of mineral oxides [114] and the uptake of liquid water, which accelerates SO_2 and NO_x gas–liquid–solid reactions and further increases the hygroscopicity of the particles [113]. In a recent study, measured nitrate to sulfate ratios in Beijing are higher than those reported a decade ago, coinciding with the increasing trend in NO_x emissions [115]. Thus, an effective strategy to control $PM_{2.5}$ and haze pollution over North China should emphasize the future control of NO_x emissions. Based on these findings, Pan et al. [34•] proposed "the NO_x hypothesis" that NO_x mitigation will not only reduce nitrate itself but also decrease secondary inorganic and organic aerosol formation [37, 112]. Wang et al. [116] found that nitrate aerosol concentration was more sensitive to NO_x emissions in the NCP and YRD, but it is equally or even more sensitive to NH_3 emissions in the PRD. Meanwhile, organic nitrate (e.g., PAN) also contributes to aerosol mass concentration in China [108••]. The reduction in NO_x emissions should also mitigate organic nitrate-induced secondary aerosols.

Recent work in the USA also reveals the importance of NH_3 in influencing the success of sulfate reduction strategies [117]. Especially in winter when oxidant concentrations are limited, enhanced levels of NH_3 which raise the pH of atmospheric condensed water can increase aqueous phase sulfate production by enhancing the importance of ozone as an oxidant. One consequence of this chemistry is that wintertime efforts to reduce sulfate pollution can be thwarted by abundant NH_3, since increases in sulfate conversion efficiency increase while SO_2 emission are reduced, due to increases in pH. This is an important lesson for China to consider as it moves to reduce SO_2 emissions with the goal of reducing haze and its associated health and visibility impacts. In terms of the impact on $PM_{2.5}$ pollution, NO_x and NH_3 influence aerosol acidity in different ways. NO_x that eventually formed nitrate increases aerosol acidity, but NH_3 actually decreases the aerosol acidity. NO_x might enhance the aqueous oxidation of dissolved SO_2 if atmospheric NH_3 elevates pH value of liquid water content in aerosol/cloud to a large extent [118].

Based on on-line and off-line aerosol measurements in urban Beijing for both clean and haze conditions, Pan et al. [34•] demonstrate that the absolute and relative concentrations of nitrate increased with visibility degradation (relative humidity), whereas the variations of organics tracked the patterns of mixing-layer height and temperature. The increasing trend of nitrate (and also sulfate) but decreasing trends of organics during haze development, together with the increase of the NO_2/SO_2 molar ratio with increasing proximity to downtown Beijing and with visibility degradation, provide regional features of NO_x-induced haze pollution in China. Such studies may provide insight into the formation of critical nuclei or the subsequent growth of freshly nucleated particles and advance our understanding of the role of nitrate in new particle formation and $PM_{2.5}$ pollution.

Contribution to O_3 Pollution

Reactive N is also an important driver for ozone (O_3) formation, since O_3 is a secondary air pollutant that is formed in the troposphere via photochemical oxidation of NO_x and volatile organic compounds (VOC) in the presence of sunlight. At a global scale, significant increasing trends of tropospheric O_3 have been derived from a synthesis of in situ observation and

remote sensing [119]. Also, elevated surface O_3 concentrations from local to regional scales, induced by large and widespread emission sources of O_3 precursors (i.e., NO_x and VOC), have been reported in China [120, 121]. In general, photochemical O_3 can be reduced by controlling emissions of its precursors, but NO_x and VOC have a non-linear relationship with O_3 formation. Namely, there are NO_x- or VOC-limited O_3 formation. The regimes are dominated by VOC/NO_x ratios, VOC reactivity, biogenic emissions, photochemical aging, and meteorological conditions. For example, VOC relative to NO_x appears to dominate the O_3 production efficiency in Central Eastern China and the Pearl River Region, whereas summer O_3 formation in the plains and mountainous areas in Northern China was sensitive to VOC and NO_x, respectively [122]. Recent research showed that O_3 formation is VOC limited in most city clusters in the NCP, YRD, and PRD regions [123, 124]. In other words, atmospheric NO_x in China's megacities exerted a titration effect on ozone formation. Unfortunately, such valuable information is still scarce, which limits our understanding of O_3 formation at a broad perspective. Therefore, O_3-VOC-NO_x chemistry over China needs to be improved through more observational and modeling studies, which is undoubtedly benefit to develop effective policies for O_3 pollution control.

Implications of N Emission Mitigation for Air Quality Improvement

Air pollution, especially $PM_{2.5}$ pollution, has captured the interest of scientists and the public alike since the worst photochemical smog in history occurred in China [108••]. As important components of $PM_{2.5}$, NH_4^+, and NO_3^- concentrations in $PM_{2.5}$ (precursors of NH_3 and NO_x) depend mainly on emission reduction.

During the Beijing Olympic Games, the daily emission of NO_x was 47% lower the emission level on June 2008 [125]. By reducing the emissions of NO_x and SO_2 from vehicles as well as coal combustion, a 69% reduction of $PM_{2.5}$ concentration and a 53% reduction of SIA (sum of SO_4^{2-}, NO_3^-, and NH_4^+) concentrations had been witnessed in Beijing during the 2008 Beijing Olympic period [126]. Also, by strict emission controls, SIA concentrations decreased significantly at the ground site and 260 m height during the first APEC episode [32]. To memorize the end of World War II and the Sino-Japanese War, a 70th anniversary victory parade was held in Beijing on 3 September 2015. During the Parade Blue period (from 20 August to 3 September 2015, with strict pollutant emission controls in Beijing and surrounding areas), reductions of 12–35% for NH_3 and 33–59% for NO_2 in different areas of Beijing city during the emission control period were observed compared with measurements in the pre- and post-Parade Blue periods without emission controls [37]. As a result of reduction of NH_3 and NO_2, NH_4^+ and NO_3^- concentrations in $PM_{2.5}$ were also significantly decreased during the emission control period. However, these short-term emission control effects on air quality improvement disappeared shortly after cancelation of those emission control measures [37, 127].

"Shifting from coal to natural gas" at Urumqi in Xinjiang provided an opportunity to examine the long-term emission reduction effects. $PM_{2.5}$ and its NH_4^+ and NO_3^- concentrations decreased by more than 60% ($p < 0.01$) in January 2013 and 2014 (heating with natural gas) compared with those in January 2011 and 2012 (heating with coal) [124]. The change of energy consumption structure at Urumqi suggests that air quality improvement needs long-term pollutant emission control measures, including the co-mitigation of NH_3, NO_x, SO_2, and VOC emissions.

Conclusions and Outlook

In general, we have tried our best to overview progress on N emissions, deposition, and air quality impacts in China, based on relevant publications especially after 2010. China's national atmospheric N emissions, mainly from agricultural activities and fossil fuel combustion, are very high and likely to further increase in the future in order to meet the requirement by the increased population. Meanwhile, the Chinese government has been making a great effort to protect the environment through the adjustment of the energy structure in urban regions and/or releasing new policies in rural regions such as zero increase plan for chemical fertilizer use by 2020 [30]. With stricter control measures of atmospheric N emissions by the government, we expect the turning point of N emissions and deposition will come soon in the near future, similar to that of North America and Europe. In conclusion, dry and wet N deposition fluxes are comparable and show equal importance in China. Atmospheric N deposition has to some extent become an important indicator of anthropogenic N emissions induced by the expanding Chinese economy. Both monitoring and modeling results reveal that the central-eastern regions of China (e.g., northern, southeast, and southwest China) are N deposition hotspots worldwide. Elevated N deposition has produced detrimental effects on the environment especially air quality (e.g., $PM_{2.5}$ and O_3 pollution) over China.

In the future, strong research needs are required to reduce the uncertainties of N emission inventories and the N emission-deposition relationship, using combined monitoring and modeling approaches. Studies on revealing condition-dependent and localized emission factors of NH_3, NO_x as well as atmospheric organic N species would significantly reduce the uncertainties in N emission inventories in China. It is crucial to reduce knowledge gaps between modeled and measured results by improving the understanding of atmospheric N emission, transport, and deposition processes (e.g., by optimizing model parameters), based on considering main factors (such as meteorological factors and landuse types) that

control those processes. It is also important for China to establish open-accessed national N deposition monitoring networks covering both wet and dry deposition using uniform monitoring methods, similar to the National Atmospheric Deposition Program of the United States (http://nadp.sws.uiuc.edu) or the Acid Deposition Network in East Asia (http://www.eanet.asia/site/index.html). Cross-site N addition experiments along with various forests, grasslands, deserts, and aquatic ecosystems are required in order to provide systematic information on the impact of elevated N deposition on both terrestrial and aquatic ecosystems against the background of climate change. The negative impacts of atmospheric N pollution on human health should be paid increasingly more attention in the future with increased premature deaths due to air pollution in China and globally. We appeal for wider international collaboration on N deposition measurements, modeling, and environmental effect evaluation. Nitrogen regulation tools and strategies should be recommended and taken into account when policy-makers consider the mitigation of anthropogenic N_r emissions and the benefits of human and ecosystem health from the mitigation.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflicts of interest.

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- •• Of major importance

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