Formation mechanism and control strategy for particulate nitrate in China

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Abstract: Over the past decade, fine particulate matter (PM) pollution in China has been abated significantly, benefiting from strict emission control measures, but particulate nitrate continues to rise. Here, we review the progress in particulate nitrate (pNO_3^-) pollution characterization, nitrate formation mechanisms, and the proposed control strategies in China. The spatial and temporal distributions of pNO_3^- are summarized. The current status of knowledge on the chemical mechanism is updated, and the significance of its formation pathways is assessed by various approaches such as field observation and modelling of nitrate production rate, as well as isotopic analysis. The factors impacting pNO_3^- formation and the corresponding pollution regulation strategies are discussed, in which the importance of atmospheric oxidation capacity and ammonia are addressed. Finally, the challenges and open questions in pNO_3^- pollution control in China are outlined.

Keywords:

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Introduction

Particulate nitrate (pNO_3^-), an important component of atmospheric fine particles, impacts the physical and chemical properties of particles (such as hygroscopicity, light absorption, acidity, etc.), atmospheric visibility, air quality and climate, as well as human health. During the past decades, winter haze has caused serious problems for the society and environment in China. For example, the severe winter haze in North and East China during 2013 affected more than 400 million people and received close attention at home and abroad (Ji et al., 2014). During the haze episodes, the visibility was less than tens of meters during the day, and the government had no choice but to shut schools, restrict road traffic, suspend flights, close expressways, and request that people stay indoors.

In order to improve the air quality in China, the government has issued ten measures since 2013 as part of the Air Pollution Prevention and Control Action Plan, and carried out a series of unprecedented air pollution control strategies nationwide, which achieved a sharp decrease in $PM_{2.5}$ from 2013 to 2017 (Wang et al., 2020d). The concentration levels of $PM_{2.5}$ in urban agglomerations such as the North China Plain (NCP), Yangtze River Delta (YRD), and Pearl River Delta (PRD) are decreasing year by year. The implementation of emission reduction measures led to the level of some primary pollutants such as CO and SO_2 being reduced significantly, and the concentration of particulate sulfate has declined due to the reduction in SO_2. However, the mitigation of particulate nitrate appears to have been less efficient. The mass proportion of nitrate in $PM_{2.5}$ did not fall but instead rose, and the mass concentration in some cities even increased (Zhou et al., 2019). The inconsistency of the changes in nitrate and sulfate reflects the complicated relationship between nitrate and its precursors, and highlights the importance of fully understanding the chemistry of particulate nitrate.

Since 2017, the Ministry of Science and Technology of China has launched a national key research and development program for understanding the air pollution mechanism and control technology, which achieved great progress in atmospheric pollution and control. By summarizing the relevant publications funded by this program, we qualitatively constructed a timeline for the investigation of nitrate pollution in China. As shown in **Fig. 1**, in the first stage, people were mainly concerned with the particle mass level, the variations in different time scales (e.g., day and seasonality), but focused less on the compositions and their detailed formation mechanism. In the second stage, with the rapid improvement of study approaches, many works tried to gain insight into the causes of nitrate pollution. In the third stage, with the amount of particle matter rising, more efforts were devoted to this issue and researchers tried to understand the detailed pollution mechanisms and search for mitigation strategies for nitrate

pollution. According to the timeline, the progress in understanding nitrate pollution characteristic, causes and related mechanisms, and control strategies are reviewed in the following sections. Finally, the open questions and future challenges in the mitigation of nitrate pollution in China are outlined.

1. The variations of particulate nitrate

1.1 Annual trend

A series of field observations of particle chemical compounds were conducted in China starting in 1997 (Hu et al., 2002). In the beginning, there were limited studies concerned with the composition of particulate matter in China, and long-term observation of the chemical compounds in particles was especially lacking. Combining the dataset from the Nationwide Nitrogen Deposition Monitoring Network (NNDMN) during 2005 to 2015 with a machine learning approach, a recent study showed a nitrate hotspot located in North China, followed by the YRD, PRD, and the Szechwan Basin region (Li et al., 2021). This reflects the close relationship between nitrate pollution and human activities, in addition to unfavorable terrain and meteorological conditions. The study also revealed that during the period 2005-2014, the national concentration of nitrate showed a clear increasing trend. Wen et al. (2018) revealed that the proportion of nitrate in $PM_{2.5}$ kept increasing in Jinan (2005-2015) and at Mt. Tai (2007-2014). The $PM_{2.5}$ components of major urban agglomerations in China showed an upward trend of nitrate content in Gucheng, Lin'an, and Chengdu in winter during the period 2010-2013, while only Panyu showed a downward trend in nitrate (Zhang et al., 2015). These results highlighted the fact that the particulate matter (PM) pollution before 2013 was severe.

This situation is a little different in Guangdong Province; just like the example of Panyu mentioned above, a long-term observation of the chemical components of particulate matter carried out in Foshan, China from 2008 to 2014 showed that the main components between 2008 and 2011 were sulfate and nitrate. With the strict implementation of control measures in 2011-2014, the principal components changed to organic compounds in Guangdong Province. During the seven-year period, the concentration of particulate matter continued to decline, and the proportion of nitrate also declined to a certain extent (Tan et al., 2016). The results indicated that the awareness of and actions on air pollution control in the PRD region are relatively advanced in China.

The secondary inorganic components of PM were dominated by sulfates before 2013 nationwide. With the vigorous reduction of SO_2 emissions in recent years, the proportion of sulfate has been exceeded by nitrates since 2015 (Dao et al., 2019). Compared with the year

2014, the absolute concentration level of particulate matter in the winter of 2016 has dropped significantly in Beijing, but the proportion of nitrate has increased significantly (Xu et al., 2019). An increasing proportion of nitrate also reported from 2014 to 2018 in Beijing (Wang et al., 2020d; Zhou et al., 2020). The mass proportion of nitrate in the haze pollution episode in the winter of 2018 in urban Beijing was 34%, which was much higher than the value of 17% in the winter of 2013 (Shang et al., 2021). In addition, studies have shown that since the beginning of the three-year action plan in 2018, the proportion of nitrates has increased significantly in both clean periods and polluted episodes (Lei et al., 2021).

1.2 Seasonal and diurnal variation

The long-term observation of PM compounds gives a comprehensive picture of the seasonal and diurnal variation of nitrate. In general, the nitrate concentration in autumn and winter is significantly higher than that in spring and summer (Griffith et al., 2015; Huang et al., 2017; Kong et al., 2020; Sun et al., 2018). The particulate matter component monitoring network was implemented by the China Environmental Monitoring Center and the manual membrane sampling work in 2+26 cities in 2017. The observation network provides very solid evidence that the concentration of particulate nitrate in winter in China is higher than that in summer, with the annual average of nitrate proportion in the range 7%-23% (Dao et al., 2019).

In North China, the diurnal changes of nitrate in spring and summer are consistent, showing nighttime and morning rises and a decline during the daytime (Hu et al., 2017). The diurnal changes in autumn and winter are consistent, that is, the concentration of nitrate increases continuously during the day and decreases at night. In Eastern and Western China, the diurnal changes of nitrate in different seasons are quite different from those in North China. For example, the diurnal variation of nitrate in both summer and winter in Nanjing and Hongkong showed a weak peak in the morning and decline during the day (Griffith et al., 2015; Sun et al., 2018). The winter case in Lanzhou is like that in Beijing in winter (Ge et al., 2017). The diurnal profiles of nitrate in different type of regions are highly varied; for example, observation showed that the profiles in urban Jinan or rural Yucheng were different from that on the top on Mt. Tai (Wen et al., 2018).

1.3 Vertical profile

Several field studies on the composition and source mechanism of particulate matter at different heights have been conducted using the meteorological tower of the Institute of Atmospheric Physics (IAP) of the Chinese Academy of Sciences in recent years, and the relationship between boundary layer evolution and extreme pollution events has been discussed (Sun, 2018). Observation revealed that the mass concentration of particles near the ground is higher than that

at 260 m, but the nitrate concentration and proportion in the particulate matter above the city are higher than those near the ground. This indicated differences in the chemical and physical mechanisms of nitrate near the ground and above the city.

It was proposed that the low temperatures above the city are conducive to the partitioning of gaseous nitric acid to the particle phase (Sun et al., 2015). This study provided observational evidence for the first time to prove that there are significant vertical differences in nitrate concentrations. Similarly, vertical observation studies in central Italy have also confirmed that high-altitude nitrate accounts for a greater proportion than near-ground nitrate (Curci et al., 2015; Ferrero et al., 2012). Very recently, Tang et al. (2021) reported the amount of nitrate in the nocturnal residual layer is much lower than that in the surface layer based on a tethered balloon measurement over the North China Plain, indicating that more comprehensive studies are needed to fully understand the differences.

1.4 Horizontal distribution

A previous observation showed that the winter fine particulate pollution in China always occurs at a large regional scale, and showed a relatively consistent level of nitrate concentrations (Dao et al., 2019). However, the horizontal differences in nitrate concentrations in the surface layer are still significant on a national scale. Considering that the overall $PM_{2.5}$ pollution is much more severe in North China that in other regions like YRD and PRD, the nitrate concentration is generally higher in the north than the south, even if the proportions of nitrate in $PM_{2.5}$ vary with the region. Sun et al. (2018) provided a comprehensive summary of the observation of nitrate nationwide, and the results confirmed that the hot spot of nitrate is located in the North China Plain, followed by the YRD and PRD regions in summer or winter. Based on a three-year measurement of $PM_{2.5}$ compounds, Kong et al. (2020) presented a fundamental dataset showing that the level of nitrate in the Szechwan Basin is comparable with that in the YRD region.

Although the NO_x precursors of nitrate have similar distribution to that of nitrate nationwide (Sun et al., 2018), the meteorological conditions, including temperature and relative humidity, may contribute to spatial differences in the distribution of nitrate through affecting the gas-particle partitioning of nitric acid, while this issue has received less attention. Finally, regional differences in ammonia emission also affect the horizontal distribution of nitrate pollution.

2. The causes of particulate nitrate pollution

The current state of knowledge of the main formation and sink pathways of particulate nitrate

is shown in **Fig. 2**. Nitrate is mainly produced by the oxidation of nitrogen oxides. During the daytime, NO_2 reacts with OH radicals to produce nitric acid, which reacts with ammonia to form ammonia nitrate and then enters the particle phase through gas-particle partitioning (R1-R3).

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (R1)$$

$$HNO_3(g) + NH_3(g) \leftrightarrow NH_4NO_3(s) \quad (R2)$$

$$HNO_3(g) + NH_3(g) \leftrightarrow NH_4^+(aq) + NO_3^-(aq) \quad (R3)$$

Nitric acid can also react with other alkaline substances in coarse particles, such as $CaCO_3$, and $MgCO_3$ or alkaline salts such as NaCl in sea salt particles to produce $CaNO_3$, $Mg(NO_3)_2$, $NaNO_3$, etc, which could be significant in certain regions (Bian et al., 2014). Since OH radicals are generally produced by photochemical processes, the gas-phase reaction OH + NO_2 mainly occurs during the daytime. At night, heterogeneous hydrolysis of N_2O_5 occurs on particle surfaces to form particulate nitrate, and both nitrate and nitryl chloride ($ClNO_2$) are produced when N_2O_5 reacts on Cl-containing aerosol surfaces. N_2O_5 is produced by reaction between NO_3 and NO_2 in thermal equilibrium, whereby NO_3 is produced by the reaction of NO_2 and O_3 (R4-R6). Besides the abovementioned two pathways, other reactions such as the reaction of NO_3 with VOCs (R7) and NO_2 uptake also produce nitrate (R8), but these pathways are regarded as not being as important as the first two in general.

$$NO_2 + O_3 \rightarrow NO_3 \quad (R4)$$

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \quad (R5)$$

$$N_2O_5 + H_2O \text{ or } Cl^-(aq) \rightarrow (2-\varphi)NO_3^-(aq) + \varphi ClNO_2 \quad (R6)$$

$$NO_3 + VOCs \rightarrow \text{products} \quad (R7)$$

$$2NO_2 + H_2O\,(aq) \rightarrow HONO + HNO_3 \quad (R8)$$

Wet and dry deposition are the main sinks of nitrate in the atmosphere; these processes are important ways by which atmospheric nitrogen enters the soil ecosystem. In addition, the photolysis of particulate nitrate has been proposed to be an important way to activate the nitrogen species to return to the atmosphere, producing nitrous acid and impacting global atmospheric oxidation (Gen et al., 2022; Ye et al., 2016).

2.1 The reaction of OH with NO_2

Due to the limitations of field measurement technologies, it is difficult to quantify the contribution of the several reaction channels to nitrate pollution under actual atmospheric conditions. With respect to the gas-phase reaction between NO_2 and OH, the level of OH is not easy to detect under ambient conditions. Several field observations conducted by the team from Peking University measuring OH by using laser-induced fluorescence reported OH levels in

major urban agglomerations in China since 2006 (Hofzumahaus et al., 2009; Lu et al., 2012). Until recently, most OH measurements were mainly carried out in summer, and the quantified nitric acid produced by OH + NO_2 in summer was found to be about 50 $\mu g/m^3$ per day on average (Wang et al., 2020a; Wang et al., 2017). Although the concentration of OH radicals in winter is relatively low (Ma et al., 2019; Tan et al., 2018b), the concentration of NO_2 during the pollution period in winter is relatively high and compensates for the decline in OH compared with summer, resulting in the contribution of the average daily production of gaseous nitric acid during polluted conditions in winter being comparable with or even exceeding that of summer (Lu et al., 2019; Wang et al., 2020a).

The above-mentioned production rate is not considered among the gas-particle partitioning processes of nitric acid, as the produced nitric acid only partially goes into the particle phase. Since the temperature during the day is higher than that at night and the relative humidity is lower, this meteorological condition is not conducive to gaseous nitric acid entering the particle phase, so the net contribution to particulate nitrate by OH + NO_2 is not as high as the calculated nitric acid production rate (Tan et al., 2021).

With the development and upgrading of the air quality monitoring network and satellite remote sensing technology, the concentration and variation of NO_2 at the regional scale can be well captured, thereby helping understand the impact of NO_x changes on nitrate formation. However, field observation of OH radical is still lacking. Less than ten OH observation datasets in some large urban agglomerations have been reported in China (Lu et al., 2019). At the same time, the source and sink mechanisms of OH radicals are very complex; although the existing mechanisms can describe the changes in the budget of OH radicals to a certain extent, there are still certain uncertainties in simulating and predicting their concentration (Lu et al., 2012; Ma et al., 2019; Tan et al., 2017; Tan et al., 2018b; Tan et al., 2019; Yang et al., 2021). Lack of information on the sources of OH radicals has led to an underestimation of modelled OH radical concentrations in the afternoon by state-of-art model simulations, which makes it difficult to accurately quantify the contribution of this gas-phase reaction pathway.

2.2 N_2O_5 heterogeneous hydrolysis

Heterogeneous N_2O_5 hydrolysis is mainly regulated by the concentration level of N_2O_5, aerosol surface area and the N_2O_5 uptake coefficient ($\gamma_{N_2O_5}$). The N_2O_5 concentration and γ_{N2O5} are the key sources of uncertainty in the quantification of nocturnal nitrate formation. The field measurement of N_2O_5 and the levels in different regions are well summarized in Wang et al. (2015). Previous field studies have found that $\gamma_{N_2O_5}$ varies from 10^{-4} to 0.1, which spans more

than three orders of magnitude. A large number of laboratories have shown that ambient temperature, humidity, particulate matter components (NO_3^-, Cl^-, SO_4^{2-}, aerosol liquid water content, organic matter), and particulate matter mixing state are the factors that affect the heterogeneous uptake of N_2O_5 (Folkers et al., 2003; Mitroo et al., 2019; Thornton and Abbatt, 2005; Wahner et al., 1998; Wang et al., 2020b). In follow-up field studies, the effects of these factors on N_2O_5 uptake were observed and discussed (Morgan et al., 2015; Phillips et al., 2016; Riedel et al., 2012; Tham et al., 2018; Xia et al., 2020; Xia et al., 2019; Yan et al., 2019), and the inhibitory effect of nitrate content on the N_2O_5 uptake was well confirmed (Wagner et al., 2013). An inhibitory effect on the uptake coefficient by high aerosol organic content was observed under low humidity environments (Bertram et al., 2009), but due to the large variability of the complicated composition of organics in different air masses, this issue is not well characterized at the present.

Based on the above-mentioned mechanisms, the existing parameterizations have been purposed and applied in model prediction and atmospheric impact assessment. However, the coupling effects from various factors on the N_2O_5 uptake are quite complicated. Compared with measured N_2O_5 uptake coefficients, most predictions can only reflect the change trend of the uptake coefficient, but have difficulty accurately predicting the values (McDuffie et al., 2018; Morgan et al., 2015; Phillips et al., 2016; Riedel et al., 2012; Wang et al., 2020b). This indicates the non-linear response of N_2O_5 uptake to these factors in the actual atmosphere, and reflects the lack of a full understanding of the mechanism of N_2O_5 uptake in ambient aerosol.

The existing parameterization schemes have difficulty accurately predicting the uptake coefficient of N_2O_5, which leads to uncertainties in the simulation of key chemical processes in regional and global models. The gap may be caused by the use of parameterization schemes established based on laboratory experimental results on model aerosol, with limited representativeness compared with ambient aerosols. It seems that the influence of organic matter and particle mixing state on the uptake coefficient are important sources of uncertainty in the parameterization. Recently, Yu et al. (2020) used multiple field observations of N_2O_5 uptake coefficients and related parameter dataset constraints to improve the existing parameterization scheme, which improved the accuracy of the parameterization of N_2O_5 uptake coefficients in China, and provided an applicable approach to assess the contribution of N_2O_5 uptake to nitrate formation.

2.3 NO_2 heterogeneous hydrolysis

NO_2 uptake on aerosol surfaces is a pathway for the formation of nitrate aerosol along with nitrous acid (Kleffmann et al., 1998). Many studies have reported NO_2 uptake coefficients (γ_{NO_2})

on various types of aerosols spanning more than five orders of magnitude, with values ranging from 10^{-9} to $>10^{-4}$ (Kleffmann et al., 1998; Knopf et al., 2011; Yu et al., 2021). However, most of the studies derived γ_{NO2} based on model aerosols and the result are hard to extrapolate to ambient conditions. Moreover, the large variation in γ_{NO_2} value tends to cause large uncertainties when assessing its contribution to nitrate formation. Previous works revealed that γ_{NO_2} and the yield of nitrate is affected by aerosol properties, temperature, RH and other factors (Borensen et al., 2000; Gross and Bertram, 2008; Wu et al., 2013; Yu et al., 2021).

Due to the reported low values of γ_{NO_2}, the contribution of nitrate from NO_2 uptake is regarded as much less important than that from N_2O_5 uptake. Therefore, most of the previous studies focused on its role in HONO formation rather than nitrate pollution. At present, for a better simulation of HONO, many works have updated and adjusted the parameterization of γ_{NO_2}, which then led to a considerable amount of nitrate formation due to NO_2 uptake (Fu et al., 2020; Zhai et al., 2019). While we cannot confirm whether NO_2 uptake is indeed as significant a contributor to nitrates as models now predict, it does deserve more attention to gain insight into this issue by comprehensive approaches in future works. The importance of bridging the gap in the parameterization of ambient γ_{NO_2} as well as the parameter γ_{N2O5} should be emphasized (Xie et al., 2022).

2.4 The reaction of NO_3 with VOCs

NO_3 reacts with alkanes through hydrogen abstraction and forms HNO_3, while the reaction rate is much lower than that of its reaction with alkenes; thus, it is believed that reaction with alkanes contributes little to nitrate. NO_3 mainly reacts with alkenes rapidly by addition to a double bond, and the products are in general peroxy radicals (RO_2) after the addition of molecular oxygen to the resulting radicals (Wayne et al., 1991). These RO_2 favor the production of peroxy nitrates (ANs) at night and contribute to secondary organic aerosol (Kiendler-Scharr et al., 2016). At the same time, the hydrolysis of ANs (not only including those initiated by NO_3 oxidation, but also by OH and O_3 oxidation) is regarded as a source of HNO_3 and discussed in several studies; this pathway could be substantial in the low NO_x regime and even comparable with OH + NO_2 (Browne et al., 2013). However, the detailed mechanism and relevant kinetic parameters including hydrolysis rate and HNO_3 yield are still lacking.

2.5 Gas-particle partitioning of nitric acid

Nitric acid is volatile, and partitions between gaseous and particle phases (R3). The partitioning process of nitrate is affected by multiple factors, such as temperature, humidity, the content of NH_3, liquid water and particle acidity. Nitric acid favors partitioning to the particle phase under

low temperature and high humidity conditions and vice versa, and these factors affect the dissociation constants directly (Li et al., 2018). The role of NH_3 in nitrate pollution is complicated. Ammonium acts as the dominant cation of nitrate in particulate matter; if there is insufficient NH_3 in the atmosphere, nitric acid preferentially exists in the gaseous form, while when NH_3 is abundant, HNO_3 mostly exists in the particle phase. However, the partitioning ratio of nitrate is not linearly dependent on the level of gaseous NH_3. Ammonia helps stabilize the particle pH to decrease aerosol acidity (Shi et al., 2019), which affects the partitioning indirectly. The level of ammonium in the aerosol was proposed to be limited more by thermodynamics than the source under ammonium-rich conditions (Shi et al., 2017). Due to the high hygroscopicity of ammonium nitrate, ammonia enhances the feedback effect between aerosol liquid water content and nitrate formation through heterogeneous reactions and partition processes during the pollution episode (Ge et al., 2019). Other compounds, such as sulfate, have also an indirect effect on nitrate formation by affecting the particle hygroscopicity and ammonium distribution in particles (Jia et al., 2021; Li et al., 2018).

3. Critical processes and control strategies

3.1 The dominant nitrate formation pathway

During a winter pollution episode, the nitrate concentration tends to undergo an explosive increase. As the pollution intensifies, the mass proportion of nitrate continues to increase. The concentration of particulate matter grows from tens to hundreds of $\mu g/m^3$ in a few hours. By comparing the growth rates of other pollutants during polluted and clean episodes, an increasing ratio of nitrate to sulfate, ammonium and organic matter was observed during polluted days (Dao et al., 2019; Tan et al., 2018a). With the aggravation of pollution, the ratio of NO_3^-/SO_4^{2-} keeps rising, and the ratio exceeds 200% under some conditions (Li et al., 2018).

Nitrate pollution snowballs during the pollution episode; that is, in the beginning, the PM level goes up and enhances the aerosol surface area, and with the feedback of changes in precursors and meteorological conditions, such as relative humidity and temperature inversions, the formed nitrate further enhances the aerosol water content (ALWC) and aerosol surface area (S_a) through its high hygroscopicity. ALWC and S_a provide positive feedback to heterogeneous N_2O_5 uptake and nitrate formation (Huang et al., 2020b; Wang et al., 2020c). In the end, the reactions are limited by the N_2O_5 production rate due to low O_3. Overall, the heavier the pollution, the higher the proportion of nitrate, making nitrate a key component of particulate matter during heavy haze episodes (Zheng et al., 2015). For example, an observation in winter in Beijing showed that the proportion of ammonium nitrate exceeded 50% in a heavy haze episode (Lu et al., 2019).

Many studies have shown that the gas-phase chemical reaction of OH + NO_2 and the heterogeneous reaction of N_2O_5 are important nitrate generation pathways (Pathak et al., 2011; Pathak et al., 2009; Sun et al., 2013; Wen et al., 2015). Based on comprehensive measurement of the precursors of nitrate such as OH, NO_2, N_2O_5 and related parameters, the nitrate formation potential can be determined and the contribution of different formation pathways can be quantified. Wang et al. (2017) revealed that N_2O_5 uptake contributed to nitrate formation comparable to that of OH + NO_2 during the PM and O_3 pollution in Autumn Beijing, where the elevated O_3 and PM conducive to N_2O_5 produced N_2O_5 uptake reactions. Field measurements in Heshan in winter showed a similar result (Yun et al., 2018). All the cases in which N_2O_5 uptake contributed to nitrate significantly occurred with high O_3 and high PM loading as well as less-cold conditions. Field observation revealed that nitrate formation by N_2O_5 uptake in the surface layer in urban and suburban regions is less than 10% and 30% respectively during the wintertime in North China. Measurement on the IAP tower showed that nitrate production rate in the residual layer (150-240 m) is about four times higher than in the surface layer (Chen et al., 2020b; Wang et al., 2018), indicating an active nitrate formation zone in the residual layer. But even without the contribution from the residual layer, the nitrate formation still dominated by the daytime pathway by ~70%. The result is quite different from the situation in the US, in which N_2O_5 uptake contributed to more than half of the nitrate production (Kim et al., 2014; McDuffie et al., 2019; Prabhakar et al., 2017; Pusede et al., 2016; Stanier et al., 2012).

Isotope technology provides a solution based on the isotope value of oxygen atoms ($\delta^{18}O$) in different chemical conversion pathways and the nitrogen isotope value of NO_x emitted by different pollution sources ($\delta^{15}N$). According to the isotope analysis, it was found that the proportion of nitrate formation by the OH pathway during the polluted period was less than 50% (Fan et al., 2021; Fan et al., 2020; He et al., 2018; Zhang et al., 2021). For example, Fan et al. (2020) used the concentrations of chemical components and stable nitrogen and oxygen isotope values to analyze the formation mechanism and potential sources of nitrate during heavy pollution. Combining the observed isotope values and the Bayesian model, they revealed that OH + NO_2 and N_2O_5 heterogeneous reactions made the same contribution to nitrate formation on average. The contribution of N_2O_5 uptake to the nitrate formation during a haze episode (64%) was significantly higher than during a clean period (39%). Besides, Wang et al. (2019) showed that NO_3 gas-phase oxidation, the OH + NO_2 process, and heterogeneous N_2O_5 uptake accounted for the same proportions on annual average, which is consistent with the results of recent isotope studies based on different heights (Fan et al., 2021). However, another study that also applied the isotope method showed that NO_3 gas-phase oxidation is not a significant

formation pathway for nitrate (Zhang et al., 2021), which indicated that there are still discrepancies in the quantification of the nitrate formation distribution by the current isotope-based method.

By considering a state-of-the-art parameterization scheme of the N_2O_5 uptake coefficient (Yu et al., 2020) and updated HONO formation mechanisms, the CMAQ model was recently used to simulate winter nitrate pollution in North China. Fu et al. (2020) found that the OH gas-phase oxidation channel and the N_2O_5 heterogeneous reaction channel played important roles in the formation of nitrate. Vertical structure analysis also confirmed that the N_2O_5 uptake in the residual layer has a higher contribution to nitrate formation than near the ground, while the dominant pathway in the surface layer is OH + NO_2. Liu et al. (2019) used WRF-CHEM to simulate the nitrate pollution during the heavy haze in North China in February 2014, and showed N_2O_5 uptake contributes nearly 30% of nitrate when considering the suppressing effect on this reaction by organic coatings on the aerosol surface, and this result is in good agreement with the previous model conclusions (Su et al., 2017).

3.2 Mitigation strategies for nitrate pollution

Due to the complex responses between nitrate and its NO_x precursors, single and simple precursor control measures may not effectively alleviate severe nitrate pollution. Based on the understanding of the chemical formation mechanism of nitrate, many studies have begun to look for insight into the reason and regulation strategy for nitrate pollution. Taking the nitrate pollution in Beijing as an example, the concentration of OH radicals decreased during the heavy pollution episode, but the turnover rate of OH was increasing (Lu et al., 2019)， and was even comparable to the average summer case in North China (Tan et al., 2017). HONO and HCHO are important sources of HO_x radicals in winter; they are the maintenance factors for high atmospheric oxidation in winter to a certain extent (Tan et al., 2018b). Since HONO is closely related to NO_2 heterogeneous processes and is always elevated during pollution episodes, the strong atmospheric oxidation in winter pollution can be regarded as feedback for haze to some extent. These results indicate that the formation of nitrate in winter is a comprehensive result of the deep coupling of atmospheric photochemistry and heterogeneous chemistry, and highlights the importance of atmospheric oxidation capacity in nitrate formation (Zang et al., 2021).

The recent epidemic (COVID-19) also provides an opportunity to understand the impact of changes in anthropogenic emissions on air pollution. With the sharp reduction in NOx emissions, the winter atmospheric oxidation was enhanced effectively, which led to particulate nitrate pollution, further confirming that atmospheric oxidation regulates air pollution (Huang

et al., 2020a).

The different dominant pathways for nitrate formation between China and US reflect different atmospheric oxidation characteristics in the two countries. Excessive NO_x enhances the reaction rate of OH + NO_2 and daytime nitrate formation. At the same time, NO_x acts as a terminus for HO_x radical, which shortens the cycle length of HO_x radical and inhibits the formation of OH and O_3. The trade-off effect of the two aspects lead to the daytime nitrate formation in Beijing, which is not initially responsive to NO_x change. Therefore, the reduction of NO_x emissions at the regional level in recent years weakened the titration of O_3, and therefore the increase in atmospheric oxidants sped up the conversion of NO_x to nitrates with higher efficiency; this is the reason why nitrate has not decreased consistently with NO_x in recent years (Fu et al., 2020).

In addition, the reduction in NO_x also impacts nighttime chemistry; long-term observations found that the increase in O_3 accompanied by a decline in NO_2 enhanced the winter N_2O_5 uptake during the nighttime, which also helps explain the elevated nitrate observed in recent years (Chen et al., 2020a; Wang et al., 2021). **Fig. 3** shows examples of the response of O_3 and nitrate to NO_x and VOC in different seasons in North China. The reduction of NO_x only in winter is helpful to mitigate nitrate but has an adverse effect on O_3; the reduction of VOC only in summer can decrease O_3 but increase nitrate. It is recommended that NO_x and VOC be reduced synergistically to alleviate nitrate and O_3 pollution (Fu et al., 2020; Lu et al., 2019). In the western US, however the reduction in NO_x has an adverse effect on both nitrate and max O_3 (Womack et al., 2019).

A very recent study demonstrated that the main reason for the increase in the proportion of winter nitrate in China is that reductions were made in NO_x and SO_2 but were not significant for NH_3. The GEOS-CHEM simulation showed that the total amount of nitric acid produced did not change significantly, and the decline in sulfate led to excessive NH_3, which further promoted more nitrate being partitioned to the particle phase, going from 90% in 2013 to 98% in 2017. The atmospheric lifetime of nitrate has greatly increased year by year since the deposition of particulate nitrate is far slower than nitric acid (Zhai et al., 2021). Based on the framework, it was revealed that although reducing one of the three pollutants NO_x or VOC or NH_3 can reduce the concentration of nitrate, only the coordinated control all of them provides a chance to find the best path to control nitrate pollution. However, the emission features of each region are quite different, which means the reduction proportion of these precursors needed may vary and that the detailed measures may need to be adjusted to suit local conditions.

4. Conclusions and outlook

In this paper, we illustrate the reality of severe nitrate pollution in China. The control of nitrate pollution could be the milestone needed to alleviate fine particulate matter pollution in the forthcoming years. However, the non-linear response of nitrate to precursors shows the big challenges to be faced in controlling nitrate pollution. Overall, a scientific consensus has been formed to a certain extent, that is, both the gas-phase oxidation of OH and the N_2O_5 heterogeneous reaction process are key channels for the formation of nitrate, which was confirmed by measurement and regional model simulations. Under the current framework of particulate nitrate chemistry, winter nitrate pollution control should focus on the importance of atmospheric oxidation and ammonia emissions. Considering that the overall atmospheric environment in China is quite different from that in Europe and America, a proper control route should be uncovered by refining the reduction weights of NO_x, VOC and NH_3. Several critical issues to help deal with the nitrate pollution in China are outlined below.

(1) Improving the observation of aerosol compounds and identifying the characteristics of nitrate pollution from multiple methodological and spatiotemporal perspectives.

(2) Strengthening the understanding of radical chemistry and atmospheric oxidation, and developing a regulation theory based on atmospheric oxidation capacity for nitrate pollution control.

(3) Addressing the mechanisms of heterogeneous processes related to nitrate formation and identifying the key factors. Uncovering the role of gas-particle partitioning and ammonia in regulating the budget of nitrate aerosols.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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List of Figures

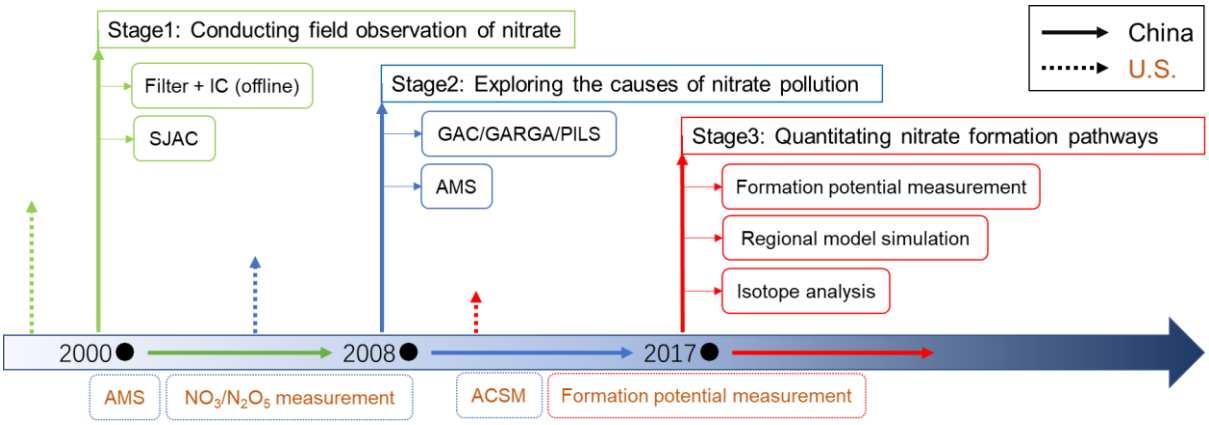

Fig. 1 Roadmap for the study of particulate nitrate pollution in China.

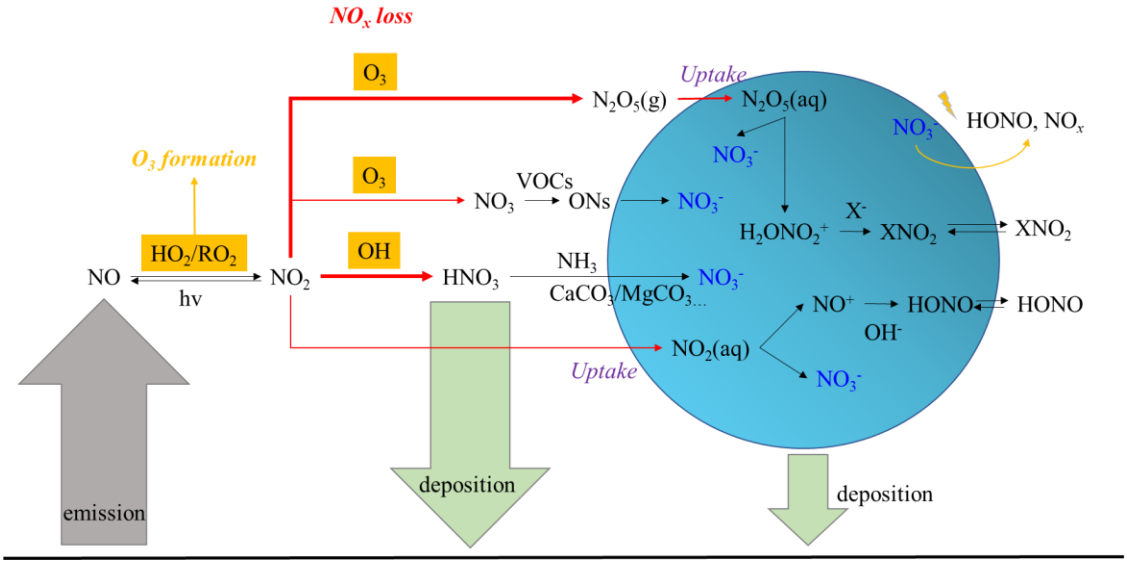

Fig. 2 Schematic of the formation and sinks of particulate nitrate in the atmosphere.

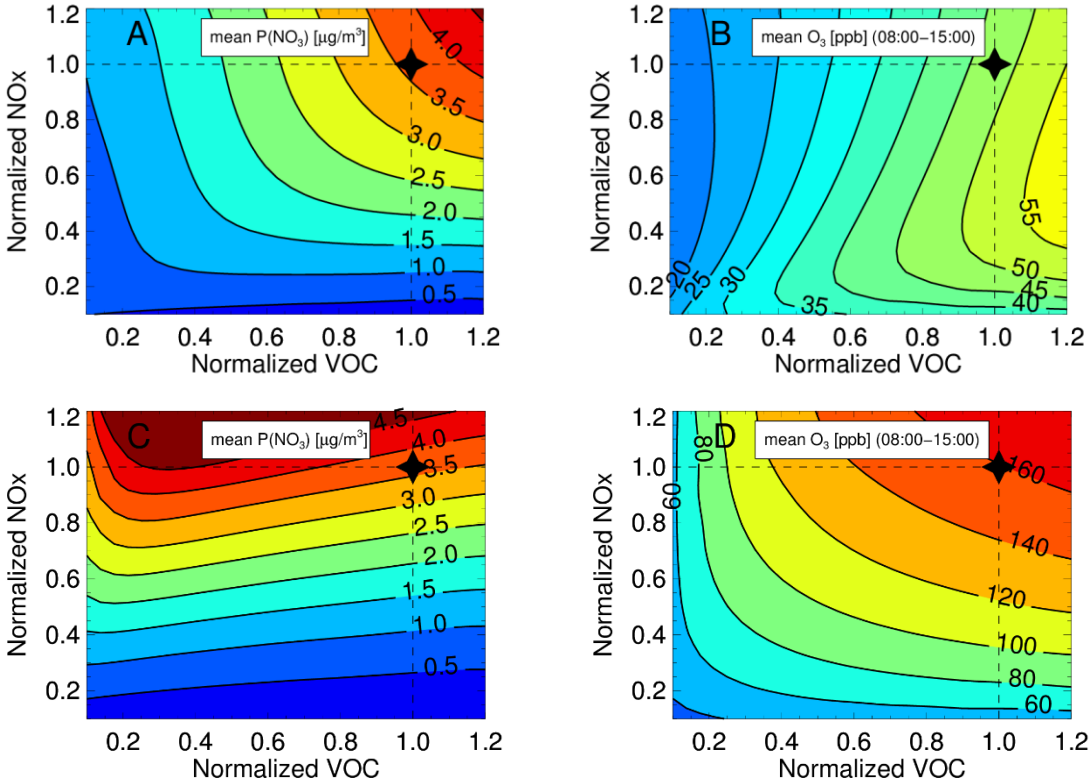

Fig. 3 Projection of the impact of emission reductions for NO_x and VOCs on the photochemical production rates of secondary pollutants under the conditions of a haze event during winter (A-B) and summer (C-D) in North China. (A, C) Daily average of particulate nitrate. (B, D) average ozone from 08:00 - 15:00.