

Formation mechanism and source apportionment of nitrate in atmospheric aerosols

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ABSTRACT

Atmospheric particulate nitrate is relevant to various atmospheric processes and shows profound impacts on regional air quality and global climate change. Exploring the formation mechanism and sources of nitrate in atmospheric particulate matter is essential for the successful mitigation of nitrate. This review summarises the different formation mechanisms, sources, and source apportionment methods of nitrate. In particular, the current progress of the nitrogen/oxygen (N/O) isotope technique coupled with the Bayesian isotopic mixing model (MixSIAR) is fully depicted. The limitations of the current source apportionment methods are also presented and the promising direction for the source apportionment of nitrate is proposed. As such, this review provides a thorough understanding of nitrate formation mechanisms and sources, which is particularly helpful for mitigating nitrate pollution in polluted cities such as those in East Asia.

KEYWORDS

Source apportionment, formation mechanism, isotope, MixSIAR, PMF



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HIGHLIGHTS

- Detailed formation mechanisms of atmospheric nitrate are presented.
- The application of the N/O isotope technique in source apportionment is reviewed.
- The isotope method is compared with the PMF method to reach a promising direction.

1. INTRODUCTION

Nitrate (NO_3^-) in atmospheric aerosols is closely related to atmospheric environmental problems. Particulate NO_3^- can scatter sunlight radiation and pose direct radiative forcing on the radiation system of the earth's surface. Being an important hygroscopic component of fine particulate matter, NO_3^- can also act as cloud condensation nuclei and indirectly affect the radiation budget of the earth-atmosphere system. Increasing the mass percentage of particulate NO_3^- in $\text{PM}_{2.5}$ can increase the hygroscopicity of $\text{PM}_{2.5}$, which consequently increases the light extinction coefficients of $\text{PM}_{2.5}$ and reduces atmospheric visibility. Given the same mass concentration of $\text{PM}_{2.5}$, the atmospheric visibility is decreased with the increase of the mass percentage of NO_3^- in $\text{PM}_{2.5}$ when $\text{PM}_{2.5} > 20 \mu\text{g m}^{-3}$ (Hu et al., 2021). Moreover, the condensation of nitric acid and ammonium can produce ammonium nitrate nanoparticles, which is an important process during the new particle formation event in urban areas, particularly in winter (Wang et al., 2020). The same process also plays an important role in the new particle formation in the free troposphere, where the presence of water vapour facilitates the fast-growing of ammonium nitrate nanoparticles.

HNO_3 was perceived as the permanent sink of NO_x (NO and NO_2). However, the reverse oxidation cycle of HNO_3 has been proven to be able to produce NO_x (Wang, Zhang, Nenes, & Fountoukis, 2012; Kumar et al., 2014). According to the laboratory results of Ye et al. (2016), the photolysis rate of particulate NO_3^- into NO_x was two orders of magnitude higher than the photolysis rate of gaseous

NO_3^- . Under typical marine atmospheric boundary layer conditions, the reverse oxidation cycle of HNO_3 maintains the observed levels of HONO and NO_x during noon time. As over 70% of the earth is covered by the sea, the photolysis of particulate NO_3^- could be an important source of NO_x in the troposphere. The photolysis of NO_3^- can not only affect the oxidation capacity of the atmospheric boundary layer in the polar, marine, and terrestrial areas (Domine & Shepson, 2002; Ye et al., 2016), but also impact the NO_x and $\bullet\text{OH}$ budgets in the remote atmosphere (Shi et al., 2021) and promote the formation of SO_4^{2-} (Xue et al., 2019; Zheng et al., 2020). In addition, the photolysis of NO_3^- in the water film of atmospheric particulate matter or atmospheric hydrometeors can produce reactive oxygen species and reactive nitrogen species, which contributes to the photooxidation of atmospheric organic compounds and subsequently the formation of brown carbon (BrC) (Yang, Au, Law, Lam, & Nah, 2021). For example, in the presence of inorganic nitrate, guaiacol and 5-nitroguaiacol, which are two typical phenolic compounds, can quickly react under irradiation to form BrC, and the reaction rate and yield of BrC are dependent on the initial concentration of inorganic nitrate (Yang et al., 2021).

Regarding the significant role of nitrate in the atmospheric environment and the related environmental impact, as shown in Figure 1, it is, therefore, important to understand the formation mechanism and sources of atmospheric nitrate. This review summarises the different formation mechanisms, sources, and source apportionment methods of nitrate. In particular, the current progress of the

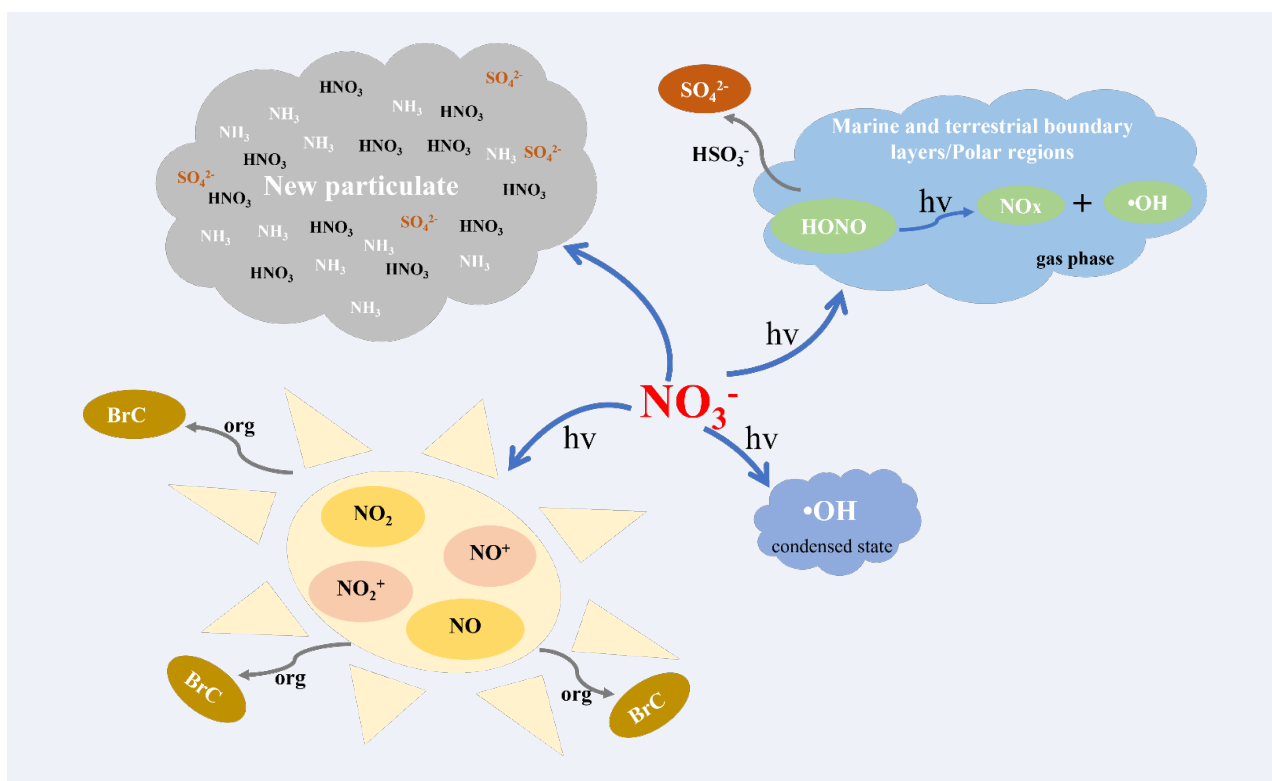


FIGURE 1. Environmental processes and impacts of atmospheric nitrate.

nitrogen/oxygen (N/O) isotope technique coupled with the Bayesian isotopic mixing model (MixSIAR) is fully depicted. As such, this review would be helpful for mitigating nitrate pollution in polluted cities such as those in East Asia.

2. FORMATION MECHANISM OF NITRATE

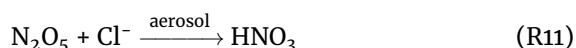
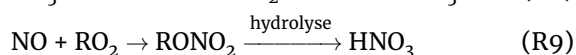
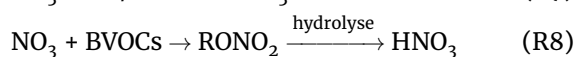
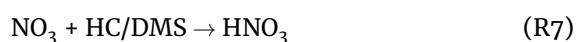
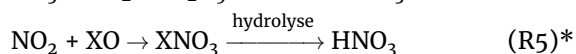
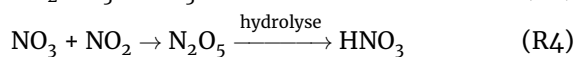
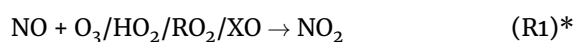
NO_x is the major precursor of atmospheric nitrate. Once emitted into the atmosphere, NO can be quickly oxidised into NO_2 by atmospheric oxidants such as O_3 , $\text{HO}_2\cdot$, $\text{RO}_2\cdot$, and halogen oxides (XO, X representing Br, Cl, and I), as demonstrated by the Chemical Equation (R1). Meanwhile, NO_2 can also photolyze at $\lambda < 398$ nm to form $\text{NO} + \text{O}$ during the day. The conversion rate of NO_x between NO and NO_2 during the day is several orders of magnitude higher than the oxidation rate of NO_x to form NO_3^- (Michalski, Scott, Kabling, & Thiemens, 2003).

As shown in the chemical equations, the major oxidation pathways from NO_x to NO_3^- include the oxidation by $\cdot\text{OH}$ (R2) during the day and hydrolysis of N_2O_5 (R3–R4) at night (Alexander et al., 2009). According to the reactive halogen chemistry

simulated using tropospheric chemical models, inorganic nitrate produced through the hydrolysis of halogen nitrate (XNO_3 , X representing Br, Cl, and I) (R5) is also an important sink of NO_x , which can further affect the formation of tropospheric O_3 , $\cdot\text{OH}$, reactive halogen, and aerosols (von Glasow & Crutzen, 2004; Yang et al., 2005; Parrella et al., 2012; Saiz-Lopez et al., 2012; Long et al., 2014; Schmidt et al., 2016; Sherwen et al., 2016). Other formation pathways of inorganic nitrate include the heterogeneous uptake of NO_2 and NO_3 (R6), reaction between NO_3 radical and hydrocarbons (HC) or dimethyl sulfide (DMS) (R7), hydrolysis of organic nitrate (R8–R9), direct oxidation of NO by $\text{HO}_2\cdot$ (R10) and heterogeneous reaction between N_2O_5 and particulate Cl^- (R11) (Atkinson, 2000). The two major oxidation pathways from NO_x to NO_3^- , i.e., oxidation by $\cdot\text{OH}$ and hydrolysis of N_2O_5 , contribute equally to the formation of NO_3^- globally in the lower atmosphere with altitude < 1 km, while the total contribution of other formation pathways of NO_3^- is generally less than 6% globally (Alexander et al., 2020). However, exceptions could occur in particular regions during a particular time. For

example, Luo et al. (2020) found that the formation pathways of NO_3^- via $\text{N}_2\text{O}_5 + \text{H}_2\text{O}/\text{Cl}^-$, $\text{NO}_3 + \text{VOCs}$, and $\text{ClNO}_3 + \text{H}_2\text{O}$ contributed around 53%–89% to NO_3^- formation during the severely polluted period in Beijing, but $\bullet\text{OH} + \text{NO}_2$ was the dominant formation pathway of NO_3^- during the non-polluted period with the contribution of 37%–69% to NO_3^- formation.

The partition between gaseous HNO_3 and particulate NO_3^- depends on the abundance of aerosols, aerosol water content and chemical composition, and temperature. The inorganic nitrate returns to the earth's surface through dry and wet deposition, and the life cycle for deposition is around 3–4 days (Park, Jacob, Field, Yantosca & Chin, 2004).



* In Reactions 1 and 5, XO represents halogen oxides, with X representing Br, Cl, and I.

3. SOURCE APPORTIONMENT OF NITRATE

3.1. Sources of nitrate

Nitrate is dominantly formed by the gaseous precursor NO_x through secondary reactions in the atmosphere. Therefore, the sources of nitrate are virtually the sources of NO_x , except that some emission sources, such as the ammonium nitrate fertiliser plants, can also release nitrate into the atmosphere directly.

Anthropogenic emission sources such as fossil fuel combustion, biofuel combustion and agricultural fertilisation are the major sources of NO_x

in the atmosphere (Jaegle, Steuberger, Martin, & Chance, 2005). The anthropogenic emissions of NO_x varied with time historically. At the end of the 20th century, fossil fuel combustion took 95% of the total NO_x emission globally (Anenberg et al., 2017), with 90% in Europe (Sutton et al., 2011), 88% in East Asia (Ohara et al., 2007), and 96% in North America (Air Pollutants Emissions Inventory, 2023), respectively. However, the contribution of non-fossil fuel sources to NO_x emission has greatly increased in recent years. According to the work of Song et al. (2021), non-fossil fuel sources took over 50% of the total NO_x emission globally; the annual emission of NO_x from non-fossil fuel sources was 21.6 ± 16.6 Mt in East Asia, 7.4 ± 5.5 Mt in Europe, and 21.8 ± 18.5 Mt in North America, respectively. The anthropogenic emissions of NO_x also show great spatial variability globally. Vehicular emission used to be the major source of NO_x in developed countries in North America and Europe. However, with the implementation of control measures targeting stationary and mobile emission sources, non-fossil fuel sources have shown an increased contribution to NO_x . The soil-related sources, such as agricultural land, forest, and animal manure emissions, now contribute highly to NO_x in developed countries (Almaraz et al., 2018; Guo et al., 2020; Skiba et al., 2021). In comparison, in many developing countries, fossil fuel combustion remains the major source of NO_x due to the growing urbanisation and industrialisation processes. For example, the energy and industry sectors were India's dominant source of NO_x , followed by vehicular emission (Garg, Bhattacharya, Shukla, & Dadhwal, 2001). Similarly, the mobile source took 46.1% of total NO_x emission in Tehran, Iran (Shahbazi, Hassani, & Hosseini, 2019), and the roadside NO_x emission flux could reach as high as $(36.46 \pm 12.86) \times 10^{24}$ molec./s in Beijing, China (Huang et al., 2020).

Because atmospheric nitrate is dominantly formed through the reactions of NO_x , the sources of nitrate show similar spatial and temporal variability to NO_x . However, the formation mechanism of nitrate is complicated, and some primary sources also contribute to nitrate in the atmosphere.

Therefore, it may not be completely effective to control atmospheric nitrate pollution by merely understanding the sources of NO_x . A recent study conducted in the North China Plain showed that with a considerable reduction of NO_x by 31.8% in 2010–2017, the atmospheric surface concentration of NO_3^- only decreased by 0.2% (Fu et al., 2020). A thorough understanding of the sources and formation mechanisms of nitrate is essential for the successful mitigation of nitrate.

3.2. Source apportionment of nitrate based on isotope analysis

Since nitrate is dominantly formed in the atmosphere, it is difficult to apply the common source apportionment methods of atmospheric aerosols, such as emission inventories, receptor models, and source diffusion models, to identify nitrate sources and formation mechanisms in the atmosphere. Particularly, the nitrogen/oxygen (N/O) isotope technique coupled with the Bayesian isotopic mixing model (MixSIAR) is a powerful tool to trace nitrate aerosols' sources and formation pathways. The isotope technique was first developed in the 1950s and used to apportion the sources of nitrate in rainwater (Eriksson, 1959; Freyer, 1978; Freyer, 1991). Later, with the aggravation of air pollution worldwide, the isotope technique was applied to apportion the sources of nitrate in TSP, PM_{10} , and $\text{PM}_{2.5}$ (Widory, 2007; Zong et al., 2017; Lin et al., 2021). With the establishment of the N/O isotopic composition data pool of different sources and the development of source apportionment models, the nitrogen/oxygen (N/O) isotope technique has now been widely used to trace the sources of $\text{NO}_3^-/\text{NO}_x$ in the atmosphere (Song et al., 2019; Zong et al., 2020a; Lin et al., 2021).

The nitrogen stable-isotope composition of nitrate ($\delta^{15}\text{N}-\text{NO}_3^-$) is influenced by the sources of NO_x and shows spatial and temporal variability due to the impact of different human activities (Felix et al., 2012; Felix & Elliott, 2014; Walters, Goodwin, & Michalski, 2015; Fibiger & Hastings, 2016; Zong et al., 2020b). The $\delta^{15}\text{N}-\text{NO}_3^-$ technique has been well extended with the continuous investigation of

the nitrogen isotopic compositions of NO_x . Felix et al. measured $\delta^{15}\text{N}-\text{NO}_x$ of coal-fired power plant (Felix, Elliott, & Shaw, 2012) and that of NO_x emitted from soil and animal manure (Felix & Elliott, 2014), finding that the $\delta^{15}\text{N}-\text{NO}_x$ value of coal-fired power plant was higher than that of NO_x from other emission sources. Walters and Michalski (2015) measured $\delta^{15}\text{N}-\text{NO}_x$ of gasoline and diesel vehicles and found negative correlations between $\delta^{15}\text{N}-\text{NO}_x$ and the NO_x concentration as well as the vehicle running time. Miller et al. (2018) revealed a significant difference of $\delta^{15}\text{N}-\text{NO}_x$ in the agricultural land applied with different fertilisers, which was affected by nitrification and NO consumption. In general, the $\delta^{15}\text{N}-\text{NO}_x$ value of NO_x from coal combustion is higher than that from vehicular or soil emissions.

The nitrogen isotope fractionation is related to the oxygen isotope fractionation during the reaction of NO_x to form NO_3^- . Therefore, the measurement of oxygen isotope can be used to evaluate the nitrogen isotope fractionation effect (Walters & Michalski, 2015, 2016). Generally, the oxygen stable-isotope composition of nitrate ($\delta^{18}\text{O}-\text{NO}_3^-$) is dependent on the contributions of different reaction pathways to NO_3^- formation. Thus the stable oxygen isotope is a powerful tool to efficiently evaluate the contributions of different formation mechanisms of nitrate. According to the current research findings, the formation of NO_3^- is highly affected by the gaseous oxidation of NO_x by $\cdot\text{OH}$ during the day and hydrolysis of N_2O_5 at night (Alexander et al., 2009). Besides, the reaction of $\text{NO}_3 + \text{HC/DMS}$ may also contribute highly to NO_3^- formation under heavy pollution conditions. According to the work of Hastings, Sigman, and Lipschultz (2003), for NO_3^- formed during the reaction of $\cdot\text{OH} + \text{NO}_2$, 2/3 of $\delta^{18}\text{O}-\text{NO}_3^-$ comes from NO_x and 1/3 of $\delta^{18}\text{O}-\text{NO}_3^-$ comes from $\cdot\text{OH}$; meanwhile, for NO_3^- formed during the hydrolysis of N_2O_5 , 5/6 of $\delta^{18}\text{O}-\text{NO}_3^-$ comes from O_3 and 1/6 of $\delta^{18}\text{O}-\text{NO}_3^-$ comes from H_2O . Generally, higher $\delta^{18}\text{O}-\text{NO}_3^-$ is associated with O_3 (+90‰–+122‰ $\delta^{18}\text{O}$) oxidation, while lower $\delta^{18}\text{O}-\text{NO}_3^-$ is associated with $\cdot\text{OH}$ (-25‰–0‰ $\delta^{18}\text{O}$) oxidation (He et al., 2018; Wu et al., 2021; Zhang et al., 2021). Zong et al. (2020b) measured $\delta^{18}\text{O}-\text{NO}_3^-$

in five megacities in China in 2013–2014 and observed significant seasonal variation of $\delta^{18}\text{O}-\text{NO}_3^-$. The $\bullet\text{OH} + \text{NO}_2$ reaction contributed highly to NO_3^- in summer, with the contribution reaching $58.0 \pm 9.82\%$, but the contribution of $\bullet\text{OH} + \text{NO}_2$ was relatively low in winter, with a contribution of $11.1 \pm 3.99\%$. Zhang et al. (2021) estimated the contributions of different mechanisms to NO_3^- formation in Beijing during the winter of 2017–2018, and the contributions of $\bullet\text{OH} + \text{NO}_2$, $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$, and $\text{NO}_3 + \text{HC}$ to NO_3^- formation were 45.3%, 46.5%, and 8.2%, respectively.

3.3. Limitations of the source apportionment methods of nitrate

By tracing the direct emission sources of NO_x , the nitrogen/oxygen (N/O) isotope technique coupled with the Bayesian isotopic mixing model can be effectively used to apportion the sources of NO_3^- . However, the sources resolved by this method are limited by the availability of N/O isotopic composition of each source. The MixSIAR model can only quantify the contributions of sources with known isotopic composition. Previous studies mostly included vehicular emission, coal combustion, biomass burning, and soil biogenic emission as the sources of NO_3^- (Liu et al., 2017; Song et al., 2019; Zong et al., 2020a, 2020b; Lin et al., 2021; Rai et al., 2021). However, other emission sources, such as industrial emissions and mineral dust, can also contribute to NO_3^- in the atmosphere. Besides, when the number of sources > the number of isotopic tracers + 1, the MixSIAR model results would not be sole, and the sources resolved by the model could show a significant negative correlation. The significant negative correlation between the resolved sources indicates overlap and overestimation of such sources (Stock et al., 2018; Lin et al., 2021). For example, in previous studies, there were occasions when vehicular emission and biomass burning (Zhang et al., 2021) or coal combustion and biomass burning (Lin et al., 2021) could not be differentiated using the MixSIAR model.

In addition to the MixSIAR model based on the isotopic technique, the positive matrix factorization

(PMF) model based on chemical tracers is also a powerful tool for apportioning the sources of atmospheric aerosols (Zong et al., 2018). Based on a large quantity of samples and careful selection of source tracers, PMF can provide a full view of the sources of atmospheric aerosols. Therefore, the PMF source apportionment result may compensate for the limited sources resolved by the isotope technique. However, while the PMF model can differentiate primary sources and secondary formation, it is difficult to link the species that are largely formed in the atmosphere to the direct emission sources, which happens to be the strength of the isotope technique (Zhu et al., 2018). Therefore, combining the two methods, isotope/MixSIAR and PMF, appears to be a promising direction for apportioning the sources of NO_3^- , which will not only provide complete information on the contributing sources but also quantify the primary and secondary contributions of different sources.

4. IMPLICATIONS FOR AIR POLLUTION CONTROL

Major cities in East Asia, such as Beijing and Ulaanbaatar, are still facing severe air pollution problems. In recent years, strict measures on air pollutant mitigation have been implemented in China, leading to a rapid transition of energy demand from solid fuels to cleaner energy, such as natural gas. For example, Beijing has 100% completed the Clean Heating Plan for Northern China in Winter and used natural gas instead of coal for central heating in winter (Ai et al., 2023). In Beijing, owing to the efforts on air pollution mitigation, the particulate SO_4^{2-} has decreased by 63% (from $24.0 \mu\text{g m}^{-3}$ to $7.4 \mu\text{g m}^{-3}$) and the particulate NH_4^+ has decreased by 51% (from $15.5 \mu\text{g m}^{-3}$ to $7.6 \mu\text{g m}^{-3}$) in 2013–2020. Compared to SO_4^{2-} and NH_4^+ , NO_3^- showed a smaller reduction of 44% (from $24.9 \mu\text{g m}^{-3}$ to $14.0 \mu\text{g m}^{-3}$) and has become the dominant inorganic species in $\text{PM}_{2.5}$ (Lei et al., 2021). During the haze episodes, the mass percentage of NO_3^- in $\text{PM}_{2.5}$ can reach as high as 50% (Sun et al., 2015), indicating that NO_3^- could be one of the key factors driving the occurrence of heavy pollution. In Ulaanbaatar, SO_4^{2-}

is still the dominant inorganic species in $PM_{2.5}$ due to the high dependence on coal combustion. However, the government has implemented several mitigation measures to reduce air pollutants, mainly targeting stationary sources with coal combustion. It is predictable that NO_3^- will also become the major pollutant in $PM_{2.5}$ in Ulaanbaatar as a result of the control measures, similar to the evolution of air pollution in Beijing. Therefore, understanding the pollution characteristics and sources of NO_3^- in the atmosphere would help to formulate effective measures to mitigate local air pollution.

5. ACKNOWLEDGEMENT

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