We thank the reviewers for the valuable time and comments. Below, we respond to the reviewers’ comments in detail and attach a marked-up manuscript (from page 8 to page 44) which highlights the changes made. Referee comments are in black, italic text. Our response to referees is in black, plain text.

Referee #1

Comment 1:
Current application of stable isotopes in atmospheric particulate nitrate to partition NOx source contributions generally presupposes that nitrogen isotopic fractionation during the conversion of NOx to NO3⁻ is minor. Here Chang et al. present a comprehensive evaluation of the nitrogen isotope fractionation during gas-to-particle conversion of NOx to NO3⁻. The computational quantum chemistry is applied to calculate the net N isotope effect (ÔSN) associated with the conversion between NOx and NO3⁻, and validated through a source-specific monitoring campaign. The applicability of this method to atmospheric aerosol samples from a megacity shows satisfactory results, which are in line to atmospheric chemistry modeling and to what one can expect in terms of source impact in a traffic-intensive environment. The source apportionment model to calculate nitrate fractions of different NOx sources is presented in a clear and concise way and is easily applicable by other researchers for similar studies. Great benefit with the method compared to other δ15N-based source apportionment studies of atmospheric nitrate is the fact that coal combustion may be substantively overestimated in previous studies when the N isotope fractionation during atmospheric nitrate formation is neglected. This makes the study with more profound implications. I recommend this manuscript to be published in ACP with minor revision.

Reply: We appreciate the reviewer for the recognition of this work, which give us a sense of accomplishment. Below please see our point-by-point reply.

Comment 2:
Title: replace “gas-particle” by “gas-to-particle”

Reply: We think that it is generally appropriate to use “gas-particle” here. In the revised
MS, we’ve replaced “gas-particle” by “gas-to-particle”.

Comment 3:
L54: delete “nationwide,”
Reply: Revised accordingly.

Comment 4:
L103: add relevant reference
Reply: We added Morin et al. (2008) in the revised MS.

Comment 5:
L154-155: to my understanding, the source apportionment study of pNO\textsubscript{3} was only performed in Nanjing
Reply: Sorry for our mistake. We change “in order to elucidate ambient NO\textsubscript{x} sources in two distinct areas of China” to “in order to elucidate ambient NO\textsubscript{x} sources in Nanjing City of Eastern China”.

Comment 6:
L190: it is a bit awkward to use “heartland” here
Reply: We deleted “the heartland of” in the revised MS.

Comment 7:
L203-207: I didn’t find the data of dicarboxylic acids and related compounds. No need to mention the method here
Reply: We deleted the description of this method in the revised MS.

Comment 8:
L317: enough credits should be given to previous researchers. L319-321: although described in the SI, relevant references should be added.

Reply: Agree. Several relevant references have been added in the revised MS:


Comment 9:

Figure 2b: what “MSA” stands for.

Reply: “MSA” stands for “methyl sulphonate”. We’ve added in the revised MS.

Comment 10

Figure 6: replace “ mã€šN”

Reply: We guess “ mã€šN” stands for “£N”, and the reviewer want us to replace “£N” by “£N”. We revised Fig. 6 as follow:
Referee #2

Comment 1:
Chang et al. propose a novel method to qualitatively determine the nitrogen isotope fractionation factor associated with NOx oxidation to form nitrate aerosols. The authors argue that the nitrogen isotope fractionation is a fundamentally important but overlooked factor in terms of influencing the source apportionment of particulate nitrate, particularly in urban polluted atmosphere. The explanations given are supported by strong observations, theory, and modeling. Overall, this work contributes a potentially powerful new tool for the investigation of atmospheric nitrate sources, and the isotopic fractionation that occurs during chemical processing. I have no major concerns regarding this manuscript. As mentioned by the first reviewer, it is well written, well presented and it makes sound. Beyond the remarks given by the first reviewer upon which I agree, I would appreciate if the authors can also consider the following points:

Reply: We are thankful for the favorable comments. Below please see our point-by-point reply.

Comment 2:
I assume that the authors have wrote a program that incorporated all of the equations
in the MS to calculate the nitrogen isotope fractionation factor and estimate nitrate
source attribution. I believe it will be a valuable asset if the authors could make such
program publicly available;

Reply: This work was financially supported by the National Key Research and
Development Program of China, which require the submission of relevant software. We
have the plan to make such program publicly available. However, we prefer not to
publish the software at the present stage in order to avoid compromising the future of
ongoing software registration. We are willing to share the software with the reviewer
for reviewing purpose.

In “Data availability”, we will remind readers to download the software through our
group website (atmosgeochem.com) after the finish of software registration.

Comment 3:
compiled from previous studies, it is surprising to see no significant difference of δ15N
values among different phases of nitrate. How the authors explain my doubt;

Reply: We agree with the reviewer that different phases of nitrate generally have
different variation range of δ15N values. We only compiled the δ15N data of particulate
nitrate and precipitation nitrate from previous publications in this study. As a
compromise, below we show the variation range of δ15N values of NHx in all phases
(paper in preparation). Firstly, gaseous NOx is as soluble as NH3 in rainwater, and the
ambient concentrations of HONO and HNO3 are much lower than that of particulate
nitrate. Thus, nitrate in precipitation is largely derived from particulate nitrate. In this
regard, the difference of δ15N values between particulate nitrate and precipitation nitrate
can be expected to lower than the difference of δ15N values between particulate
ammonium and precipitation ammonium. Secondarily, in this study, we have no
intention to accurately the determine the location-specific values for εN in previous
studies. Instead, the εN was assigned by a large range of δ15N values (from 0‰ to 20‰),
which could significantly diminish the potential effects of the δ15N gap between
particulate nitrate and precipitation nitrate on the results of nitrate source apportionment.
Comment 4:

the use of two pathways to explain the nitrogen isotope fractionation is classic and maybe correct to a large extent. I was wondering if other pathways to influence the nitrogen isotope fractionation and subsequently contribute to nitrate formation need to be mentioned at least;

Reply: We’ve enriched the discussion regarding the pathways of nitrate formation in the introduction section. Indeed, the co-editor also pointed out that the direct reactive uptake of NO\textsubscript{3} radicals by aerosol particles also contribute to particulate nitrate. Knopf et al. (2006, 2011) and Shiraiwa et al. (2012) have shown that NO\textsubscript{3} can be taken up efficiently by organic (e.g., levoglucosan) aerosol and may dominate oxidation of aerosol in the polluted urban nighttime (Kaiser et al., 2011). Globally, theoretical modeling results show that nearly 76%, 18%, and 4% of annual inorganic nitrate are formed via pathways/reactions involving OH, N\textsubscript{2}O\textsubscript{5}, and DMS or HC (NO\textsubscript{3} reacts with dimethylsulfide (DMS) or hydrocarbons (HC) predominantly at night) (e.g., Alexander et al., 2009). The stable O isotopic composition of atmospheric nitrate is a powerful proxy for assessing which oxidation pathways are important for converting NO\textsubscript{3} into nitrate under changing environmental conditions (e.g., polluted, volcanic events, climate change). In the same line, in this study, the average $\delta^{18}$O value of $p$NO\textsubscript{3} in Nanjing City was 83.0 ± 11.2‰ (see discussion later), suggesting that $p$NO\textsubscript{3} formation is dominated by the pathways of “OH + NO\textsubscript{2}” and the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5}.

Reference


Comment 5:
Reply: Revised accordingly.
Nitrogen isotope fractionation during gas-particle conversion of NO\textsubscript{x} to NO\textsubscript{3}\textsuperscript{−} in the atmosphere – implications for isotope-based NO\textsubscript{x} source apportionment

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Abstract

Atmospheric fine-particle (PM$_{2.5}$) pollution is frequently associated with the formation of particulate nitrate (pNO$_3^-$), the end product of the oxidation of NO$_x$ gases (=NO+NO$_2$) in the upper troposphere. The application of stable nitrogen (N) (and oxygen) isotope analyses of pNO$_3^-$ to constrain NO$_x$ source partitioning in the atmosphere requires the knowledge of the isotope fractionation during the reactions leading to nitrate formation. Here we determined the $\delta^{15}$N values of fresh pNO$_3^-$ ($\delta^{15}$N-pNO$_3^-$) in PM$_{2.5}$ at a rural site in Northern China, where atmospheric pNO$_3^-$ can be attributed exclusively to biomass burning. The observed $\delta^{15}$N-pNO$_3^-$ (12.17±1.55‰; n=8) was much higher than the N isotopic source signature of NO$_x$ from biomass burning (1.04±4.13‰). The large difference between $\delta^{15}$N-pNO$_3^-$ and $\delta^{15}$N-NO$_x$ ($\Delta(\delta^{15}$N)) can be reconciled by the net N isotope effect ($\varepsilon_N$) associated with the gas-particle conversion from NO$_x$ to NO$_3^-$. For the biomass-burning site, a mean $\varepsilon_N$ ($\approx\Delta(\delta^{15}$N)) of 10.99±0.74‰ was assessed through a newly-developed computational quantum chemistry (CQC) module. $\varepsilon_N$ depends on the relative importance of the two dominant N isotope exchange reactions involved (NO$_2$ reaction with OH versus hydrolysis of dinitrogen pentoxide (N$_2$O$_5$) with H$_2$O), and varies between regions, and on a diurnal basis. A second, slightly higher CQC-based mean value for $\varepsilon_N$ (15.33±4.90‰) was estimated for an urban site with intense traffic in Eastern China, and integrated in a Bayesian isotope mixing model to make isotope-based source apportionment estimates for NO$_x$ at this site. Based on the $\delta^{15}$N values (10.93±3.32‰, n=43) of ambient pNO$_3^-$ determined for the urban site, and considering the location-specific estimate for $\varepsilon_N$, our results reveal that the relative contribution of coal combustion and road traffic to urban NO$_x$ are 32±11% and 68±11%, respectively. This finding agrees well with a regional bottom-up emission inventory of NO$_x$. Moreover, the variation pattern of OH contribution to ambient pNO$_3^-$ formation calculated by the CQC module is consistent with that simulated by the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem), further confirming the robustness of our estimates. Our investigations also show that, without the consideration of the N isotope effect during pNO$_3^-$ formation, the observed $\delta^{15}$N-
\( \rho \text{NO}_x \) at the study site would erroneously imply that \( \text{NO}_x \) is derived almost entirely from coal combustion. Similarly, reanalysis of reported \( \delta^{15}\text{N-NO}_3 \) data throughout China and its neighboring areas suggests that, nationwide, \( \text{NO}_x \) emissions from coal combustion may be substantively overestimated (by >30\%) when the N isotope fractionation during atmospheric \( \rho \text{NO}_3 \) formation is neglected.

1 Introduction

Nitrogen oxides \((\text{NO}_x = \text{NO} + \text{NO}_2)\) are among the most important molecules in tropospheric chemistry. They are involved in the formation of secondary aerosols and atmospheric oxidants, such as ozone \((\text{O}_3)\) and hydroxyl radicals \((\text{OH})\), which controls the self-cleansing capacity of the atmosphere (Galloway et al., 2003; Seinfeld and Pandis, 2012; Solomon et al., 2007). The sources of \( \text{NO}_x \) include both anthropogenic and natural origins, with more than half of the global burden \((\sim 40 \text{ Tg N yr}^{-1})\) currently attributed to fossil fuel burning \((22.4-26.1 \text{ Tg N yr}^{-1})\) and the rest primarily derived from nitrification/denitrification in soils \((8.9 \pm 1.9 \text{ Tg N yr}^{-1})\), biomass burning \((5.8 \pm 1.8 \text{ Tg N yr}^{-1})\), lightning \((2-6 \text{ Tg N yr}^{-1})\), and oxidation of \( \text{N}_2\text{O} \) in the stratosphere \((0.1-0.6 \text{ Tg N yr}^{-1})\) (Jaegle et al., 2005; Richter et al., 2005; Lamsal et al., 2011; Price et al., 1997; Yienger and Levy, 1995; Miyazaki et al., 2017; Duncan et al., 2016; Anenberg et al., 2017; Levy et al., 1996). The main/ultimate sinks for \( \text{NO}_x \) in the troposphere are the oxidation to nitric acid \((\text{HNO}_3)\) and the formation of aerosol-phase particulate nitrate \((\rho \text{NO}_3)\) (Seinfeld and Pandis, 2012), the partitioning of which may vary on diurnal and seasonal time scales (Morino et al., 2006).

Emissions of \( \text{NO}_x \) occur mostly in the form of \( \text{NO} \) (Seinfeld and Pandis, 2012; Leighton, 1961). During daytime, transformation from \( \text{NO} \) to \( \text{NO}_2 \) is rapid \( (\text{few minutes})\) and proceeds in a photochemical steady state, controlled by the oxidation of \( \text{NO} \) by \( \text{O}_3 \) to \( \text{NO}_2 \), and the photolysis of \( \text{NO}_2 \) back to \( \text{NO} \) (Leighton, 1961):

\[
\text{(R1)} \quad \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

\[
\text{(R2)} \quad \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}
\]
(R3) \[ O + O_2 \xrightarrow[M]{\text{M}} O_3, \]

where M is any non-reactive species that can take up the energy released to stabilize O. NOx oxidation to HNO3 is governed by the following equations. During daytime:

(R4) \[ \text{NO}_2 + \text{OH} \xrightarrow[M]{\text{M}} \text{HNO}_3, \]

and during nighttime:

(R5) \[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

(R6) \[ \text{NO}_3 + \text{NO}_2 \xrightarrow[M]{\text{M}} \text{N}_2\text{O}_5 \]

(R7) \[ \text{N}_2\text{O}_5 + \text{H}_2\text{O}_{(\text{aq})} \xrightarrow{\text{aq}} \rightarrow 2\text{HNO}_3. \]

HNO3 then reacts with gas-phase NH3 to form ammonium nitrate (NH4NO3) aerosols.

If the ambient relative humidity (RH) is lower than the efflorescence relative humidity (ERH) or crystallization relative humidity (CRH), solid-phase NH4NO3(s) is formed (Smith et al., 2012; Ling and Chan, 2007):

(R8a) \[ \text{NH}_2\text{NO}_3 \Leftrightarrow \text{HNO}_3(g) + \text{NH}_3(g). \]

If ambient RH exceeds the ERH or CRH, HNO3 and NH3 dissolve into the aqueous phase (aq) (Smith et al., 2012; Ling and Chan, 2007):

(R8b) \[ \text{HNO}_3(g) + \text{NH}_3(g) \Leftrightarrow \text{NO}_3^-_{(aq)} + \text{NH}_4^+_{(aq)}. \]

Whilst global NOx emissions are well constrained, individual source attribution and their local or regional role in particulate nitrate formation are difficult to assess due to the short lifetime of NOx (typically less than 24 hr), and the high degree of spatiotemporal heterogeneity with regards to the ratio between gas-phase HNO3 and particulate NO3- (pNO3-) (Duncan et al., 2016; Lu et al., 2015; Zong et al., 2017; Zhang et al., 2003). Given the conservation of the nitrogen (N) atom between NOx sources and sinks, the N isotopic composition of pNO3- can be related to the different origins of the
emitted NO\textsubscript{x}, and thus provides valuable information on the partitioning of the NO\textsubscript{x} sources \cite{Morin2008}. Such N isotope balance approach works best if the N isotopic composition of various NO\textsubscript{x} sources display distinct $^{15}\text{N}/^{14}\text{N}$ ratios (reported as $\delta^{15}\text{N}$). The $\delta^{15}\text{N}$ of NO\textsubscript{x} of coal-fired power plant (+10‰ to +25‰) \cite{Felix2012, Heaton1990, Felix2013}, vehicle (+3.7‰ to +5.7‰) \cite{Heaton1990, Walters2015, Felix2014, Felix2013, Wojtal2016}, and biomass burning (-7‰ to +12‰) emissions \cite{Fibiger2016}, for example, are generally higher than that of lightning (-0.5‰ to +1.4‰) \cite{Hoering1957} and biogenic soil (-48.9‰ to -19.9‰) emissions \cite{Li2008, Felix2014, Felix2013}, allowing the use of isotope mixing models to gain insight on the NO\textsubscript{x} source apportionment for gases, aerosols, as well as the resulting nitrate deposition (-15‰ to +15‰) \cite{Elliott2007, Zong2017, Savarino2007, Morin2008, Elliott2009, Park2018, Altieri2013}. In addition, because of mass-independent fractionation during its formation \cite{Thiemens1999, Thiemens1983}, ozone possesses a strong isotope anomaly ($\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$), which is propagated into the most short-lived oxygen-bearing species, including NO\textsubscript{x} and nitrate. Therefore, the oxygen isotopic composition of nitrate ($\delta^{18}\text{O}, \Delta^{17}\text{O}$) can provide information on the oxidants involved in the conversion of NO\textsubscript{x} to nitrate \cite{Michalski2003, Geng2017}. \citeauthor{Knopf2006} (2006, 2011) and \citeauthor{Shiraiwa2012} (2012) have shown that NO\textsubscript{2} can be taken up efficiently by organic (e.g., levoglucosan) aerosol and may dominate oxidation of aerosol in the polluted urban nighttime \cite{Kaiser2011}. Globally, theoretical modeling results show that nearly 76%, 18%, and 4% of annual inorganic nitrate are formed via pathways/reactions involving OH, N\textsubscript{2}O\textsubscript{5}, and DMS or HC (NO\textsubscript{3} reacts with dimethylsulfide (DMS) or hydrocarbons (HC) predominantly at night) \cite{Alexander2009}. The stable O isotopic composition of atmospheric nitrate is a powerful proxy for assessing which oxidation pathways are important for converting NO\textsubscript{x} into nitrate under changing environmental conditions (e.g., polluted, volcanic events, climate change). In the same line, in this study, the average $\delta^{18}\text{O}$ value of $\rho$NO\textsubscript{x}}
in Nanjing City was 83.0 ± 11.2‰ (see discussion later), suggesting that $p$NO$_3^-$ formation is dominated by the pathways of “OH + NO$_2$” and the heterogeneous hydrolysis of N$_2$O$_5$.

$\delta^{15}$N-based source apportionment of NO$_x$ requires knowledge of how kinetic and equilibrium isotope fractionation may impact $\delta^{15}$N values during the conversion of NO$_x$ to nitrate (Freyer, 1978; Walters et al., 2016). If these isotope effects are considerable, they may greatly limit the use of $\delta^{15}$N values of $p$NO$_3^-$ for NO$_x$ source partition (Walters et al., 2016). Previous studies didn’t take into account the potentially biasing effect of N isotope fractionation, because they assumed that changes in the $\delta^{15}$N values during the conversion of NO$_x$ to nitrate are minor (without detailed explanation) (Kendall et al., 2007; Morin et al., 2008; Elliott et al., 2007) or relatively small (e.g., +3‰) (Felix and Elliott, 2014; Freyer, 2017). However, a field study by Freyer et al. (1993) has indicated that N isotope exchange may have a strong influence on the observed $\delta^{15}$N values in atmospheric NO and NO$_2$, implying that isotope equilibrium fractionation may play a significant role in shaping the $\delta^{15}$N of NO$_3^-$ species (the family of oxidized nitrogen molecules in the atmosphere, including NO$_x$, NO$_2$, NO$_3^-$, peroxyacetyl nitrate etc.). The transformation of NO$_x$ to nitrate is a complex process that involves several different reaction pathways (Walters et al., 2016). To date, few fractionation factors for this conversion have been determined. Recently, Walters and Michalski (2015) and Walters et al. (2016) used computational quantum chemistry methods to calculate N isotope equilibrium fractionation factors for the exchange between major NO$_x$ molecules and confirmed theoretical predictions that $^{15}$N isotopes enrich in the more oxidized form of NO$_3^-$, and that the transformation of NO$_x$ to atmospheric nitrate (HNO$_3$, NO$_3^-$ (aq), NO$_3^-$ (g)) continuously increases the $\delta^{15}$N in the residual NO$_x$ pool.

As a consequence of its severe atmospheric particle pollution during the cold season, China has made great efforts toward reducing NO$_x$ emissions from on-road traffic (e.g., improving emission standards, higher gasoline quality, vehicle travel restrictions) (Li et al., 2017). Moreover, China has continuously implemented denitrogenation technologies (e.g., selective catalytic reduction or SCR) in the coal-fired power plants
sector since the mid-2000s, and has been phasing out small inefficient units (Liu et al., 2015). Monitoring and assessing the efficiency of such mitigation measures, and optimizing policy efforts to further reduce NO\textsubscript{x} emissions, requires knowledge of the vehicle- and power plant-emitted NO\textsubscript{x} to particulate nitrate in urban China (Ji et al., 2015; Fu et al., 2013; Zong et al., 2017). In this study, the chemical components of ambient fine particles (PM\textsubscript{2.5}) were quantified, and the isotopic composition of particulate nitrate (\(\delta^{15}\text{N-NO}_3\), \(\delta^{18}\text{O-NO}_3\)) was assessed in order to elucidate ambient NO\textsubscript{x} sources in Nanjing City of Eastern China two distinct areas of China. We also investigated the potential isotope effect during the formation of nitrate aerosols from NO\textsubscript{x}, and evaluated how disregard of such N isotope fractionation can bias N-isotope mixing model-based estimates on the NO\textsubscript{x} source apportionment for nitrate deposition.

2 Methods

2.1 Field sampling

In this study, PM\textsubscript{2.5} aerosol samples were collected on precombusted (450 °C for 6 hr) quartz filters (25 × 20 cm) on a day/night basis, using high-volume air samplers at a flow rate of 1.05 m\textsuperscript{3} min\textsuperscript{-1} in Sanjiang and Nanjing (Fig. 1). After sampling, the filters were wrapped in aluminum foil, packed in air-tight polyethylene bags and stored at -20 °C prior to further processing and analysis. Four blank filters were also collected. They were exposed for 10 min to ambient air (i.e., without active sampling). PM\textsubscript{2.5} mass concentration was analyzed gravimetrically (Sartorius MC5 electronic microbalance) with a ± 1 μg precision before and after sampling (at 25°C and 45 ± 5% during weighing).

The Sanjiang campaign was performed during a period of intensive burning of
agricultural residues between October 8 and 18, 2013, to examine if there is any significant difference between the $\delta^{15}$N values of $p$NO$_3^-$ and NO$_x$ emitted from biomass burning. The Sanjiang site (in the following abbreviated as SJ; 47.35°N, 133.31°E) is located at an ecological experimental station affiliated with the Chinese Academy of Sciences located in the Sanjiang Plain, a major agricultural area predominantly run by state farms in Northeastern China (Fig. 1). Surrounded by vast farm fields and bordering Far-Eastern Russia, SJ is situated in a remote and sparsely populated region, with a harsh climate and rather poorly industrialized economy. The annual mean temperature at SJ is close to the freezing point, with daily minima ranging between -31 and -15°C in the coldest month January. As a consequence of the relatively low temperatures (also during summer), biogenic production of NO$_x$ through soil microbial processes is rather weak. SJ is therefore an excellent environment where to collect biomass burning-emitted aerosols with only minor influence from other sources.

The Nanjing campaign was conducted between 17 December 2014 and 8 January 2015 with the main objective to examine whether N isotope measurements can be used as a tool to elucidate NO$_x$ source contributions to ambient $p$NO$_3^-$ during times of severe haze. Situated in the heartland of the lower Yangtze River region, Nanjing is, after Shanghai, the second largest city in Eastern China. The aerosol sampler was placed at the rooftop of a building on the Nanjing University of Information Science and Technology campus (in the following abbreviated as NJ; 18 m a.g.l.; 32.21° N, 118.72° E; Fig. 1), where NO$_x$ emissions derive from both industrial and transportation sources.

### 2.2 Laboratory analysis

The mass concentrations of inorganic ions (including SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, and Na$^+$), carbonaceous components (organic carbon or OC, elemental carbon or EC), and water-soluble organic carbon or WSOC were determined using an ion chromatograph (761 Compact IC, Metrohm, Switzerland), a thermal/optical OC/EC analyzer (RT-4 model, Sunset Lab. Inc., USA), and a TOC analyzer (Shimadzu, TOC-VCSH, Japan), respectively. Importantly, levoglucosan, a molecular marker for the
biomass combustion aerosols was detected using a Dionex™ ICS-5000+ system (Thermo Fisher Scientific, Sunnyvale, USA). In addition, a homologous series of dicarboxylic acids (C$_2$-C$_{11}$) and related compounds (oxoacids, α-dicarbonyls and fatty acids) were analyzed using an Agilent 7890 gas chromatography and GC-MS detection (Agilent Technologies, Wilmington, USA), employing a dibutyl ester derivatization technique. Chemical aerosol analyses, including sample pre-treatment, analytical procedures, protocol adaption, detection limits, and experimental uncertainty were described in detail in our previous work (Cao et al., 2016; Cao et al., 2017).

For isotopic analyses of aerosol nitrate, aerosol subsamples were generated by punching 1.4-cm disks out of the filters. In order to extract the NO$_3^-$, sample discs were placed in acid-washed glass vials with 10 ml deionized water and placed in an ultra-sonic water bath for 30 min. Between one and four disks were used for NO$_x$ extraction, dependent on the aerosol NO$_3^-$ content on the filters, which was determined independently. The extracts were then filtered (0.22 μm) and analyzed the next day. N and O isotope analyses of the extracted/dissolved aerosol nitrate ($^{15}$N/$^{14}$N, $^{18}$O/$^{16}$O) were performed using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, sample NO$_3^-$ is converted to nitrous oxide (N$_2$O) by denitrifying bacteria that lack N$_2$O reductase activity (Pseudomonas chlororaphis ATCC# 13985; formerly Pseudomonas aureofaciens, referred to below as such). N$_2$O is extracted, purified, and analyzed for its N and O isotopic composition using a continuous-flow isotope ratio mass spectrometer (Thermo Finnigan Delta+®, Bremen, German). Nitrate N and O isotope ratios are reported in the conventional δ-notation with respect to atmospheric N$_2$ and standard mean ocean water (V-SMOW) respectively. Analyses are calibrated using the international nitrate isotope standard IAEA-N3, with a δ$^{15}$N value of 4.7‰ and a δ$^{18}$O value of 25.6‰ (Böhlke et al., 2003). The blank contribution was generally lower than 0.2 nmol (as compared to 20 nmol of sample N). Based on replicate measurements of standards and samples, the analytical precision for δ$^{15}$N and δ$^{18}$O was generally better than ±0.2‰ and ±0.3‰ (1σ), respectively.

The denitrifier method generates δ$^{15}$N and δ$^{18}$O values of the combined pool of NO$_3^-$.
and NO$_2^-$. The presence of substantial amounts of NO$_2^-$ in NO$_3^-$ samples may lead to errors with regards to the analysis of $\delta^{18}$O (Wankel et al., 2010). We refrained from including a nitrite-removal step, because nitrite concentrations in our samples were always < 1% of the NO$_3^-$ concentrations. In the following $\delta^{15}$N$_{NOx}$ and $\delta^{18}$O$_{NOx}$ are thus referred to as nitrate $\delta^{15}$N and $\delta^{18}$O (or $\delta^{15}$N$_{NO3}$ and $\delta^{18}$O$_{NO3}$).

In the case of atmospheric/aerosol nitrate samples with comparatively high $\delta^{18}$O values, $\delta^{15}$N values tend to be overestimated by 1-2‰ (Hastings et al., 2003), if the contribution of $^{14}$N to the N$_2$O mass 45 signal is not accounted for during isotope ratio analysis. For most natural samples, the mass-dependent relationship can be approximated as $\delta^{17}$O $\approx$ 0.52 $\times$ $\delta^{18}$O, and the $\delta^{18}$O can be used for the $^{17}$O correction. Atmospheric NO$_3^-$ does not follow this relationship but inhabits a mass-independent component. Thus, we adopted a correction factor of 0.8 instead of 0.52 for the $^{17}$O to $^{18}$O linearity (Hastings et al., 2003).

2.3 Calculation of N isotope fractionation value ($\varepsilon_N$)

As we described above, the transformation process of NO$_x$ to HNO$_3$/NO$_3^-$ involves multiple reaction pathways (see also Fig. S1) and is likely to undergo isotope equilibrium exchange reactions. The measured $\delta^{15}$N$_{NO3}$ values of aerosol samples are thus reflective of the combined N isotope signatures of various NO$_x$ sources ($\delta^{15}$N-NO$_x$) plus any given N isotope fractionation. Recently, Walter and Michalski (2015) used a computational quantum chemistry approach to calculate isotope exchange fractionation factors for atmospherically relevant NO$_y$ molecules, and based on this approach, Zong et al. (2017) estimated the N isotope fractionation during the transformation of NO$_x$ to pNO$_3^-$ at a regional background site in China. Here we adopt, and slightly modify, the approach by Walter and Michalski (2015) and Zong et al. (2017), and assumed that the net N isotope effect $\varepsilon_N$ (for equilibrium processes A$\leftrightarrow$B: $\varepsilon_{A\leftrightarrow B} = \left(\frac{\text{heavy isotope/light isotope}}{\text{heavy isotope/light isotope}}\right)_A - 1\right) \times 1000$‰; $\varepsilon_N$ refers to $\varepsilon_N$(NO$_x$,$\leftrightarrow$NO$_3^-$) in this study unless otherwise specified) during the gas-to-particle conversion from NO$_x$ to
\[ p_{NO_3} \text{ formation (} \Delta \delta^{15}N \text{)}_{p_{NO_3}} = \delta^{15}N_{p_{NO_3}} - \delta^{15}N_{NO_3} \approx \varepsilon_N \] can be considered a hybrid of the isotope effects of two dominant N isotopic exchange reactions:

\[ \varepsilon_N = \frac{\gamma e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}}}{1 - \gamma} + \frac{1 - \gamma}{1 - \gamma} e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \quad (1) \]

where \( \gamma \) represents the contribution from isotope fractionation by the reaction of NO\(_x\) and photo-chemically produced OH to form HNO\(_3\) (and \( p_{NO_3} \)), as shown by

\[ e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} (e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}}) \]. The remainder is formed by the hydrolysis of N\(_2\)O\(_5\) with aerosol water to generate HNO\(_3\) (and \( p_{NO_3} \)), namely, \( e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \) (\( e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \)). Assuming that kinetic N isotope fractionation associated with the reaction between NO\(_x\) and OH is negligible, \( e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \) can be calculated based on mass-balance considerations:

\[ e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} = e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} = e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \]

\[ = 1000 \left[ \frac{15 \alpha_{\text{NO}_3/\text{NO}} - 1}{1 - f_{\text{NO}_3}} \right] \quad (2) \]

where \( 15 \alpha_{\text{NO}_3/\text{NO}} \) is the temperature-dependent (see equation 7 and Table S1) equilibrium N isotope fractionation factor between NO\(_2\) and NO, and \( f_{\text{NO}_3} \) is the fraction of NO\(_3\) in the total NO\(_x\). \( f_{\text{NO}_3} \) ranges from 0.2 to 0.95 (Walters and Michalski, 2015). Similarly, assuming a negligible kinetic isotope fractionation associated with the reaction N\(_2\)O\(_5\) + H\(_2\)O + aerosol \( \rightarrow \) 2HNO\(_3\), \( e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} \) can be computed from the following equation:

\[ e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} = e_{N_N(\text{NO}_3,\text{HNO}_3)_{\text{air}}} = 1000 \left( 15 \alpha_{\text{NO}_3/\text{NO}} - 1 \right) \quad (3) \]
where $^{15}\alpha_{\text{N}_2\text{O}_5/\text{NO}_2}$ is the equilibrium isotope fractionation factor between N$_2$O$_5$ and NO$_2$, which also is temperature-dependent (see equation 7 and Table S1).

Following Walter and Michalski (2015) and Zhong et al. (2017), $\gamma$ can then be approximated based on the O isotope fractionation during the conversion of NO$_x$ to pNO$_3$:

$$
\varepsilon_{\text{O}(\text{NO}_x,\text{pNO}_3)} = \gamma \times \varepsilon_{\text{O}(\text{NO},\text{pNO})}_{\text{uu}} + (1-\gamma) \times \varepsilon_{\text{O}(\text{NO},\text{pNO})}_{\text{l-o}} 
$$

(4)

where $\varepsilon_{\text{O}(\text{NO},\text{pNO})}_{\text{uu}}$ and $\varepsilon_{\text{O}(\text{NO},\text{pNO})}_{\text{l-o}}$ represent the O isotope effects associated with pNO$_3$ generation through the reaction of NO$_x$ and OH to form HNO$_3$, and the hydrolysis of N$_2$O$_5$ on a wetted surface to form HNO$_3$, respectively. $\varepsilon_{\text{O}(\text{NO}_x,\text{pNO})}_{\text{uu}}$ can be further expressed as:

$$
\varepsilon_{\text{O}(\text{NO}_x,\text{pNO})}_{\text{uu}} = 2 \times \varepsilon_{\text{O}(\text{NO},\text{pHNO})}_{\text{uu}} + \frac{1}{3} \varepsilon_{\text{O}(\text{NO},\text{pHNO})}_{\text{l-o}} + \frac{2}{3} \left[ 1000 \left( ^{15}\alpha_{\text{NO}_2/\text{NO}} - 1 \right) \left( 1 - f_{\text{NO}_2}^{\text{NO}} \right) + \left( ^{15}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2}^{\text{NO}} \right) \right] + \left( ^{15}\alpha_{\text{NO}_3/\text{NO}} \times f_{\text{NO}_3}^{\text{NO}} \right) 
$$

(5)

and $\varepsilon_{\text{O}(\text{NO}_x,\text{pNO})}_{\text{l-o}}$ can be determined as follows:

$$
\varepsilon_{\text{O}(\text{NO}_x,\text{pNO})}_{\text{l-o}} = \varepsilon_{\text{O}(\text{NO},\text{pHNO})}_{\text{l-o}} + \frac{5}{6} \left( ^{15}\alpha_{\text{N}_2\text{O}_5/\text{NO}} \right) + \frac{1}{6} \left( ^{15}\alpha_{\text{OH}/\text{H}_2\text{O}} \right) 
$$

(6)

where $^{15}\alpha_{\text{NO}_2/\text{NO}}$ and $^{15}\alpha_{\text{OH}/\text{H}_2\text{O}}$ represent the equilibrium O isotope fractionation factors between NO$_2$ and NO, and OH and H$_2$O, respectively. The range of $\delta^{18}$O-H$_2$O can be approximated using an estimated tropospheric water vapor $\delta^{18}$O range of -25‰-0‰. The $\delta^{18}$O values for NO$_2$ and N$_2$O$_5$ range from 90‰ to 122‰ (Zong et al. 2017).
and

\[
1000 \left( \delta^18O_{\text{pNO}_3} - 1 \right) = \frac{A}{T^4} \times 10^9 + \frac{B}{T^3} \times 10^9 + \frac{C}{T^2} \times 10^9 + \frac{D}{T} \times 10^4
\]

(7)

where A, B, C, and D are experimental constants (Table S1) over the temperature range of 150-450 K (Walters and Michalski, 2015; Walters et al., 2016; Walters and Michalski, 2016; Zong et al., 2017).

Based on Equations 4-7 and measured values for \( \delta^18O_{\text{pNO}_3} \) of ambient PM\(_{2.5} \), a Monte Carlo simulation was performed to generate 10000 feasible solutions. The error between predicted and measured \( \delta^18O \) was less than 0.5‰. The range (maximum and minimum) of computed contribution ratios (\( \gamma \)) were then integrated in Equation 1 to generate an estimate range for the nitrogen isotope effect \( \epsilon_N \) (using Equations 2-3). \( \delta^{15}N_{\text{pNO}_3} \) values can be calculated based on \( \epsilon_N \) and the estimated \( \delta^{15}N \) range for atmospheric NO\(_x\), (see section 2.4).

### 2.4 Bayesian isotope mixing model

Isotopic mixing models allow estimating the relative contribution of multiple sources (e.g., emission sources of NO\(_x\)) within a mixed pool (e.g., ambient pNO\(_3\)). By explicitly considering the uncertainty associated with the isotopic signatures of any given source, as well as isotope fractionation during the formation of various components of a mixture, the application of Bayesian methods to stable isotope mixing models generates robust probability estimates of source proportions, and are often more appropriate when targeting natural systems than simple linear mixing models (Chang et al., 2016a). Here the Bayesian model MixSIR (a stable isotope mixing model using sampling-importance-resampling) was used to disentangle multiple NO\(_x\) sources by generating potential solutions of source apportionment as true probability distributions, which has been widely applied in a number of fields (e.g., Parnell et al., 2013; Phillips et al., 2014; Zong et al., 2017). Details on the model frame and computing methods are given in SI.
Here, coal combustion (13.72 ± 4.57‰), transportation (-3.71 ± 10.40‰), biomass burning (1.04 ± 4.13‰), and biogenic emissions from soils (-33.77 ± 12.16‰) were considered to be the most relevant contributors of NOx (Table S2 and Text S2). The δ15N of atmospheric NOx is unknown. However, it can be assumed that its range in the atmosphere is constrained by the δ15N of the NOx sources and the δ15N of pNO3- after equilibrium fractionation conditions have been reached. Following Zong et al. (2017), δ15N-NOx in the atmosphere was determined performing iterative model simulations, with a simulation step of 0.01 times the equilibrium fractionation value based on the δ15N(NOx) values of the emission sources (mean and standard deviation) and the measured δ15N-pNO3- of ambient PM2.5 (Fig. S2).

3 Results

3.1 Sanjiang in Northern China

The δ15N-pNO3- and δ18O-pNO3- values of the eight samples collected from the Sanjiang biomass burning field experiment, ranged from 9.54 to 13.77‰ (mean: 12.17‰) and 57.17 to 75.09‰ (mean: 63.57‰), respectively. In this study, atmospheric concentrations of levoglucosan quantified from PM2.5 samples collected near the sites of biomass burning in Sanjiang vary between 4.0 and 20.5 µg m⁻³, two to five orders of magnitude higher than those measured during non-biomass burning season (Cao et al., 2017; Cao et al., 2016). Levoglucosan is an anhydrosugar formed during pyrolysis of cellulose at temperatures above 300 °C (Simoneit, 2002). Due to its specificity for cellulose combustion, it has been widely used as a molecular tracer for biomass burning (Simoneit et al., 1999; Liu et al., 2013a; Jedynska et al., 2014; Liu et al., 2014). Indeed, the concentrations of levoglucosan and aerosol nitrate in Sanjiang were highly correlated (R² = 0.64; Fig. 2a), providing compelling evidence that particulate nitrate measured during our study period was predominately derived from biomass burning emissions.
3.2 Nanjing in Eastern China

The mass concentrations (mean$_{\text{nm}}$ ± 1σ, n = 43) of PM$_{2.5}$ and pNO$_3^-$ measured in Nanjing City were 122.1$_{39.0}^{27.8}$ ± 47.9 and 17.8$_{10.3}^{45.2}$ ± 10.3 μg m$^{-3}$, respectively. All PM$_{2.5}$ concentrations exceeded the Chinese Air Quality Standard for daily PM$_{2.5}$ (35 μg m$^{-3}$), suggesting severe haze pollution during the sampling period. The corresponding δ$^{15}$N-pNO$_3^-$ values (raw data without correction) ranged between 5.39‰ and 17.99‰, indicating significant enrichment in $^{15}$N relative to rural and coastal marine atmospheric NO$_3^-$ sources (Table S4). This may be due to the prominent contribution of fossil fuel-related NO$_x$ emissions with higher δ$^{15}$N values in urban areas (Elliott et al., 2007; Park et al., 2018).

4 Discussion

4.1 Sanjiang campaign: theoretical calculation and field validation of N isotope fractionation during pNO$_3^-$ formation

To be used as a quantitative tracer of biomass-combustion-generated aerosols, levoglucosan must be conserved during its transport from its source, without partial removal by reactions in the atmosphere (Hennigan et al., 2010). The mass concentrations of non-sea-salt potassium (nss-K$^+$ = K$^+$ - 0.0355*Na$^+$) is considered as an independent/additional indicator of biomass burning (Fig. 2b). The association of elevated levels of levoglucosan with high nss-K$^+$ concentrations underscores that the two compounds derived from the same proximate sources, and that thus aerosol levoglucosan in Sanjiang was indeed pristine and represented a reliable source indicator that is unbiased by altering processes in the atmosphere. Moreover, in our previous work (Cao et al., 2017), we observed that there was a much greater enhancement of atmospheric NO$_3^-$ compared to SO$_4^{2-}$ (a typical coal-related pollutant). This additionally points to biomass burning, and not coal-combustion, as the dominant pNO$_3^-$ source in the study area, making SJ and ideal “quasi single source” environment for calibrating...
the N isotope effect during $p$NO$_3^-$ formation.

Our $\delta^{18}$O-$p$NO$_3^-$ values are well within the broad range of values in previous reports (Zong et al., 2017; Geng et al., 2017; Walters and Michalski, 2016). However, as depicted in Fig. 3, the $\delta^{15}$N values of biomass burning-emitted NO$_3^-$ fall within the range of $\delta^{15}$N-NO$_x$ values typically reported for emissions from coal combustion, whereas they are significantly higher than the well-established values for $\delta^{15}$N-NO$_x$ emitted from the burning of various types of biomass (mean: $1.04 \pm 4.13\%$, ranging from -7 to +12%) (Fibiger and Hastings, 2016). Turekian et al. (1998) conducted laboratory tests involving the burning of eucalyptus and African grasses, and determined that the $\delta^{15}$N of $p$NO$_3^-$ (around 23%) was 6.6% higher than the $\delta^{15}$N of the burned biomass. This implies significant N isotope partitioning during biomass burning.

In the case of complete biomass combustion, by mass balance, the first gaseous products (i.e., NO$_x$) have the same $\delta^{15}$N as the biomass. Hence any discrepancy between the $p$NO$_3^-$ and the $\delta^{15}$N of the biomass can be attributed to the N isotope fractionation associated with the partial conversion of gaseous NO$_x$ to aerosol NO$_3^-$. Based on the computational quantum chemistry (CQC) module calculations, the N isotope fractionation $\epsilon_N$ determined from the Sanjiang data was $10.99^{+2.54}_{-0.30} \pm 0.74\%o$. After correcting the primary $\delta^{15}$N-$p$NO$_3^-$ values under the consideration of $\epsilon_N$, the resulting mean $\delta^{15}$N of $1.17^{+2.90}_{-1.30} \pm 1.95\%o$ is very close to the N isotopic signature expected for biomass burning-emitted NO$_x$ ($1.04 \pm 4.13\%o$) (Fig. 3) (Fibiger and Hastings, 2016). The much higher $\delta^{15}$N-$p$NO$_3^-$ values in our study compared to reported $\delta^{15}$N-NO$_x$ values for biomass burning can easily be reconciled when including N isotope fractionation during the conversion of NO$_x$ to NO$_3^-$. Put another way, given that Sanjiang is an environment where we can essentially exclude
NO\textsubscript{x} sources other than biomass burning at the time of sampling, the data nicely validate our CQC module-based approach to estimate $\epsilon_N$.

**Figure 3.**

### 4.2 Source apportionment of NO\textsubscript{x} in an urban setting using a Bayesian isotopic mixing model

Due to its high population density and intensive industrial production, the Nanjing atmosphere was expected to have high NO\textsubscript{x} concentrations derived from road traffic and coal combustion (Zhao et al., 2015). However, the raw $\delta^{15}$N-\textit{p}NO\textsubscript{x} values (10.93 ± 3.32‰) fell well within the variation range of coal-emitted $\delta^{15}$N-NO\textsubscript{x} (Fig. 3). It is tempting to conclude that coal combustion is the main, or even sole, \textit{p}NO\textsubscript{x} source (given the equivalent $\delta^{15}$N values), yet, this is very unlikely. The data rather confirm that significant isotope fractionation occurred during the conversion of NO\textsubscript{x} to NO\textsubscript{3} and that, without consideration of the N isotope effect, traffic-related NO\textsubscript{x} emissions will be markedly underestimated.

In the atmosphere, the oxygen atoms of NO\textsubscript{x} rapidly exchanged with O\textsubscript{3} in the NO/NO\textsubscript{2} cycle (see equations R\textsubscript{1}-R\textsubscript{3}) (Hastings et al., 2003), and the $\delta^{18}$O-\textit{p}NO\textsubscript{3} values are determined by its production pathways (R\textsubscript{4}-R\textsubscript{7}), rather than the sources of NO\textsubscript{x} (Hastings et al., 2003). Thus, $\delta^{18}$O-\textit{p}NO\textsubscript{3} can be used to gain information on the pathway of conversion of NO\textsubscript{x} to nitrate in the atmosphere (Fang et al., 2011). In the computational quantum chemistry module used here to calculate isotope fractionation, we assumed that two-thirds of the oxygen atoms in NO\textsubscript{3} derive from O\textsubscript{3} and one-third from •OH in the •OH generation pathway (R\textsubscript{4}) (Hastings et al., 2003); correspondingly, five sixths of the oxygen atoms then derived from O\textsubscript{3} and one sixth from •OH in the O\textsubscript{3}/H\textsubscript{2}O pathway (R\textsubscript{5}-R\textsubscript{7}). The assumed range for $\delta^{18}$O-O\textsubscript{3} and $\delta^{18}$O-H\textsubscript{2}O values were
90%–122‰ and -25%–0‰, respectively (Zong et al., 2017). The partitioning between the two possible pathways was then assessed through Monte Carlo simulation (Zong et al., 2017). The estimated range was rather broad, given the wide range of $\delta^{18}$O-O$_3$ and $\delta^{18}$O-H$_2$O values used. Nevertheless, the theoretical calculation of the average contribution ratio ($\gamma$) for nitrate formation in Nanjing via the reaction of NO$_2$ and •OH is consistent with the results from simulations using the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) (Fig. 4; see Text S3 for details). A clear diurnal cycle of the mass concentration of nitrate formed through •OH oxidation of NO$_2$ can be observed (Fig. S3), with much higher concentrations between 12:00 and 18:00. This indicates the importance of photochemically produced •OH during daytime. Yet, throughout our sampling period in Nanjing, the average $p$NO$_3^-$ formation by the heterogeneous hydrolysis of N$_2$O$_5$ (12.6 μg m$^{-3}$) exceeded $p$NO$_3^-$ formation by the reaction of NO$_2$ and •OH (4.8 μg m$^{-3}$), even during daytime, consistent with recent observations during peak pollution periods in Beijing (Wang et al., 2017). Given that the production rates of N$_2$O$_5$ in the atmosphere is governed by ambient O$_3$ concentrations, reducing atmospheric O$_3$ levels appears to be one of the utmost important measures to take for mitigating $p$NO$_3^-$ pollution in China’s urban atmospheres.

Figure 4.

In Nanjing, dependent on the time-dependent, dominant $p$NO$_3^-$ formation pathway, the average N isotope fractionation value calculated using the computational quantum chemistry module varied between 10.77‰ and 19.34‰ (15.33‰ on average). Using the Bayesian model MixSIR, the contribution of each source can be estimated, based on the mixed-source isotope data under the consideration of prior information on the site (see Text S1 for detailed information regarding model frame and computing method). As described above, theoretically, there are four major sources, i.e., road
traffic, coal combustion, biomass burning, and biogenic soil, potentially contributing to
ambient NO$_x$. As a start, we tentatively integrated all four sources into MixSIR (data
not shown). The relative contribution of biomass burning to the ambient NO$_x$ (median
value) ranged from 28% to 70% (average 42%), representing the most important source.
The primary reason for such apparently high contribution by biomass burning is that
the corrected $\delta^{15}$N-$p$NO$_3^-$ values of $-4.29^{+4.42}_{-0.32} \pm 3.66‰$ are relatively close to the N
isotopic signature of biomass burning-emitted NO$_x$ ($1.04 \pm 4.13‰$) compared to the
other possible sources. Based on $\delta^{15}$N alone, the isotope approach can be ambiguous if
there are more than two sources. The N isotope signature of NO$_x$ from biomass burning
falls right in between the spectrum of plausible values, with highest $\delta^{15}$N for emissions
from coal combustion on the one end, and much lower values for automotive and soil
emissions on the other, and will be similar to a mixed signature from coal combustion
and NO$_x$ emissions from traffic.

We can make several evidence-based pre-assumption to better constrain the emission
sources in the mixing model analysis: (1) sampling at a typical urban site in a major
industrial city in China, we can assume that the sources of road traffic and coal
combustion are dominant, while the contribution of biogenic soil to ambient NO$_x$
should have minimal impact, or can be largely neglected (Zhao et al., 2015); (2) there
is no crop harvest activity in Eastern China during the winter season. Furthermore,
deforestation and combustion of fuelwood has been discontinued in China’s major
cities (Chang et al., 2016a). Therefore, the contribution of biomass burning-emitted
NO$_x$ during the sampling period should also be minor. Indeed, Fig. S4 shows that the
mass concentration of biomass burning-related $p$NO$_x$ is not correlated with the fraction
of levoglucosan that contributes to OC, confirming a weak impact of biomass burning
on the variation of $p$NO$_x$ concentration during our study period.

In a second, alternative, and more realistic scenario, we excluded biomass burning and
soil as potential source of NO$_x$ in MixSIR (see above). As illustrated in Fig. 5a,
assuming that NO$_x$ emissions in urban Nanjing during our study period originated
solely from road traffic and coal combustion, their relative contribution to the mass concentration of $p$NO$_3^-$ is $12.5 \pm 9.1 \mu g m^{-3}$ (or $68 \pm 11\%$) and $4.9 \pm 2.5 \mu g m^{-3}$ (or $32 \pm 11\%$), respectively. These numbers agree well with a city-scale NO$_x$ emission inventory established for Nanjing recently (Zhao et al., 2015). Nevertheless, on a nation-wide level, relatively large uncertainties with regards to the overall fossil fuel consumption and fuel types propagate into large uncertainties of NO$_x$ concentration estimates and predictions of longer-term emission trends (Li et al., 2017). Current emission-inventory estimates (Jaegle et al., 2005; Zhang et al., 2012; Liu et al., 2015; Zhao et al., 2013) suggest that in 2010 NO$_x$ emissions from coal-fired power plants in China were about 30% higher than those from transportation. However, our isotope-based source apportionment of NO$_x$ clearly shows that in 2014 the contribution from road traffic to NO$_x$ emissions, at least in Nanjing (a city that can be considered representative for most densely populated areas in China) is twice that of coal combustion. In fact, due to changing economic activities, emission sources of air pollutants in China are changing rapidly. For example, over the past several years, China has implemented an extended portfolio of plans to phase out its old-fashioned and small power plants, and to raise the standards for reducing industrial pollutant emissions (Chang, 2012). On the other hand, China continuously experienced double-digit annual growth in terms of auto sales during the 2000s, and in 2009 it became the world’s largest automobile market (Liu et al., 2013b; Chang et al., 2017; Chang et al., 2016b). Recent satellite-based studies successfully analyzed the NO$_x$ vertical column concentration ratios for megacities in Eastern China and highlighted the importance of transportation-related NOx emissions (Reuter et al., 2014; Gu et al., 2014; Duncan et al., 2016; Jin et al., 2017). Moreover, long-term measurements of the ratio of NO$_3^-$ versus non-sea-salt SO$_4^{2-}$ in precipitation and aerosol jointly revealed a continuously increasing trend in Eastern China throughout the latest decade, suggesting decreasing emissions from coal combustion (Liu et al., 2013b; Itahashi et al., 2017). Both coal combustion- and road traffic-related $p$NO$_3^-$ concentrations are highly correlated with their corresponding tracers (i.e., SO$_2$ and CO, respectively), confirming the validity of our MixSIR modelling results. With justified confidence in our Bayesian isotopic model
results, we conclude that previous estimates of NO$_x$ emissions from automotive/transportation sources in China based on bottom-up emission inventories may be too low.

### Figure 5.

#### 3.3 Previous $\delta^{15}$N-NO$_3$-based estimates on NO$_x$ sources

Stable nitrogen isotope ratios of nitrate have been used to identify nitrogen sources in various environments in China, often without large differences in $\delta^{15}$N between rainwater and aerosol NO$_3^-$ (Kojima et al., 2011). In previous work, no consideration was given to potential N isotope fractionation during atmospheric $p$NO$_3^-$ formation.

Here, we reevaluated 700 data points of $\delta^{15}$N-NO$_3^-$ in aerosol ($-0.77 \pm 4.52\%o$, $n = 308$) and rainwater ($3.79 \pm 6.14\%o$, $n = 392$) from 13 sites that are located in the area of mainland China and the Yellow and East and South China Seas (Fig. 1), extracted from the literature (see SI Table S4 for details). To verify the potentially biasing effects of neglecting N isotope fractionation (i.e. testing the sensitivity of ambient NO$_x$ source contribution estimates to the effect of N isotope fractionation), the Bayesian isotopic mixing model was applied a) to the original NO$_3^-$ isotope data set and b) to the corrected nitrate isotope data set, accounting for the N isotope fractionation during NO$_x$ transformation. All 13 sampling sites are located in non-urban areas; therefore, apart from coal combustion and on-road traffic, the contributions of biomass burning and biogenic soil to nitrate needs to be taken into account.

Although most of the sites are located in rural and coastal environments, using the original data set without the consideration of N isotope fractionation in the Bayesian isotopic mixing model, fossil fuel-related NO$_x$ emissions (coal combustion and on-road traffic) appear as the largest contributor at all the sites (data are not shown). This is
particularly true for coal combustion: Everywhere, except for the sites of Dongshan Islands and Mt. Lumin, NO$_x$ emissions seem to be dominated by coal combustion. Very high contribution from coal combustion (on the order of 40-60%) particularly in Northern China may be plausible, and can be attributed to a much larger consumption of coal. Yet, rather unlikely, the highest estimated contribution of coal combustion (83%) was calculated for Beihuang Island (a full-year sampling at a coastal island that is 65 km north of Shandong Peninsula and 185 km east of the Beijing-Tianjin-Hebei region) and not for mainland China. While Beihuang may be an extreme example, we argue that, collectively, the contribution of coal combustion to ambient NO$_x$ in China as calculated on the basis of isotopic analyses in previous studies without the consideration of N isotope fractionation represent overestimates.

As a first step towards a more realistic assessment of the actual partitioning of NO$_x$ sources in China in general (and coal combustion-emitted NO$_x$ in particular), it is imperative to determine the location-specific values for $\epsilon_N$. Unfortunately, without $\delta^{18}$O-NO$_3^-$ data in hand, as well as data on meteorological parameters that correspond to the 700 $\delta^{15}$N-NO$_3^-$ values used in our meta-analysis, it is not possible to estimate the $\epsilon_N$ values through the above-mentioned CQC module. As a viable alternative, we adopted the approximate values for $\epsilon_N$ as estimated in Sanjiang (10.99‰) and Nanjing (15.33 ± 4.90‰). As indicated in Fig. 6, the estimates on the source partitioning is sensitive to the choice of $\epsilon_N$. Whereas with increasing $\epsilon_N$, estimates on the relative contribution of on-road traffic and biomass burning remained relatively stable; estimates for coal combustion and biogenic soil changed significantly, in opposite directions. More precisely, depending on $\epsilon_N$, the average estimate of the fractional contribution of coal combustion decreased drastically from 43% ($\epsilon_N = 0‰$) to 5% ($\epsilon_N = 20‰$) (Fig. 6), while the contribution from biogenic soil to NO$_x$ emissions increased in a complementary way. Given the lack of better constraints on $\epsilon_N$ for the 13 sampling sites, it cannot be our goal here to provide a robust revised estimate on the partitioning of NO$_x$ sources throughout China and its neighboring areas. But we have very good reasons to assume that disregard of N isotope fractionation during $\rho$NO$_3^-$ formation in
previous isotope-based source apportionment studies has likely led to overestimates of
the relative contribution of coal combustion to total NO\textsubscript{x} emissions in China. For what
we would consider the most conservative estimate, i.e. lowest calculated value for the
N isotope fractionation during the transformation of NO\textsubscript{x} to pNO\textsubscript{3} (ε\textsubscript{N} = 5‰), the
approximate contribution from coal combustion to the NO\textsubscript{x} pool would be 28%, more
than 30% less than N isotope mixing model-based estimates would yield without
consideration of the N isotope fractionation (i.e., ε\textsubscript{N} = 0‰) (Fig. 6).

**Figure 6.**

4 Conclusion and outlook

Consistent with theoretical predictions, δ\textsuperscript{15}N-pNO\textsubscript{3} data from a field experiment where
atmospheric pNO\textsubscript{3} formation could be attributed reliably to NO\textsubscript{x} from biomass burning
only, revealed that the conversion of NO\textsubscript{x} to pNO\textsubscript{3} is associated with a significant net
N isotope effect (ε\textsubscript{N}). It is imperative that future studies, making use of isotope mixing
models to gain conclusive constraints on the source partitioning of atmospheric NO\textsubscript{x},
will consider this N isotope fractionation. The latter will change with time and space,
depending on the distribution of ozone and OH radicals in the atmosphere and the
predominant NO\textsubscript{x} chemistry. The O-isotope signatures of pNO\textsubscript{3} is mostly chemistry-
(and not source) driven (modulated by O-isotope exchange reactions in the atmosphere),
and thus, O isotope measurements do not allow addressing the ambiguities with regards
to the NO\textsubscript{x} source that may remain when just looking at δ\textsuperscript{15}N values alone. However,
δ\textsuperscript{18}O in pNO\textsubscript{3} will help assessing the relative importance of the dominant pNO\textsubscript{3} formation pathway. Simultaneous δ\textsuperscript{15}N and δ\textsuperscript{18}O measurements of atmospheric nitrate
thus allow reliable information on ε\textsubscript{N} and in turn on the relative importance of single
NO$_x$ sources. For example, for Nanjing, which can be considered representative for other large cities in China, dual-isotopic and chemical-tracer evidence suggest that on-road traffic and coal-fired power plants, rather than biomass burning, are the predominant sources during high-haze pollution periods. Given that the increasing frequency of nitrate-driven haze episodes in China, our findings are critically important in terms of guiding the use of stable nitrate isotope measurements to evaluate the relative importance of single NO$_x$ sources on regional scales, and for adapting suitable mitigation measures. Future assessments of NO$_x$ emissions in China (and elsewhere) should involve simultaneous $\delta^{15}$N and $\delta^{18}$O measurements of atmospheric nitrate and NO$_x$ at high spatiotemporal resolution, allowing us to more quantitatively reevaluate former N-isotope based NO$_x$ source partitioning estimates.

**Competing interests**

The authors declare that they have no competing interests.

**Data availability**

Data are available from the corresponding author on request. We prefer not to publish the software of calculating the nitrogen isotope fractionation factor and estimating nitrate source attribution at the present stage in order to avoid compromising the future of ongoing software registration. Readers can download the software through the website atmosgeochem.com after the finish of software registration.

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**Reference**


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Figure 1. Location of the sampling sites Sanjiang and Nanjing. The black dots indicate the location of sampling sites (sites are located in the area of mainland China and the Yellow and East and South China Seas) with $\delta^{15}$N-NO$_x$ data from the literature (see also Table S4).
Figure 2. (a) Correlation analysis between the mass concentrations of levoglucosan and aerosol nitrate during the Sanjiang sampling campaign; (b) Variation of fractions of various inorganic species (MSA stands for methyl sulphonate) during day-night samplings at Sanjiang between 8 and October 2013 18 (sample ID 1 to 8, respectively). The higher relative abundances of nss-K⁺ and Cl⁻ are indicative for a biomass-burning dominated source. For sample ID information and exact sampling dates, refer to Table S3.
Figure 3. Original $\delta^{15}$N values ($\delta^{15}$N$_{ini}$) for $p$NO$_3^-$, calculated values for the N isotope fractionation ($\epsilon_N$) associated with the conversion of gaseous NO$_x$ to $p$NO$_3^-$, and corrected $\delta^{15}$N values ($\delta^{15}$N$_{corr}$; $^{15}$N$_{ini}$ minus $\epsilon_N$) of $p$NO$_3^-$ for each sample collected during the Sanjiang sampling campaign. The colored bands represent the variation range of $\delta^{15}$N values for different NO$_x$ sources based on reports from the literature (Table S2). See Table S3 for the information regarding sample ID.
Figure 4. Comparison between the theoretical calculation and WRF-Chem simulation of the average contribution ratio ($\gamma$) for nitrate formation in Nanjing via the reaction of NO$_2$ and photochemically produced •OH.
Figure 5. (a) Time-series variation of coal combustion and road traffic contribution to the mass concentrations of ambient $p$NO$_3^-$ in Nanjing, as estimated through MixSIR; (b) Correlation analysis between the mass concentrations of coal combustion-related $p$NO$_3^-$ and SO$_2$; (c) Correlation analysis between the mass concentrations of road traffic-related $p$NO$_3^-$ and CO.
Figure 6. Estimates of the relative importance of single NO$_x$ sources (mean ± 1σ) throughout China based on the original δ$^{15}$N-NO$_3^-$ values extracted from the literature ($ɛ_N = 0‰$) and under consideration of significant N isotope fractionation during NO$_x$ transformation ($ɛ_N = 5‰$, 10‰, 15‰ or 20‰).