Supplement of

Nitrogen isotope fractionation during gas-particle conversion of NO_x to NO_3^- in the atmosphere – implications for isotope-based NO_x source apportionment

Y. H. Chang et al.

Correspondence to: Yanlin Zhang dryanlinzhang@outlook.com

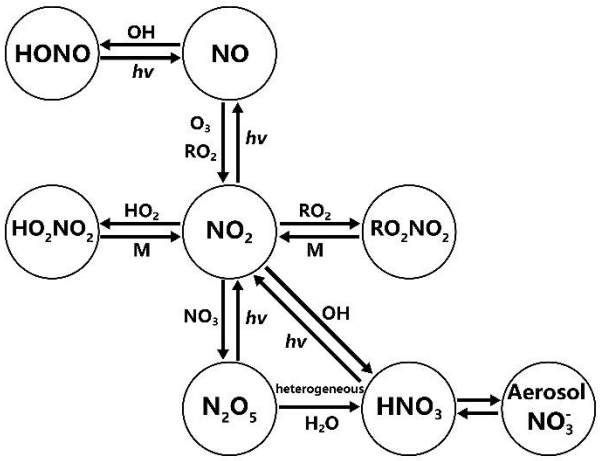

Figure S1. Possible NO_x to NO_3^- transformation pathways

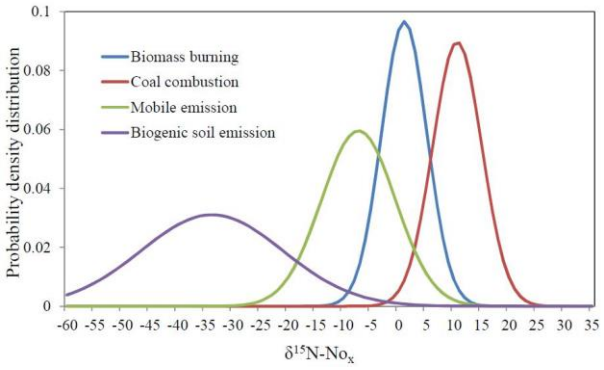

Figure S2. Probability density distribution of δ^{15}N-NO_x emitted from the four NO_x sources considered in this study.

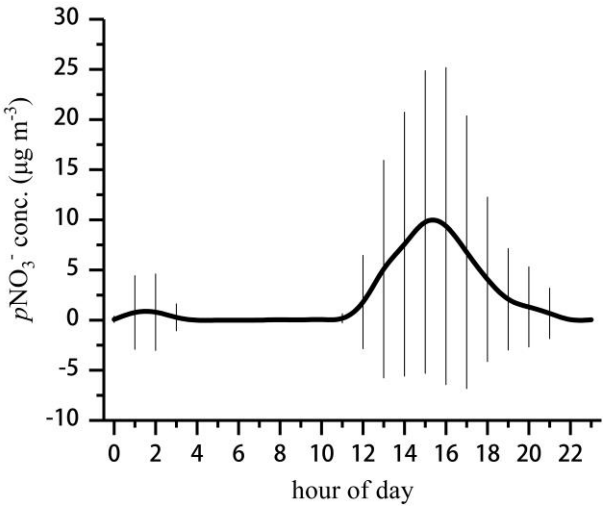

Figure S3. Diurnal variation of the mass concentration (mean ± 1σ) of nitrate formed through •OH oxidation of NO_2 in Nanjing City.

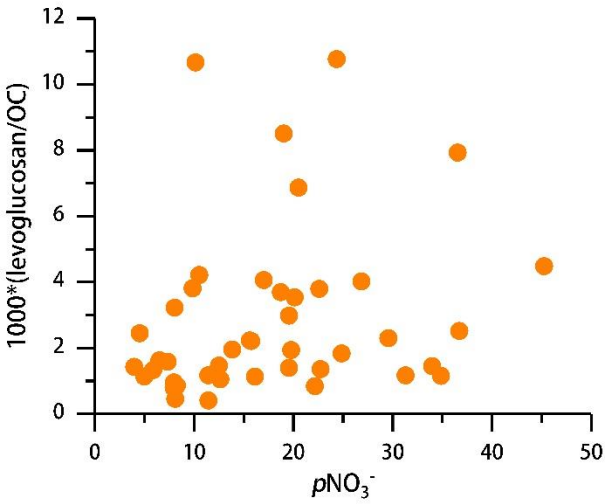

Figure S4. Scatter plot between the mass concentrations of $p\mathrm{NO_3^-}$ (μg $\mathrm{m^{-3}}$) and 1000*(levoglucosan/OC) during the Nanjing sampling campaign. The absence of any significant correlation indicates that biomass-burning can be excluded as major $p\mathrm{NO_3^-}$ source.

Table S1. Values for the coefficients A, B, C, D used for the calculation of $^{15}\alpha_{NO_2/NO}$, $^{15}\alpha_{N_2O_5/NO_2}$, $^{18}\alpha_{NO_2/NO}$, and $^{18}\alpha_{OH/H_2O}$ over the settled temperature range (150-450 K) (see main text).

$^{m}\alpha_{X/Y}$	A	B	C	D	equation
$^{15}NO_2/NO$	3.8834	-7.7299	6.0101	-0.17928	2
$^{15}N_2O_5/NO_2$	0.69398	-1.9859	2.3876	0.16308	3
$^{18}NO/NO_2$	-0.04129	1.1605	-1.8829	0.74723	5
$^{18}H_2O/OH$	2.1137	-3.8026	2.5653	0.59410	5

Table S2. Typical δ^{15}N-NO_x from coal combustion, mobile source and biomass burning based on literature values.

Source types	Mean	Standard deviation	Statistic number	Distribution	Reference
Coal combustion	13.72	4.57	47	Figure S2	1-3
Mobile source	-7.25	7.80	151	Figure S2	3-6
Biomass burning	1.04	4.13	24	Figure S2	7-9
Biogenic soil emission	-33.77	12.16	6	Figure S2	2, 7

Table S3. Sample information for Sanjiang sampling campaign

Sample ID	Day/Night	Start (local time)	End (local time)
1	Day	2013/10/8 10:20	2013/10/8 16:20
2	Night	2013/10/8 16:00	2013/10/9 06:00
3	Night	2013/10/9 19:35	2013/10/10 07:35
4	Day	2013/10/10 08:30	2013/10/10 15:30
5	Night	2013/10/10 15:51	2013/10/11 05:51
6	Day	2013/10/11 08:15	2013/10/11 15:45
7	Night	2013/10/17 16:24	2013/10/18 06:24
8	Day	2013/10/18 08:59	2013/10/18 15:59

Table S4. Site information and descriptive statistics for $\delta^{15}N$ values for atmospheric NO_3^- extracted from the literature.

Site name	Type	Phase	N	Mean	SD	Minimum	Median	Maximum	Reference
Yongxing Island	marine	aerosol	53	1.19	1.65	-2.45	1.36	4.88	11
Mt. Lulin	background	aerosol	174	-3.50	3.74	-17.21	-3.05	6.50	12
Jeju Island	marine	aerosol	81	3.81	2.51	0.59	3.28	15.33	13
Dongsha Island	marine	rainwater	18	-4.86	1.40	-7.51	-5.03	-1.77	14
Botanical Garden	background	rainwater	105	3.70	2.48	-4.90	3.88	10.35	15
Beihuang Island	marine	rainwater	120	8.20	6.18	-1.72	5.95	23.98	16
experimental field	suburban	rainwater	30	1.62	2.99	-3.24	1.24	7.25	17
Dongbeiwang	suburban	rainwater	21	6.82	5.78	-1.88	6.40	20.94	17
Changping	rural	rainwater	28	2.53	5.48	-3.80	1.30	20.81	17
Quzhou	rural	rainwater	24	-1.40	3.77	-8.33	-0.20	4.07	17
Wuqiao	rural	rainwater	24	-1.05	3.81	-7.49	-1.71	6.41	17
Wanzhou	rural	rainwater	12	0.23	8.07	-6.46	-3.13	21.92	18
Dade	rural	rainwater	10	-0.65	9.57	-6.88	-3.75	25.00	18

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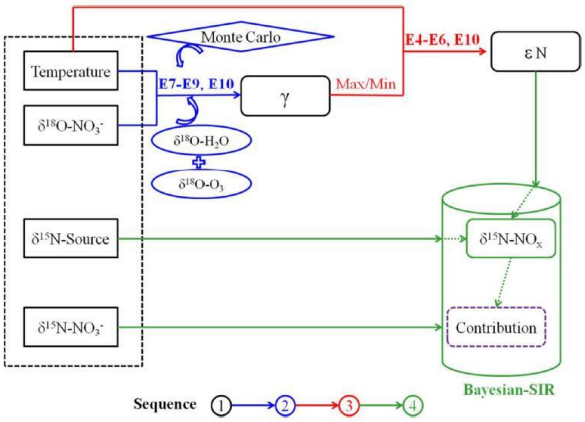
Text S1.

The Bayesian mixing model makes use of stable isotope data to determine the probability distribution of source contributions to a mixture, explicitly accounting for uncertainties associated with multiple sources, their isotopic signatures, and isotope fractionation during transformations.[26] The model has been widely used in ecological studies, such as food-web analyses.[27] In Bayesian theorem, the contribution of each source is calculated based on mixed data and prior information, such that:

$$P(f_q|data) = \theta(data \mid f_q) \times p(f_q) / \sum\theta(data \mid f_q) \times p(f_q)$$

where θ(data|fq) and p(fq) refer to the likelihood of the given mixed isotope signature, and the pre-determined probability of the given state of nature, based on prior information, respectively. The denominator represents the numerical approximation of the marginal probability of the data. In a Bayesian model (stable isotope mixing models using sampling-importance-resampling; MixSIR), isotope signatures from the mixed data pool are assumed to be normally distributed. Uncertainty in the distribution of isotope sources and their associated fractionation are factored into the model by defining respective mean (μ) and standard deviation (σ) parameters. Prior knowledge about proportional source contributions (f_q) are defined using the Dirichlet distribution, with an interval of [0, 1]. To assess the likelihood of the given f_q, the proposed proportional contribution is combined with a user-specified isotope distribution of sources and their associated isotope effects to develop a proposed isotope distribution for the mixture. The posterior probability of proportional source contributions (f_q) is calculated by the Hilborn sampling-importance-resampling method. For the detailed model frame and computing method, readers should refer to Moore et al.[28] Based on work by Walters and Michalski,[29] a computation module evaluating the fractionation of the equilibrium/Leighton reaction was incorporated into MixSIR (Figure below and main text).



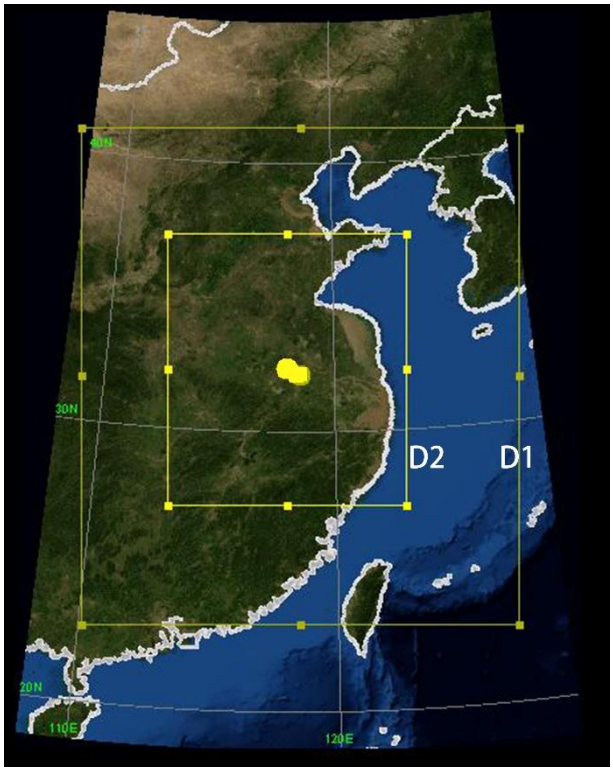
Principle of the Bayesian model approach used in this study.

Text S2.

As potential NO_x sources from emission inventories, coal combustion, mobile source, biomass burning and biogenic soil emissions were considered the dominant contributors to NO_x in this study (see discussion in the main text). The mean and standard deviations (SD) of δ^{15}N-NO_x for the four type sources (Fig. S2) were calculated based on data from the literature (see Table S2). In this study, the δ^{15}N-NO_x range of vehicle exhaust is considered representative of automotive NO_x sources in general.

Text S3.

The WRF-Chem (Weather Research and Forecasting model coupled with Chemistry) model v3.6.1[19] was used for simulating the contribution of the two major pathways to form nitrate: NO_2 oxidation by OH and O_3, respectively. The simulation was adopted from a mother domain with a 27 × 27 km horizontal resolution over eastern China, and nested down to a second domain of 9 × 9 km covering the Yangtze River Delta region. Lambert conformal conic projection was used with true latitude limits of 30.0°N and 60.0°N and standing longitude of 118.0°E. The coverage of the two-way nested domains is shown below. The number of vertical grids used was 30, and the number of horizontal grids was 66 × 75 and 109 × 124, respectively. For formulation of the tropospheric gas and aerosol chemistry ("mechanism") the gas-phase chemical mechanism CBMZ[20] was used, coupled with the 4-bin sectional MOSAIC model with aqueous chemistry.[21] MOSAIC integrates all the important aerosol species, including sulfate, nitrate, chloride, ammonium, sodium, black carbon, primary organic mass, liquid water and other inorganic mass.[21] Other physical parameterization options include Morrison 2-moment[22], RRTMG short and long wave radiation,[23] Noah land surface model, and the Yonsei University planetary boundary layer parameterization[24]. Data from the National Center for Environmental Prediction (NCEP) Final (FNL) Operational Global Analysis data set (http://rda.ucar.edu/datasets/ds083.2/) with a horizontal resolution of 1°×1° were incorporated as initial and boundary conditions for the model. The chemical initial and boundary conditions are provided by The Model for Ozone and Related chemical Tracers, version 4 (MOZART-4) .[25]



Two-way nested modeling domains at 27-km (East Asia: D1), 9-km (Yangtze River Delta: D2) resolutions. Yellow cycle represents the observation site in Nanjing City

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