Supplement of Atmos. Chem. Phys., 25, 8719–8742, 2025
https://doi.org/10.5194/acp-25-8719-2025-supplement

Supplement of

Enhanced atmospheric oxidation and particle reductions driving changes to nitrate formation mechanisms across coastal and inland regions of north China

Zhenze Liu et al.

Correspondence to: Jianhua Qi (qjianhua@ouc.edu.cn) and Xiaohuan Liu (liuxh1983@ouc.edu.cn)

Text S1

Our isotope blank measurements followed the same procedure as the sample isotope analysis. Specifically, in the sample measurements, after purging with high-purity nitrogen, 20 nmol of nitrogen was added to the headspace vial containing the *Pseudomonas aureofaciens* (ATCC13985) strain. For the blank measurements, no sample was added, and after 24 hours, 10 M NaOH was directly injected to quench the reaction before the analysis. The peak area in the chromatogram represents the absolute amount of N_2O reduced by the strain, and the $\delta^{15}N$ and $\delta^{18}O$ values correspond to the $\delta^{15}N$ and $\delta^{18}O$ values of the sample. The peak area for the samples was around 10, while the peak areas for the two blank measurements were only 0.371 and 0.336, indicating an influence on the isotope values of less than 5%, which is negligible and thus not considered.

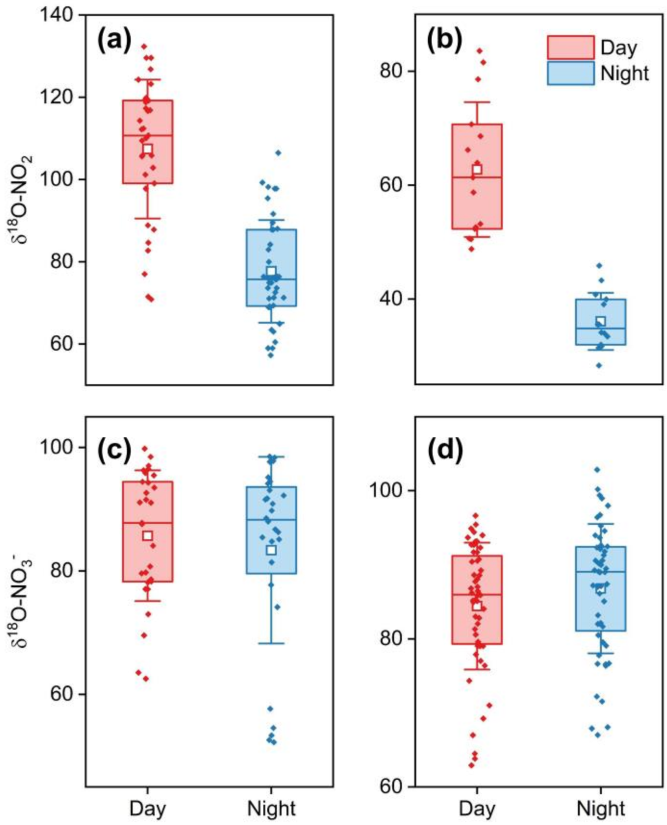

Figure S1. The diurnal values of atmospheric $\delta^{18}O$-NO_2 in Hefei winter (Zhang et al., 2025) (a) and in Nanchang summer (Cao, 2022) (b), and $\delta^{18}O$-NO_3^- in Tianjin winter (Feng et al., 2020) (c) and in Nanjing winter (Zhang et al., 2022) (d).

Text S2

In most studies, the tropospheric δ^{15}N-NOx was often assumed as 0‰ following Walters and Michalski (2016), Luo et al. (2023) and Deng et al. (2024). In addition, the tropospheric δ^{18}O-$H_2O_{(g)}$ in Beijing in winter was determined as −27.9‰ in Wen et al. (2010), and in Qingdao, it was determined as −18.6‰ in Wang et al. (2022). The tropospheric δ^{18}O-NOx ranged from 112‰ to 122‰ (Michalski et al., 2014; Walters and Michalski, 2016). The f_{NO2} values in Beijing and Qingdao were 0.655 (Luo et al., 2023) and 0.786 (Lian et al., 2022) in winter, respectively.

$$\begin{aligned}\delta^{15}N-NO_3^- &= \gamma\times[\delta^{15}N-NO_3^-]_{OH}+(1-\gamma)\times[\delta^{15}N-NO_3^-]_{N_2O_5}\\ &= \gamma\times[\delta^{15}N-HNO_3]_{OH}+(1-\gamma)\times[\delta^{15}N-HNO_3]_{N_2O_5}\end{aligned}\quad (S1)$$

$$\begin{aligned}\delta^{18}O-NO_3^- &= \gamma\times[\delta^{18}O-NO_3^-]_{OH}+(1-\gamma)\times[\delta^{18}O-NO_3^-]_{N_2O_5}\\ &= \gamma\times[\delta^{18}O-HNO_3]_{OH}+(1-\gamma)\times[\delta^{18}O-HNO_3]_{N_2O_5}\end{aligned}\quad (S2)$$

$$\begin{aligned}&[\delta^{15}N-HNO_3]_{OH}=\delta^{15}N-NO_2\\ &=1000\times\left[\frac{\left({}^{15}a_{\mathrm{NO_2/NO}}-1\right)\left(1-f_{NO_2}\right)}{\left(1-f_{NO_2}\right)+\left({}^{15}a_{\mathrm{NO_2/NO}}\times f_{NO_2}\right)}\right]+\delta^{15}N-NOx\end{aligned}\quad (S3)$$

$$[\delta^{15}N-HNO_3]_{N_2O_5}=1000\times\left({}^{15}a_{N_2O_5/NO_2}-1\right)+\delta^{15}N-NOx \quad (S4)$$

$$\begin{aligned}&[\delta^{18}O-HNO_3]_{OH}=\frac{2}{3}\times[\delta^{18}O-NO_2]_{OH}+\frac{1}{3}\times[\delta^{18}O-OH]_{OH}\\ &=\frac{2}{3}\times\left[\frac{1000\times\left({}^{18}\alpha_{NO_2/NO}-1\right)\times\left(1-f_{NO_2}\right)}{\left(1-f_{NO_2}\right)+\left({}^{18}a_{NO_2/NO}\times f_{NO_2}\right)}+[\delta^{18}O-NOx]\right]\\ &\quad+\frac{1}{3}\times\left[\left(\delta^{18}O-H_2O_{(g)}\right)+1000\times\left({}^{18}\alpha_{OH/H_2O_{(g)}}-1\right)\right]\end{aligned}\quad (S5)$$

$$[\delta^{18}O-HNO_3]_{N_2O_5}=\left(\delta^{18}O-NO_2+1000\times\left({}^{18}\alpha_{N_2O_5/NO_2}-1\right)\right)\times\frac{5}{6}+\delta^{15}N-H_2O\times\frac{1}{6} \quad (S6)$$

$$1000\left({}^{m}a_{x/y}-1\right)=\frac{A}{T^4}\times10^{10}+\frac{B}{T^3}\times10^{8}+\frac{C}{T^2}\times10^{6}+\frac{D}{T}\times10^{4} \quad (S7)$$

Table S1. Values of $\delta^{18}O$ from atmospheric components.

Components	Values (‰)	References
O_3	From 80 to 130	Michalski et al., 2011
O_2	23.5	Kroopnick and Craing; 1972
H_2O (g) in Beijing winter	−27.9	Wen et al., 2010
H_2O (g) in Qingdao winter	−18.6	Wang et al., 2022
·OH in Beijing winter	From −72.4 to −64.9	$\delta^{18}O\text{-}OH = \delta^{18}O\text{-}H_2O_{(g)} + 1000(^{18}\alpha_{X/Y} - 1)$
·OH in Qingdao winter	From −61.2 to −57.8	(Walters and Michalski, 2016)

Table S2. $^{15}\alpha_{A/B}$ and $^{18}\alpha_{A/B}$ regression coefficients as a function of the temperature (150 K ≤ T ≤ 450 K) (Walters and Michalski, 2015, 2016).

		A	B	C	D
$^{15}\alpha_{A/B}$	N_2O_5/NO_2	0.69398	-1.9859	2.3876	0.16308
	NO_2/NO	3.8834	-7.7299	6.0101	-0.17928
$^{18}\alpha_{A/B}$	NO/NO_2	-0.04129	1.1605	-1.8829	0.74723
	$\cdot OH/H_2O_{(g)}$	2.1137	-3.8026	2.5653	0.5941
	N_2O_5/NO_2	-0.54136	0.13073	1.2477	-0.1272

Table S3. Equations for calculating the statistical evaluation indices.

Statistical index	**Formula**
1. Mean Bias	$\mathrm{MB} = \frac{1}{N}\sum_{1}^{N}(\mathrm{Sim} - \mathrm{Obs})$
2. Root Mean Square Error	$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{1}^{N}(Sim - Obs)^2}$
3. Index of agreement, IOA	$\mathrm{IOA} = 1 - \frac{\sum_{i=1}^{N}(Sim-Obs)^2}{\sum_{i=1}^{N}(\lvert Sim-\overline{Obs}\rvert+\lvert Obs-\overline{Obs}\rvert)^2}$
4. Normalized Mean Bias	$\mathrm{NMB} = \frac{1}{N}\sum_{1}^{N}\left(\frac{Sim - Obs}{Obs}\right)$
5. Normalized Mean Error	$\mathrm{NME} = \frac{1}{N}\sum_{1}^{N}\left\lvert\frac{Sim - Obs}{Obs}\right\rvert$
6.Correlation coefficient (R)	$\mathrm{R} = \frac{1}{N}\sum_{i=1}^{N}\left[\frac{(Sim-\overline{Sim})(Obs-\overline{Obs})}{S_p S_o}\right]$ $S_P = \left[\frac{1}{N}\sum_{i=1}^{N}(Sim - \overline{Sim})^2\right]^{\frac{1}{2}}$ $S_o = \left[\frac{1}{N}\sum_{i=1}^{N}(Obs - \overline{Obs})^2\right]^{\frac{1}{2}}$

Table S4. Sources of nitrate observation data for the winter of 2013 and the winter of 2018 in the NCP.

City	Winter, 2013	Winter, 2018
Beijing	Song et al. (2019)	Fan et al. (2020)
Tianjin	Yao et al. (2020)	Observation
Shijiahzuang	Wang et al. (2016)	Zhou et al. (2020)
Jinan	Cheng et al. (2021)	Observation
Zhengzhou	Wei et al. (2019)	Dong et al. (2020)
Qingdao	Observation	Observation
Yantai	/	/

The NO_3^- observation data collected during the winter of 2018 for Tianjin were sourced from direct observations by the group of Li Xiaodong at Tianjin University (sampling site: Building 19 rooftop, Tianjin University; coordinates: 39.11°N, 117.16°E). The NO_3^- observation data collected during the winter of 2018 in Jinan were sourced from observations by the group of Xue Likun at Shandong University (sampling site: Jinan City Environmental Monitoring Station; coordinates: 36.66°N, 117.05°E). For Qingdao, NO_3^- observation data for both the winter of 2018 and the winter of 2013 were derived from our own observations.

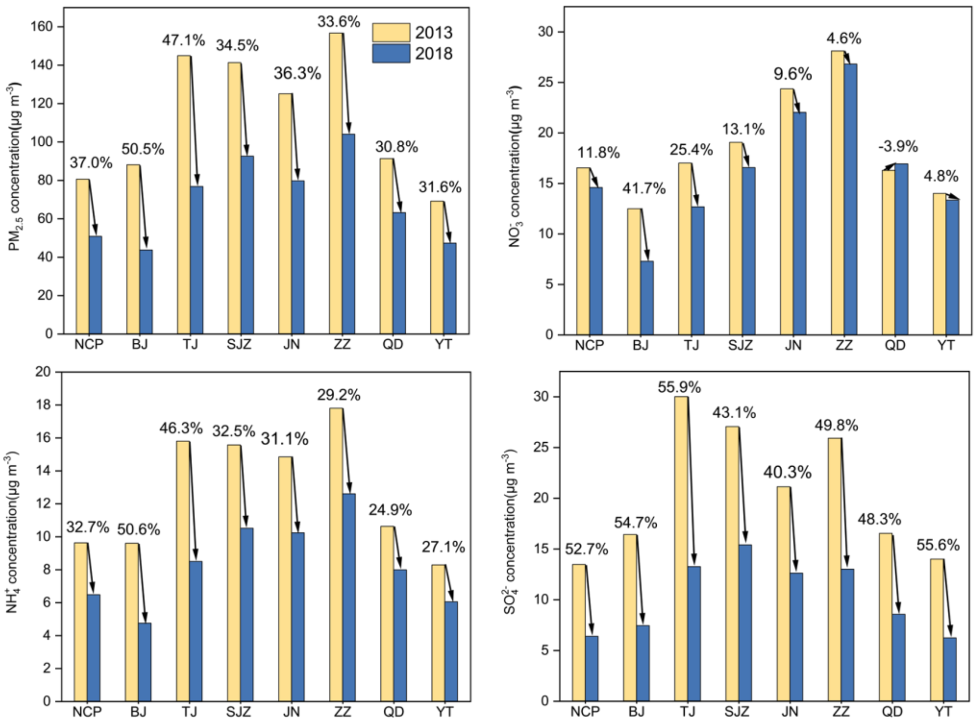

Figure S2. Concentrations of $PM_{2.5}$ and its components in seven major cities in the NCP region during the winters of 2013 and 2018.

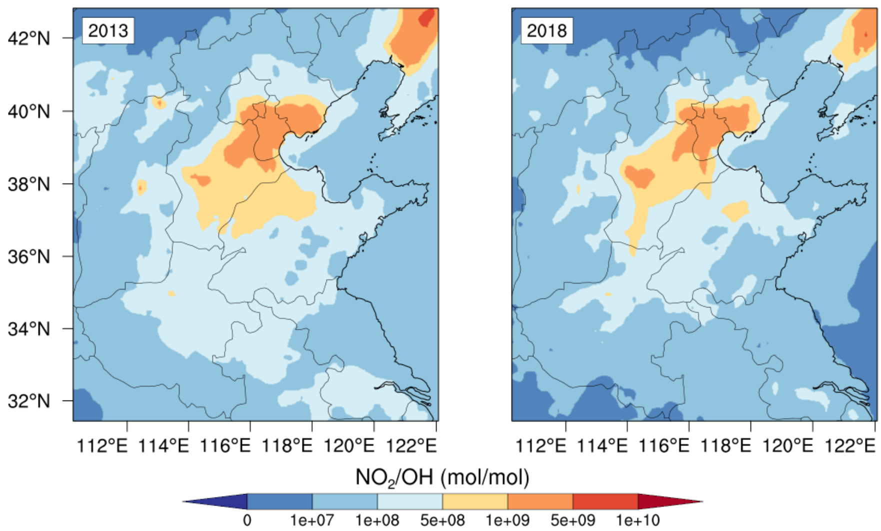

Figure S3. Spatial distribution of the NO_2/OH molar ratio in the NCP region during the winters of 2013 and 2018.

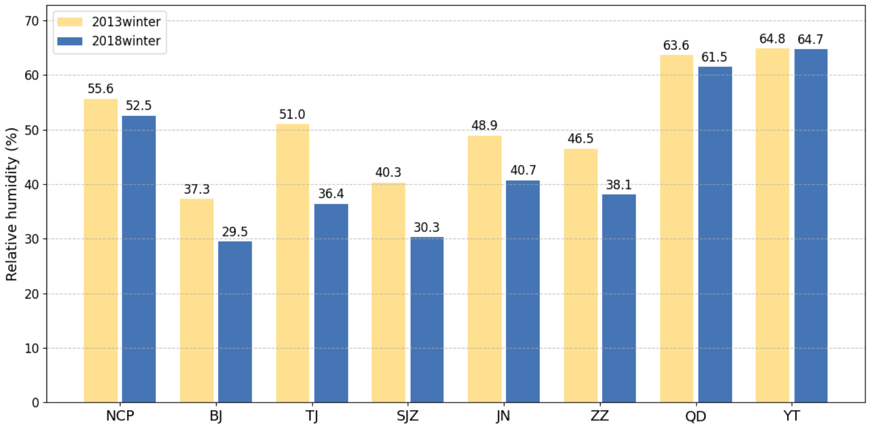

Figure S4. Relative humidity in the NCP and seven major cities (2013, 2018).

Reference

Cheng, M., Tang, G., Lv, B., Li, X., Wu, X., Wang, Y., and Wang, Y.: Source apportionment of $PM_{2.5}$ and visibility in Jinan, China, Journal of Environmental Sciences, 102, 207-215, https://doi.org/10.1016/j.jes.2020.09.012, 2021.

Deng, M., Wang, C., Yang, C., Li, X., and Cheng, H.: Nitrogen and oxygen isotope characteristics, formation mechanism, and source apportionment of nitrate aerosols in Wuhan, Central China, Science of The Total Environment, 921, 170715, https://doi.org/10.1016/j.scitotenv.2024.170715, 2024.

Dong, Z., Su, F., Zhang, Z., and Wang, S.: Observation of chemical components of $PM_{2.5}$ and secondary inorganic aerosol formation during haze and sandy haze days in Zhengzhou, China, J Journal of Environmental Sciences, 88, 316-325, https://doi.org/10.1016/j.jes.2019.09.016, 2020.

Fan, M.-Y., Zhang, Y.-L., Lin, Y.-C., Cao, F., Zhao, Z.-Y., Sun, Y., Qiu, Y., Fu, P., and Wang, Y.: Changes of Emission Sources to Nitrate Aerosols in Beijing After the Clean Air Actions: Evidence From Dual Isotope Compositions, Journal of Geophysical Research: Atmospheres, 125, e2019JD031998, https://doi.org/10.1029/2019JD031998, 2020.

Lian, C., Wang, W., Chen, Y., Zhang, Y., Zhang, J., Liu, Y., Fan, X., Li, C., Zhan, J., Lin, Z., Hua, C., Zhang, W., Liu, M., Li, J., Wang, X., An, J., and Ge, M.: Long-term winter observation of nitrous acid in the urban area of Beijing, Journal of Environmental Sciences, 114, 334-342, https://doi.org/10.1016/j.jes.2021.09.010, 2022.

Luo, L., Wu, S., Zhang, R., Wu, Y., Li, J., and Kao, S.-j.: What controls aerosol $\delta^{15}N\text{-}NO_3^-$? NOx emission sources vs. nitrogen isotope fractionation, Science of The Total Environment, 871, 162185, http://dx.doi.org/10.1016/j.scitotenv.2023.162185, 2023.

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NOx cycle and the tropospheric ozone isotope anomaly: an experimental investigation, Atmos. Chem. Phys., 14, 4935-4953, https://doi.org/10.5194/acp-14-4935-2014, 2014.

Song, W., Wang, Y.-L., Yang, W., Sun, X.-C., Tong, Y.-D., Wang, X.-M., Liu, C.-Q., Bai, Z.-P., and Liu, X.-Y.: Isotopic evaluation on relative contributions of major NOx sources to nitrate of $PM_{2.5}$ in Beijing, Environmental Pollution, 248, 183-190, https://doi.org/10.1016/j.envpol.2019.01.081, 2019.

Walters, W. W. and Michalski, G.: Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NOy molecules, Geochimica et Cosmochimica Acta, 164, 284-297, https://doi.org/10.1016/j.gca.2015.05.029, 2015.

Walters, W. W. and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NOy molecules, OH, and H_2O and its implications for isotope variations in atmospheric nitrate, Geochimica et Cosmochimica Acta, 191, 89-101, https://doi.org/10.1016/j.gca.2016.06.039, 2016.

Wang, X., Zhou, Y., Cheng, S., and Wang, G.: Characterization and regional transmission impact of water-soluble ions in $PM_{2.5}$ during winter in typical cities, China Environmental Science, 36, 2289-2296, 2016.

Wang, Y., Cui, B.-l., Li, D.-s., Wang, Y.-x., Yu, W.-x., and Zong, H.-h.: Stable Isotopes Reveal Water Vapor Sources of Precipitation over the Jiaolai Plain, Shandong Peninsula, China, Asia-Pacific Journal of Atmospheric Sciences, 58, 227-241, https://doi.org/10.1007/s13143-021-00253-2, 2022.

Wei, X., Gao, m., and Tong, j.: Characterization of water-soluble ions of $PM_{2.5}$ in Zhengzhou, Chinese journal of quantum, 36, 495-499, 2019.

Wen, X.-F., Zhang, S.-C., Sun, X.-M., Yu, G.-R., and Lee, X.: Water vapor and precipitation isotope ratios in Beijing, China, Journal of Geophysical Research: Atmospheres, 115, https://doi.org/10.1029/2009JD012408, 2010.

Yao, Q., Liu, Z., Han, S., Cai, Z., Liu, J., Hao, T., Liu, J., Huang, X., and Wang, Y.: Seasonal variation and secondary formation of size-segregated aerosol water-soluble inorganic ions in a coast megacity of North China Plain, Environmental Science and Pollution Research, 27, 26750-26762, https://doi.org/10.1007/s11356-020-09052-0, 2020.

Zhou, J., Duan, J., Wang, J., Liu, H., LI, M., and Jin, W.: Analysis of pollution characteristics and sources of $PM_{2.5}$ during heavey pollution in Shijiazhuang city around New Year's Day 2019, Environmental Science, 41, 39-49, https://doi.org/10.13227/j.hjkx.201906085, 2020.

Cao, L. Nitrogen and oxygen isotope tracing of urban atmospheric nitrate sources and atmospheric processes—taking Beijing and Nanchang as examples. Dissertation for master’s degree of East China University of Technology.

Feng, X., Li, Q., Tao, Y., Ding, S., Chen, Y., and Li, X.: Impact of Coal Replacing Project on atmospheric fine aerosol nitrate loading and formation pathways in urban Tianjin: Insights from chemical composition and ^{15}N and ^{18}O isotope ratios, Sci. Total Environ., 708, 134797, https://doi.org/10.1016/j.scitotenv.2019.134797, 2020.

Zhang, Y., Zhang, W., Fan, M., Li, J., Fang, H., Cao, F., Lin, Y., Wilkins, B. P., Liu, X., Bao, M., Hong, Y., and Michalski, G.: A diurnal story of $\Delta^{17}O(NO_3^-)$ in urban Nanjing and its implication for nitrate aerosol formation, npj Climate and Atmospheric Science, 5, 50, https://doi.org/10.1038/s41612-022-00273-3, 2022.

Zhang, Z., Zhou, T., Jiang, Z., Ma, T., Su, G., Ruan, X., Wu, Y., Cao, Y., Wang, X., Liu, Z., Li, W., Zhang, H., Lin, M., Liu, P., and Geng, L.: High-Resolution Measurements of Multi-Isotopic Signatures ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) of Winter NO_2 in a Megacity in Central China, Environ. Sci. Technol., 59, 3634-3644, https://doi.org/10.1021/acs.est.4c07724, 2025.

Kroopnick, P., and Craig, H.: Atmospheric Oxygen: Isotopic Composition and Solubility Fractionation, Science, 175, 54-55, https://doi.org/10.1126/science.175.4017.54, 1972.

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NOx cycle and the tropospheric ozone isotope anomaly: an experimental investigation, Atmos. Chem. Phys., 14, 4935-4953, https://doi.org/10.5194/acp-14-4935-2014, 2014.

Michalski, G., Bhattacharya, S. K., and Mase, D. F.: Oxygen Isotope Dynamics of Atmospheric Nitrate and Its Precursor Molecules, in: Handbook of Environmental Isotope Geochemistry: Vol I, edited by: Baskaran, M., Springer Berlin Heidelberg, Berlin, Heidelberg, 613-635, https://doi.org/10.1007/978-3-642-10637-8_30, 2012.

Walters, W. W., and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NO molecules, OH, and H_2O and its implications for isotope variations in atmospheric nitrate, Geochim. Cosmochim. Ac., 191, 89-101, https://doi.org/10.1016/j.gca.2016.06.039, 2016.