Supplementary Material for

Source Apportionment and Evolution of N-containing Aerosols at a Rural Cloud Forest in Taiwan by Isotope Analysis

by
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Contents of this file

$\delta^{18}O$ variation in NO_3^- oxidation processes

The oxidation processes for aerosol NO_3^- formation can be represented as follows and shown as R1 to R10 in Fig. 1:

$NO + O_3 \longrightarrow NO_2 + O_2$ (R1)

$NO_2 + h\nu \longrightarrow NO + O$ (R2)

$O + O_2 \xrightarrow{M} O_3$ (R3)

OH radical oxidation:

$NO_2 + OH \xrightarrow{M} HNO_3$ (R4)

N_2O_5 hydrolysis at nighttime:

$NO_2 + O_3 \longrightarrow NO_3 + O_2$ (R5)

$NO_2 + NO_3 \xrightarrow{M} N_2O_5$ (R6)

$N_2O_5 + H_2O \longrightarrow 2HNO_3$ (R7)

OH formation:

$O_3 + h\nu \longrightarrow O + O_2$ (R8)

$O + H_2O \longrightarrow 2OH$ (R9)

peroxyl radical oxidation:

$NO + RO_2 \longrightarrow NO_2 + RO$ (R10)

If both oxygen atoms of NO_2 are from O_3 oxidation (R1), the O of NO_3^- would be 2/3 from O_3 and 1/3 from OH via OH oxidation (R4). On the other hand, if NO_3^- is formed via N_2O_5 hydrolysis during nighttime (R7), O atoms on NO_3^- would be 5/6 from O_3 and 1/6 from H_2O. Hastings et al. (2003) suggested that the $\delta^{18}O$ of OH radical was close to that of atmospheric H_2O (from -15‰ to 0‰ over the Asian continent, Global Network of Isotopes in Precipitation, IAEA); therefore, $\delta^{18}O$ of NO_3^- from OH oxidation (where $\delta^{18}O$ = +55‰ ~ +81.3‰) would be lower than that from N_2O_5 hydrolysis at night (where $\delta^{18}O$ = +72.5‰ ~ +101.67‰), as shown as yellow blocks in Fig. S6 and S7 (Hastings et al., 2003; Fang et al., 2011). However, if atmospheric OH radicals are mainly produced via R8 & R9, the $\delta^{18}O$ value of atmospheric OH could be the mean value of O_3 and H_2O in the range of +37.5‰ ~ +61.0‰ (half from O_3 and the other half from H_2O). The calculation would result in the same $\delta^{18}O$ (+72.5‰ ~ +101.67 ‰) of NO_3^- formed through the OH oxidation and N_2O_5 hydrolysis pathways.

If NO_2 has a significant contribution via the reaction of NO with peroxyl radicals (hydroperoxyl radical HO_2 or organic peroxyl radical RO_2) as R10, O atoms of HO_2 or RO_2 are supposed to have a similar $\delta^{18}O$ with atmospheric O_2 ($\delta^{18}O$ = +23.5‰, Luz and Barkan (2011)) as the O atom of the peroxyl radical is originated from atmospheric O_2 ($H + O_2 + M \rightarrow HO_2 + M$). Therefore, NO_2 from R10 reacting OH can produce NO_3^- with a lower $\delta^{18}O$ (could be low as +28.2‰ ~ +36.0‰) compared to that of NO_2 from R5 (+90‰ to +122‰). If the NO ↔ NO_2 cycle has rapidly exchanged through O_3 oxidation and NO_2 photolysis during the daytime, $\delta^{18}O$ of NO_2 would be close to that of O_3 after 7-8 times of reactions (Fig. S8). Therefore, $\delta^{18}O$ of formed NO_3^- would be +72.50-101.67‰ after either OH radical oxidation or nighttime N_2O_5 hydrolysis shown as

(P4) and (P6) in Fig. S6. If RO_2 radicals involve the oxidation processes, NO_3^- $\delta^{18}O$ could be low to +28.17‰ shown as (P7) in Fig. S7.

Table S1. Mass weighted isotope value (‰) of each group of samples.

	02D	**02N**	**13N**	**14D**	**14N**	**15D**	**20N**	**21D**	**22D**	**22N**
$\delta^{15}N$, NH_4^+	14.38	9.93	13.33	16.30	12.30	14.92	11.32	7.61	10.43	8.94
$\delta^{15}N$, PM_{1-10}-NO_3^-	2.72			3.70		4.24	1.85	5.20		
$\delta^{15}N$, PM_1-NO_3^-			1.46	1.50		1.93				
$\delta^{18}O$, PM_{1-10}-NO_3^-	70.05			70.75		72.45	74.82	72.52		
$\delta^{18}O$, PM_1-NO_3^-			79.81	69.07		72.01				
$\delta^{15}N$, NO_3^-	2.72		1.46	2.29		2.83	1.85	5.20		
$\delta^{18}O$, NO_3^-	70.05		79.81	69.67		72.18	74.82	72.52		

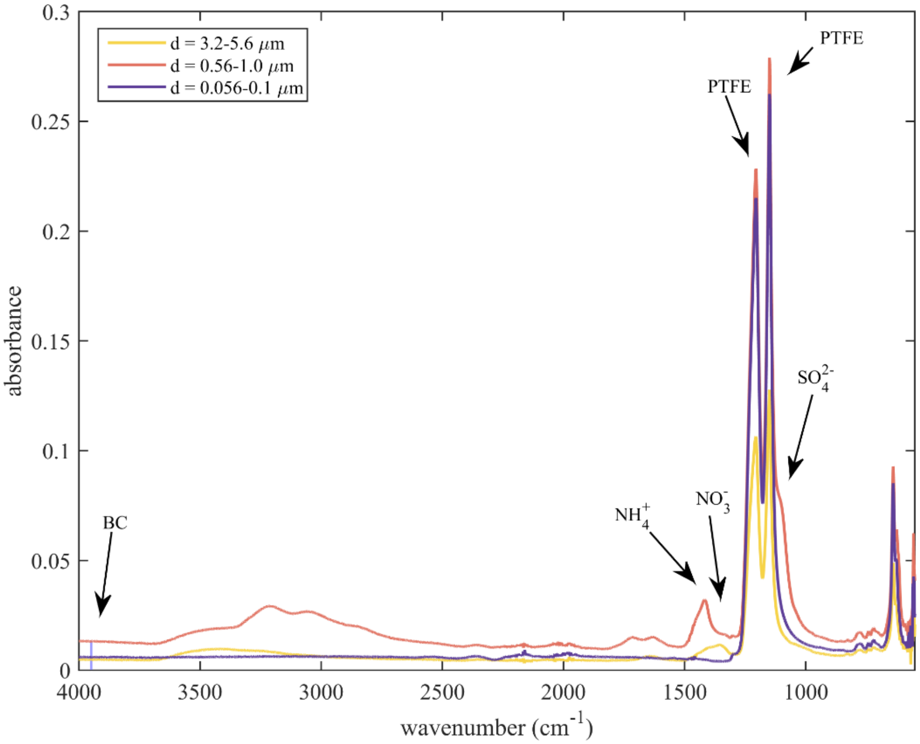

Figure S1. IR spectra of 3 collected samples on 2 December 2018. The absorption peaks for curve fitting are 2-curve fit for NH_4^+, NO_3^-; 3-curve fit for polytetrafluoroethylene (PTFE) and SO_4^{2-}; the absorbance of BC is determined by the average absorption of 3950 ± 5 cm^{-1} where have less interference by the absorption of other chemical species.

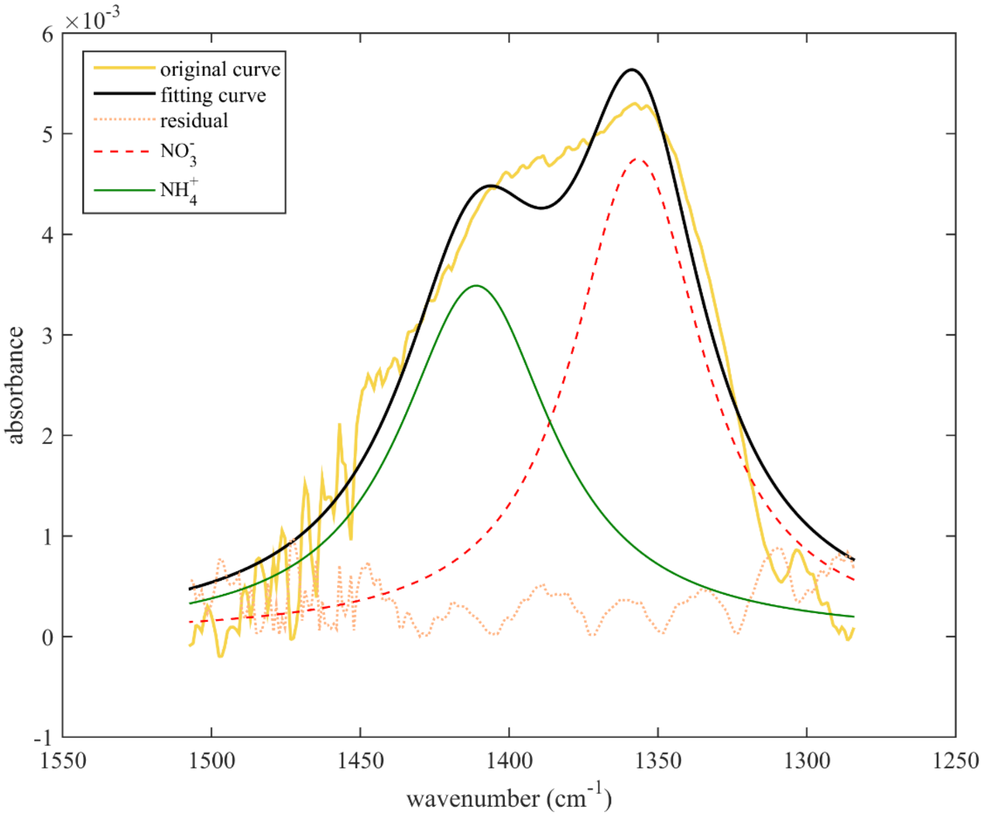

Figure S2. The Lorentzian fitting curve of the absorption curve of NH_4^+ and NO_3^-. The yellow thick curve is the background-corrected IR spectrum. Red and green curves are the fitted NH_4^+ and NO_3^- absorption curves, respectively. The black curve is the add-up of NH_4^+ and NO_3^- absorption, and the orange one represents the absolute value of the fitting curve minus the original curve.

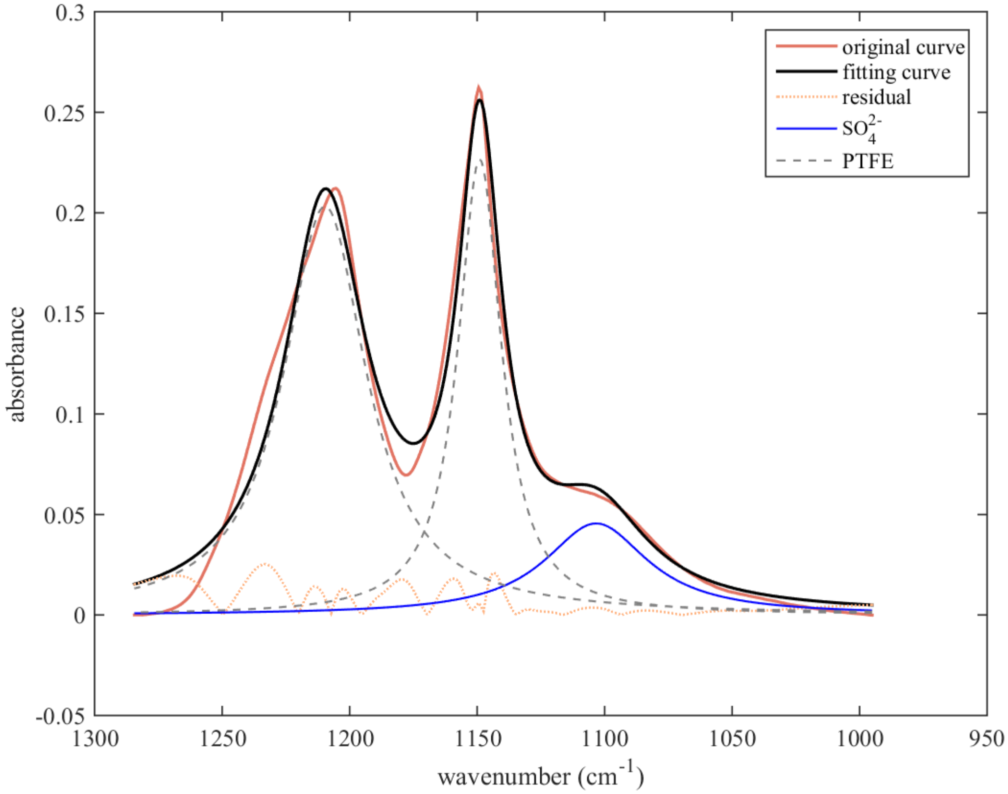

Figure S3. The Lorentzian fitting curve of the absorption curve of SO_4^{2-} and polytetrafluoroethylene (PTFE). The red curve is the baseline-corrected absorption curve. Two gray curves are the fitting curve of PTFE filter absorption, and the green line is that of SO_4^{2-}. The black thick curve is the add-up of absorption curves, and the orange one represents the absolute value of the fitting curve minus the original curve.

Concentration comparison between different methods

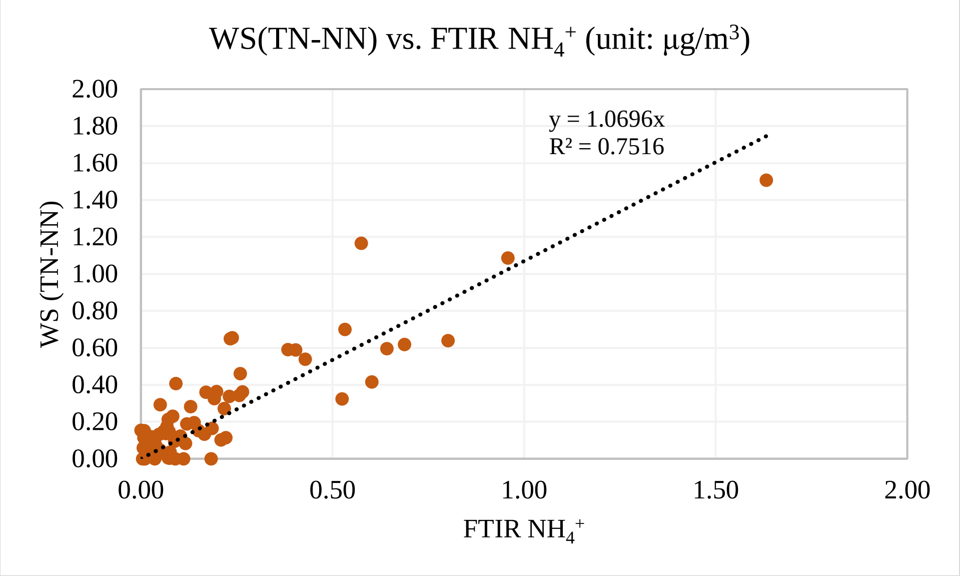

Figure S4. Comparison between the measured water-soluble (TN minus NN) and FTIR measured NH_4^+ concentration.

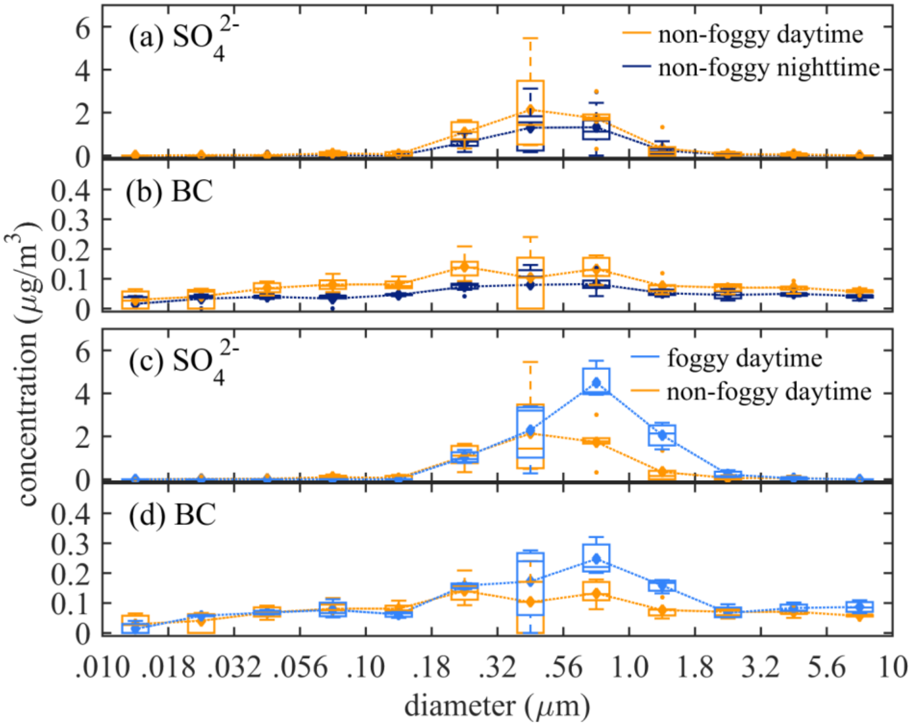

Figure S5. Statistic box plot of concentration of (A) SO_4^{2-}, (B) black carbon (BC) in non-foggy daytime and nighttime, and (C) SO_4^{2-}, (D) BC in the foggy and non-foggy daytime condition in different cut-off sizes. (diamond: mean value; outliers: < 1st quartile Q1-1.5 interquartile range (IQR) or > 3rd quartile Q3+1.5 IQR).

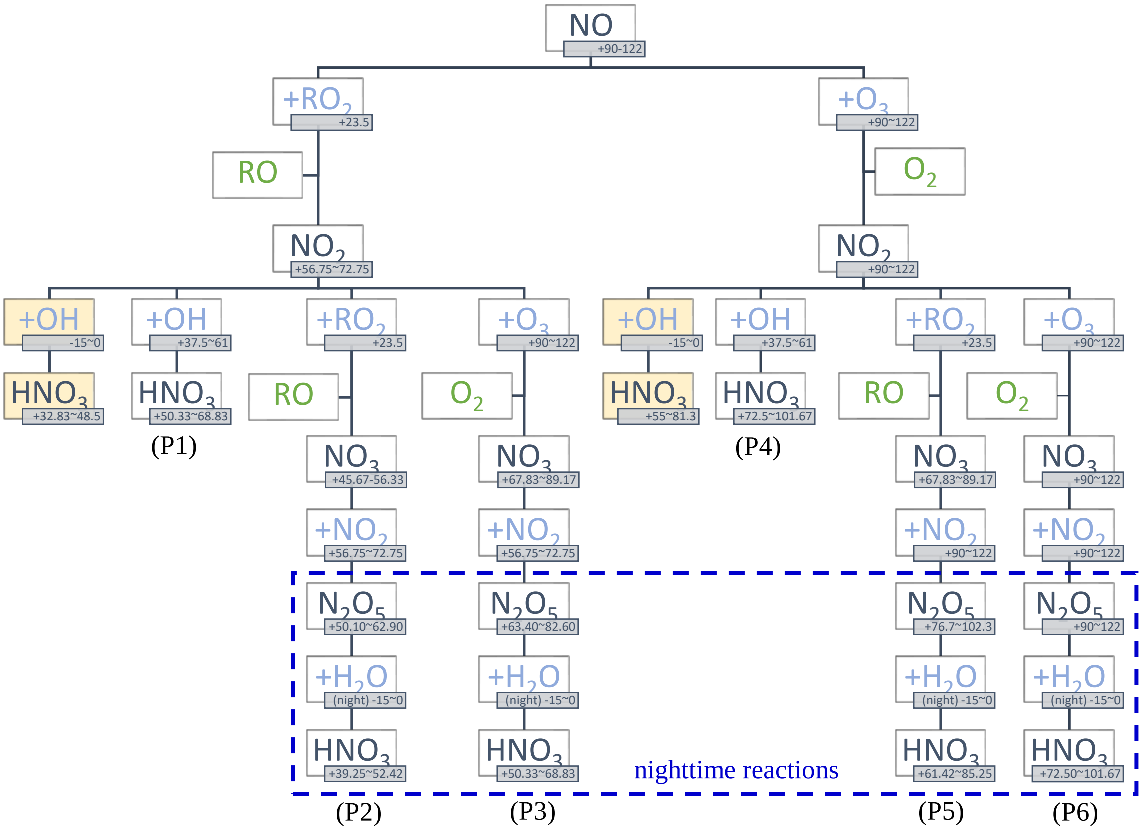

Figure S6. The predicted $\delta^{18}O$ (gray shaded bottom-right boxes) of products during HNO_3 formation pathways assuming the $\delta^{18}O$ of initial NO is 90~122‰ (i.e., fully reacted with O_3). Products are in dark-blue font color, reactants in light-blue, and by-products in green. The yellow-shaded boxes are based on the assumption of water-originated O atom of OH radical, whereas the O atoms of P1 and P4 are assuming that the OH is from O_3 and H_2O. The reactions in the dashed boxes are related to N_2O_5 hydrolysis occurring during nighttime.

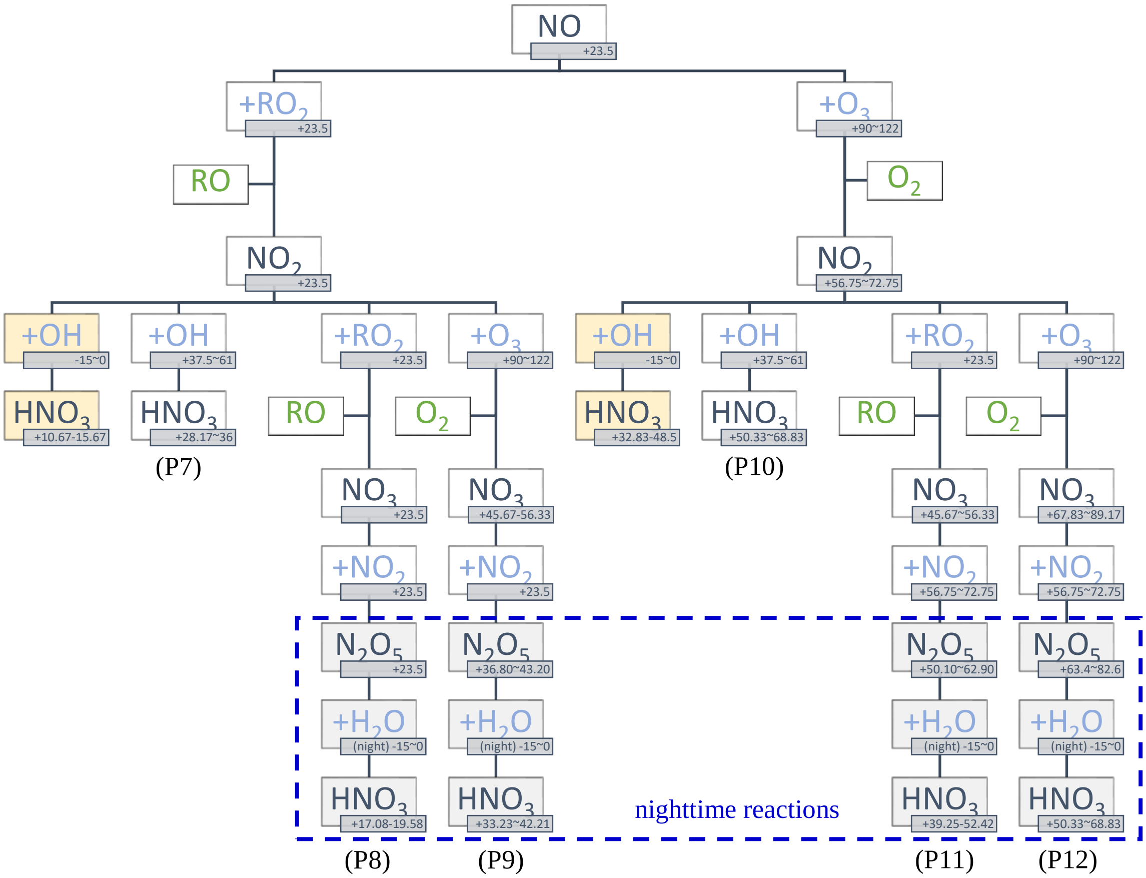

Figure S7. The predicted δ^{18}O (gray shaded bottom-right blocks) of products during HNO_3 formation pathways assuming the δ^{18}O of initial NO is +23.5‰ (i.e., freshly emitted and close to that of atmospheric O_2). Products are in dark-blue font color, reactants in light-blue, and by-products in green. The yellow-shaded blocks are based on the assumption of water-originated O atom of OH radical, whereas the O atoms of P7 and P10 are assuming that the OH is from O_3 and H_2O. The reactions in the dashed squares are related to N_2O_5 hydrolysis, where the reactions only occur at night.

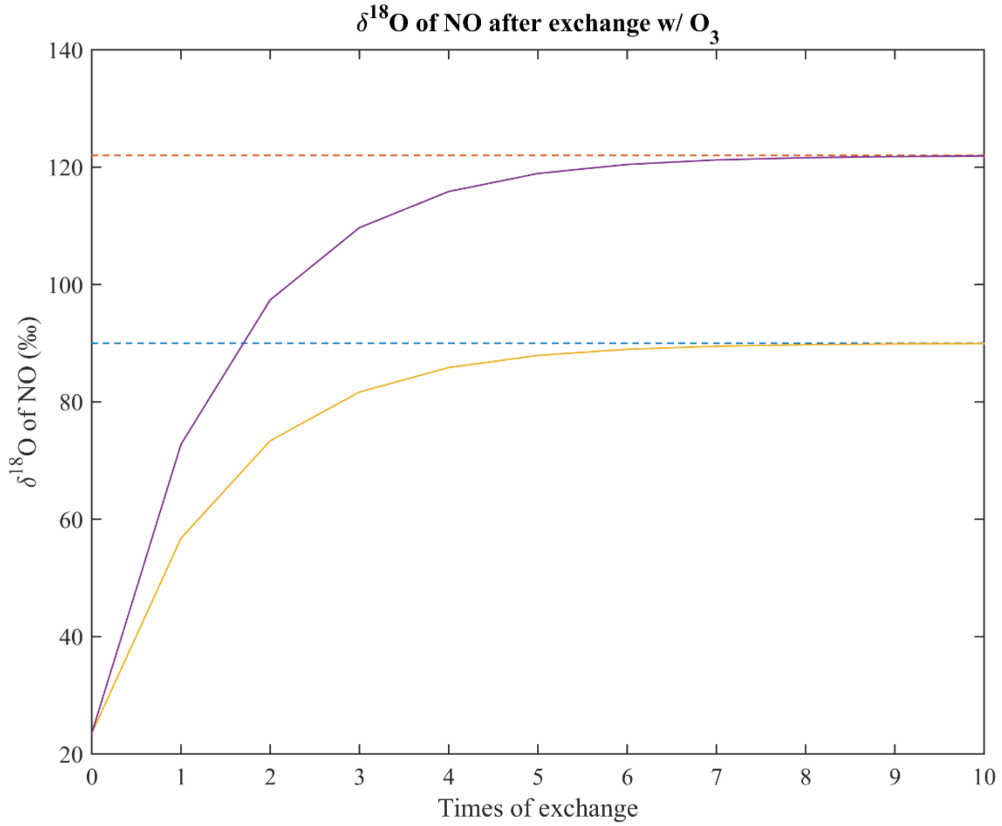

Figure S8. The predicted δ^{18}O of freshly formed NO (assume the δ^{18}O close of atmospheric O_2 = 23.5‰) after exchanging with O_3 (where δ^{18}O = 90~122‰).

References

Fang, Y. T., Koba, K., Wang, X. M., Wen, D. Z., Li, J., Takebayashi, Y., Liu, X. Y., and Yoh, M.: Anthropogenic imprints on nitrogen and oxygen isotopic composition of precipitation nitrate in a nitrogen-polluted city in southern China, Atmospheric Chemistry and Physics, 11, 1313-1325, 10.5194/acp-11-1313-2011, 2011.

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