1 **Oxidation pathways and emission sources of atmospheric particulate nitrate in Seoul:**

2 **based on $\delta^{15}N$ and $\varDelta^{17}O$ measurements**

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10

11 **Abstract**

12 $PM_{2.5}$ haze pollution driven by secondary inorganic NO_3^- has been a great concern in East Asia. It is,

13 therefore, imperative to identify its sources and oxidation processes, for which nitrogen and oxygen

14 stable isotopes are powerful tracers. Here, we determined the $\delta^{15}N$ (NO_3^-) and $\varDelta^{17}O$ (NO_3^-) of $PM_{2.5}$ in

15 Seoul during the summer of 2018 and the winter of 2018-2019, and estimated quantitatively the relative

16 contribution of oxidation pathways for particulate NO_3^- and investigated major NO_x emission sources.

17 In the range of $PM_{2.5}$ mass concentration from 7.5 μg m^{-3} (summer) to 139.0 μg m^{-3} (winter), the mean

18 $\delta^{15}N$ was -0.7 ± 3.3 ‰ and 3.8 ± 3.7 ‰, and the mean $\varDelta^{17}O$ was 23.2 ± 2.2 ‰ and 27.7 ± 2.2 ‰ in the

19 summer and winter, respectively. While OH oxidation was the dominant pathway for NO_3^- during the

20 summer (87 %), nighttime formation via N_2O_5 and NO_3 was relatively more important (38 %) during

21 the winter, when aerosol liquid water content (AWLC) and nitrogen oxidation ratio (NOR) were higher.

22 Interestingly, the highest $\varDelta^{17}O$ was coupled with the lowest $\delta^{15}N$ and highest NOR during the record-

23 breaking winter $PM_{2.5}$ episodes, revealing the critical role of photochemical oxidation process in severe

24 winter haze development. For NOx sources, atmospheric $\delta^{15}N$ (NO_x) estimated from measured $\delta^{15}N$

25 (NO_3^-) considering isotope fractionation effects indicates vehicle emissions as the most important

26 emission source of NO_x in Seoul. The contribution from biogenic soil and coal combustion was slightly

27 increased in summer and winter, respectively. Our results built on multiple-isotope approach provide

28 the first explicit evidence for NO_3^- formation processes and major NO_x emission sources in Seoul

29   megacity and suggest an effective mitigation measure to improve PM$_{2.5}$ pollutions.

30   **Keywords**: nitrate, NO$_x$, oxidation processes, emission sources, PM$_{2.5}$ haze, triple oxygen isotope,
31   nitrogen stable isotope

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33

1. Introduction

35   In Northeast Asia, air pollution characterized by high PM$_{2.5}$ (particulate matters with aerodynamic
36   diameter smaller than 2.5 μm) and ozone concentrations has received significant attention due to its
37   serious effects on human health (Lelieveld et al., 2015; Xie et al., 2019). As a result of extensive efforts
38   by East Asian countries to improve the ambient air quality, anthropogenic emissions of SO$_x$, NO$_x$, and
39   CO has been significantly reduced, particularly in China (Cheng et al., 2019). Nonetheless, the number
40   of severe haze events and the duration have been increased, which is not understood clearly.

41   It is also noteworthy that there are common chemical and meteorological characteristics in the
42   occurrence of the PM$_{2.5}$ haze pollution in northeast Asia, such as inorganic species-dominated chemical
43   composition (Liu et al., 2018; Shao et al., 2018; Wang et al., 2019a) and transboundary transport of
44   haze aerosol depending on the synoptic atmospheric circulation (Quan et al., 2020; Shi et al., 2020;
45   Zheng et al., 2019). Overall, approximately 40% of PM$_{2.5}$ consists of NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ (secondary
46   inorganic aerosol, "SIA") in both urban and background sites in China (Liu et al., 2018) for the period
47   of 2012-2013. The mass contribution of SIA was further augmented up to 69% at urban Beijing and
48   island sites (Changdao) in North China Plain ("NCP") during the 2016 spring (Lim et al., 2020). A large
49   increase in SIA mass is particularly associated with efficient formation of NO$_3^-$ in cold months (most
50   frequently in Dec. to Mar.), leading to a rapid increase in PM$_{2.5}$ concentration and developing a
51   persistent haze pollution on a regional scale (Li et al., 2018; Xu et al., 2019). Recent studies suggest
52   that the regional occurrence of the PM$_{2.5}$ haze events derived by NO$_3^-$ across Asian continent has been
53   associated with long-range transport of air pollutants promoted by cold fronts and their intrusion in
54   downward regions by the development of the atmospheric boundary layer (Kang et al., 2019; Lee et al.,
55   2019). However, scientific understanding is still limited because the rapid increase of fine-aerosol NO$_3^-$
56   is the result of complex interplay of oxidation and transformation mechanisms producing NO$_3^-$ from
57   various fossil and non-fossil sources of NO$_x$ with micro-to-synoptic meteorology creating the conditions
58   for NO$_3^-$ formation. In addition, considering that NO$_x$ emissions from bottom-up emission inventory are

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59   smaller than top-down estimates by satellites (e.g.,Goldberg et al., 2019), our understanding of NO_x

60   emissions is poor.

61   In order to better understand processes of NO_3^- formation including NO_x emission sources in East Asia,

62   a growing number of recent studies have suggested nitrogen and oxygen stable isotope-based

63   measurement as a robust and useful tool for providing important clues for NO_3^- formation as well as

64   NO_x emission sources (He et al., 2018; Lim et al., 2019, 2020; Song et al., 2019; Zong et al., 2017,

65   2020). The isotopic composition is expressed in parts per thousand (‰) and reported as δ (‰)

66    $=(R_{sample}/R_{standard}-1) \times 1000$ with R being the ratio of the heavy isotope over the light isotope (e.g., $^{15}N/^{14}N$,

67    $^{18}O/^{16}O$, $^{17}O/^{16}O$) in a sample (R_{sample}) and in the international standard ($R_{standard}$). The international

68   standards are the Vienna Standard Mean Ocean Water, VSMOW and atmospheric N_2 for oxygen and

69   nitrogen ratios, respectively. In terms of NO_x emission sources, the major NO_x sources are distinguished

70   in their nitrogen isotopic compositions; biogenic soil (driven by fertilizer use; -35.1‰ ± 10.2‰) (Felix

71   and Elliott, 2014; Li and Wang, 2008; Yu and Elliott, 2017), biomass burning (1.8‰ ±1.8‰) (Fibiger

72   and Hastings, 2016), vehicle emissions (-2.5‰ ± 1.5‰) (Walters et al., 2015), and coal combustion

73   (14.2‰ ± 4.5‰) (Felix et al., 2012; Heaton, 1990). Despite evidences that $\delta^{15}N$ (NO_x) can serve as a

74   useful tracer of NO_x emission sources, during NO_y photochemical cycling and its loss processes, the

75    $\delta^{15}N$ of initial NO_x can be significantly altered by both kinetic and equilibrium isotopic fractionation

76   effects (ε_N), complicating the link between $\delta^{15}N$ (NO_3^-) and $\delta^{15}N$ (NO_x) (Freyer et al., 1993; Li et al.,

77   2020).

78   The formation processes of HNO_3 in the atmosphere consist of NO-NO_2 photochemical cycle (R1-R3)

79   and post NO_2 oxidation reactions (R4-R8). During the NO_x cycling, nitrogen isotopic fractionation is

80   affected by unidirectional reactions of Leighton cycle and NO_x isotope exchange equilibrium. A recent

81   laboratory experiment has shown that the Leighton cycle isotope effect (LCIE) associated solely with

82   O_3 reaction (R1) and equilibrium isotopic effect (EIE) were -10 ‰ and 28.9 ‰ at room temperature,

83   respectively (Li et al., 2020). The relative importance of these two effects on $\delta^{15}N$ (NO_2) also depends

84   on NO_x levels, leading to increase (decrease) in $\delta^{15}N$ (NO_2) relative to $\delta^{15}N$ (NO_x) values at high (low)

85   NO_x conditions (Kamezaki et al., 2019; Li et al., 2020; Walters et al., 2018). Overall, the nitrogen

86   isotope exchange equilibrium has been suggested to be the dominant fractionation process in NO-NO_2

87   cycling at urban atmosphere (Freyer et al., 1993) and oxidation reactions forming nitric acid (HNO_3)

88   and particulate NO_3^- (Savarino et al., 2013).

89    $NO + O_3 \rightarrow NO_2 + O_2$ (R1)

90    $NO + RO_2 (HO_2) \rightarrow NO_2 + RO (OH)$ (R2)

91	$NO_2 + h\nu \rightarrow NO + O\,(^3P)$	(R3)
92	$NO_2 + OH \rightarrow HNO_3\,(g)$	(R4)
93	$NO_2 + O_3 \rightarrow NO_3 + O_2$	(R5)
94	$NO_2 + NO_3 + M \leftrightarrow N_2O_5$	(R6)
95	$N_2O_5 + H_2O \;\xrightarrow{aerosol}\; 2HNO_3\,(aq)$	(R7)
96	$NO_3 + RH \rightarrow HNO_3\,(g) + R$	(R8)

97   The kinetic fractionation effect during daytime oxidation of NO_2 to HNO_3 (R4) is relatively minor,
98   being estimated to be -3‰ (Freyer, 1991). During the nighttime when most NO is oxidized to NO_2
99   without NO_x photolysis, the isotopic equilibrium between NO_2, NO_3, and N_2O_5 should be achieved (R6).
100   The nighttime thermal equilibrium likely favors the partitioning of ^{15}N into N_2O_5 relative to NO_2 and
101   consequently induces a large isotopic fractionation effect of 25.5‰ (Walters and Michalski, 2015, R5-
102   R6). On the other hand, the nitrogen partitioning between NO_2 and NO_3 (R5) may induces a
103   fractionation effect of about -18‰ (Walters and Michalski, 2015). These N isotope fractionation effects
104   should be first evaluated to explore NO_x source contributions, which should be based on combining
105   with a robust tracer for the contributions of NO_3^- oxidation pathways.

106   Lately, $\Delta^{17}O\,(NO_3^-)$ has been used for tracing NO_3^- oxidation pathways (Alexander et al., 2009, 2020;
107   Morin et al., 2009; Savarino et al., 2007, 2013). Earlier researches observed that atmospheric NO_3^- is
108   anomalously enriched in ^{17}O (Michalski et al., 2003), which stems from O_3 formation reactions, where
109   a rare isotope effect leads to excess ^{17}O enrichment relative to what is expected based on the ^{18}O
110   enrichments (Thiemens, 1999, 2006). This enrichment is quantified by $\Delta^{17}O$ notation (^{17}O-excess,
111   defined as $\delta^{17}O - 0.52 \times \delta^{18}O$). Since non-zero $\Delta^{17}O$ strictly reflects a photochemical effect, NO_3^-
112   produced by denitrification in soils should have $\Delta^{17}O$ of zero. The mass-independent $\Delta^{17}O$ signature of
113   O_3 is transferred to NO_x, in which the number of oxygen atom from O_3 is involved in NO_x. In this way,
114   the $\Delta^{17}O\,(NO_3^-)$ is served as a conservative marker to track the chemical formation of atmospheric NO_3^-.
115   Photochemical formation by peroxy radicals (HO_2 and RO_2) leads to a relatively low $\Delta^{17}O\,(NO_3^-)$,
116   whereas nighttime formation through N_2O_5 and NO_3 results in high $\Delta^{17}O$ (Michalski et al., 2003; Morin
117   et al., 2009; Savarino et al., 2007). Consequently, the difference in $\Delta^{17}O\,(NO_3^-)$ suggests approaching a
118   proportional contribution of daytime and nighttime oxidation of NO_3^-.

119   To date, few field studies have coupled $\Delta^{17}O\,(NO_3^-)$ and $\delta^{15}N\,(NO_3^-)$ to investigate NO_x-to-NO_3^-
120   oxidation processes and emission sources of NO_x, e.g., field researches in Japan (Nelson et al., 2018),
121   west Virginia USA (Rose et al., 2019), Shanghai , China (He et al., 2020) and Beijing, China (He et al.,

122　　2018; Song et al., 2020).

123　　In this study, we present the measurement results of $\delta^{15}N$ and $\Delta^{17}O$ of NO_3^- in Seoul during the summer

124　　of 2018 and the winter of 2018-2019, when we encountered the record-breaking $PM_{2.5}$ concentrations.

125　　Then, the $\delta^{15}N$ and $\Delta^{17}O$ measurements are used to evaluate seasonally distinct atmospheric oxidation

126　　pathways of NO_3^- and to explore major NO_x source contributions in the study region.

127

2.　Measurements and methods

129　　### 2.1. Sampling

130　　We collected $PM_{2.5}$ filter samples on the rooftop of six-story Asan science building at Korea University

131　　campus located in northeast Seoul, the capital of South Korea (37.59° N, 127.02° E; Figure 1) during

132　　the summer 2018 (26 May to 22 Aug.; n = 13) and the winter 2018-2019 (27 Dec. to 8 Mar.; n = 18).

133　　Seoul is a metropolitan area with a population of 9.77 million and known to be influenced by heavy

134　　road traffic all around. The $PM_{2.5}$ particulates were collected on quartz filters (20 cm x 25 cm ; Pallflex

135　　Products, Putnam, USA) at a nominal flow rate of 96 m^3 hr^{-1} for 1 to 3 days using a high-volume air

136　　sampler (3000 series, Ecotech, Australia). Filters were analyzed for water-soluble ions, carbonaceous

137　　compounds, total nitrogen (TN) and carbon (TC), and stable nitrogen and oxygen isotopic ratios.

138　　Reactive gases including O_3, NO, NO_2, SO_2, and CO, and meteorological suite including air temperature,

139　　relative humidity, and wind speed and direction were measured hourly at the nearby monitoring sites

140　　run by the National Institute of Environmental Research (NIER) and the Korea Meteorological

141　　Administration (KAM), respectively. These data were averaged daily for comparison with filter-based

142　　chemical composition data, if necessary.

143

144　　### 2.2. Chemical analyses

145　　Filters were stored in a freezer pending chemical analysis. Chemical composition of $PM_{2.5}$ was

146　　determined for 8 water-soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) by ion

147　　chromatography (IC; Eco-IC, Metrohm, Switzerland); OC and EC by an OC-EC analyzer (Sunset

148　　Laboratory Inc., US) using the thermo-optical transmittance method (NIOSH870); and TC and total

149　　nitrogen (TN) by an elemental analyzer (EA, Fisons NA-1500NC, Thermo, Waltham, MA, USA). Mass

150　　concentrations of these constituents were corrected for laboratory and field blanks. The detection limit,

151   determined as three standard deviations (SD) above blank concentrations, was <0.1 ppm for ionic

152   species, 0.5 µg cm^{-3} for TC (the sum of OC and EC), and 0.8g µgN and 0.5 µgC per punched filter area

153   for TN and TC, respectively. Details of the analytical methods can be found elsewhere (Lim et al., 2020).

154   Following the bacterial denitrifier method (Casciotti et al., 2002; McIlvin and Casciotti, 2011),   the

155    $\Delta^{17}O$ of NO_3^- was measured simultaneously with $\delta^{18}O$ and $\delta^{15}N$ coupled with an IRMS measurement

156   using an in-house peripheral system at the Université Grenoble Alpes (Morin et al., 2009). In brief,

157   NO_3^- of samples was converted to N_2O via bacterial denitrification and the N_2O was further converted

158   into O_2 and N_2, which were separated via a gas chromatography column before being introduced to the

159   IRMS system (Thermo Finnigan MAT 253 Isotope Ratio Mass Spectrometer). Samples were measured

160   in batch with reference materials following strictly the identical treatment principles, including the same

161   water matrix for standards and samples. Together with samples, a subset of international nitrate

162   reference materials (US Geological Survey 32, 34, and 35, as well as their mixtures) was measured for

163   correction and calibration of $\Delta^{17}O$ and $\delta^{18}O$ values relative to VSMOW and $\delta^{15}N$ values relative to air

164   N_2. The overall accuracy of the method is estimated as the reduced standard deviation of the residuals

165   from the linear regression between the measured reference materials and their expected values (Morin

166   et al., 2009). For these sets of analyses, the obtained uncertainties values (1σ) were 0.4 ‰ and 0.3 ‰

167   for $\Delta^{17}O$ (NO_3^-) and $\delta^{15}N$ (NO_3^-), respectively. The analytical procedure used in this study strictly

168   followed the method described in Morin et al. (2009) which adheres to the new standard bacterial

169   method coupled with the gold catalyst for the thermal decomposition of N_2O into N_2 and O_2 (Kaiser et

170   al., 2007).

171

172   **2.3. Quantifying isotope fractionation effects**

173   **2.3.1. Isotope fractionation effects of NO$_2$ oxidation to atmospheric particulate NO$_3^-$:**

174   **$\delta^{15}N$ (NO$_3^-$)**

175   The HNO$_3$ forms through three major pathways including (i) OH pathway, (ii) O$_3$ pathway associated

176   with N$_2$O$_5$, and (iii) O$_3$ pathway associated with NO$_3$.

177

178   **OH pathway**

179   When NO and NO$_2$ coexist in similar quantities due to the Leighton cycle, ^{15}N is preferentially

180   partitioned into NO$_2$ via the equilibrium isotope effect, leading to higher $\delta^{15}N$ in NO$_2$ relative to NO

181 and NO_x (Freyer et al., 1993; Walters et al., 2016). Considering the comparable concentrations of NO

182 and NO_2 over a year in Seoul (Figure S1), the N isotope effects on $\delta^{15}N$ (NO_3^-) should be significantly

183 affected by NO_x photochemical interactions. The relative importance of EIE and LCIE to $\delta^{15}N(NO_2)$

184 can be assessed by comparing lifetimes of NO_2 with respect to isotope exchange with NO ($\tau_{exchange}$) and

185 photolysis ($\tau_{NO2+h\nu}$). In this regard, the "A" factor was defined as $\tau_{exchange}/\tau_{NO2+h\nu} = j_{NO2}/ k_1 \times$ [NO] (k_1=

186 8.14×10^{-14} cm^3 s^{-1}, Sharma et al., 1970) by Li et al. (2020, 2021). These studies demonstrated that A

187 was as small as 0.01-0.5 in EIE-dominated regime with $NO_x > 20$ ppbv and the ratio of NO_2/NO_x <0.6.

188 In Seoul, to simply evaluate the relative importance of EIE and LCIE only (not for ^{15}N correction), A

189 factor was estimated to be 0.08 ± 0.20 (median ± standard deviation) and 0.60 ± 0.51 during the winter

190 and summer months, respectively, indicating the significant influence of the equilibrium isotope effect

191 on NO-NO_2 isotopic fractionation. The time series j_{NO2} was calculated using the Master Chemical

192 Mechanisms (MCM) model (Saunders et al., 2003).

193 After photochemical NO_x photochemical cycling, NO_2 is oxidized by the reaction with OH radical to

194 form atmospheric HNO_3 ("HNO_3 (R4) pathway"). The N fractionation effect of particulate NO_3^-

195 produced via HNO_3 (R4) pathway (ε_1, unit in ‰) can be expressed as the following, neglecting kinetic

196 isotope effects associated with HNO_3 (R4) pathway (Walters and Michalski, 2016):

197 $\delta^{15}N$ (HNO_3) (R4) = $\delta^{15}N$ (NO_2) = $\delta^{15}N$ (NO_x) + ε_1 (Eq. 1-1)

198 $\varepsilon_1 = ((^{15}\alpha_{NO2/NO} - 1) (1 - f_{NO2}))/ ((1 - f_{NO2}) + (^{15}\alpha_{NO2/NO} \times f_{NO2}))$ (Eq. 1-2)

199 , where f_{NO2} is the fraction of NO_2 relative to the total NO_x, and $^{15}\alpha_{NO2/NO}$ is the temperature-dependent

200 isotope equilibrium exchange fractionation factor for NO_2/NO (Walters et al., 2016). In the present

201 study, the measured f_{NO2} was used individually for summer samples and a seasonal mean f_{NO2} (0.69)

202 was applied to winter samples due to the lack of availability of continuous NO-NO_2 measurement data.

203 Oxidation of NO_x to HNO_3 is regarded as the formation pathway of particulate NO_3^- via the "HNO_3

204 (R4) pathway" due to the unconstrained isotope fractionation effect between HNO_3 and NO_3^-, resulting

205 in the following equation:

206 $\delta^{15}N$ (HNO_3) (R4) = $\delta^{15}N$ (NO_3^-) (R4)   (Eq. 1-3)

207

208 **O_3 pathways associated with N_2O_5, and NO_3.**

209 During the nighttime when NO is oxidized into NO_2 without photolyzing back to NO and fresh

210 emissions of NO is negligible, NO_x exists almost as NO_2 and thus, $\delta^{15}N$ (NO_2) should be reflective of

211 the $\delta^{15}N$ of NO_x sources. If NO_2 is oxidized to N_2O_5, the isotopic equilibrium is likely to be achieved

212 between NO_2, NO_3, and N_2O_5 by chemical equilibrium (R6) and the $\delta^{15}N$ values of N_2O_5 and NO_3 will

213 reflect the isotope equilibrium fractionation factors relative to NO_2 (i.e., $^{15}\alpha_{N2O5/NO2}$ and $^{15}\alpha_{NO3/NO2}$,

214 values were adopted from supplementary Table S5 in Walters and Michalski, 2016). Finally, $\delta^{15}N$ of

215 particulate NO_3^- produced from dark pathways can be expressed as the following, neglecting currently

216 unconstrained kinetic isotopic fractionation associated with R7 and R8 (Walters and Michalski, 2016).

217

218 $\delta^{15}N$ (HNO_3) (R7) $= \delta^{15}N$ (N_2O_5) $= \delta^{15}N$ (NO_2) $+ \varepsilon_2$ (Eq. 2-1)

219 $\varepsilon_2 = (^{15}\alpha_{N2O5/NO2} - 1)$ (Eq. 2-2)

220 $\delta^{15}N$ (HNO_3) (R7) $= \delta^{15}N$ (NO_3^-) (R7) (Eq. 2-3)

221 $\delta^{15}N$ (HNO_3) (R8) $= \delta^{15}N$ (NO_3) $= \delta^{15}N$ (NO_2) $+ \varepsilon_3$ (Eq. 3-1)

222 $\varepsilon_3 = (^{15}\alpha_{NO3/NO2} - 1)$ (Eq. 3-2)

223 $\delta^{15}N$ (HNO_3) (R8) $= \delta^{15}N$ (NO_3^-) (R8) (Eq. 3-3)

224

225 Therefore, the $\delta^{15}N$ (NO_x) in the atmosphere can be expressed using measured $\delta^{15}N$ (NO_3^-) and the net

226 N isotope fractionation effect, ε_N.

227 $\delta^{15}N$ (NO_x)$_{atmosphere} = \delta^{15}N$ (NO_3^-) $_{measured} - \varepsilon_N$ (Eq. 4-1)

228 $\varepsilon_N = \varepsilon_1 \times f_1 + \varepsilon_2 \times f_2 + \varepsilon_3 \times f_3$ (Eq. 4-2)

229 , where ε_1, ε_2, and ε_3 are abovementioned N isotope fractionation effect of pathways (i), (ii), and (iii),

230 respectively, and the proportional contributions (f_1, f_2, and f_3) of the three NO_3^- formation pathways

231 were estimated from $\Delta^{17}O$ measurements (Sect. 2.3.2).

232

233 **2.3.2. Proportional contributions of three formation pathways to atmospheric particulate**

234 **NO_3^-: $\Delta^{17}O$ (NO_3^-)**

235　Due to its mass-independent nature, $\Delta^{17}O$ of particulate NO_3^- is a conservative tracer of photochemical

236　NO_3^- formation (Michalski et al., 2003, 2004). At photochemical steady state, the $\Delta^{17}O$ of NO_2 is

237　determined by the relative production rate of NO_2 via O_3 oxidation (R1) in NO_2 production (R1 and R2)

238　(f_{O3}) and the mass-independent $\Delta^{17}O$ anomaly transferred from O_3 during R1 ($\Delta^{17}O\text{-}O_3^*$):

239　$\Delta^{17}O\ (NO_2)\ (‰) = f_{O3} \times \Delta^{17}O\text{-}O_3^*$ 　　　　　　　　　　　　　　　　(Eq. 5)

240　f_{O3} was adopted from a previous study conducted in Beijing (Wang et al., 2019b), where the seasonal

241　mean was 0.858 and 0.918 for summer and winter, respectively. $\Delta^{17}O\text{-}O_3^*$ can be approximated as 1.5

242　$\times \Delta^{17}O\text{-}O_3$ because of the isotopic asymmetry of O_3 (Michalski and Bhattacharya, 2009). In this study,

243　the $\Delta^{17}O\text{-}O_3^*$ is $37.5 \pm 2.2‰$ (mean ± SD) averaged from literature sources as the isotopic composition

244　of ozone shows a remarkable stability in the lower troposphere (Ishino et al., 2017; Vicars et al., 2012;

245　Vicars and Savarino, 2014)

246　The $\Delta^{17}O$ of particulate NO_3^- produced via the three formation pathways can be predicted by distinct

247　$\Delta^{17}O$ transfer functions as the following (Morin et al., 2011):

248　$\Delta^{17}O\ (NO_3^-)\ (1)\ (‰) = 2/3\ \Delta^{17}O(NO_2) = 2/3\ f_{O3} \times \Delta^{17}O\text{-}O_3^*$ 　　　　　　　(Eq. 6-1)

249　$\Delta^{17}O\ (NO_3^-)\ (2)\ (‰) = 5/6\ \Delta^{17}O(N_2O_5) = 1/3\ \Delta^{17}O(NO2) + 1/2\ \Delta^{17}O(NO_3) = 1/6\ \Delta^{17}O\text{-}O_3^*\ (4\ f_{O3} +1)$

250　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　(Eq. 6-2)

251　$\Delta^{17}O\ (NO_3^-)\ (3)\ (‰) = \Delta^{17}O(NO_3) = 2/3\ \Delta^{17}O(NO_2) + 1/3\ \Delta^{17}O\text{-}O_3^* = 1/3\ \Delta^{17}O\text{-}O_3^*\ (2\ f_{O3} +1)$ 　(Eq. 6-3)

252　Finally, the $\Delta^{17}O\ (NO_3^-)$ can be expressed as the following:

253　$\Delta^{17}O\ (NO_3^-)_{measured} = \Delta^{17}O\ (NO_3^-)\ (R4) \times f_1 + \Delta^{17}O\ (NO_3^-)\ (R7) \times f_2 + \Delta^{17}O\ (NO_3^-)\ (R8) \times f_3$

254　(Eq. 7)

255　where $\Delta^{17}O\ (NO_3^-)_{measured}$ is the measured value in this study and the three endmember values of $\Delta^{17}O$

256　$(NO_3^-)\ (R4)$, $\Delta^{17}O\ (NO_3^-)\ (R7)$, and $\Delta^{17}O\ (NO_3^-)\ (R8)$ are calculated using Eqs. (6-1 to 6-3). The

257　proportional contributions of the three NO_3^- formation pathways ($f_1 + f_2 + f_3 = 1$) were estimated by the

258　SIAR model (Sect. 2.5.) for the winter and the summer months.

259

2.4. Estimation of PM$_{2.5}$ Aerosol Liquid Water Content (ALWC) and aerosol pH

ISORROPIA-II is a thermodynamic equilibrium model for the Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Ca^{2+}, Mg^{2+}, and H$_2$O aerosol system (Fountoukis and Nenes, 2007). In the present study, the model was run as a "forward" and "metastable" mode to calculate aerosol liquid water content (ALWC) and pH. The detailed information of the model is found in Fountoukis and Nenes (2007). As input parameters, the concentrations of water-soluble ions that were measured by NIER and ambient RH and temperature were used for the model.

2.5. Bayesian stable isotope mixing model (stable isotope analysis in R, SIAR)

For quantifying proportional contribution of three NO$_3^-$ formation pathways (f_1, f_2, and f_3 in Eq. 4-2), we used the Bayesian stable isotope mixing model (Parnell et al., 2013) implemented using the SIMMR package in R software, which is available at https://cran.r-project.org/web/packages/simmr/index.html. The Bayesian Markov Chain Monte Carlo approach is adequate to provide the relative contribution of the endmembers. Detailed information of the SIAR can be found in Parnell et al. (2010). As input data, measured Δ^{17}O (NO$_3^-$) and estimated Δ^{17}O (NO$_3^-$) endmember values of each pathway were treated in SIAR model. Similar use of the SIAR model can be found elsewhere (Song et al., 2020; Wang et al., 2019b).

2.6. Backward airmass trajectory

Two-day air mass backward trajectories were analyzed using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model with meteorological input from the global data assimilation system (a regular 1° x 1° longitude-latitude grid) (Stein et al., 2015; https://ready.arl.noaa.gov/HYSPLIT.php) . The trajectories were calculated every 6 h at an elevation of 500 m above sea level. The potential source contribution function (PSCF) was then applied to calculate the probable source location (latitude i and longitude j), which is determined here as the ratio of the number of trajectory end points associated with measured δ^{15}N (NO$_3^-$) values higher than a threshold value (set to 95th percentile of δ^{15}N (NO$_3^-$) (m_{ij}) to the total number of points (n_{ij}) in the $i\,j$ th grid cell). The PSCF calculation and gridded trajectory frequencies was made in the openair package, R software

289 (https://cran.r-project.org/web/packages/openair/index.html) (Carslaw and Ropkins, 2012).

290

3. Results and discussion

3.1. Seasonal characteristics of PM$_{2.5}$ concentration, $\delta^{15}N$ (NO$_3^-$), and $\Delta^{17}O$ (NO$_3^-$)

PM$_{2.5}$ mass concentration varied from 7.5 μg m^{-3} to 139.0 μg m^{-3} for the whole sampling period. According to the typical synoptic weather patterns of East Asia (Kim et al., 2007), the measurements are divided into summer (May-Aug) and winter (Oct.-Mar.) groups. A clear seasonal difference in PM$_{2.5}$ concentration and its composition were observed with significantly higher concentrations of mass and inorganic constituent in the winter than in the summer (Table 1 and Figure S1).

During the summer, PM$_{2.5}$ concentration ranged from 7.5 μg m^{-3} to 34.5 μg m^{-3} with a mean of 22.7 ± 6.9 μg m^{-3}. The mean concentration of TC and TN was 4.6 ± 1.4 μgC m^{-3} and 1.9 ± 1.0 μgN m^{-3}, respectively, resulting in the mean TC/TN ratio of 2.7 ± 2.0. The mass concentrations of all measured species were much higher in the winter, during which PM$_{2.5}$ concentration was raised up to 139.0 μg m^{-3} from 10.6 μg m^{-3} with a mean of 61.7 ± 39.2 μg m^{-3}. Accordingly, the mean of TC and TN was 15.2 ± 4.5 μgC m^{-3} and 11.8 ± 7.7 μgN m^{-3}, respectively and the mean TC/TN ratio of 0.9 ± 0.7 was noticeably lower than that of the summer.

For the entire experiment, the mean mass fraction against PM$_{2.5}$ was the highest for NO$_3^-$ (26% ± 23%), followed by SO$_4^{2-}$ (20% ± 1%) and NH$_4^+$ (14% ± 1%), highlighting the contribution of SIA to PM$_{2.5}$ mass. The NO$_3^-$ mass concentration varied from 0.2 μg m^{-3} to 69.3 μg m^{-3} with a mean of 17.6 ± 22.1 μg m^{-3}. Seasonally, the NO$_3^-$ concentration was significantly higher in the winter (29.7 ± 22.1 μg m^{-3}) than summer (0.8 ± 0.9 μg m^{-3}). TN existed completely as inorganic N from both NO$_3^-$ and NH$_4^+$ during the winter (regression slope of 1.0). During the summer, NO$_3^-$ and NH$_4^+$ comprised 67% of TN and the rest (33 %) was assumed to be organic nitrogen (ON) components. In contrast, the mass fraction of SO$_4^{2-}$ against PM$_{2.5}$ was higher in the summer (23%) than winter (19%). The seasonal characteristics of chemical composition implies the significant role of inorganic nitrogen species in PM$_{2.5}$ mass increase in winter and ON and sulfate in summer.

Both $\delta^{15}N$ (NO$_3^-$) and $\Delta^{17}O$ (NO$_3^-$) exhibited an inverse correlation with ambient temperature (r= -0.87 and r= -0.55, respectively). The $\delta^{15}N$ (NO$_3^-$) exhibited higher values in winter with a weight-mean of -0.7‰ ± 3.3 ‰ and 3.8‰ ± 3.7 ‰ in the summer and the winter, respectively. This seasonal pattern of

318   $\delta^{15}N$ (NO_3^-) has been typically observed in East Asia regions (Li et al., 2019; Song et al., 2019; Zong et

319   al., 2020). Analysis of backward airmass trajectory indicates that the lower and the upper bound of $\delta^{15}N$

320   (NO_3^-) were associated with air masses from the ocean by southerly and easterly winds in the summer

321   and from Siberia by northerly winds in winter, respectively (Figure S3). In comparison with urban China

322   (Figure 2a), averaged summer $\delta^{15}N$ (NO_3^-) values were comparable between Seoul and all urban

323   Chinese sites reported here, whereas in winter, $\delta^{15}N$ (NO_3^-) of Seoul was similar to those of Shanghai

324   and Guangzhou rather than $\delta^{15}N$ (NO_3^-) of Beijing that were higher than 10‰. Another observation at

325   a mountain station in Taiwan shows that the highest $\delta^{15}N$ (NO_3^-) was found in spring when the level of

326   anthropogenic constituents were elevated (Guha et al., 2017). These observations over East Asia may

327   suggest at some extent that the seasonal pattern of $\delta^{15}N$ (NO_3^-) is basically associated with synoptic

328   meteorological condition that controls the type and strength of emission sources, where low and high

329   $\delta^{15}N$ (NO_3^-) values indicate biogenic soil emissions and fossil-combustion, respectively. (Elliott et al.,

330   2019)(Elliott et al., 2019)

331   Along with nitrogen isotope, heavier oxygen isotopes were also enriched in NO_3^- during the winter

332   compared to the summer, when the weight-mean of $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ in NO_3^- were 70.4‰ ± 5.4 ‰,

333   82.0‰ ± 6.2 ‰, and 27.7‰ ± 2.2 ‰ for the winter and 57.3‰ ± 4.9 ‰, 65.7‰ ± 6.2 ‰, and 23.2‰ ±

334   2.2 ‰ for the summer. These results of high winter and low summer $\Delta^{17}O$ (NO_3^-) were consistent with

335   previous observations at urban Beijing (He et al., 2018; Wang et al., 2019b; Figure 2b), indicative of

336   relatively greater contribution of nighttime oxidation pathways in winter. It is also noteworthy that our

337   summer and winter $\Delta^{17}O$ (NO_3^-) values were similar to annual $\Delta^{17}O$ (NO_3^-) values of an urban (Sapporo)

338   and a rural (Rishiri) site in Japan, respectively (Nelson et al., 2018). It is likely suggestive that the winter

339   $\Delta^{17}O$ value in Seoul has undergone a considerable atmospheric processing on a regional scale.

340   Given that $PM_{2.5}$ concentrations reflect the seasonality, atmospheric chemical composition and

341   meteorological properties were examined in relation to $PM_{2.5}$ concentrations (Figure 3). Clearly, for the

342   winter samples with $PM_{2.5}$ concentration greater than 40 μg m^{-3}, meteorological conditions varied

343   relative to low $PM_{2.5}$ samples; relatively high temperature and RH staying at 0 °C to 10 °C and 45 % to

344   65 %, respectively, and low wind speed of 1 m s^{-1} to 2 m s^{-1}, representing the meteorological

345   characteristics of winter $PM_{2.5}$ episodes. Particularly in winter, a strong linearity of $PM_{2.5}$ was found

346   with most chemical constituents considered in this study, such as SIA species, TN, NOR, and SOR.

347   However, although being elevated in levels, NO_2 and O_3 mixing ratios showed non-linearity with $PM_{2.5}$

348   concentrations. Isotope ratios were correlated either linearly or inversely with $PM_{2.5}$ concentrations. In

349   winter, $\Delta^{17}O$ (NO_3^-) showed the best correlation with $PM_{2.5}$ concentrations but $\delta^{15}N$ (NO_3^-) was

350   inversely related with PM$_{2.5}$ level.

351

3.2. Graphical representation of dual isotopes: Δ^{17}O and δ^{15}N of NO$_3^-$

353   The isotope ratios of source endmembers are scarce in the study region and in the aerosol measurements

354   and the isotope fractionation effect during gas-to-particle conversion is often estimated with

355   thermodynamic constants and reasonable assumptions. In this regard, the graphical representation of

356   dual isotopes enables the complex signatures of atmospheric samples to be distinguished and allows

357   their oxidation processes to be constrained. Figure 4 displayed measured δ^{15}N (NO$_3^-$) and Δ^{17}O (NO$_3^-$)

358   coordinates with related chemical parameters in colors.

359   In Figure 4a and b, the range of Δ^{17}O (NO$_3^-$) endmembers for the three NO$_3^-$ oxidation pathways

360   calculated in Sect. 2.3.2. are presented by black dotted boxes, which are successfully distinguished. The

361   Δ^{17}O (NO$_3^-$) of all samples fell into the predicted ranges of the Δ^{17}O endmembers, but were separated

362   into seasonal groups. Most of summer Δ^{17}O (NO$_3^-$) values indicate NO$_3^-$ (R4) pathway. It is in

363   accordance with what has been reported in temperate areas during summer (Alexander et al., 2009;

364   Michalski et al., 2003). In field measurements of δ^{15}N (NO$_3^-$) and δ^{18}O (NO$_3^-$) in Chinese cities, the

365   proportional contribution of OH-oxidation pathway was significantly correlated with latitudes (Zong et

366   al., 2020), confirming the evidence of the NO$_3^-$ formation through OH oxidation depending on UV

367   radiation intensity.

368   In comparison, more than half of winter samples are located in the domains indicating NO$_3^-$ (R7) and

369   (R8) pathways. Particularly, for winter samples with NO$_3^-$ mass concentration higher than ~ 30 μg m^{-3},

370   Δ^{17}O (NO$_3^-$) values clearly represent the (R7) pathway. The winter Δ^{17}O (NO$_3^-$) was proportional to

371   nitrogen oxidation ratio (NOR, Figure 4c), indicative of efficient conversion of NO$_x$ to NO$_3^-$ via O$_3$

372   oxidation pathways. In the summer periods when NO$_3^-$ concentrations were relatively high (above ~ 3

373   μg m^{-3}), the contributions of O$_3$ oxidation pathways became elevated, which is a similar pattern to what

374   was observed in the winter. This result suggests that the O$_3$ oxidation pathways are likely to be

375   responsible for the rapid conversion of particulate NO$_3^-$ observed during winter and summer PM$_{2.5}$

376   episodes in the study region.

377   The formation of N$_2$O$_5$ (R6) is dependent on both NO$_2$ and O$_3$, which are reciprocally correlated in

378   source regions. The equilibrium of R6 shifts to N$_2$O$_5$ at low temperature and its lifetime against

379   photolysis is long under the low sunlight. For these reasons, the dark formation of NO$_3^-$ (R7) would be

380 favorable in urban outflows in winter. The hydrolysis of N_2O_5 on aerosol surface (R7) is highly
381 dependent on RH, aerosol liquid water content (AWLC), and chemical composition (Hallquist et al.,
382 2003; Wahner et al., 1998). To evaluate the $\Delta^{17}O$ (NO_3^-) signature observed, we calculated ALWC and
383 acidity of aerosol, pH using ISORROPIA II model (Sect. 2.4.). Given the high concentration of nano-
384 particles from various sources in the urban areas, it is assured that aerosol surface is enough for NO_3^-
385 (R7) pathway. The calculated ALWC was higher by 90 % (19.1 ± 22.8 µg m^{-3}) in the winter and lower
386 by 21 % (7.8 ± 5.2 µg m^{-3}) in the summer relative to the annual mean of the two years. When NO_3^- mass
387 concentrations were greater than ~ 3 µg m^{-3} in the summer and ~ 30 µg m^{-3} in the winter, ALWC was
388 14.3 µg m^{-3} and 31.7 µg m^{-3}, respectively, which were greater by 166 % and 183 % than the seasonal
389 mean, respectively (Figure 4d). Furthermore, the high $\Delta^{17}O$ (NO_3^-) and ALWC coincided with lower
390 bound (about 4) of winter pH varying from 4 to 6, whereas aerosol pH was 2-3 during the summer. The
391 low aerosol pH concurrent with the high $\Delta^{17}O$ (NO_3^-) and ALWC is coherent with the aqueous-phase
392 HNO_3 formation on liquid aerosol through R7.

393 While $\Delta^{17}O$ (NO_3^-) allows insights into the oxidation pathway of NO_3^-, $\delta^{15}N$ (NO_3^-) values are affected
394 by various factors, most of which are not well constrained due to the complicated chemistry and key
395 roles of nitrogen oxides in the Earth's environment. In this study, $\delta^{15}N$ (NO_3^-) variability versus $PM_{2.5}$
396 concentration resembled the variability of NO_2 versus $PM_{2.5}$ concentration (Figure 3f and o), implying
397 a close link between NO_2 oxidation and $\delta^{15}N$ (NO_3^-). Therefore, in addition to the role of $\Delta^{17}O$ (NO_3^-)
398 as a tracer of NO_3^- oxidation pathway, we evaluated whether a variation of $\delta^{15}N$ (NO_3^-) indicates NO_x
399 oxidation efficiency between NO and NO_2 (Freyer et al., 1993; Nelson et al., 2018; Walters et al., 2016).
400 A possible effect on $\delta^{15}N$ during NO_x photochemical cycling cannot be predicted in the same way under
401 varying conditions, e.g., depending on abundances of NO, NO_2, and O_3. The shift in $\delta^{15}N$ (NO_2) relative
402 to $\delta^{15}N$ (NO_x) in the atmosphere will change depending on f_{NO2} and temperature-dependent $\alpha_{NO2/NO}$
403 (Freyer et al., 1993; Li et al., 2020; Walters et al., 2016). When O_3 mixing ratio is high, NO is almost
404 completely oxidized to NO_2, leading to an increasing f_{NO2} value, and the $\delta^{15}N$ (NO_2) should correspond
405 to the $\delta^{15}N$ of NO_x sources (Freyer et al., 1993).

406 In the dual isotope coordinates of $\delta^{15}N$ (NO_3^-) and $\Delta^{17}O$ (NO_3^-) (Figure 4), it is evident that the samples
407 taken during a record-breaking winter $PM_{2.5}$ pollution events are associated with the lower bound values
408 of $\delta^{15}N$ (NO_3^-) (-1 to 4 ‰) and the highest $\Delta^{17}O$ (NO_3^-) values (28 to 31 ‰). Simultaneous
409 measurements of PM_1 chemical composition in Seoul and Beijing demonstrated that the regionally-
410 processed air masses were long-range transported to Seoul within approximately 2 days during these
411 episodes (Kim et al., 2020a). Their NO_2/O_3 ratio (1 to 2) was clearly lower with higher f_{NO2} (0.7 to 0.8)

compared to the other winter samples (Figure 4g and h). This result implies that O_3 level was high enough to efficiently oxidize NO to NO_2 during the severe $PM_{2.5}$ pollution events. In this condition, the shift in $\delta^{15}N$ (NO_2) relative to $\delta^{15}N$ (NO_x) is insignificant and consequently, $\delta^{15}N$ (NO_2) would be lower than those of other winter samples unless both emission sources and $\alpha_{NO2/NO}$ changed significantly. Considering that NO_3^- is the key driver of the high $PM_{2.5}$ in Seoul, the higher degree of NO_x oxidation efficiency is worth highlighting, in conjunction with a strong linear relationship between $\Delta^{17}O$ (NO_3^-) and NOR (Figure 4c) revealing an efficient conversion of NO_2 to NO_3^- through NO_3^- pathway (R5+R6+R7+R8) via O_3.

3.3. Contributions of major HNO₃ oxidation pathways

Combining the $\Delta^{17}O$ (NO_3^-) measurements and the calculation of $\Delta^{17}O$ transferred from O_3 to HNO_3, the contributions of three major NO_3^- formation pathways were quantitatively accounted, despite the inherent uncertainties in the calculation (Sect. 2.5.).

NO_3^- pathway (R4) dominated the total NO_3^- formation (87 ± 6 %) in summer. In contrast, the nighttime pathways through N_2O_5 and NO_3 (pathways R7 and R8) were responsible for 24 % and 14 % of the NO_3^- formation in the winter, respectively. The contributions increased further to 40 % and 30 %, respectively, on haze days when $PM_{2.5}$ concentration exceeded 75 $\mu g\ m^{-3}$, national air quality standard for "very bad" alert. The significant nighttime oxidation of NO_3^- has been observed broadly at urban sites in Northeast Asia. The results of this study are consistent with those conducted in Beijing, showing low $\Delta^{17}O$ values in summertime (about 17 ‰ to 25 ‰) and substantially high $\Delta^{17}O$ values (about 25 ‰ to 34 ‰) in wintertime when NO_3^--driven $PM_{2.5}$ haze pollution occurred (He et al., 2018; Song et al., 2020; Wang et al., 2019b). In general, nighttime pathways accounted for more than 60 % and up to 97 % in Beijing (He et al., 2018; Song et al., 2020; Wang et al., 2019b). From a global perspective, the chemical transport model demonstrated that N_2O_5 heterogeneous hydrolysis was comparably important as NO_2 + OH (41 %) for NO_3^- formation at below 1km altitude (Alexander et al., 2020).

It is noteworthy that although the seasonal patterns are similar in Northeast Asia, the average proportional contributions estimated from $\Delta^{17}O$ (NO_3^-) are highly sensitive to input parameters (i.e, f_{O3} and $\Delta^{17}O$-O_3*). In this study, the seasonal f_{O3} was assumed to be equal to those estimated for Beijing and set to 0.858 ± 0.05 and 0.918 ± 0.05 for the warm and cold months, respectively (Wang et al., 2019b), which are comparable to other estimates for Beijing (0.86) and Shanghai (0.97) (He et al., 2018, 2020) and the annual-mean of 0.85 in a global model (Alexander et al., 2020).

443   The uncertainty associated with $\Delta^{17}O\text{-}O_3^*$ has been recognized as the largest source of uncertainty in

444   estimating NO_3^- production pathways from $\Delta^{17}O$ (NO_3^-) (Alexander et al., 2009, 2020). In this study,

445   the $\Delta^{17}O\text{-}O_3^*$ of 37.5 ± 2.2 ‰ was averaged from previous observations, corresponding to $\Delta^{17}O\text{-}bulk$

446   O_3 of 25 ‰ (Ishino et al., 2017; Vicars et al., 2012; Vicars and Savarino, 2014). Our mean $\Delta^{17}O\text{-}O_3^*$ of

447   37.5 ‰ was 2.8 ‰ higher and 1.5 ‰ lower than what was used in the field studies (Song et al., 2020;

448   Wang et al., 2019b) and the studies (He et al., 2018, 2020), respectively, for urban Beijing and Shanghai.

449   When sensitivity test was conducted for the proportional contribution of the three oxidation pathways,

450   a 2.8 ‰ change in $\Delta^{17}O\text{-}O_3^*$ value caused 1.6 ‰, 2.1 ‰, and 2.5 ‰ change in the endmember for (R4),

451   (R7), and (R8) pathway, respectively. As a result, the average contribution of the nighttime pathways,

452   including NO_3^- (R7) and NO_3^- (R8), increased to 23 % in summer and 65 % in winter. This suggests

453   that a proper use of key parameters driving endmember values is pre-requisite for more realistic

454   quantification of NO_3^- oxidation pathway contributions.

455

456   3.4. Major NO_x emission sources

457   To investigate major emission sources of atmospheric NO_x in Seoul, $\delta^{15}N$ (NO_x) in the atmosphere

458   ($\delta^{15}N$ (NO_x)$_{atmosphere}$) was estimated from measured $\delta^{15}N$ (NO_3^-) considering nitrogen isotopic

459   fractionation effects (ε_N) based on a dual isotopes approach ($\Delta^{17}O$ and $\delta^{15}N$). Estimated ε_N values were

460   5.9 ± 1.5 ‰ and of 12.2 ± 0.5 ‰ and accordingly, the $\delta^{15}N$ (NO_x)$_{atmosphere}$ was -8.7 ± 3.3 ‰ and -5.8 ±

461   4.2 ‰ in summer and winter, respectively. The larger winter ε_N reveals the enhanced contribution of

462   nighttime oxidation pathway via N_2O_5. As a result, a seasonal difference in $\delta^{15}N$ (NO_x)$_{atmosphere}$ was as

463   small as 2.9 ‰ on average, which is suggestive of little seasonal difference in major NO_x emission

464   source in Seoul.

465   Figure 5 displays the measured $\delta^{15}N$ (NO_3^-) and estimated $\delta^{15}N$ (NO_x)$_{atmosphere}$ of individual samples

466   together with $\delta^{15}N$ (NO_x) domains of emission source endmembers reported in literature; biogenic soil

467   (driven by fertilizer use, -35.1 ± 10.2 ‰; Felix and Elliott, 2014; Li and Wang, 2008; Yu and Elliott,

468   2017), biomass burning (1.8 ± 1.8 ‰; Fibiger and Hastings, 2016), vehicle emissions (-2.5 ± 1.5 ‰;

469   Walters et al., 2015), and coal combustion (14.2 ± 4.5 ‰; Felix et al., 2012; Heaton, 1990). Both in

470   summer and winter, $\delta^{15}N$ (NO_x)$_{atmosphere}$ values are the closest to the domain of vehicle emissions $\delta^{15}N$

471   (NO_x), highlighting the largest contribution of vehicle emissions to NO_x in Seoul (Figure 5). However,

472   the winter $\delta^{15}N$ (NO_3^-) without isotope fractionation effect apparently point to coal emissions, which

473   could lead to misleading conclusions about major NO_x sources. This result is supported by a better

474   correlation of NO_2 with CO than with SO_2 for both seasons. According to a (anthropogenic) bottom-up

475   emissions inventory, the Clean Air Policy Support System (CAPSS), total mobile sources account for

476   about two-third of NO_x emissions in Korea, followed by combustion sources such as energy and

477   manufacturing industries (33 %). The highest NO_2 column densities are distinct in Seoul Metropolitan

478   Areas (SMA), which is mostly due to the emissions from transportation (Kim et al., 2020b). Our results

479   of the isotope measurements are in fairly good agreement with the national emission inventories and

480   satellite observations, highlighting the largest contribution of vehicle emissions to NO_x sources in Seoul.

481   Other than vehicle emissions, the lower bound summer $\delta^{15}N$ $(NO_x)_{atmosphere}$ and the upper bound winter

482    $\delta^{15}N$ $(NO_x)_{atmosphere}$ were relatively closer to the $\delta^{15}N$ (NO_x) of fertilized soil emissions and coal-

483   combustion, respectively. These seasonally distinct contributions from soil emissions and coal

484   combustion were consistent with the results from previous studies conducted in China, revealing

485   common seasonal emission characteristics on a regional scale in East Asia. It was evident that the upper

486   bound winter $\delta^{15}N$ $(NO_x)_{atmosphere}$ coincided with elevated SO_4^{2-}/ NO_3^- mass ratio by 2-3 times. During

487   these periods, trajectory analysis indicates that air masses originated from cold regions in northeastern

488   China, such as Liaoning province, where heavy and coal-fired industries are located. In Beijing located

489   in northeastern China, coal combustion is an important fossil-fuel source as the highest contribution

490   source to atmospheric NO_x emissions during winter, about 30 to 40 %, regardless of approaches used

491   for estimating NO_3^- oxidation pathways, either $\Delta^{17}O$ or $\delta^{18}O$ (Li et al., 2019; Song et al., 2019, 2020;

492   Zong et al., 2020). Thus, in this study, the upper bound winter $\delta^{15}N$ $(NO_x)_{atmosphere}$ suggests enhanced

493   contributions of coal combustion to atmospheric NO_x emissions. It is particularly noteworthy that the

494   lower winter $\delta^{15}N$ (NO_3^-) and thus relatively lower contribution of coal combustion of the present study

495   confirms the recent trend that emissions from coal combustion have been reduced in China (Cheng et

496   al., 2019; Tong et al., 2018). Our study was conducted in later years (2018-2019) than their studies

497   (2013-2017), of which $\delta^{15}N$ (NO_3^-) values were rather comparable to the winter mean $\delta^{15}N$ (NO_3^-)

498   observed in Seoul during January 2014 ~ February 2016 (11.9 ± 2.5 ‰; Park et al., 2018). The lower

499   bound of winter $\delta^{15}N$ (NO_3^-) values associated with the highest NO_3^- and $PM_{2.5}$ concentrations (Figures

500   3 and 4) was considered a result of complex effects of isotopic fractionation, as discussed above.

501   This study region is under influence of various biomass burning sources throughout a year, such as

502   agricultural combustion in vicinities of Seoul and over eastern China from spring to fall (Chen et al.,

503   2017; Zhao et al., 2017), wild fires over Siberia and Russian Far East in summer (van der Werf et al.,

504   2010), and residential biomass combustion for heating over east Asia in winter. Some winter $\delta^{15}N$

505    $(NO_x)_{atmosphere}$ values fell in the $\delta^{15}N$ (NO_x) range of biomass burning endmember (Fibiger and Hastings,

506 2016; Figure 5). When assessing contributions of biomass burning based on few endmember $\delta^{15}N$ (NO$_x$),

507 however, caution should be exerted considering the fact that $\delta^{15}N$ (NO$_x$) varied among biomass types

508 from -7 to 12‰ (Fibiger and Hastings, 2016) and there is currently a lack of   understanding of biomass

509 combustion that could potentially affect air quality in Seoul.

510

511 4. Conclusions and outlook

512 5. Our $\delta^{15}N$ and $\Delta^{17}O$-based study confirms that vehicle emissions are the main source of NO$_3^-$ in PM$_{2.5}$ in

513 Seoul during the summer and the winter. In addition, the qualitative estimates of NO$_x$ emission sources

514 provide suggestive evidence for enhanced contributions from coal combustion and biogenic soil

515 emissions in the winter and the summer, respectively. Moreover, severe winter haze events with daily

516 PM$_{2.5}$ exceeding 100 μg m^{-3} were mainly driven by NO$_3^-$ (up to ~60 % in PM$_{2.5}$). Reducing NO$_x$

517 emissions from vehicles is, therefore, essential for an effective mitigation measure to improve fine

518 aerosol pollution in the study region. Particularly, the highest PM$_{2.5}$ was concurrent with the lowest $\delta^{15}N$

519 (NO$_3^-$) and the highest $\Delta^{17}O$ (NO$_3^-$) and NOR, revealing the efficient NO-to-NO$_2$ conversion and

520 heterogeneous conversion of HNO$_3$ to particulate NO$_3^-$ through O$_3$ oxidation pathway during the winter

521 haze episodes. The multiple-isotope signatures of particulate NO$_3^-$, including ^{17}O, ^{18}O, and ^{15}N,

522 highlight the secondary nature of fine aerosol pollution intimately coupled with the photochemical

523 oxidation process.

524 While our results demonstrate that $\delta^{15}N$ and $\Delta^{17}O$ are robust tracers for major NO$_x$ sources, quantitative

525 source apportionment using the isotope method requires further elaboration of isotope

526 equilibrium/kinetic fractionation effects involved in photochemical cycling of nitrogen oxides and $\delta^{15}N$

527 of NO$_x$ source endmembers representing local or regional emissions in East Asia. In well-designed field

528 studies, the $\delta^{15}N$ and $\Delta^{17}O$ measurements of multiphase and their vertical structures allow us to test the

529 isotope fractionation effects suggested by laboratory experiments and theoretical calculations, and to

530 characterize the atmospheric processing that influence them. In addition, there is an urgent need to

531 document the $\delta^{15}N$ (NO$_x$) values of emissions from vehicles with/without selective catalytic reduction

532 (SCR) and from biomass combustion as a function of biomass type and combustion conditions.

533 Consequently, a comprehensive and quantitative understanding of the oxidation pathways and emission

534 sources of nitrogen oxides using $\delta^{15}N$ and $\Delta^{17}O$ measurements will be able to elucidate detailed

535 mechanisms driving severe haze development in megacities of northeast Asia, including Seoul.

536

Table and figures

Tables

549

550 **Table 1. Measurement summary of PM$_{2.5}$ chemical constituents and isotopic compositions in Seoul**
551   **during the sampling period of May. 2018-Mar. 2019. Arithmetic mean ± 1 standard**
552   **deviation (mass fraction, %) for mass concentrations and concentration-weight mean ± 1**
553   **standard deviation for isotope ratios.**

554

Constituents	Summer (n = 13)	Winter (n = 18)
PM$_{2.5}$ (μg m^{-3})	22.7 ± 6.9	61.7 ± 39.2
TC	4. 6 ± 1.4 (20 %)	15.2 ± 4.5 (25 %)
TN	1.9 ± 1.0 (8 %)	11.8 ± 7.7 (19 %)
NO$_3^-$	0.8 ± 0.9 (4 %)	29.7 ± 22.1 (48 %)
NH$_4^+$	1.9 ± 0.8 (8 %)	11.7 ± 8.4 (19 %)
SO$_4^{2-}$	5.3 ± 2.1 (23 %)	11.5 ± 9.2 (19 %)
[NH$_4^+$]/([SO$_4^{2-}$]+[NO$_3^-$]) equiv. ratio	0.83 ± 0.08	0.94 ± 0.09
δ^{15}N (NO$_3^-$)	-0.7 ± 3.3	3.8 ± 3.7
δ^{17}O	57.3 ± 4.9	70.4 ± 5.4
δ^{18}O	65.7 ± 6.2	82.0 ± 6.2
Δ^{17}O	23.2 ± 2.2	27.7 ± 2.2

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557   **Figures.**

558   **Figure 1. Location of the study region. (a) Seoul metropolitan area in South Korea; the map was**
559   **generated using open source software R (http:// www.R-project.org/).   (b) Sampling site**
560   **of Korea University campus in the northeast Seoul; the map was taken from Kakao maps**
561   **(https://map.kakao.com/).**

562   **Figure 2. (a) $\delta^{15}N$ (NO_3^-) and (b) $\Delta^{17}O$ (NO_3^-) $PM_{2.5}$ observed in Northeast Asia are compared:**
563   **Seoul in this study (red), Beijing (brown), Shanghai (orange), and Guangzhou (light) in**
564   **China, and Rishiri (green) and Sapporo (blue) in Japan during summer (circle) and**
565   **winter (square). Marker indicates mean value (concentration-weighted average for**
566   **Seoul samples of the present study), and lower and upper whiskers denote minimum**
567   **and maximum values (This study; He et al., 2018; Lim et al., 2020; Nelson et al., 2018),**
568   **mean ± standard deviation (Song et al., 2019; Wang et al., 2019b), or 25th and 75th**
569   **percentiles (Zong et al., 2020). Different marker shapes indicate different seasons.**

570   **Figure 3. Relationships of $PM_{2.5}$ mass concentration with meteorological parameters (a-c),**
571   **concentrations of reactive gases (d-f, k) and aerosol chemical constituents (g-j, l-n),**
572   **and N and O isotopic compositions (o-q) measured in Seoul during the summer (open**
573   **circle) and the winter (blue ribbon).**

574   **Figure 4. Relationship of measured $\delta^{15}N$ (NO_3^-) and $\Delta^{17}O$ (NO_3^-) values with key parameters**
575   **during the summer (open circle) and winter (closed ribbon). The predicted $\Delta^{17}O$ (NO_3^-)**
576   **values are presented as dotted rectangles for the tree major NO_3^- formation pathways**
577   **(R4, R7, and R8, see Sect. 2.3.2 for details) in (a) summer and (b) winter. Data are color**
578   **coded by (a) and (b) nitrate concentrations, (c) NOR, (d) ALWC, (e) pH, (f)**
579   **$[NH_4^+]/([SO_4^{2-}]+[NO_3^-])$ equivalent ratio, (g) NO_2/O_3 ratio, and (h) f_{NO2}. Marker size is**
580   **proportional to $PM_{2.5}$ concentration ranging from 10 μg m^{-3} to 100 μg m^{-3}.**

581   **Figure 5. Variations in measured $\delta^{15}N$ (NO_3^-) (open) and estimated $\delta^{15}N$ (NO_x)$_{atmosphere}$ (closed) in**
582   **Seoul during the summer (circle) and winter (triangle). The $\delta^{15}N$ (NO_x) range (mean ±**
583   **1sd) of source-endmembers are distinguished by dotted boxes in different colors: coal**
584   **combustion (14.2 ± 4.5 ‰; Felix et al., 2012; Heaton, 1990), biomass burning (1.8 ±1.8**
585   **‰; Fibiger and Hastings, 2016), vehicle emissions (-2.5 ± 1.5 ‰; Walters et al., 2015),**
586   **and biogenic soil emissions (-35.1 ± 10.2 ‰; Felix and Elliott, 2014; Li and Wang, 2008;**
587   **Yu and Elliott, 2017).**

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