



Behavior of total peroxy and total organic nitrate concentrations at Suzu on the Noto Peninsula, Japan : Long-range transport and local photochemical production

メタデータ	言語: eng 出版者: 公開日: 2019-01-31 キーワード (Ja): キーワード (En): 作成者: Sadanaga, Yasuhiro, Ishiyama, Ayana, Takaji, Ryo, Matsuki, Atsushi, Kato, Shungo, Sato, Keiichi, Osada, Kazuo, Bandow, Hiroshi メールアドレス: 所属:
URL	http://hdl.handle.net/10466/16193

Manuscript Number: ATMENV-D-18-00957R2

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Article Type: Research Paper

Keywords: peroxy nitrates; organic nitrates; long-range transport; local photochemical production; East Asia

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Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:

Data will be made available on request

1 **Highlights**

- 2 ● Continuous observations of PNs and ONs were performed at Noto Peninsula, Japan
- 3 ● PNs and ONs showed characteristic seasonal and diurnal variations
- 4 ● The main variable factor of PNs and ONs is long-range transport in the cold season
- 5 ● PNs and ONs are influenced mainly by photochemical production in the warm season

6

1 **Behavior of total peroxy and total organic nitrate concentrations at Suzu on the**
2 **Noto Peninsula, Japan: Long-range transport and local photochemical**
3 **production**

4

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23 **Abstract**

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25 nitrates (ONs) at Suzu on the Noto peninsula, Japan. It was found that PNs and ONs showed similar
26 seasonal variations with maximum concentrations in spring and minimum concentrations in summer.
27 Concentrations of PNs and ONs were high for air masses originating from the Asian continent from
28 winter to spring, whereas they were independent of air mass origin from spring to summer. In
29 summer, PNs and ONs indicated similar diurnal variations with maximum concentrations during
30 daytime and minimum concentrations during nighttime. Such diurnal variations of PNs and ONs
31 were small in winter. Diurnal variations of PNs in spring were similar to those in summer, whereas
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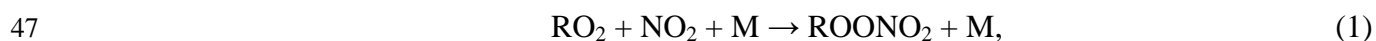
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38 **Keywords:** peroxy nitrates; organic nitrates; long-range transport; local photochemical production;
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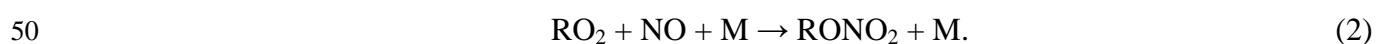
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41 **1. Introduction**

42 Total peroxy nitrates (PNs = ROONO₂; R means an organic group) and total organic nitrates (ONs
43 = RONO₂) are major constituents in total odd nitrogen species (NO_y). The major formation process
44 of PNs and ONs is photochemical reaction in the presence of nitrogen oxides (NO_x) and volatile
45 organic compounds. Primarily, PNs are produced by the reaction of a peroxy radical (RO₂) and
46 NO₂:



48 where M represents a third body molecule, whereas ONs are generated mainly by the reaction of a
49 peroxy radical and NO:

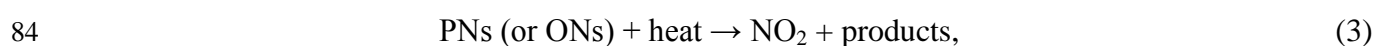


51 In the East Asia region, NO_x emissions have increased over the previous few decades. For
52 example, Kurokawa et al. (2013) developed an emission inventory for Asia (REAS ver. 2), and they
53 estimated that NO_x emissions in Asia and China during 2000–2008 have increased by 54% and 89%,
54 respectively. Concentrations of NO_x in East Asia remain high, although recent satellite observations
55 have indicated that the level of NO₂ over China has decreased at a rate of about 6% y⁻¹ since 2011
56 (Irie et al., 2016). NO_x originating from the Asian continent undergo chemical transformations as
57 they are transported over long distances to other regions such as Japan. The atmospheric lifetimes of
58 NO_x are about 1 d and thus, the scope for their long-range transport is very limited (Sadanaga et al.,
59 2017). However, inorganic total nitrate (T.NO₃: the sum of gaseous nitric acid and particulate
60 nitrate), which is one of the major descendant products of NO_x, is photochemically stable in the
61 troposphere and it has a reasonably long lifetime. Several recent studies have investigated the
62 long-range transport of T.NO₃ from the Asian continent to the western Pacific region, including
63 Japan (e.g. Takiguchi et al., 2008; Chiwa, 2010; Yuba et al., 2014; Fujiwara et al., 2014).

64 Similar to T.NO₃, PNs and ONs have reasonably long atmospheric lifetimes. The lifetimes
65 of PNs are strongly dependent on temperature and are longest under cold conditions. For example,
66 peroxyacetyl nitrate (PAN), the representative species of PNs, has a lifetime of several months in

67 the mid- and upper troposphere (Kirchner et al., 1997, 1999), and the lifetimes of ONs have been
68 estimated to range from several days to several weeks (Clemitshaw et al., 1997). Hence, PNs and
69 ONs could be transported over long distances. Therefore, some NO_x originating from the Asian
70 continent could be transported to Japan in the form of PNs and ONs, although observations of PNs
71 and ONs in Japan are very limited. This is because it is very difficult to use gas chromatography
72 with an electron capture detector (the typical method for the measurement of PNs and ONs) in field
73 observations in Japan because of legal regulations concerning radioisotopes. Tanimoto et al. (2002)
74 performed year-round observations of PAN, peroxypropionyl nitrate, and other species on Rishiri
75 Island in Hokkaido (Japan) using gas chromatography with negative ion chemical ionization mass
76 spectrometry (Tanimoto et al., 1999, 2000). This is only one example of yearly observation of PNs
77 in Japan. No yearly observations of ONs in Japan have been reported. Hence, Japan is a blank area
78 in terms of observations of PNs and ONs, and the long-range transport of PNs and ONs from the
79 Asian continent to the western Pacific region, including Japan, remains unclear.

80 Recently, we developed a system for the continuous measurement of PNs and ONs based
81 on a thermal dissociation cavity attenuated phase shift spectroscopy (TD-CAPS) technique
82 (Sadanaga et al., 2016). TD-CAPS is based on the dissociation of PNs and ONs by heating to NO₂,
83 as in reaction (3):



85 followed by direct measurement of the NO₂ concentration using a CAPS technique (Kebabian et al.,
86 2005, 2008). TD-CAPS is based on a thermal dissociation laser-induced fluorescence technique
87 (Day et al., 2002). The use of CAPS instead of laser-induced fluorescence enables automatic
88 continuous observations of PNs and ONs because the operation of CAPS is much more convenient
89 than that of laser-induced fluorescence (Sadanaga et al., 2016).

90 In the present study, we performed automatic continuous measurements of the
91 concentrations of PNs and ONs using TD-CAPS in a remote area at Suzu on the Noto Peninsula
92 (Japan). We investigated seasonal and diurnal variations of the concentrations of PNs and ONs and

93 discussed their factors in terms of long-range transport and local photochemistry. This study was the
94 first to perform continuous observations of both PNs and ONs and to investigate their behaviors in
95 Japan.

96

97 **2. Observations**

98 **2.1. Site description**

99 Observations were made at the Noto Ground-based Research Observatory (NOTOGRO) of
100 Kanazawa University in Suzu, which is in Ishikawa Prefecture, Japan (**Fig. 1**). The observatory is
101 located at 37.5°N, 137.4°E. Further details concerning the observatory can be found elsewhere
102 (Sadanaga et al., 2016; Ueda et al., 2016). Briefly, the NOTOGRO is located at the tip of Noto
103 Peninsula. There is little industrial activity on the peninsula, and the population of Suzu is low (i.e.,
104 14,625 in 2015). The site is about 117 km from the center of Kanazawa, which is the largest city in
105 Ishikawa Prefecture. The observational site is located in a remote area. The Noto Peninsula
106 protrudes into the Sea of Japan and pollution from the Asian continent can reach the NOTOGRO
107 directly. Therefore, the NOTOGRO is a site highly suitable for observing pollution outflows from
108 the Asian continent. The observations for this study were performed from December 2012 to
109 December 2015.

110

111 **2.2. System for measurement of PNs and ONs**

112 The concentrations of PNs and ONs were measured using TD-CAPS. Details of the TD-CAPS
113 measurement system are described elsewhere (Sadanaga et al., 2016), although a schematic of the
114 TD-CAPS instrument is shown in Supplementary **Fig. S1**. Briefly, this instrument includes a
115 thermal dissociation unit and an NO₂ detection unit. The thermal dissociation unit has three lines: an
116 “NO₂ line,” a “PNs line,” and an “ONs line.” The NO₂ line has a quartz tube that is not heated,
117 while the PNs and ONs lines contain quartz tubes that are heated at 433 and 633 K, respectively.
118 Ambient air is passed through a Teflon[®] filter, which is used to remove particles, before being

119 introduced into all three lines. On the NO₂ line, neither PNs nor ONs are pyrolyzed in the quartz
120 tube, and only ambient NO₂ is measured by a CAPS-NO₂ analyzer. On the PNs line, PNs are
121 thermally decomposed in the heated quartz tube to NO₂ but ONs are not dissociated. Thus, the
122 CAPS-NO₂ analyzer measures the level of NO₂ originating from the PNs as well as the ambient
123 NO₂. On the ONs line, both PNs and ONs are thermally decomposed to NO₂ in the heated quartz
124 tube, and the CAPS-NO₂ analyzer measures the NO₂ originating from both PNs and ONs as well as
125 the ambient NO₂. Therefore, the concentrations of NO₂, NO₂ + PNs, and NO₂ + PNs + ONs are
126 obtained from the analyses of the gases from the NO₂, PNs, and ONs lines, respectively. These
127 concentrations are measured sequentially by switching three-way solenoid valves. The
128 concentrations of PNs and ONs are obtained by subtracting the relevant concentrations of the other
129 compounds measured on a particular line:

$$130 \quad [\text{PNs}] = [\text{NO}_2 + \text{PNs}] - [\text{NO}_2], \quad (4)$$

$$131 \quad [\text{ONs}] = [\text{NO}_2 + \text{PNs} + \text{ONs}] - [\text{NO}_2 + \text{PNs}]. \quad (5)$$

132 Some gaseous nitric acid (HNO₃) is pyrolyzed to produce NO₂ in the ONs line (Sadanaga et al.,
133 2016), and an annular denuder coated with NaCl is placed before the heated quartz tube in the ONs
134 line to remove HNO₃. Here, a commercially available NO₂ monitor based on a CAPS method
135 (CAPS-NO₂, Shoreline Science Research Inc.; licensed by Aerodyne Research Inc.) was used as an
136 NO₂ detector without modification. Zero air was automatically introduced into the CAPS-NO₂
137 analyzer for 135 s every 30 min using a zero air supply (Shoreline Science Research Inc.) to correct
138 the zero-point of the CAPS-NO₂ analyzer. The detection limit of this instrument for the total signal,
139 i.e., the sum of NO₂, PNs, and ONs concentrations, is equal to the detection limit of NO₂, which
140 was estimated to be 15 pptv (parts per trillion by volume) (3σ) with an integration time of 2 min.
141 The detection limits for PNs and ONs using this method cannot be determined exactly because they
142 depend on variations in the NO₂ and NO₂ + PNs concentrations, respectively. In a previous article
143 (Sadanaga et al., 2016), the detection limit was estimated to be 21 pptv (3σ) with an integration
144 time of 2 min, under a constant NO₂ mixing ratio of 5 ppbv (parts per billion by volume).

145 Thieser et al. (2016) and Sobanski et al. (2016) described interferences of NO_x and O_3 to
146 PNs and ONs data for a thermal dissociation cavity ring-down spectrometer (TD-CRDS). Such
147 interferences are due to operations of TD-CRDS under high pressure (typically from 0.5 to 1 bar).
148 TD-CAPS is operated under atmospheric pressure and such interference could exist as is the case of
149 TD-CRDS. However, NO_x concentrations at the NOTOGRO were low and less than 1 ppbv in many
150 cases (accounting for 77% of the total observation period). In addition, NO_2 concentration
151 fluctuations were large in many cases under high NO_x concentrations. Current TD-CAPS instrument
152 has only one CAPS- NO_2 analyzer, and NO_2 , PNs and ONs concentrations were measured
153 sequentially by switching three-way solenoid valves as described above. In this case, precisions of
154 PNs and ONs concentrations are poor and we omitted the PNs and ONs data under large NO_2
155 concentration fluctuations. We concluded that the interference described by Thieser et al. (2016)
156 and Sobanski et al. (2016) can be negligible for the observation at the NOTOGRO.

157 Several reports (e.g, Thaler et al., 2011; Sobanski et al., 2016; Thieser et al., 2016) indicate
158 that ClNO_2 can interfere ONs data because some ClNO_2 is pyrolyzed to form NO_2 at temperatures
159 above ~ 550 K (Thaler et al., 2011; Sobanski et al., 2016). ClNO_2 is formed in the troposphere by
160 the heterogeneous reaction of N_2O_5 with chloride-containing particles such as sea salt aerosol in the
161 nighttime. It should be noted that ONs observed in this study might contain ClNO_2 , especially in the
162 nighttime and in the early morning, since the NOTOGRO is located near the seashore of the Noto
163 peninsula.

164

165 **2.3. Measurements of other species**

166 The concentrations of NO_y and T.NO_3 were measured using a scrubber-difference NO-O_3
167 chemiluminescence (SD-CL) method, the details of which are described elsewhere (Sadanaga et al.,
168 2008a, 2008b; Yuba et al., 2010). Briefly, the SD-CL method has two lines: an “ NO_y line” and an
169 “ $\text{NO}_y\text{-T.NO}_3$ line.” On the NO_y line, ambient air is introduced into a molybdenum reducing catalyst
170 heated at 598 K (Mo catalyst), which reduces NO_y to NO , and then the NO concentration is

171 measured using an NO-O₃ chemiluminescent detector (Model 42i-TL; Thermo Fisher Scientific
172 Inc.). The concentrations of NO_y are measured using the signal from the NO_y line. On the
173 NO_y-T.NO₃ line, ambient air is passed through a Teflon[®] filter and an annular denuder coated with
174 NaCl to remove particulate nitrate and HNO₃, respectively, before being introduced to another Mo
175 catalyst to reduce nitrogen species, which are then measured by the NO-O₃ chemiluminescent
176 detector. The NO_y-T.NO₃ concentrations are measured using the signal from the NO_y-T.NO₃ line.
177 The T.NO₃ concentrations are obtained by subtracting the simultaneous NO_y-T.NO₃ concentration
178 from the NO_y concentration:

$$179 \quad [T.NO_3] = [NO_y] - [NO_y-T.NO_3]. \quad (6)$$

180 The NO_x concentrations are measured using a light-emitting diode photolytic converter, in
181 combination with the NO-O₃ chemiluminescence method (Sadanaga et al., 2010). The detection
182 limits of NO_x and NO_y were 60 pptv, with a 1-min integration time (2σ). The detection limits for
183 T.NO₃ with this method cannot be determined exactly, as is the case for PNs and ONs, because they
184 depend on variations in the NO_y concentrations. The detection limit has been estimated to be 71
185 pptv, with a 10-min integration time (2σ), under an NO_y mixing ratio of 5 ppbv (Sadanaga et al.,
186 2008a).

187 Isoprene was analyzed using a Gas Chromatograph-Flame Ionization Detector (GC-FID)
188 (HP 6890; Hewlett Packard) (Kato et al., 2001, 2004). Ambient air samples were collected into 6 L
189 stainless steel canisters for analyses about every week. The sampling hours of ambient air and
190 weather conditions were assigned at random. The 500 cm³ of sampled air was concentrated into a
191 three-stage pre-concentrator (Entech7000; Entech) prior to injection into the GC-FID. The GC
192 column was an HP-1 (60-m length, 0.32-mm inner diameter, and 1-μm film thickness). Calibrations
193 were conducted using 1 ppmv (parts per million by volume) standard gas containing 58 species
194 (PAMS-J58; Sumitomoseika). The detection limits for isoprene were in the range 1–3 pptv with
195 2%–13% accuracy and 2%–15% precision.

196 Ozone and CO were measured using commercially available instruments based on UV

197 absorption (Model 49i; Thermo Fisher Scientific Inc.) and non-dispersive infrared photometer
198 (Model 48i; Thermo Fisher Scientific Inc.). For the CO measurement, zero air generated from a
199 heated Pt catalyst (Model 96; Nippon Thermo) was measured during the first 15 min of every hour,
200 to check the zero point of the CO analyzer.

201

202 **2.4. Backward trajectory analyses**

203 Backward trajectory analyses were performed using the HYSPLIT 4 model developed by the
204 American National Oceanic and Atmospheric Administration (Stein et al., 2015; Rolph et al., 2017).
205 The HYSPLIT 4 model was run with the GDAS meteorological field with a horizontal resolution of
206 $1^{\circ}\times 1^{\circ}$. The initial altitude and calculation time were set to 500 m and 120 h, respectively. Based on
207 the last coastline they crossed, the origins of the air masses reaching the observational site were
208 classified into five groups: Northeast China (NEC), Middle China and Korea (MCK), Japan (JP),
209 Russia (RU), and Sea (S) (**Fig. 1**). The groups NEC, MCK, JP, and RU were divided according to
210 the dashed lines drawn from the site in **Fig. 1**. Group S indicates air masses that neither passed
211 through the Asian continent nor the Japanese archipelago within 120 h, but would contain air
212 pollutants from the Asian continent and/or Japan because the air masses had passed between the
213 Asian continent and the Japanese archipelago (see **Fig. 1**). Air masses that meandered or did not
214 belong to any of these categories were excluded from our analysis. Trajectory data were collated
215 every 6 h, at 03:00, 09:00, 15:00, and 21:00 Japan Standard Time (JST). Concentrations of trace
216 species measured at the NOTOGRO were averaged into 6-h bins to relate them to the air masses
217 identified using backward trajectory analyses. Thus, concentration data for the time intervals of
218 00:00–6:00, 06:00–12:00, 12:00–18:00, and 18:00–24:00 were equated with trajectories for 03:00,
219 09:00, 15:00, and 21:00 JST, respectively. The percentages of each trajectory sector in each month
220 during the observation period are shown in Supplementary **Fig. S2**. Air masses from the Asian
221 continent (i.e., NEC and MCK) and Japan (i.e., JP) reached the NOTOGRO frequently in the cold
222 and warm seasons, respectively.

223

224 **3. Results and discussion**

225 **3.1. Seasonal variations of PNs and ONs**

226 The monthly averaged concentration variations of PNs and ONs are shown in **Fig. 2(a)**. Daily
227 averaged concentration variations of PNs and ONs are shown in Supplementary **Fig. S3**. The
228 missing PNs and ONs data were due to trouble with the CAPS-NO₂ analyzer used in the PNs and
229 ONs measurement system. Average mixing ratios of PNs and ONs during the observation period
230 were 0.25 and 0.19 ppbv, respectively. Overall, PNs and ONs exhibited similar seasonal cycles with
231 maximum concentrations in spring and minimum concentrations in summer. Seasonal variations of
232 PNs and ONs concentrations also had secondary local maxima in autumn and minima in winter.
233 These seasonal variations are similar to previous observations of PAN at Rishiri Island (45.07°N,
234 141.12°E) in northern Japan (Tanimoto et al., 2002). However, slight differences were found
235 between the variations of concentrations of PNs and ONs. Concentrations of ONs were higher than
236 those of PNs in summer, whereas concentrations of PNs were higher than those of ONs in other
237 seasons. The concentrations of ONs in May were comparable with those in March, but the mixing
238 ratios of PNs in May were about 0.2 ppbv lower than those in March in the same year. These
239 variations were attributed to the differences in atmospheric lifetimes between PNs and ONs (see
240 section 3.3). Daily averaged concentration variations of NO_y, T.NO₃, NO_x, O₃, and CO are also
241 shown in Supplementary **Fig. S3**. Average mixing ratios of NO_y, T.NO₃, NO_x, O₃, and CO during
242 the observation period were 1.66, 0.76, 0.41, 42.3, and 173 ppbv, respectively. Seasonal cycles of
243 NO_y, T.NO₃, O₃, and CO were similar to those of PNs and ONs. A systematic seasonal cycle was
244 not observed for NO_x. **Fig. 2(b)** shows the monthly averaged variations of PNs and ONs fractions in
245 NO_y. The missing PNs/NO_y and ONs/NO_y fraction data were due to trouble with either the NO_y
246 measurement system or the CAPS-NO₂ analyzer. PNs and ONs fractions in NO_y ranged from 7.3 to
247 27% and 8.0 to 17%, respectively.

248 The variations of concentrations of PNs and ONs associated with the five different air mass

249 origins, based on backward trajectory analyses, are shown in **Fig. 3**. In many cases, the
250 concentrations of PNs and ONs from MCK were high from winter to spring. In contrast, the
251 concentrations of PNs and ONs were found independent of air mass origin from spring to summer.
252 These results suggest that variations in the concentrations of PNs and ONs at the NOTOGRO are
253 governed by long-range transport from the Asian continent in the cold season. In the warm season,
254 the shorter atmospheric lifetimes and faster photochemical production rates of PNs and ONs reduce
255 the influence of long-range transport. Detailed discussion on the atmospheric lifetimes and rates of
256 photochemical production of PNs and ONs is presented in section 3.3.

257

258 **3.2. Diurnal variations of concentrations of PNs and ONs**

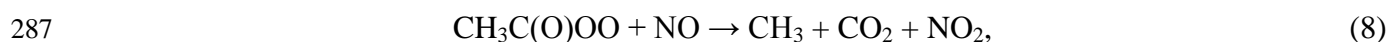
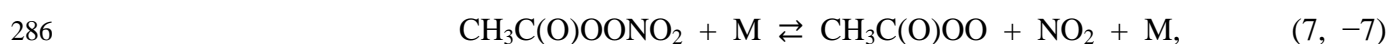
259 The average diurnal variations of concentrations of PNs and ONs in February (winter), May
260 (spring), and July (summer) 2013 are shown in **Fig. 4**. The diurnal variations in the other months
261 are presented in Supplementary **Figs. S4 and S5**. In summer, PNs and ONs exhibited similar
262 diurnal variations with maximum concentrations during daytime and minimum concentrations
263 during nighttime. However, such diurnal variations of PNs and ONs were small in winter. These
264 results suggest that variations of concentrations of PNs and ONs at the NOTGRO are governed by
265 photochemical production in summer. The rates of photochemical production of PNs and ONs in
266 summer are faster than those in winter. As described in section 3.1, the influence of long-range
267 transport on the variations of concentrations of PNs and ONs is small in summer because the
268 concentrations of PNs and ONs are independent of air mass origin. The diurnal variations of
269 concentrations of PNs in spring were found similar to those in summer. In contrast, such diurnal
270 variations were not observed for ONs in spring. Detailed discussion on the diurnal variations,
271 including the differences between concentrations of PNs and ONs in spring, is presented in section
272 3.3.

273

274 **3.3. Discussion on seasonal and diurnal variations of concentrations of PNs and ONs**

275 The seasonal and diurnal variations of concentrations of PNs and ONs, described in sections 3.1 and
 276 3.2, could be attributed to the atmospheric lifetimes and the rates of photochemical production of
 277 PNs and ONs. Variations of concentrations of PNs and ONs at the NOTOGRO are governed by
 278 local photochemical production and long-range transport from the Asian continent. PNs and ONs
 279 are produced mainly by reactions (1) and (2), respectively, and the rates of production of PNs and
 280 ONs in the atmosphere increase with a rise in the solar actinic flux. Therefore, the local
 281 photochemical production of PNs and ONs in the warm season is larger than that in the cold season.
 282 However, the main process of loss of PNs is thermal dissociation, and ONs are decomposed by OH
 283 radicals and solar ultraviolet radiation.

284 First, the atmospheric lifetime of PAN, a representative example of PNs, by thermal
 285 decomposition is discussed. PAN is decomposed by the following reactions:



288 where reactions (7) and (-7) are the forward and reverse reactions, respectively. The atmospheric
 289 lifetime of PAN (τ) based on reactions (7), (-7), and (8) can be calculated using the following
 290 formula (Orlando et al., 1992):

$$291 \quad \tau = \frac{1}{k_1} \left(1 + \frac{k_{-1} [\text{NO}_2]}{k_2 [\text{NO}]} \right), \quad (9)$$

291 where k_1 , k_{-1} and k_2 are the rate constants for reactions (7), (-7), and (8), respectively. The constants
 292 k_1 and k_{-1} depend on both pressure and temperature, whereas k_2 is dependent only on temperature.
 293 These rate constants were calculated considering temperature dependence under a constant pressure
 294 of 1 atm. We referred to Atkinson et al. (2006) as the database for the calculations of k_1 , k_{-1} , and k_2 .
 295 For example, in the cold season of this study (December 2012 to March 2013), the average
 296 temperature and the concentration ratio of NO_2 to NO were 275.8 K and 13.6, respectively. Under
 297 this condition, the lifetime of PAN was estimated as 11.9 d. In the warm season (June–August 2013),
 298 the average temperature and the concentration ratio of NO_2 to NO were 297.1 K and 11.1,

299 respectively. In this case, the lifetime of PAN was estimated as 6.6 h. Hence, the lifetime of PAN
300 varies greatly between the cold and warm seasons. In winter, PNs have long lifetimes and they can
301 be transported from the Asian continent to the NOTOGRO. Conversely, in summer, PNs from the
302 Asian continent are thermally decomposed before arriving at the NOTOGRO because of their short
303 lifetimes.

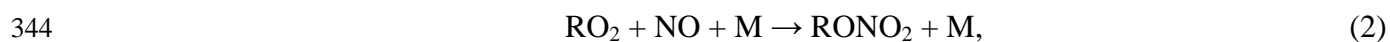
304 Second, the atmospheric lifetimes of ONs are discussed. Clemitshaw et al. (1997) reported
305 seasonal variations of the photodissociation rate coefficients and reaction rates with OH radicals for
306 saturated C₂–C₅ ONs at latitudes of 65°N, 40°N, and 0°. We estimated atmospheric lifetimes of ONs
307 using the data at the latitude of 40°N, the nearest latitude to the NOTOGRO. The lifetimes of ONs
308 ranged from 1–4 d in summer and from 10–27 d in winter. Hence, ONs have short and long
309 atmospheric lifetimes in summer and winter, respectively, as is the case for PNs.

310 The following conclusions can be stated regarding the seasonal variations of the
311 concentrations of PNs and ONs, considering their atmospheric lifetimes and production rates. From
312 winter to spring, i.e., in the cold season, PNs and ONs have long lifetimes and they can be
313 transported long distances. In addition, local photochemical production rates of PNs and ONs are
314 slow and the variations of concentrations of PNs and ONs are influenced primarily by long-range
315 transport. From spring to summer, i.e., in the warm season, PNs and ONs have short lifetimes
316 ranging from several hours to a few days, as estimated above, and the local photochemical
317 production rates of PNs and ONs are fast. Therefore, the variations of concentrations of PNs and
318 ONs are governed mainly by local photochemical production.

319 The diurnal variations of PNs and ONs also indicate a difference of the predominant factor
320 (i.e., long-range transport or local photochemical production) for the variations of concentrations
321 between seasons, as described above. In summer, PNs and ONs showed similar diurnal variations
322 with maximum concentrations during daytime and minimum concentrations during nighttime, and
323 such diurnal variations were small in winter, as described in section 3.2. As estimated above,
324 however, the atmospheric lifetimes of ONs in summer ranged from 1–4 d, which are sufficiently

325 long that such diurnal variations of ONs are unlikely to be observed, even in summer. In fact,
326 diurnal variations of ONs were not found in spring, unlike those of PNs (see **Fig. 4**). The 1-h
327 averaged values of concentrations of ONs in July 2013 showed clear daytime maxima and nighttime
328 minima on many days (**Fig. 5**). This result indicates that ONs in summer actually have diurnal
329 variations with maximum concentrations during daytime and minimum concentrations during
330 nighttime. The diurnal variations of ONs in summer might be due to an organic group of ONs. In
331 general, the reaction rate coefficients of OH with unsaturated organics are larger than those with
332 saturated organics. The atmospheric lifetimes of unsaturated ONs are shorter than 1–4 d (i.e., the
333 lifetimes of saturated C₂–C₅ ONs) in summer. Therefore, the unsaturated ONs could show diurnal
334 variation with maximum concentrations during daytime and minimum concentrations during
335 nighttime.

336 The presence of unsaturated ONs in summer could be attributed to ONs originating from
337 biogenic volatile organic compounds (BVOCs). Many types of BVOC (such as isoprene) have
338 multiple double bonds. In general, emissions of BVOCs increase with rising temperature and
339 enhanced photosynthetically active radiation (Guenther et al., 1993). There is abundant vegetation
340 near the NOTOGRO and emissions of BVOCs would increase in summer. In fact, concentrations of
341 isoprene at the NOTGRO in summer were found higher than in the other seasons (**Fig. 6**). In this
342 case, ONs originating from BVOCs could exist. ONs are generated mainly by the reaction of a
343 peroxy radical and NO. This reaction has two processes, as shown in reactions (2) and (10):



346 In general, a branching ratio of reaction (2) becomes larger as the size of an organic group of an
347 RO₂ radical increases (Atkinson et al., 1982), and RO₂ radicals originating from BVOCs would be
348 likely to produce ONs. Given the above, unsaturated ONs originating from BVOCs at the
349 NOTOGRO might exist. Therefore, ONs in summer could exhibit diurnal variation with maximum
350 concentrations during daytime and minimum concentrations during nighttime. The discussion on

351 the diurnal variation of ONs in summer is a matter for speculation, so that further research and
352 investigation are required, however.

353

354 **3.4. Influence of precipitation on concentrations of PNs and ONs**

355 Henry's law constants for PNs and ONs (of the order of 10^{-2} mol m⁻³ Pa⁻¹) are much smaller than
356 those of HNO₃ (of the order of 10^3 mol m⁻³ Pa⁻¹) (Sander, 2015); thus, the influence of wet
357 deposition on PNs and ONs would be much smaller than that on T.NO₃. To investigate the influence
358 of wet deposition on PNs, ONs, and T.NO₃, we compared the variations of concentrations of these
359 species in relation to the presence and absence of precipitation around the NOTOGRO.
360 Precipitation data from Suzu were obtained from the website of the Japan Meteorological Agency
361 (<http://www.jma.go.jp>). The variations of concentrations of PNs, ONs, and T.NO₃ with and without
362 precipitation during the observation period are shown in **Fig. 7**. Concentrations of water-soluble
363 T.NO₃ were systematically reduced by precipitation but the concentrations of PNs and ONs were
364 independent of precipitation. We conclude that the influence of wet deposition on the concentrations
365 of PNs and ONs with a low Henry's law constant is small, while the concentrations of water-soluble
366 T.NO₃ are influenced by precipitation.

367

368 **4. Conclusions**

369 Continuous observations of the concentrations of PNs and ONs were performed at the NOTOGRO
370 on the Noto Peninsula in Japan, to investigate the behaviors of PNs and ONs. Such continuous
371 observations are the first to be undertaken in Japan. We analyzed the seasonal variations, with and
372 without classification according to air mass origin based on backward trajectory analyses, and the
373 diurnal variations, and we derived the following conclusions. Variations of the concentrations of
374 PNs and ONs are influenced by long-range transport in the cold season, when there is low
375 photochemical activity and the PNs and ONs have long atmospheric lifetimes. In contrast,
376 variations of concentrations of PNs and ONs are governed by local photochemical production in the

377 warm season, when local photochemistry is active and the atmospheric lifetimes of PNs and ONs
378 are short. Diurnal variations of ONs in summer suggest that unsaturated ONs, e.g., ONs originating
379 from BVOCs, might exist around the NOTOGRO in summer because saturated ONs have
380 reasonably long atmospheric lifetimes (1–4 d); however, further observations such as direct
381 measurements of unsaturated ONs will be required to substantiate the hypothesis. We confirmed the
382 influence of wet deposition on the concentrations of PNs and ONs is negligible, whereas T.NO₃
383 concentrations are strongly influenced by precipitation.

384

385 **Acknowledgments**

386 The authors are grateful to Dr. Daisuke Akaishi, Dr. Daisuke Utsunomiya, Ms. Mika Sawano, Ms.
387 Haruka Naya (Kanazawa University), and Dr. Yoko Iwamoto (Hiroshima University) for their
388 support with the observations at the NOTOGRO supersite. This research was supported by
389 Grant-in-Aid from the Japan Society for the Promotion of Science (Grant Nos. 23241008 and
390 23310004), Steel Foundation for Environmental Protection Technology (Grant Nos. 10, 8, 15, and 9
391 in 2014, 2015, 2016, and 2017, respectively), and Cooperative Research Program of the Institute of
392 Nature and Environmental Technology, Kanazawa University (Accept Nos. 7, 2, 4, 26, and 17007 in
393 2013, 2014, 2015, 2016, and 2017, respectively). The National Oceanic and Atmospheric
394 Administration Air Resources Laboratory is acknowledged for providing the HYSPLIT 4 model and
395 READY website (<http://www.ready.noaa.gov>). We thank James Buxton MSc from Edanz Group
396 (www.edanzediting.com/ac) for editing a draft of this manuscript.

397

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509

510 **Figure captions**

511 Fig. 1. Map of East Asia and the location of the NOTOGRO showing classification of air masses
512 based on origin: Northeast China (NEC), Middle China and Korea (MCK), Japan (JP),
513 Russia (RU), and Sea (S).

514 Fig. 2. (a) Monthly averaged concentration variations of PNs and ONs from December 2012 to
515 December 2015. (b) Monthly averaged variations of PNs and ONs fractions in NO_y from
516 December 2012 to December 2015

517 Fig. 3. Variations of concentrations of PNs and ONs associated with the five different air mass
518 origins, based on backward trajectory analyses from December 2012 to December 2015.
519 NEC, MCK, RU, JP, and S mean Northeast China, Middle China and Korea, Russia, Japan,
520 and Sea air mass origins, respectively. Open symbols indicate the data number from the air
521 mass origin was $<5\%$ of the total in the month.

522 Fig. 4. Monthly averaged diurnal variations of concentrations of PNs and ONs in (a) January
523 (winter), (b) April (spring), and (c) July (summer) 2014. Dashed and gray lines show
524 concentration of PNs and ONs, respectively.

525 Fig. 5. Hourly averaged concentrations of ONs in July 2014.

526 Fig. 6. Variation of concentration of isoprene from March 2014 to September 2015.

527 Fig. 7. Monthly averaged concentration variations of PNs, ONs, and T.NO_3 with and without
528 precipitation from December 2012 to December 2015. Dashed and gray lines show with and
529 without precipitation, respectively.

530

Figure 1

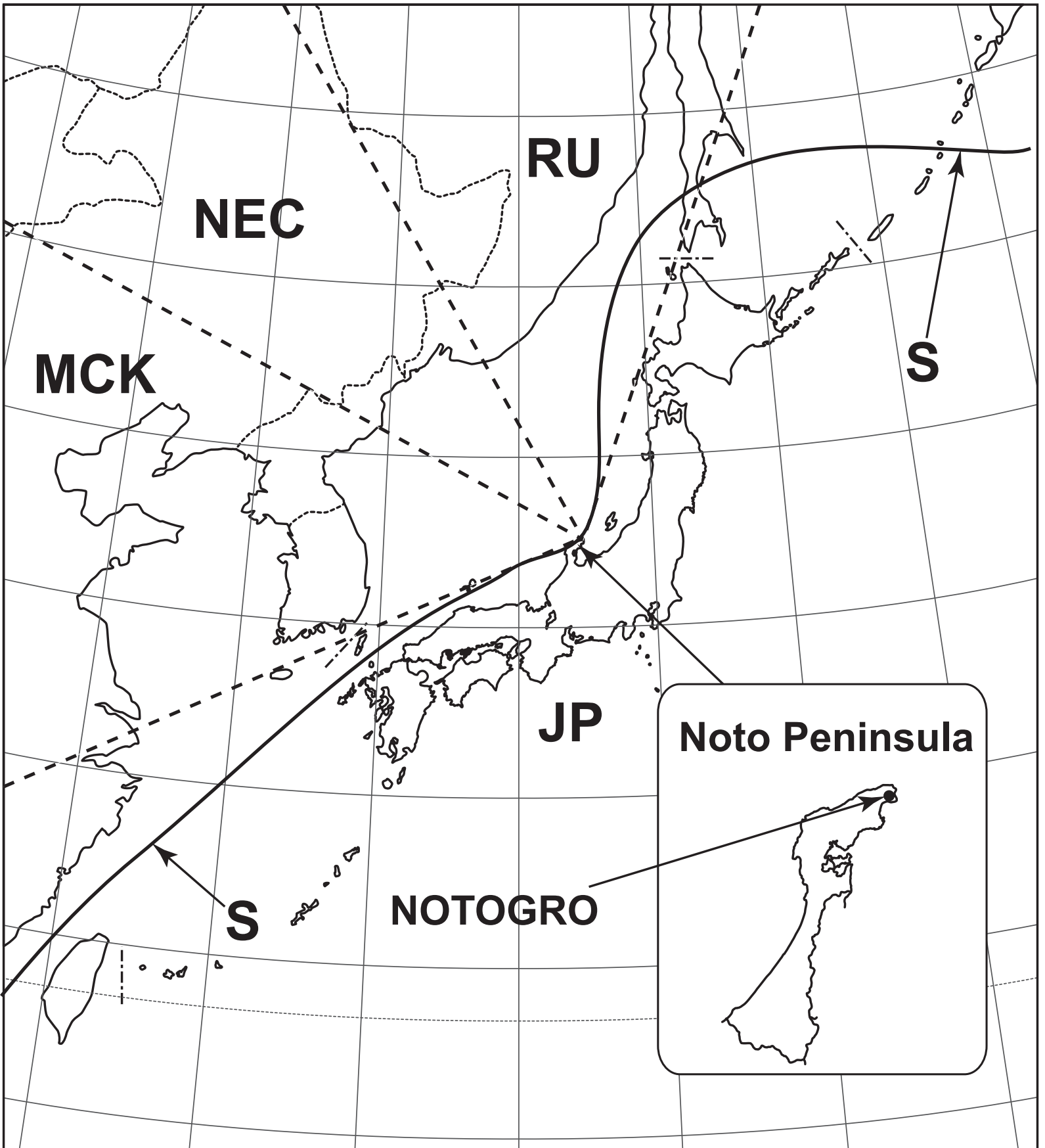


Fig. 1

Figure 2

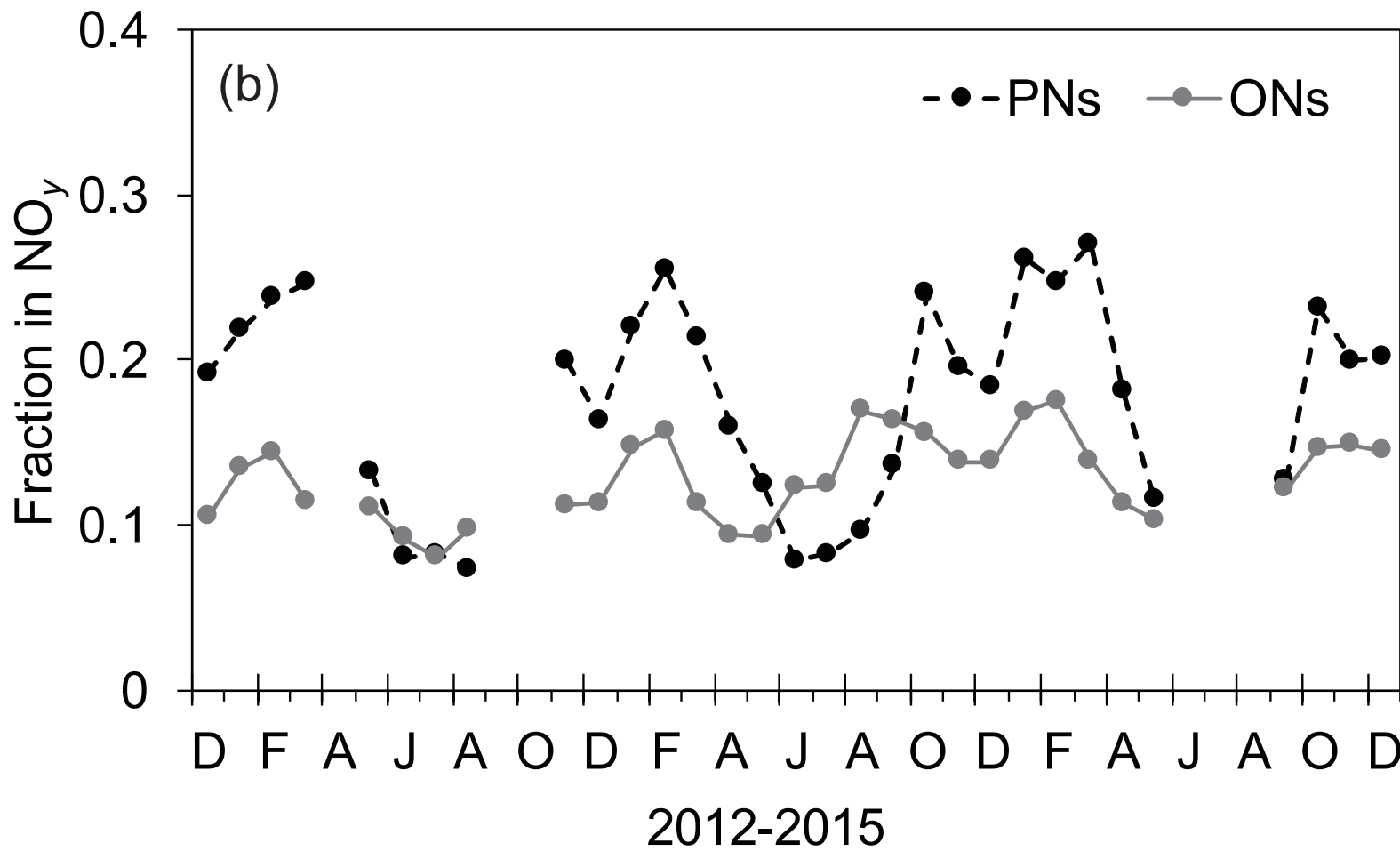
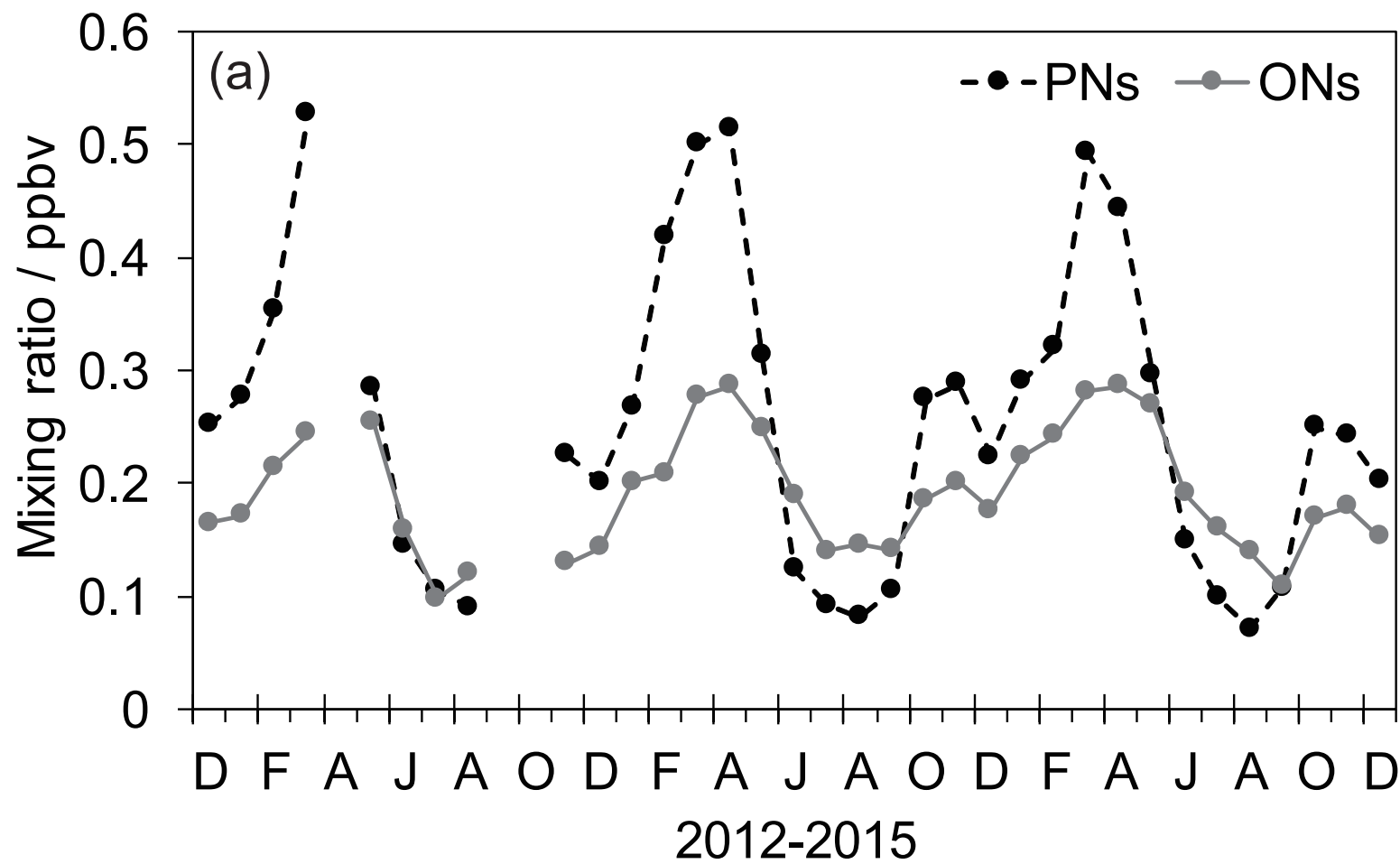


Fig. 2

Figure 3

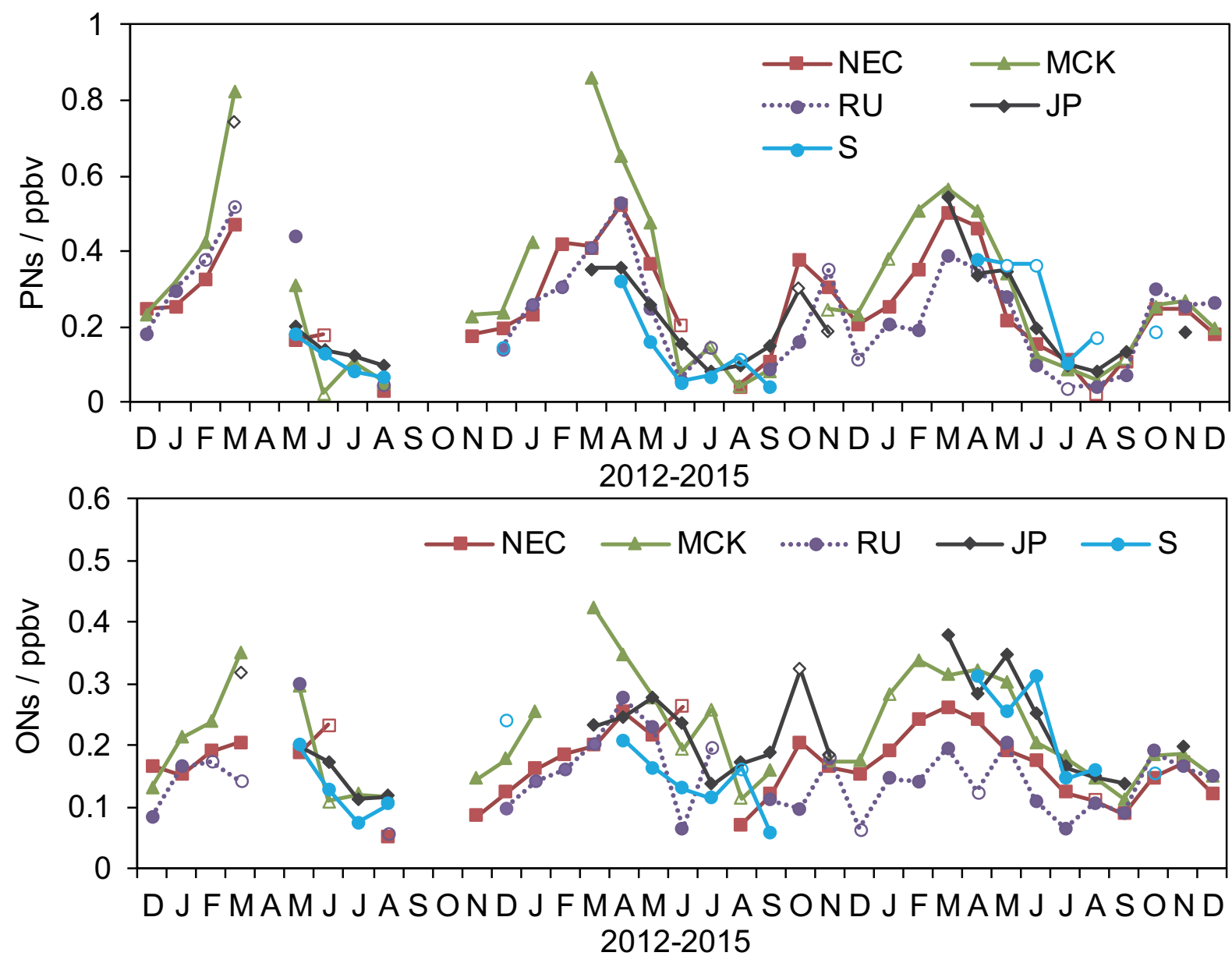


Fig. 3

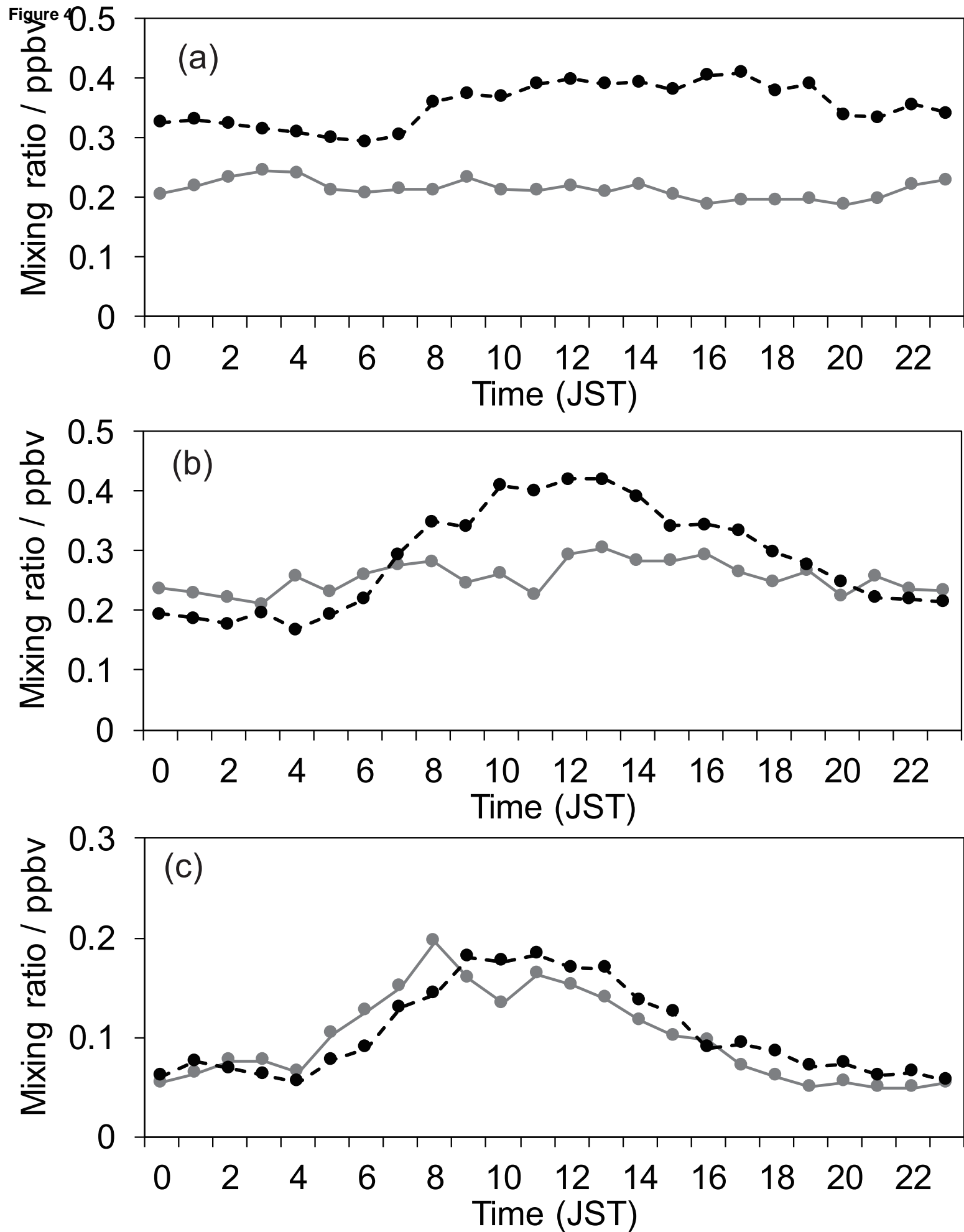


Fig. 4

Figure 5

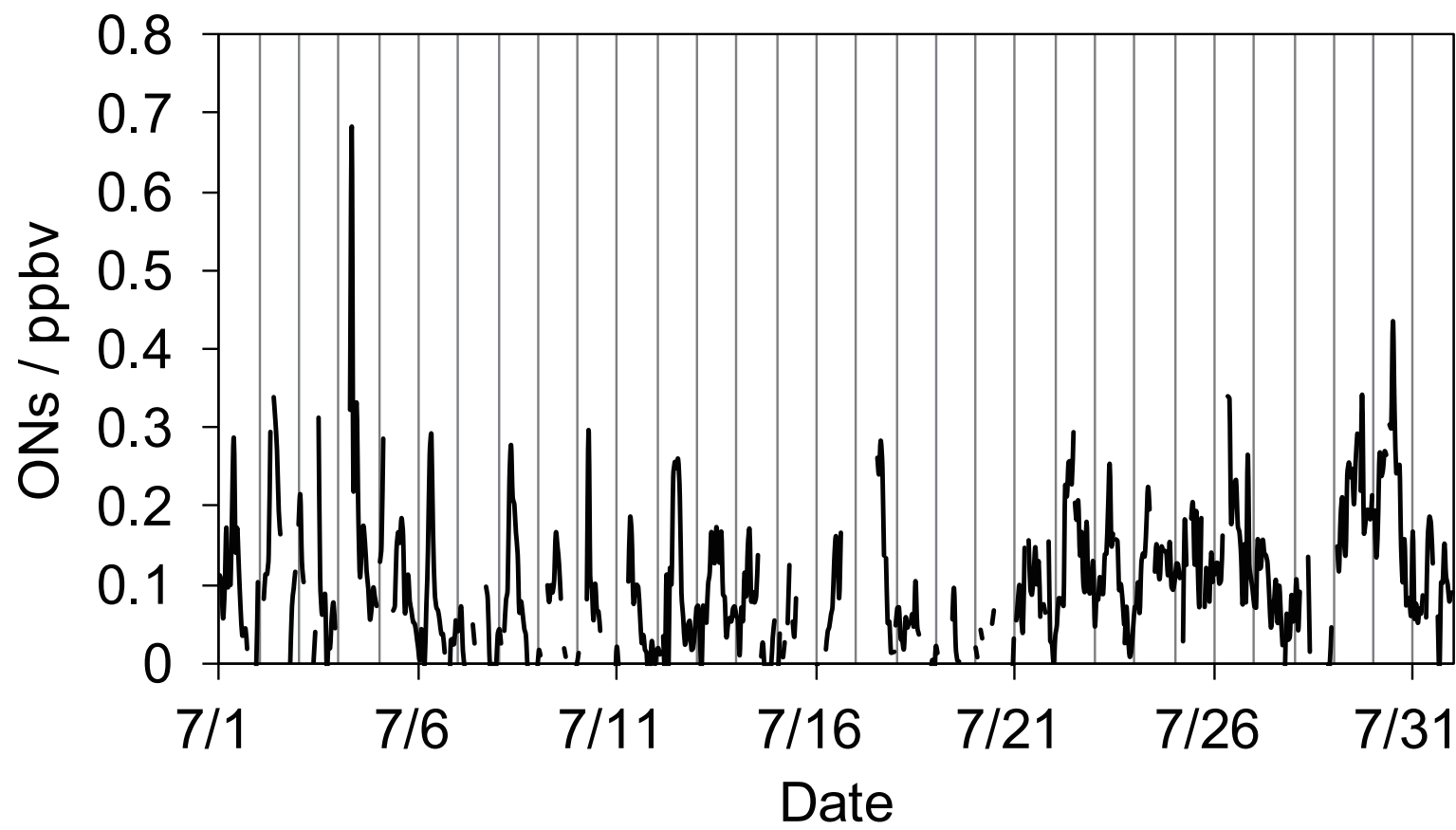


Fig. 5

Figure 7

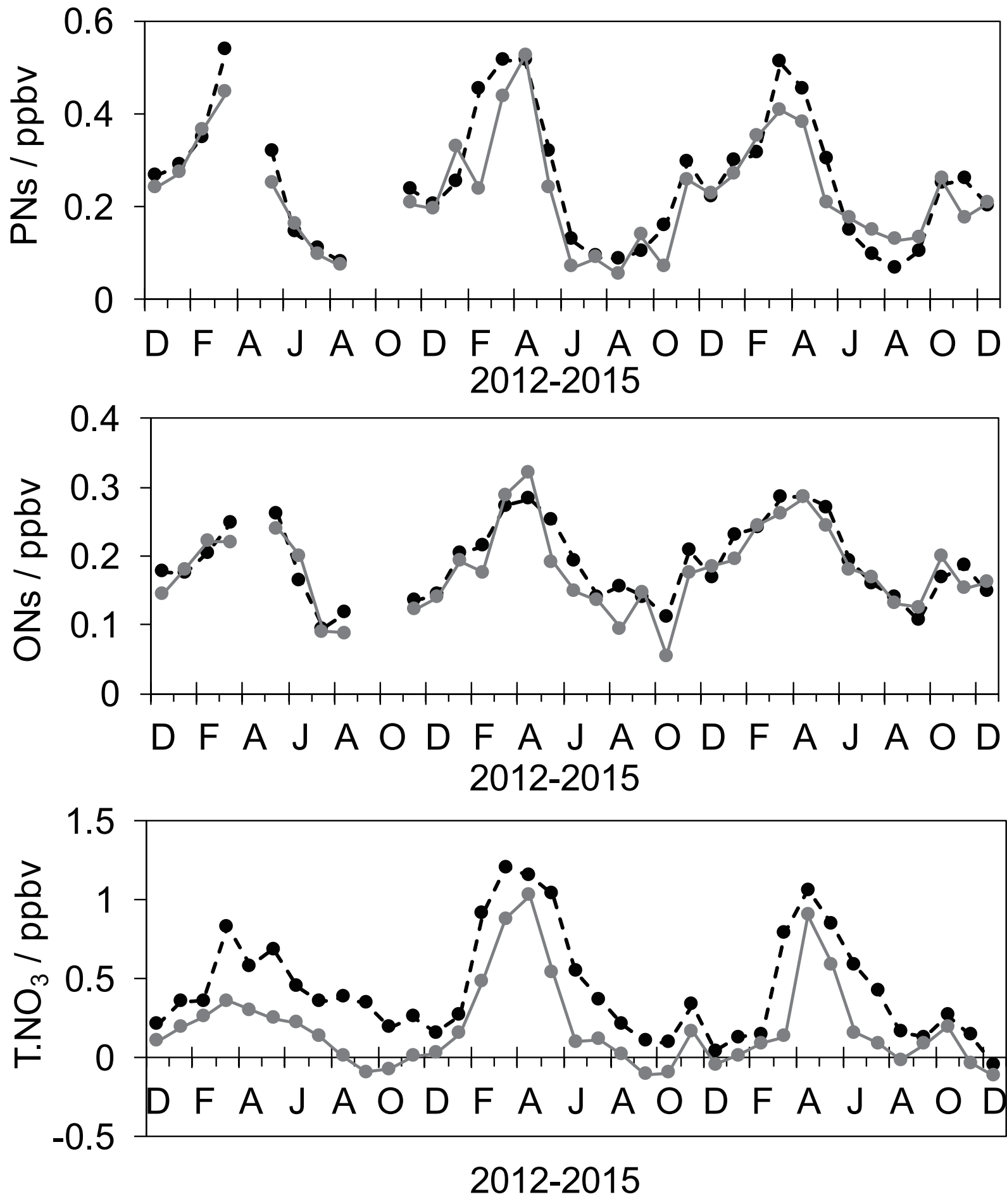


Fig. 7

Supplementary Material

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