Atmospheric chemistry of nitrogenous aerosols in northeastern Asia: biological sources and secondary formation

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Abstract. To better understand the sources of nitrogenous aerosols, particularly water-soluble organic nitrogen (WSON) and water-insoluble organic nitrogen (WION), in northeastern Asia, we measured total nitrogen (TN) and water-soluble total nitrogen (WSTN) as well as nitrogen isotope ratios (δ15N) of TN (δ15N(TN)) and WSTN (δ15N(WSTN)) in the total suspended particulate (TSP) samples collected from Sapporo, northern Japan, for a 1-year period. In general, WION was more abundant (126±117 ng m⁻³), whereas WSON was 89.7±80.6 ng m⁻³, accounting for 14±11 % and 9.2±7.3 % of TN, respectively. WSON peaked in late autumn to winter (maximum 288 ng m⁻³) and WION peaked in mid-spring to early summer (454 ng m⁻³). δ15N(TN) (21.9±4.1 ‰) and δ15N(WSTN) (25.8±8.2 ‰) showed peaks in summer with relatively high ratios in late autumn. Based on the seasonal variations in WSON and WION together with organic tracers, fossil fuel combustion and biomass burning are found to be two major sources of WSON, whereas emissions of biological particles and secondary formation by reactions of biogenic secondary organic species (carbonyls) with NH₃ are suggested as an important source of WION. The seasonality of δ15N(TN) and δ15N(WSTN) together with the comparisons to literature values, implies that chemical aging (including gas–particle partitioning) and biomass burning are the causes of the enhanced values in summer and autumn, respectively. This study demonstrates that contributions of aerosol N from fossil fuel combustion and biomass burning dominate in autumn and/or winter, whereas emission of terrestrial biological particles and secondary formation from biogenic hydrocarbons and subsequent chemical aging in the atmosphere are important in spring and/or summer in northeastern Asia.

1 Introduction

In eastern Asia, high loading of aerosol nitrogen (N) and its significant deposition onto the Earth surface are associated with the enhanced agricultural usage of nitrogenous fertilizer: 40 % of vegetation receives nitrogen deposition in excess of 1000 mg N m⁻² yr⁻¹ (threshold level), and the figure is even higher (~ 50 %) in Japan (Dentener et al., 2006; Liu et al., 2013; Morino et al., 2011). Emissions of NH₃ and NOₓ to the air have an impact on atmospheric chemistry, visibility impairment, human health and the Earth’s climate system (Rollins et al., 2012; Vitousek et al., 1997). Furthermore, N deposition over the Earth surface has a large influence on terrestrial and aquatic ecosystems via the changes in the global biogeochemical cycles (Duce et al., 2008; Galloway et al., 2004; Kim et al., 2014). Most studies of aerosol N in eastern Asia and other regions around the world have been focused on inorganic species (NO₃⁻ and NH₄⁺) (Dentener et al., 2006; Duce et al., 2008; Liu et al., 2013). Although organic nitrogen (ON) represents a significant fraction (up to 80 %) of total aerosol N and may play a critical role in biogeochemical cycles, ON has rarely been studied (Cape et al., 2011; Matsumoto et al., 2014; Zhang et al., 2008).

Aerosol ON is comprised of a wide range of nitrogenous compounds from semivolatile amines to proteins and macromolecules (Cape et al., 2011; Laskin et al., 2009; Wang et al., 2010). In addition to biomass burning, primary sources, including biological particles emitted from soil, vegetation, pollen, bacteria and the ocean surface, are important (Cape et al., 2011; Jickells et al., 2013; Miyazaki et al., 2014; Neff et al., 2002). ON can also be produced in the atmosphere via the reactions of NO₃ radical or NH₃ with biogenic and/or
anthropogenic volatile organic compounds (VOCs) followed by gas-to-particle conversion (Cornell et al., 2001; Miyazaki et al., 2014; Pratt et al., 2012). Recently, the oxidation of isoprene and monoterpene by NO$_3$ has been considered a substantial source of organic nitrates and secondary organic aerosols (SOAs) (Fry et al., 2009; Pratt et al., 2012; Rollins et al., 2009, 2012). Furthermore, chemical aging of SOA derived from both biogenic and anthropogenic precursors in the presence of NH$_3$ in the gas phase and NH$_4^+$ salts in the aqueous phase can produce light-absorbing nitrogenous compounds (defined as brown carbon) (Bones et al., 2010; Updyke et al., 2012).

However, the relative importance of anthropogenic and biogenic emissions including biomass burning is largely unknown, and the secondary formation of ON has been poorly characterized (Cape et al., 2011; Jickells et al., 2013; Kanakidou et al., 2012) and thus the land–atmosphere interactions of aerosol N are not fully understood yet because of limited measurements of aerosol ON. Previous studies of ON have focused on water-soluble ON (WSON), but very little is known about the abundances and sources of water-insoluble ON (WION) particularly in continental aerosols. Interestingly, WION is much more abundant (on average $3.4$ nmol N m$^{-3}$) than WSON (4.5 nmol N m$^{-3}$) in aerosols from Lewes, Delaware, the mid-Atlantic US coast (Russell et al., 2003) and marine aerosols (55 ± 16 % of total N) over the western North Pacific (Miyazaki et al., 2011). Hence, it is of interest to investigate the seasonal variations in WSON and WION.

Here, we present total N (TN), water-soluble TN (WSTN), WSON and WION and nitrogen isotope ratios ($\delta^{15}N$) of TN ($\delta^{15}N_{\text{TN}}$) and WSTN ($\delta^{15}N_{\text{WSTN}}$) measured in ambient aerosols (TSP) collected from Sapporo, northern Japan, over a 1-year period. The isotope studies are helpful in understanding the origins and atmospheric processing of N (Kawamura et al., 2004; Pavuluri et al., 2010). Based on WSON and WION data together with various organic tracers, $\delta^{15}N$ values and air mass trajectories as well as the comparison with previous studies, we discuss the atmospheric chemistry of nitrogenous aerosols and their possible sources, with a major focus on WSON and WION in northeastern Asia.

2 Materials and methods

2.1 Aerosol sampling

Total suspended particulate (TSP) samples were collected from Sapporo in the western part of Hokkaido Island, northern Japan (43.07°N, 141.36°E), an ideal location for collecting the air masses delivered from northeastern Asian regions: Siberia, the Russian Far East, China, and the surrounding oceans (Aggarwal and Kawamura, 2008; Yamamoto et al., 2011). The geographic details of the sampling site are described elsewhere (Pavuluri et al., 2013). TSP sampling ($n = 21$) was performed on the rooftop of the three-story building of the Institute of Low Temperature Science (ILTS), Hokkaido University, Sapporo, from 2 September 2009 to 5 October 2010 using a pre-combusted ($450°C$, 4 h) quartz fiber filter and high-volume ($∼65 m^3 h^{-1}$) air sampler. Each sample was collected for ca. 2 consecutive weeks in order to obtain sufficient amounts of carbon for radiocarbon ($^{14}C$) analyses at organic molecular levels, another objective of this research. Filter samples were placed in a pre-combusted glass jar with a Teflon-lined screw cap and stored in a dark room at $-20°C$ prior to analysis.

It should be noted that aerosol samples collected on quartz fiber filters might have positive (adsorption of gaseous HNO$_3$ and NH$_3$ and WSON) and negative (evaporation of particulate NH$_4^+$ salts such as NH$_4$NO$_3$ and WSON) sampling artifacts (Matsumoto et al., 2014; Squizzato et al., 2013). Since the sampling time is long ($∼2$ weeks) in this study, the evaporative loss from the particles should be more significant than the adsorbed gases by quartz fiber filter and thus the reported concentrations may be underestimated. However, the ambient temperatures encountered in Sapporo are rather low (range of averages of each sample period: $-3.30$ to $24.5°C$) (Pavuluri et al., 2015), and thus may not cause a significant evaporative loss of N species during the sampling period because quartz filters show a good retention for semivolatile NH$_4$NO$_3$ sampled at an air temperature up to $21°C$ and $∼30$% at an elevated air temperature of $35°C$ (Schaap et al., 2004). Therefore, we believe that our sampling technique does not have serious sampling artifacts even in summer.

2.2 Chemical analyses

2.2.1 Determination of TN and WSTN and their N isotope ratios

TN and WSTN contents and their isotope ratios ($\delta^{15}N_{\text{TN}}$ and $\delta^{15}N_{\text{WSTN}}$, respectively) in TSP samples were determined using an elemental analyzer (EA) (Carlo Erba NA 1500) and an isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus), respectively, as described elsewhere (Kawamura et al., 2004; Pavuluri et al., 2010). An aliquot of filter sample (1.8 cm in diameter disc $×3$) was extracted for WSTN with $∼15$ mL Milli Q water ($>18.3 M\Omega$) under ultrasonication for 20 min and filtrated with a syringe filter (GL Sciences Chromatodisc Type A, 0.45 μm). The extracts were adjusted to pH 8–9 with $∼0.5$ mL of 0.05 M KOH, concentrated to dryness using a rotary evaporator under vacuum and then redissolved in 200 μL Milli Q water. An aliquot of filter sample (1.0 cm diameter disc for TN and 50 μL of water extract, a subsample of the 200 μL redissolved extract, adsorbed onto $20$ mg of pre-combusted Chromosorb for WSTN) was placed in a pre-cleaned tin cup and introduced into the EA. The resulting N$_2$ gas was measured with a thermal conductivity detector in the EA and transferred to IRMS.
via an interface (ConFlo II) for $^{15}$N/$^{14}$N measurement. The blank levels in TN measurements are found to be 0.0 µg N. The analytical uncertainties (i.e., relative standard deviation) in a single set of duplicate analyses of filter samples were within 6% for TN, 3% for WSTN, 0.28% for $\delta^{15}$N$_{TN}$ and 1.34% for $\delta^{15}$N$_{WSTN}$. The detection limit of the EA determined by the sensitivity of the detector is 0.4 µg N (Neuwenhuize et al., 1994).

We also measured WSTN using a total organic carbon (TOC)/total nitrogen (TN) analyzer (Shimadzu TOC-Vcsh), as reported by Miyazaki et al. (2011). Briefly, an aliquot of filter (1.4 cm in diameter disc) was extracted with 10 mL Milli Q water under ultrasonication for 20 min. The extracts were filtered with a syringe filter (GL Sciences Chromatodisc Type A, 0.45 µm) and then injected into a TOC/TN analyzer. The analytical uncertainty in duplicate analyses of filter samples was within 5%.

Concentrations of WSTN measured by the EA are lower by 23 ± 5% than those measured by the TOC/TN analyzer. The difference was significant when the concentration of WSTN was greater than 0.5 µg m$^{-3}$. The difference may have arisen from different combustion temperatures (1400 °C for the EA vs. 680 °C for the TOC/TN analyzer) and different procedures. We consider that the WSTN measured by the EA may be underestimated due to possible evaporative loss of N species such as NH$_3$ and HNO$_3$ during the concentration step and/or the loss of N species that remain on glass walls. In fact, if the evaporative loss of N species, e.g., NH$_3$, is significant, $\delta^{15}$N of the remaining WSTN should vary significantly, proportionally to the loss of WSTN because of isotopic fractionation caused by an NH$_4^+$–NH$_3$ exchange (phase partitioning) reaction (Hoefs, 2009). Under equilibrium conditions, $\delta^{15}$N values of NH$_4^+$ become higher than those of NH$_3$, where the isotopic enrichment factor ($\varepsilon_{\text{NH}_4^+}$–NH$_3$) is estimated to be +33 ‰ (Heaton et al., 1997). However, $\delta^{15}$N$_{WSTN}$ did not show any abnormal deviation in its temporal trend, which is comparable to that of $\delta^{15}$N$_{TN}$ (see Fig. 2b), suggesting that the evaporative loss of N species and thus the impact of WSTN loss on its $\delta^{15}$N are not important. Here, we use WSTN measured by the TOC/TN analyzer to minimize the uncertainties in the estimation of WSON and WION.

### 2.2.2 Measurements of inorganic ions

Details of the measurements of inorganic ionic species such as NO$_3^-$, NH$_4^+$ and methanesulfonate (MSA$^-$, CH$_3$SO$_4^-$) are described elsewhere (Pavuluri et al., 2015). Briefly, an aliquot of filter sample was extracted with Milli Q water under ultrasonication and filtrated with a syringe filter (GL Sciences Chromatodisc Type A, 0.45 µm). The filtrates were then injected into an ion chromatograph (761 Compact IC, Metrohm). A calibration curve was prepared with a set of authentic standards to calculate the concentrations for the samples. The analytical precision was within 4%.

### 2.2.3 Estimation of WSON and WION

Amounts of inorganic N (IN), i.e., the sum of NO$_3^-$-N and NH$_4^+$-N, were calculated from the concentrations of NO$_3^-$ and NH$_4^+$ ions (Pavuluri et al., 2015). The amounts of ON, WSON and WION were estimated by the following equations (Miyazaki et al., 2011):

$$\text{ON} = \text{TN} - \text{IN}$$
$$\text{WSON} = \text{WSTN} - \text{IN}$$
$$\text{WION} = \text{TN} - \text{WSTN}.$$  

Using the propagating errors of each parameter, the precision of ON, WSON and WION was estimated to be within 8%.

### 2.2.4 Measurements of organic tracers

Organic tracers such as hopanes, isoprene- and monoterpen oxidation products were determined using a capillary gas chromatograph (Hewlett-Packard 6890) coupled to a mass spectrometer (Hewlett-Packard 5973) (GC/MS) as described elsewhere (Fu et al., 2010). Briefly, organic tracer compounds were extracted from the filter samples with dichloromethane/methanol (2:1; v/v) under ultrasonication. The hydroxyl and carboxyl functional groups were derivatized to trimethylsilyl (TMS) ethers and esters, respectively, with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10 µL of pyridine. The TMS derivatives were then measured using a GC/MS. The analytical errors in duplicate analyses were less than 10%.

All the data reported here are corrected for the field blank collected in each season.

### 3 Results and discussion

#### 3.1 Source regions of Sapporo aerosols

Ten-day backward air mass trajectories arriving in Sapporo at 500 m above the ground level (a.g.l.) were computed for every 48 h during each sample period using the HYSPLIT model (Draxler and Rolph, 2012) and are plotted in Fig. 1. The trajectories show that the air masses mostly originated from Siberia and passed over northeastern Asian regions and the Sea of Japan during autumn, winter and spring (Fig. 1). In summer, they originated from the East China Sea and/or western North Pacific passing over the coastal region and/or Honshu of Japan (Fig. 1). The air parcels mostly traveled at a height of less than 2000 m a.g.l. in all seasons, and hence there should be significant advection of these parcels from distant source regions to the receptor site.

In fact, the radiocarbon analyses showed that the percentage of modern carbon (pMC) of total carbon and watersoluble organic carbon in our aerosols started to increase...
Aerosols are consistent with those of TSP from winter to mid-variations in crustal metals, e.g., Al, Ca and Fe, in Sapporo eastern Asia (Pavuluri et al., 2013). In addition, temporal of biomass burning aerosols via long-range transport from ing winter has been mainly attributed to the contributions etation is unlikely in winter, such an increase in pMC dur-
Because the contribution of modern carbon from local veg-
summer, with a peak in early spring, indicating a signific-
ant atmospheric transport of Asian dust from arid regions in Mongolia and China (Pavuluri et al., 2015). Therefore, we consider that the Sapporo aerosols were probably mainly influenced by air masses from distant sources that were trans-
Imported a long way over northeastern Asia. However, the characteristics and seasonal variations in Sapporo aerosols could reflect the regional scenario and we do not preclude an impact from the local sources during the campaign.

3.2 Total nitrogen (TN) and water-soluble total nitrogen (WSTN)
Concentrations of TN and WSTN ranged from 348 to 1750 ng m⁻³ (average 1020 ± 466 ng m⁻³) and 293 to 1520 ng m⁻³ (893 ± 443 ng m⁻³), respectively, in Sapporo aerosols during the study period (n = 21). The mass fractions of TN in TSP ranged from 1.20 to 8.66 % (average 3.81 ± 2.28 %). As shown in Fig. 2a, although the temporal trends in TN and WSTN did follow a seasonal pattern, except for few samples, their increasing and decreasing trends are not quite distinct from season to season. However, on average, they were higher in winter, followed by spring, summer and autumn (Table 1). Similarly, TN/TSP mass ratios did not show any clear temporal trend during the study period but showed a drastic increase from mid-autumn (1.31 %) to winter (8.66 %). TN/TSP mass ratios (average 3.8 %, range 1.2–8.7 %) observed in Sapporo aerosols during the campaign are lower than those (average 5 %, range 2–15 %) reported for urban aerosols from Tokyo (Kawamura et al., 1995), where anthropogenic source contributions are expected to be the major source. However, wintertime TN/TSP mass ratios in Sapporo aerosols (≥ 7.8 %) are close to that reported from urban Tokyo, suggesting that the contributions from anthropogenic
Table 1. Seasonal and annual averages with standard deviation of the concentrations of nitrogenous components and $^{15}$N isotope ratios of TN and WSTN in atmospheric aerosol (TSP) samples collected from 2 September 2009 to 5 October 2010 in Sapporo, northern Japan.

<table>
<thead>
<tr>
<th>Component</th>
<th>Autumn ($n=8$)</th>
<th>Winter ($n=3$)</th>
<th>Spring ($n=5$)</th>
<th>Summer ($n=5$)</th>
<th>Annual ($n=19$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentrations (ng m$^{-3}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>$790 \pm 480$</td>
<td>$1456 \pm 298$</td>
<td>$1116 \pm 434$</td>
<td>$1023 \pm 433$</td>
<td>$1074 \pm 454$</td>
</tr>
<tr>
<td>WSTN</td>
<td>$714 \pm 496$</td>
<td>$1388 \pm 247$</td>
<td>$986 \pm 356$</td>
<td>$789 \pm 351$</td>
<td>$950 \pm 427$</td>
</tr>
<tr>
<td>NO$_3^-$-N</td>
<td>$284 \pm 120$</td>
<td>$362 \pm 55.2$</td>
<td>$395 \pm 182$</td>
<td>$73.8 \pm 24.1$</td>
<td>$279 \pm 172$</td>
</tr>
<tr>
<td>NH$_4^+$-N</td>
<td>$338 \pm 347$</td>
<td>$896 \pm 97.2$</td>
<td>$511 \pm 191$</td>
<td>$647 \pm 310$</td>
<td>$576 \pm 314$</td>
</tr>
<tr>
<td>ON</td>
<td>$168 \pm 77.1$</td>
<td>$198 \pm 186$</td>
<td>$212 \pm 221$</td>
<td>$302 \pm 149$</td>
<td>$220 \pm 157$</td>
</tr>
<tr>
<td>WSON</td>
<td>$91.6 \pm 73.6$</td>
<td>$130 \pm 139$</td>
<td>$84.7 \pm 99.5$</td>
<td>$67.8 \pm 39.8$</td>
<td>$96.0 \pm 81.9$</td>
</tr>
<tr>
<td>WION</td>
<td>$77.5 \pm 50.9$</td>
<td>$68.4 \pm 51.3$</td>
<td>$130 \pm 141$</td>
<td>$234 \pm 144$</td>
<td>$125 \pm 123$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope ratios ($%$)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{15}$N$_{TN}$</td>
<td>$18.91 \pm 3.17$</td>
<td>$19.72 \pm 3.56$</td>
<td>$23.42 \pm 1.63$</td>
<td>$26.82 \pm 1.95$</td>
<td>$22.47 \pm 3.98$</td>
</tr>
<tr>
<td>$\delta^{15}$N$_{WSTN}$</td>
<td>$19.17 \pm 6.45$</td>
<td>$23.84 \pm 4.13$</td>
<td>$26.82 \pm 2.46$</td>
<td>$36.88 \pm 2.46$</td>
<td>$26.71 \pm 8.16$</td>
</tr>
</tbody>
</table>

3.3 Water-soluble organic nitrogen (WSON) and water-insoluble organic nitrogen (WION)

3.3.1 Concentrations and mass fractions in TN

Concentrations of WSON and WION in Sapporo aerosols ranged from below the detection limit (BDL) to 569 ng m$^{-3}$ (215 ± 150 ng m$^{-3}$) during the study period. High abundances of ON in TN rather than WSTN indicate that WION is significant in Sapporo aerosols. Furthermore, WSTN showed a stronger linear relation with IN ($r^2 = 0.97$) than that ($r^2 = 0.90$) between TN and IN in Sapporo aerosols (Fig. 3). Such deviation in the linearity suggests that the origins and/or secondary formation processes of WION (i.e., TN − WSTN) may be different from that of WSTN (including WSON). Therefore, it is apparent that the atmospheric loading and impacts of aerosol N in northeastern Asia is significantly influenced by the sources and seasonality of ON.
Table 2: Concentrations of water-soluble organic nitrogen (WSON) and the mass fractions of WSON in water-soluble total nitrogen (WSTN) in Sapporo aerosols together with those in atmospheric aerosols from different sites around the world.

<table>
<thead>
<tr>
<th>Location</th>
<th>Study period</th>
<th>Aerosol size</th>
<th>WSON (ng m(^{-3}))</th>
<th>WSON/WSTN (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapporo, Japan</td>
<td>September 2009 to October 2010</td>
<td>TSP</td>
<td>89.7 ± 80.6</td>
<td>10.5 ± 7.5</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>August 1997 to July 1998</td>
<td>PM(_{2.5})</td>
<td>265 ± 190</td>
<td>23</td>
<td>Zhang et al. (2002)</td>
</tr>
<tr>
<td>Kofu, Japan</td>
<td>August 2009 to January 2013</td>
<td>PM(_{10})</td>
<td>221</td>
<td>14</td>
<td>Matsumoto et al. (2014)</td>
</tr>
<tr>
<td>Rondônia, Brazil</td>
<td>March–May 1999</td>
<td>PM(_{10})</td>
<td>49 ± 64.4</td>
<td>45 ± 35</td>
<td>Mace et al. (2003a)</td>
</tr>
<tr>
<td></td>
<td>September–October 1999(^b)</td>
<td>PM(_{10})</td>
<td>854 ± 938</td>
<td>43 ± 31</td>
<td>Mace et al. (2003a)</td>
</tr>
<tr>
<td>Sapporo, Japan</td>
<td>June 2009 to December 2011</td>
<td>TSP</td>
<td>157 ± 127</td>
<td>20 ± 11</td>
<td>Miyazaki et al. (2014)</td>
</tr>
<tr>
<td>Fujiyoshida, Japan</td>
<td>August 2009 to January 2013</td>
<td>PM(_{10})</td>
<td>101</td>
<td>11</td>
<td>Matsumoto et al. (2014)</td>
</tr>
<tr>
<td>Erdemli, Turkey</td>
<td>March–May 2000</td>
<td>TSP</td>
<td>406 ± 588</td>
<td>~ 26 ± 28</td>
<td>Mace et al. (2003c)</td>
</tr>
<tr>
<td>Qingdao, China</td>
<td>March–April 2006</td>
<td>TSP</td>
<td>2520 ± 1760</td>
<td>~ 20</td>
<td>Shi et al. (2010)</td>
</tr>
<tr>
<td>Yellow Sea(^c)</td>
<td>March 2005</td>
<td>TSP</td>
<td>2860 ± 1780</td>
<td>~ 17</td>
<td>Shi et al. (2010)</td>
</tr>
<tr>
<td>Yellow Sea(^c)</td>
<td>April 2006</td>
<td>TSP</td>
<td>1220 ± 812</td>
<td>~ 17</td>
<td>Shi et al. (2010)</td>
</tr>
<tr>
<td>South China Sea(^c)</td>
<td>April 2005</td>
<td>TSP</td>
<td>910 ± 280</td>
<td>~ 34</td>
<td>Shi et al. (2010)</td>
</tr>
<tr>
<td>East China Sea(^c)</td>
<td>September–October 2002</td>
<td>TSP(^a)</td>
<td>756 ± 504</td>
<td>~ 24</td>
<td>Nakamura et al. (2006)</td>
</tr>
<tr>
<td>East China Sea and western North Pacific(^c)</td>
<td>March 2004</td>
<td>TSP(^a)</td>
<td>224 ± 266</td>
<td>~ 10</td>
<td>Nakamura et al. (2006)</td>
</tr>
<tr>
<td>Cape Grim, Australia</td>
<td>November–December 2000</td>
<td>TSP</td>
<td>50.4 ± 79.8</td>
<td>~ 21</td>
<td>Mace et al. (2003b)</td>
</tr>
<tr>
<td>Cape Grim, Australia</td>
<td>November–December 2000</td>
<td>TSP</td>
<td>13.0 ± 13.3</td>
<td>~ 25</td>
<td>Mace et al. (2003b)</td>
</tr>
<tr>
<td>Oahu, Hawaii</td>
<td>July–August 1998</td>
<td>PM(_{10})</td>
<td>46.2 ± 28</td>
<td>~ 33</td>
<td>Cornell et al. (2001)</td>
</tr>
<tr>
<td>Western North Pacific</td>
<td>August–September 2008</td>
<td>TSP</td>
<td>~ 17.5</td>
<td></td>
<td>Miyazaki et al. (2011)</td>
</tr>
</tbody>
</table>

\(^a\) Total of fine- and coarse-mode particles. \(^b\) Dry (biomass burning) season. \(^c\) Asian outflow region.

3.3.2 Comparisons with previous studies from different locations

As seen from Table 2, the average concentration of WSON in Sapporo aerosols is lower than that reported in urban aerosols from Davis, California, and Kofu, Japan, as well as from coastal sites: Erdemli in Turkey, Crete in Greece, and Qingdao in China. It is also lower than that reported in the forest aerosols collected from Rondônia, Brazil during an intensive biomass burning period (dry season) (Mace et al., 2003a) and from Sapporo, Japan, and lower than in the marine aerosols over the Asian outflow regions: the Yellow Sea, South China Sea and the western North Pacific (Table 2). In contrast, the average concentration of WSON in Sapporo aerosols is comparable to that of forest aerosols from Fujiyoshida, Japan, but higher than that from Rondônia, Brazil, during the wet season. It is also higher than that of the marine aerosols from pristine oceanic regions: Cape Grim, Australia (Mace et al., 2003b), and Oahu, Hawaii (Cornell et al., 2001), and over the western North Pacific (Miyazaki et al., 2011) (Table 2). In addition, the higher end (maximum 288 ng m\(^{-3}\)) of WSON is comparable to average WSON concentration reported in
and 2-methylerythritol, whereas concentrations of butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol drocarbons. Concentrations of isoprene-SOA tracers are the data of organic molecular tracers are from Pavuluri et al. (2013)

Seasonal variations in Figure 4.

Therefore, we consider that WSON in Sapporo aerosols may be mainly derived from anthropogenic emissions including biomass burning, although emissions from biological sources and secondary formation from gaseous hydrocarbon precursors cannot be excluded. Meanwhile, WION may originate from emissions of biological particles and secondary formation from biogenic hydrocarbons. We further examine the possible contributions from such sources in the following section based on comparisons between them and the source tracers.
3.4 Comparisons of WSON and WION with organic tracers

3.4.1 Possible sources of WSON

The temporal trend in WSON is found to be somewhat similar to that of hopanes (C_{27}-C_{32} hopanoid hydrocarbons), specific biomarkers of petroleum and coal (Schauer et al., 2002), particularly in autumn and wintertime Sapporo aerosols (Fig. 4c). Furthermore, WSON showed a linear relationship with hopanes with moderate but significant correlation during the campaign (Fig. 5a). On the other hand, the temporal variation in WSON from mid-autumn to mid-winter is somewhat similar to that of levoglucosan (Fig. 4d), a tracer for biomass burning (Simoneit, 2002), and showed a weak linear relation throughout the campaign (Fig. 5b). Contributions of WSON to TN are higher in the above seasons (Fig. 4a). In contrast, WSON was abundant in few spring (from mid-April to mid-May) and summer (late June and late July) samples (Fig. 4a), despite the lower levels of both hopanes and levoglucosan throughout the spring and summer (Fig. 4c, d). The lower levels of levoglucosan in spring and summer, and thus a weak correlation of WSON with levoglucosan during the campaign, was probably caused, in part, by the decomposition of levoglucosan (Hoffmann et al., 2010) because contributions of biomass burning emissions to Sapporo aerosols were considered to be significant during these periods (Pavuluri et al., 2015).

The temporal trend in WSON from late spring to early summer (Fig. 4a) is similar to that of sucrose (Fig. 4e), which is a tracer of pollens emitted from terrestrial higher plants (Fu et al., 2012). The seasonal trend in WSON (Fig. 4a) is also similar to those of biogenic secondary organic aerosols (SOA), i.e., α-pinene-SOA tracers (Kleindienst et al., 2007), and MSA− in late spring to early autumn (Fig. 4f, g). MSA− is produced in the atmosphere by photochemical oxidation of dimethyl sulfide (DMS) (Bates et al., 1992), which is emitted from terrestrial higher plants (Geng and Mu, 2006), soil in forests (Yi et al., 2010) and phytoplankton bloom in oceans (Bates et al., 1992). Therefore, MSA− can be considered a tracer to understand the importance of secondary production of WSON (and WION) from biogenic organics, although neither DMS nor MSA− contain nitrogen. Interestingly, WSON showed a linear relation with sucrose (r = 0.71, p ≤ 0.05), α-pinene SOA tracers and MSA− during spring and summer (Fig. 5c–e). In fact, the Spearman’s rank correlations of WSON with α-pinene SOA tracers (r = 0.71) and MSA− (r = 0.62) in spring and summer (n = 10) are statistically significant (p ≤ 0.05). Furthermore, it showed a positive Spearman’s rank correlation with isoprene SOA tracers (r = 0.33) and β-caryophyllenic acid (r = 0.37). However, WSON shows no relation with sucrose, isoprene- and α-pinene-SOA tracers, β-caryophyllenic acid and MSA−...
Table 3. Spearman’s rank correlation of WSON and WION with source tracers in Sapporo aerosols during the study period \((n = 21)\). Significant correlation coefficients at 0.05 level are shown in bold.

<table>
<thead>
<tr>
<th>Source tracer</th>
<th>Correlation coefficient ((r))</th>
<th>WSON</th>
<th>WION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hopanes</td>
<td>0.48</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>0.18</td>
<td>-0.57</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>-0.02</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>Isoprene-SOA tracers</td>
<td>-0.12</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>(\alpha)-pinene-SOA tracers</td>
<td>0.21</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>(\beta)-caryophyllinic acid</td>
<td>0.06</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>MSA(^{-})</td>
<td>0.09</td>
<td>0.59</td>
<td></td>
</tr>
</tbody>
</table>

when we consider the total data set \((n = 21)\), which includes all seasons during the campaign (Table 3).

The above comparisons of WSON with source tracers imply that anthropogenic emissions including biomass burning are major sources of WSON in Sapporo aerosols. Their contributions to Sapporo aerosols may have been enhanced in autumn and winter when the air masses enriched with forest fire and fossil fuel combustion products are often delivered from Siberia, passing over northeastern China (Fig. 1a, b). In fact, fossil fuel consumption is significantly higher in winter than in any other season in eastern Asia (Zhang et al., 2009). Furthermore, emissions of biological particles and secondary production by the reaction of biogenic hydrocarbons with NO\(_3^-\) radicals (Fry et al., 2009; Pratt et al., 2012) could contribute to WSON in late spring and late spring or early autumn, respectively, although we do not preclude a minor contribution from biomass burning emissions. In fact, levels of NO\(_2^-\) in Sapporo aerosols declined in late spring to summer followed by a gradual increase toward early autumn (Pavuluri et al., 2015). The lower levels of NO\(_2^-\) in summer may be in part caused by NO\(_2^-\) active involvement in the reactions with hydrocarbons (Fry et al., 2009; Pratt et al., 2012; Rollins et al., 2009) to result in secondary WSON, although clean air masses from oceanic regions often arrive in Sapporo during summer (Fig. 1d).

3.4.2 Possible source and formation processes of WION

The results of Spearman’s rank correlation analysis between WION and source tracers are presented in Table 3. WION shows a significant inverse correlation with hopanes and levoglucosan during the campaign (Table 3). By contrast, the temporal trend in WION is similar to those of sucrose (Fig. 4e) during late spring to early summer and of biogenic SOA tracers (isoprene- and \(\alpha\)-pinene-SOA tracers and \(\beta\)-caryophyllinic acid, Fig. 4f) and MSA\(^{-}\); Fig. 4g) throughout the year. Furthermore, WION showed a moderately significant positive Spearman’s correlation with sucrose, isoprene SOA and MSA\(^{-}\) during the study period \((n = 21)\) (Table 3) and also with \(\beta\)-caryophyllinic acid in spring and summer \((r = 0.62, p \leq 0.05; n = 10)\).

Based on the above comparisons of WION with source tracers, we suggest that the WION in Sapporo aerosols is mainly derived from emissions of biological particles such as pollens and from secondary production by the reactions of biogenic hydrocarbons (containing carbonyls) with NH\(_3\) in the atmosphere (Bones et al., 2010; Updyke et al., 2012). WSON could be abundantly produced if the oxidation of biogenic hydrocarbons by NO\(_3^-\) radicals were prominent. However, the SOA preferably produced by O\(_3^-\)-initiated oxidation of biogenic hydrocarbons (e.g., isoprene and monoterpenes) contains carbonyl groups that can react with reduced nitrogen species such as NH\(_3\) (g), NH\(_4^+\) and amino acids and produce high-molecular-weight N-containing organics (Bones et al., 2010; Updyke et al., 2012), which may not be fully water-soluble. For example, glyoxal has been reported to form an imidazole (Galloway et al., 2009) and also undergo oligomerization reactions (Noziere et al., 2009) to form high-molecular-weight N-containing organics in the presence of NH\(_3\). In fact, Wang et al. (2010) observed high-molecular-weight N-containing organic salts (\(m/z\) range of 250–500) at substantial intensities in the positive-ion mass spectra in urban aerosols from Shanghai, China. They interpreted such high-molecular-weight organic salts formation by Mannich reaction rather than the oligomerization of imidazole alone.

Based on observations under controlled environmental conditions, Husted and Schjoerring (1996) reported that NH\(_3\) emission from plants is enhanced with increasing leaf temperature and light intensity, which is similar to the emission of organic compounds from higher plants (Guenther, 1997). On the other hand, the net emission of NH\(_3\) from soil is enhanced in summer due to increasing soil temperatures (Wentworth et al., 2014). Therefore, enhanced emissions of biogenic hydrocarbons and NH\(_3\) during the growing season (mid-spring to midsummer) are very likely in spring and summer followed by the subsequent reactions and production of WION in the atmosphere. In fact, the air masses arriving in Sapporo originate from Siberia in spring from oceanic regions and pass over the Japanese Honshu in summer (Fig. 1c, d). They should be enriched with the components derived from terrestrial and/or oceanic emissions. In addition to biogenic SOA and MSA\(^{-}\) (Fig. 4f, g), abundances of NH\(_4^+\) are relatively high in spring and summer (Pavuluri et al., 2015). Hence, secondary production of WION by the reactions of SOA (carbonyls) with NH\(_3\) (NH\(_3\) ↔ NH\(_2\)) (Noziere et al., 2009) should be accelerated during the warmer seasons in northeastern Asia. However, there is a need to conduct measurements of WION and source tracers at different locations in order to fully understand the main source(s) of WION in atmospheric aerosols, which is a subject of future research.
3.5 Nitrogen isotope ratios of TN and WSTN: implications for source and chemical aging

3.5.1 Seasonal variations

δ¹⁵N⁰⁰ was from 15.5 to 29.4 %e (average 21.9 ± 4.1 %e), whereas δ¹⁵NWSTN was from 12.2 to 39.1 %e (25.8 ± 8.2 %e) in Sapporo aerosols during the campaign period (n = 21). As shown in Fig. 2b, temporal trends in δ¹⁵N⁰⁰ and δ¹⁵NWSTN were highly comparable. They both show peaks in summer with relatively high values in late autumn (Fig. 2b). Their averages, except for δ¹⁵N⁰⁰ in autumn and winter, varied significantly from season to season with higher δ¹⁵N in summer, followed by spring, winter and autumn (Table 1). The seasonal trends in δ¹⁵N⁰⁰ and δ¹⁵NWSTN suggest that aerosol N is significantly influenced by season-specific source(s) and/or the chemical aging of N species.

We also found that δ¹⁵NWSTN is higher than δ¹⁵N⁰⁰ throughout the campaign, except for few samples in autumn (Fig. 2b). An enrichment of ¹⁵N in WSTN over TN is more significant in summer than in other seasons (Table 1). It has been reported that the aerosol particles collected over controlled laboratory burns of the vegetation, which significantly contribute to WSTN, are enriched with ¹⁵N ranging from −1.3 to 13.1 %e (average 6.6 %e) compared to the source vegetation (Turekian et al., 1998). Furthermore, chemical aging of N species, including gas-to-particle exchange (e.g., NH₄⁺ ↔ NH₃) reactions during long-range transport causes the enrichment of ¹⁵N in aerosol N (Pavuluri et al., 2010). In addition, δ¹⁵N of terrestrial plants, which significantly contributes to WION, is relatively low (e.g., −3.4 to 12.2 %e in plants from the San Francisco Bay area) (Cloern et al., 2002). Therefore, higher δ¹⁵NWSTN values than δ¹⁵N⁰⁰ in Sapporo aerosols suggest that contributions of biomass burning to WSTN and biological sources to WION (i.e., TN-WSTN) may be significant and aerosol N has been subjected to significant chemical aging during long-range transport. The enhanced aging (particularly NH₄⁺ ↔ NH₃) of nitrogenous aerosols under higher ambient temperature in summer may have caused further enrichment of ¹⁵N in WSTN (Pavuluri et al., 2010).

As seen from Fig. 6, δ¹⁵N⁰⁰ (and δ¹⁵NWSTN) showed an inverse relation with the mass fractions of NO₃⁻-N and WSON in TN but showed a linear relation with NH₄⁺-N/TN and WION during the study period. Their relations with NO₃⁻-N/TN and NH₄⁺-N/TN are statistically significant at

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Scatterplots between δ¹⁵N⁰⁰ (and δ¹⁵NWSTN) and mass fractions of nitrogenous components (NO₃⁻-N, NH₄⁺-N; WSON and WION) in TN in Sapporo aerosols.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Range or mean N isotope ratios in the particles emitted from point sources, source substance, and atmospheric aerosols from different sites around the world. One, two and three asterisks show gaseous NH₃, particulate NH₄⁺ and WSTN, respectively.
the 99% (p ≤ 0.01) level but not in the other two cases (Fig. 6). Such relations imply that δ15N_{TN} and δ15N_{WSTN} are mainly controlled by their sources, chemical aging of nitrogenous species and abundances of NO3−-N and NH4+.-N. It is well recognized that NO3− originates mainly from fossil fuel combustion and biomass burning, whereas NH4+ originates from biomass burning, agricultural activities and biological emissions (Delon et al., 2012; Hertel et al., 2012). In fact, NO3− is more abundant in mid-autumn to early spring, whereas NH4+ maximizes in mid-spring to summer (Pavuluri et al., 2015). These results are consistent with those of source tracers (Fig. 4), again suggesting that the contributions from biomass burning and fossil fuel combustion are important in autumn and winter, whereas the biological particles are important in spring and biogenic emissions of gaseous species (hydrocarbons and NH3) and subsequent secondary production are important in spring/summer.

3.5.2 Comparison with literature values

Figure 7 compares the range (or mean) of δ15N values reported for the particles emitted from point sources in mid-latitudes as well as those observed in atmospheric aerosols from different locations around the world, including Sapporo aerosols. δ15N_{TN} values observed in Sapporo aerosols are significantly higher than those (−19.4 to 15.4 ‰) reported for the particles emitted from point sources of fossil fuel combustion and waste incineration burning (Fig. 7). They are also higher than those reported in urban aerosols from Paris, France, where fossil fuel combustion was expected as a major source (Widory, 2007), and the marine aerosols over the western North Pacific, which are considered to be mainly derived from sea-to-air emissions (Miyazaki et al., 2011) (Fig. 7).

However, δ15N_{TN} in Sapporo aerosols are comparable to the higher ends of the δ15N_{TN} reported in atmospheric aerosols from Jeju Island, Korea (Fig. 7), which were attributed to the significant atmospheric processing of N species, emitted mainly from China, during long-range transport (Kundu et al., 2010b). Furthermore, the lower ends of δ15N_{TN} in Sapporo aerosols are comparable to the higher ends of δ15N_{TN} reported for the particles emitted from the controlled burning of C3 (range, 2.0 to 19.5 ‰) and C4 (9.8 to 22.7 ‰) plant species in a laboratory study and to those of atmospheric aerosols from Piracicaba and the Amazon basin, Brazil, where biomass burning is a dominant source (Martinelli et al., 2002) (Fig. 7). In addition, they compare well to δ15N_{TN} reported in the forest aerosols from Rondônia, Brazil, where biomass burning was expected as a dominant source (Kundu et al., 2010a), and urban aerosols from Chennai and Mumbai, India, which were considered to mainly originate from biomass burning and to have been subjected to aging (Aggarwal et al., 2013; Pavuluri et al., 2010) (Fig. 7).

On the other hand, lower values of δ15N_{WSTN} observed in Sapporo aerosols are comparable to those reported in the forest aerosols from Sapporo experimental forest, Japan (Fig. 7). Although their seasonal patterns (winter minimum and summer maximum) are similar, the enrichment of 15N in Sapporo aerosols (Fig. 2b) is significantly higher than that (range of monthly averages: 9.0 to 26.0 ‰) reported for the Sapporo forest aerosols (Miyazaki et al., 2014). Furthermore, the range of δ15N_{WSTN} values observed in Sapporo aerosols is highly comparable to δ15N of aerosol NH4+, which is much higher than that of gaseous NH3, in the atmosphere measured at the Maki monitoring station, Niigata, Japan (Fig. 7). The large difference in δ15N between NH3 and NH4+ has been attributed to gas-to-particle (equilibrium) exchange reactions in the atmosphere (Hayasaka et al., 2004) because under equilibrium conditions, particulate NH4+ is more enriched with 15N than gaseous NH3, where the isotopic enrichment factor (ε_{NH4+}-NH3) was estimated to be +33 ‰ (Heaton et al., 1997). Such comparisons suggest that aerosol N in Sapporo aerosols might have originated to a significant extent from biogenic sources, including biomass burning, and subjected to chemical aging during long-range transport, although we do not preclude a contribution from fossil fuel combustion.

4 Summary and conclusions

Water-soluble organic nitrogen (WSON) and water-insoluble organic nitrogen (WION) and N isotope ratios of total nitrogen (δ15N_{TN}) and water-soluble TN (δ15N_{WSTN}) were obtained for TSP aerosol samples collected from Sapporo, northern Japan, from September 2009 to October 2010. WSON and WION ranged from BDL to 288 ng m−3 (average 89.7 ± 80.6 ng m−3) and from BDL to 454 ng m−3 (126 ± 117 ng m−3). Although their temporal variations did not show clear seasonal trends, average WSON was found to be higher in winter, followed by autumn, spring and summer, whereas WION maximized in summer followed by spring, with much lower concentration in autumn and winter. δ15N_{TN} ranged from 15.5 to 29.4 ‰ (average 21.9 ± 4.1 ‰), whereas δ15N_{WSTN} ranged from 12.2 to 39.1 ‰ (25.8 ± 8.2 ‰). Their seasonal variations showed high ratios in summer and late autumn. Comparisons of seasonal variations in WSON and WION with anthropogenic and biological source tracers together with air mass trajectories suggest that fossil fuel combustion and biomass burning are major sources of WSON, whereas emissions of biological particles and secondary reactions of biogenic hydrocarbons (carbonyls) with NH3 significantly contribute to WION in northeastern Asia. Seasonal variations in δ15N_{TN} and δ15N_{WSTN} and their relations to mass fractions of nitrogenous components in TN suggest that aerosol N in Sapporo aerosols mainly originated from biogenic sources, including biomass burning, and was subjected to chemical aging during long-range transport, although a contribution from fossil fuel combustion is important particularly in winter.
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