Atmospheric chemistry of nitrogenous aerosols in Northeast 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 Northeast Asia, we measured total nitrogen (TN) and water-soluble total nitrogen (WSTN) as well as nitrogen isotope ratios ($\delta^{15}N$) of TN ($\delta^{15}N_{TN}$) and WSTN ($\delta^{15}N_{WSTN}$) in the total suspended particles (TSP) collected from Sapporo, northern Japan for one-year period. In general, WION was more abundant (126 ± 117 ng m^{-3}) whereas WSON (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}). $\delta^{15}N_{TN}$ (21.9 ± 4.1‰) and $\delta^{15}N_{WSTN}$ (25.8 ± 8.2‰) showed peaks in summer with relatively high ratios in late autumn. Based on the seasonal variations of 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 NH_3 are suggested as important source of WION. The seasonality of $\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$, 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/winter whereas emission of terrestrial biological particles and secondary formation from biogenic hydrocarbons and subsequent chemical aging in the atmosphere are important in spring/summer in Northeast Asia.

1 Introduction

In East Asia, high loading of aerosol nitrogen (N) and its significant deposition onto the Earth surface are associated with 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 even more (~50%) in Japan (Dentener et al., 2006; Liu et al., 2013; Morino et al., 2011). Emissions of NH_3 and NO_x 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). Further, N deposition over the Earth surface has 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 East Asia and other regions in the world have been focused on inorganic species (NO_3^- and NH_4^+) (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 semi-volatile amines to proteins and macromolecules (Cape et al., 2011; Laskin et al., 2009; Wang et al., 2010). In addition to biomass burning, the 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 NO_3 radical or NH_3 with biogenic/anthropogenic volatile organic compounds (VOCs) followed by gas-to-particle conversion (Cornell et al., 2001; Miyazaki et al., 2014; Pratt et al., 2012). Recently, oxidation of isoprene and monoterpenes by NO_3 is considered as a substantial source of organic nitrates and secondary organic aerosols (SOA) (Fry et al., 2009; Pratt et al., 2012; Rollins et al., 2009; Rollins et al., 2012). Further, chemical aging of SOA derived from both biogenic and anthropogenic precursors in the presence of NH_3 in gas phase and NH_4^+ salts in 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 secondary formation of ON has been poorly characterized (Cape et al., 2011; Jickells et al., 2013; Kanakidou et al., 2012) and thus 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 34.0 nmol N m^{-3}) than WSON (4.5 nmol N m^{-3}) in aerosols from Lewes, Delaware on 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 of 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 ($\delta^{15}N_{TN}$) and WSTN ($\delta^{15}N_{WSTN}$) measured in ambient aerosols (TSP) collected from Sapporo, northern Japan over one-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 Northeast Asia.

2 Materials and methods

2.1 Aerosol sampling

Total suspended particles (TSP) 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 Northeast Asian regions: Siberia, the Russian Far East, China, and 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 during 2 September 2009 and 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 amount 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_4NO_3 and WSON) sampling artifacts (Matsumoto et al., 2014; Squizzato et al., 2013). Since the sampling time is longer 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: -3.30ºC to 24.5ºC) (Pavuluri et al., 2015) that may not cause a significant evaporative loss of N species during the sampling period, because quartz filters show a good retention for semi-volatile NH_4NO_3 sampled at an air temperature up to 21°C and ~30% at even 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 ($\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$, respectively) in TSP samples were determined using an elemental analyzer (EA) (Carlo Erba NA 1500) and EA/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 MΩ) under ultrsonication 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 and concentrated to dryness using a rotary evaporator under vacuum and then re-dissolved 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 sub-sample of the 200 μl re-dissolved extract, adsorbed onto ~20 mg of pre-combusted Chromosorb for WSTN) was placed in a pre-cleaned tin cup and introduced into EA. The resulting N_2 gas was measured with thermal conductivity detector in 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 μgN. The analytical uncertainties (i.e., RSD) 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 EA determined by the sensitivity of the detector is 0.4 μg N (Nieuwenhuize 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 syringe filter (GL Sciences Chromatodisc Type A, 0.45 μm) and then injected into TOC/TN analyzer. The analytical uncertainty in duplicate analyses of filter samples was within 5%.

Concentrations of WSTN measured by EA are lower by 23 ± 5% than those measured by TOC/TN analyzer. The difference was significant when the concentration of WSTN was greater than 0.5 μg m^{-3}. The difference may be arisen from different combustion temperature: 1400°C for EA v.s. 680°C for TOC/TN analyzer and different procedures. We consider that the WSTN measured by 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 sticking loss of N species 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 be significantly varied in proportionate to loss of WSTN, because of isotopic fractionation caused by 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 ($\varepsilon_{NH4+-NH3}$) 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 TOC/TN analyzer to minimize the uncertainties in the estimation of WSON and WION.

2.2.2 Measurements of inorganic ions

Details in the measurements of inorganic ionic species such as NO_3^-, NH_4^+ and methanesulfonate: MSA^- ($CH_3SO_3^-$) 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., 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);

$$ON = TN - IN$$

$$WSON = WSTN - IN$$

$$WION = TN - WSTN$$

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

2.2.4 Measurements of organic tracers

Organic tracers such as hopanes, isoprene- and monoterpene-oxidation products were determined using a capillary gas chromatograph (Hewlett-Packard 6890) coupled to 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)triflouroacetamide (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 (AGL) were computed for every 48 h during each sample period using HYSPLIT model (Draxler and Rolph, 2012) and are plotted in Fig. 1. The trajectories show that the air masses were mostly originated from Siberia passing over Northeast Asian regions and the Japan Sea 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 the Main Island of Japan (Fig. 1). The air parcels were mostly travelled at lower than 2000 m AGL in all seasons and hence their advection from distant source regions to the receptor site should be significant.

In fact, the radiocarbon analyses showed that percent modern carbon (pMC) of total carbon and water-soluble organic carbon in our aerosols started to increase from mid to late winter toward spring (Pavuluri et al., 2013), although the growing season starts in May in Hokkaido when daily average temperatures are ≥10°C (Toma et al., 2011). Because the contribution of modern carbon from local vegetation is unlikely in winter, such increase in pMC during winter has been mainly attributed to the contributions of biomass burning aerosols via long-range transport from East Asia (Pavuluri et al., 2013). In addition, temporal variations of crustal metals, e.g., Al, Ca and Fe, in Sapporo aerosols are consistent with those of TSP from winter to mid summer with a peak in early spring, indicating a significant atmospheric transport of Asian dust from arid regions in Mongolia and China (Pavuluri et al., 2015). Therefore, we consider that the Sapporo aerosols should have largely influenced by long-range transported air masses from distant sources over Northeast Asia. However, the characteristics and seasonal variations of 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 1,750 ng m^{-3} (average 1020 ± 466 ng m^{-3}) and 293 to 1,520 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 of 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 sources such as fossil fuel combustion may be significant in winter.

As seen from Fig. 3, WSTN contains mostly IN (i.e., $\sum NO_3^-$-N + NH_4^+-N) (range 70.8–-100%, average 89.7 ± 7.74%) whereas TN consists of a significant amount of ON (average 22.7 ± 17.7%, maximum 44.7%,) that ranged from below detection limit (BDL)–569 ng m^{-3} (215 ± 150 ng m^{-3}) during the study period. High abundances of ON in TN rather than WSTN indicate a significance of WION in Sapporo aerosols. Further, 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 Northeast Asia is significantly influenced by the sources and seasonality of ON.

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 BDL to 288 ng m^{-3} and BDL to 454 ng m^{-3}, respectively. On average, WION is more abundant (126 ± 117 ng m^{-3}) than WSON (89.7 ± 80.6 ng m^{-3}). Although the temporal variations did not show any clear seasonal pattern, WSON maximized in late autumn to mid winter whereas WION peaked in mid spring to early summer (i.e., in growing season) (Fig. 4a). Further, seasonally averaged concentrations of WSON are higher in winter followed by autumn, spring and summer whereas those of WION are higher in summer followed by spring and much lower in autumn and winter, although the seasonal differences are not statistically significant (Table 1). On average, mass fraction of WION in TN is 13.9 ± 11.1% (range BDL–33.1%) and WSON/TN ratio is 9.13 ± 7.29% (BDL–30.2%) during the study period. Temporal variations of the mass fractions of WSON and WION in TN (Fig. 4b) are similar to those of the concentrations (Fig. 4a).

3.3.2 Comparisons with previous studies from different locale

As seen from Table 2, 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 the 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 intensive biomass burning period (dry season) (Mace et al., 2003a) and from Sapporo, Japan, and in the marine aerosols over the Asian outflow regions: the Yellow Sea, South China Sea and western North Pacific (Table 2). In contrast, 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 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 urban aerosols from Davis, California and Kofu, Japan and in coastal urban aerosols from Crete, Greece (Table 2). However, average mass fraction of WSON in WSTN in Sapporo aerosols is found to be comparable or close to those reported for urban aerosols from Kofu, Japan, coastal urban aerosols from Crete, Greece, forest aerosols from Fujiyoshida, Japan and the marine aerosols over the Yellow Sea, China Sea and western North Pacific (Table 2).

Higher concentrations of WSON reported for urban aerosols from Davis, California, during late fall and winter are attributed to increased amounts of atmospheric liquid water, which promote a partition of gaseous WSON to particles (Zhang et al., 2002). In Kofu and Fujiyoshida (forest site), Japan, emissions from combustion sources including biomass burning and plant-derived particles as well as secondary formation through the reaction of NO_2 with volatile organics are considered as potential sources of WSON (Matsumoto et al., 2014). In the Mediterranean atmosphere, atmospheric dust from north Africa was expected as dominant source of WSON at Erdemli, Turkey (Mace et al., 2003c) whereas in Crete, Greece, fossil fuel combustion and biomass burning are also considered (Violaki and Mihalopoulos, 2010). Over the marginal seas of China (Asian outflow region): Qingdao, the Yellow Sea and Sea of China, anthropogenic sources are considered as dominant origin of WSON with minor contributions from marine and crustal sources (Nakamura et al., 2006; Shi et al., 2010). In the forest aerosols from Sapporo, Japan, emissions of biological particles are considered as major source of WSON in autumn whereas secondary formation of WSON from biogenic hydrocarbons is considered as dominant source in summer (Miyazaki et al., 2014).

On the other hand, average concentration of WION (126 ± 117 ng m^{-3}) found in Sapporo aerosols is comparable to that (112 ± 61 ng m^{-3}) reported in the marine aerosols over the western North Pacific, where the sea-to-air emissions are considered as the major source as well as the secondary production via the reactions of gaseous hydrocarbons with NH_3 (Miyazaki et al., 2011). In addition, the higher end (maximum 454 ng m^{-3}) of WION in Sapporo aerosols is comparable to the average WION (476 ng m^{-3}) reported in the coastal aerosols from Lewes, Delaware, where biological and mineral particles are expected as major source (Russell et al., 2003).

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 be originated 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 their comparisons with the source tracers.

3.4 Comparisons of WSON and WION with organic tracers

3.4.1 Possible sources of WSON

The temporal trend of 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 winter time Sapporo aerosols (Fig. 4c). Further, WSON showed a linear relationship with hopanes with moderate but significant correlation during the campaign (Fig. 5a). On the other hand, temporal variation of 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. 4b). 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, should have been 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).

Temporal trend of 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 of 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) that emits 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 as a tracer to understand the importance of secondary production of WSON (and WION) from biogenic organics, although both DMS and MSA^- do not contain nitrogen. Interestingly, WSON showed a linear relation with sucrose ($r = 0.71$, $p \leq 0.05$), 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 ($p \leq 0.05$). Further, it showed a positive Spearman's rank correlation with isoprene SOA tracers ($r = 0.33$) and β-caryophylinic acid ($r = 0.37$).

However, WSON shows no relation with sucrose, isoprene- and α-pinene-SOA tracers, β-caryophylinic acid and MSA$^-$ when we consider the total data set (n = 21) that include 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 Northeast China (Fig. 1a, b). In fact, fossil fuel consumption is significantly higher in winter than any other season in East Asia (Zhang et al., 2009). Further, 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-early autumn, respectively, although we do not preclude a minor contribution from biomass burning emissions. In fact, levels of NO_3^- 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_3^- in summer may be in part caused by its 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 inversed correlation with hopanes and levoglucosan during the campaign (Table 3). On the contrary, temporal trend of WION is similar to those of sucrose (Fig. 4e) during late spring to early summer and of biogenic SOA tracers: isoprene- and α-pinene-SOA tracers and β-caryophyllinic acid, (Fig. 4f) and MSA$^-$

(Fig. 4g) throughout the year. Further, WION showed a moderate significant positive Spearman's correlation with sucrose, isoprene SOA and MSA^- during the study period (n = 21) (Table 3) and also with β-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 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 oxidation of biogenic hydrocarbons by NO_3 radicals is 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 the formation of such high molecular weight organic salts by Mannich reaction rather than imidazole salts 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, 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 growing season (mid spring to mid summer) 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 to Sapporo originate from Siberia in spring and oceanic region passing over the Japanese Main Island 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 ($NH_4^+ \leftrightarrow NH_3$) (Noziere et al., 2009) should be accelerated during the warmer seasons in Northeast Asia. However, there is a need to conduct the measurements of WION and source tracers at different locale 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

$\delta^{15}N_{TN}$ ranged from 15.5 to 29.4‰ (average 21.9 ± 4.1‰) whereas $\delta^{15}N_{WSTN}$ ranged from 12.2 to 39.1‰ (25.8 ± 8.2‰) in Sapporo aerosols during the campaign period (n = 21). As shown in Fig. 2b, temporal trends of $\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$ were highly comparable. They both show peaks in summer with relatively high values in late autumn (Fig. 2b). Their averages, except for $\delta^{15}N_{TN}$ in autumn and winter, were significantly varied from season-to-season with higher $\delta^{15}N$ values in summer followed by spring, winter and autumn (Table 1). The seasonal trends of $\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$ suggest that aerosol N is significantly influenced by season-specific source(s) and/or chemical aging of N species.

We also found that $\delta^{15}N_{WSTN}$ are higher than $\delta^{15}N_{TN}$ throughout the campaign, except for few samples in autumn (Fig. 2b). An enrichment of ^{15}N in WSTN over TN is more significant in summer than other seasons (Table 1). It has been reported that the aerosol particles collected over the controlled laboratory burns of the vegetation, which significantly contribute to WSTN, are enriched with ^{15}N ranging from -1.3 to 13.1‰ (average 6.6‰) compared to the source vegetation (Turekian et al., 1998). Further, chemical aging of N species, including gas-to-particle exchange (e.g., $NH_4^+ \leftrightarrow NH_3$) reactions during long-range transport causes the enrichment of ^{15}N in aerosol N (Pavuluri et al., 2010). In addition, $\delta^{15}N$ of terrestrial plants, which significantly contribute to WION, is relatively low (e.g., -3.4 to 12.2‰ in plants from the San Francisco Bay area) (Cloern et al., 2002). Therefore, higher $\delta^{15}N_{WSTN}$ values than $\delta^{15}N_{TN}$ 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 $NH_4^+ \leftrightarrow NH_3$) of nitrogenous aerosols under higher ambient temperature in summer may have caused further enrichment of ^{15}N in WSTN (Pavuluri et al., 2010).

As seen from Fig. 6, $\delta^{15}N_{TN}$ (and $\delta^{15}N_{WSTN}$) showed an inverse relation with the mass fractions of NO_3^--N and WSON in TN, but showed a linear relation with NH_4^+-N/TN and WION/TN during the study period. Their relations with NO_3^--N/TN and NH_4^+-N/TN are statistically significant at 99% ($p \leq 0.01$) level but not in other two cases (Fig. 6). Such relations imply that the $\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$ are mainly controlled by their sources, chemical aging of nitrogenous species and abundances of NO_3^--N and NH_4^+-N. It is well recognized that NO_3^- originates mainly from fossil fuel combustion and biomass burning whereas NH_4^+ from biomass burning, agricultural activities and biological emissions (Delon et al., 2012; Hertel et al., 2012). In fact, NO_3^- is more abundant in mid autumn to early spring whereas

NH_4^+ maximize 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 in spring and biogenic emissions of gaseous species (hydrocarbons and NH_3) and subsequent secondary production in spring/summer are important.

3.5.2 Comparison with literature values

Figure 7 compares the range (or mean) of $\delta^{15}N$ values reported for the particles emitted from point sources in mid-latitudes as well as those observed in atmospheric aerosols from different locale over the world including Sapporo aerosols. $\delta^{15}N_{TN}$ 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, they are comparable to the higher ends of the $\delta^{15}N_{TN}$ reported in atmospheric aerosols from Jeju Island, Korea (Fig. 7), which were attributed to significant atmospheric processing of N species, emitted mainly from China, during long-range transport (Kundu et al., 2010b). Further the lower ends of $\delta^{15}N_{TN}$ in Sapporo aerosols are comparable to the higher ends of $\delta^{15}N_{TN}$ reported for the particles emitted from controlled burning of C_3 (range, 2.0‰ to 19.5‰) and C_4 (9.8‰ to 22.7‰) plant species in a laboratory study and those of atmospheric aerosols from Piracicaba and Amazon basin, Brazil, where biomass burning is a dominant source (Martinelli et al., 2002) (Fig. 7). In addition, they are well comparable to those 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 be mainly originated from biomass burning and subjected for aging (Aggarwal et al., 2013; Pavuluri et al., 2010) (Fig. 7).

On the other hand, lower values of $\delta^{15}N_{WSTN}$ 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 ^{15}N in Sapporo aerosols (Fig. 2b) is significantly higher than that (range of monthly averages, 9.0‰ to 26.0‰) reported in the Sapporo forest aerosols (Miyazaki et al., 2014). Further, the range of $\delta^{15}N_{WSTN}$ values observed in Sapporo aerosols are highly comparable with $\delta^{15}N$ of aerosol NH_4^+, which is much higher than that of gaseous NH_3, in the atmosphere from the Maki monitoring station, Niigata, Japan (Fig. 7). The large difference in $\delta^{15}N$ between NH_3 and NH_4^+ has been attributed to gas-to-particle (equilibrium) exchange reactions in the atmosphere (Hayasaka et al., 2004) because under equilibrium conditions, particulate NH_4^+ is more enriched with ^{15}N than gaseous NH_3, where the isotopic enrichment factor ($\varepsilon_{NH4+-NH3}$) was estimated to be +33‰ (Heaton et al., 1997). Such comparisons suggest that aerosol N in Sapporo aerosols might have significantly originated 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 ($\delta^{15}N_{TN}$) and water-soluble TN ($\delta^{15}N_{WSTN}$) were obtained for TSP aerosol samples collected from Sapporo, northern Japan during September 2009 and October 2010. WSON and WION ranged from 0.00 to 288 ng m^{-3} (average 89.7 ± 80.6 ng m^{-3}) and from 0.00 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. $\delta^{15}N_{TN}$ ranged from 15.5 to 29.4‰ (average 21.9 ± 4.1‰) whereas $\delta^{15}N_{WSTN}$ 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 of 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 NH_3 significantly contribute to WION in Northeast Asia. Seasonal variations of $\delta^{15}N_{TN}$ and $\delta^{15}N_{WSTN}$ and their relations to mass fractions of nitrogenous components in TN suggest that aerosol N in Sapporo aerosols is mainly originated from biogenic sources including biomass burning and subjected to chemical aging during long-range transport, although a contribution from fossil fuel combustion is important particularly in winter.

Acknowledgements. This study was in part supported by Japan Society for the Promotion of Science (Grant-in-Aid Nos. 1920405 and 24221001) and the Environment Research and Technology Development Fund (B903) of the Ministry of the Environment, Japan.

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Table 1. Seasonal and annual averages with standard deviation of concentrations of nitrogenous components and ^{15}N isotope ratios of TN and WSTN in atmospheric aerosol (TSP) samples collected during 2 September 2009 and 5 October 2010 from Sapporo, northern Japan.

Component	Autumn (n = 8)	Winter (n = 3)	Spring (n = 5)	Summer (n = 5)	Annual (n =19)
Concentrations (ng m^{-3})					
TN	790 ± 480	1456 ± 298	1116 ± 434	1023 ± 433	1074 ± 454
WSTN	714 ± 496	1388 ± 247	986 ± 356	789 ± 351	950 ± 427
NO_3^-–N	284 ± 120	362 ± 55.2	395 ± 182	73.8 ± 24.1	279 ± 172
NH_4^+–N	338 ± 347	896 ± 97.2	511 ± 191	647 ± 310	576 ± 314
ON	168 ± 77.1	198 ± 186	212 ± 221	302 ± 149	220 ± 157
WSON	91.6 ± 73.6	130 ± 139	84.7 ± 99.5	67.8 ± 39.8	96.0 ± 81.9
WION	77.5 ± 50.9	68.4 ± 51.3	130 ± 141	234 ± 144	125 ± 123
Isotope ratios (‰)					
$\delta^{15}N_{TN}$	18.91 ± 3.17	19.72 ± 3.56	23.42 ± 1.63	26.82 ± 1.95	22.47 ± 3.98
$\delta^{15}N_{WSTN}$	19.17 ± 6.45	23.84 ± 4.13	26.82 ± 2.46	36.88 ± 2.46	26.71 ± 8.16

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 in the world. [a]Total of fine and coarse mode particles, [b]Dry (biomass burning) season, [c]Asian outflow region.

Locale	Study Period	Aerosol Size	WSON (ng m^{-3})	WSON/WSTN (%)	Reference
Urban sites					
Sapporo, Japan	Sept 2009 to Oct 2010	TSP	89.7 ± 80.6	10.5 ± 7.5	This study
Davis, California	Aug 1997 to Jul 1998	$PM_{2.5}$	265 ± 190	23	Zhang et al. (2002)
Kofu, Japan	Aug 2009 to Jan 2013	PM_{10}[a]	221	~14	Matsumoto et al. (2014)
Forest sites					
Rondônia, Brazil	Mar–May 1999	PM_{10}	49 ± 64.4	45 ± 35	Mace et al. (2003a)
Rondônia, Brazil	Sept–Oct 1999[b]	PM_{10}	854 ± 938	43 ± 31	Mace et al. (2003a)
Sapporo, Japan	Jun 2009 to Dec 2011	TSP	157 ± 127	20 ± 11	Miyazaki et al. (2014)
Fujiyoshida, Japan	Aug 2009 to Jan 2013	PM_{10}[a]	101	~11	Matsumoto et al. (2014)
Coastal sites					
Erdemli, Turkey	Mar–May 2000	TSP	406 ± 588	~26 ± 28	Mace et al., (2003c)
Crete, Greece	2005–2006	PM_{10}[a]	~239	13	Violaki & Mihalopoulos (2010)
Qingdao, China	Mar–Apr 2006	TSP	2520 ± 1760	~20	Shi et al. (2010)
Oceanic sites					
Yellow Sea[c]	Mar 2005	TSP	2860 ± 1780	~17	Shi et al. (2010)
Yellow Sea[c]	Apr 2006	TSP	1220 ± 812	~17	Shi et al. (2010)
South China Sea[c]	Apr 2005	TSP	910 ± 280	~34	Shi et al. (2010)
East China Sea[c]	Sept–Oct 2002	TSP[a]	756 ± 504	~24	Nakamura et al. (2006)
East China Sea and western North Pacific[c]	Mar 2004	TSP[a]	224 ± 266	~10	Nakamura et al. (2006)
Cape Grim, Australia	Nov–Dec 2000	TSP	50.4 ± 79.8	~21	Mace et al. (2003b)
Cape Grim, Australia	Nov–Dec 2000	TSP	13.0 ± 13.3	~25	Mace et al. (2003b)
Oahu, Hawaii	Jul–Aug 1998	PM_{10}	46.2 ± 28	~33	Cornell et al. (2001)
Western North Pacific	Aug–Sept 2008	TSP	~17.5		Miyazaki et al. (2011)

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.

Source tracer	Correlation coefficient (ρr)	
	WSON	WION
Hopanes	**0.48**	**-0. 50**
Levoglucosan	0.18	**-0.57**
Sucrose	-0.02	**0.38**
Isoprene-SOA tracers	-0.12	**0.50**
α-Pinene-SOA tracers	0.21	0.14
β-Caryophylinic acid	0.06	0.30
MSA^-	0. 09	**0.59**

Figure captions

Fig. 1. Plots of 10-day backward air mass trajectories arriving over Sapporo at 500 AGL.

Fig. 2. Seasonal variations in (a) concentrations of TN and WSTN and (b) N isotope ratios of TN ($\delta^{15}N_{TN}$) and WSTN ($\delta^{15}N_{WSTN}$).

Fig. 3. Linear relations of IN (sum of NO_3^--N and NH_4^+-N) to (a) WSTN and (b) TN.

Fig. 4. Seasonal variations of (a) concentrations of WSON and WION, (b) mass fractions of WSON and WION in TN, and (c-e) concentrations of organic molecular tracers and MSA^- in Sapporo aerosols. Concentrations of hopanes are sum of the concentrations of C_{27}-C_{32} hopanoid hydrocarbons. Concentrations of isoprene-SOA tracers are sum of the concentrations of 2-methylglyceric acid, cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol whereas concentrations of α-pinene-SOA tracers are sum of the concentrations of 3-hydroxyglutaric, pinonic, pinic and 3-methyl-1,2,3-butanetricarboxylic acids. The data of organic molecular tracers are from Pavuluri et al. (2013) and MSA^- is from Pavuluri et al. (2015).

Fig. 5. Linear relations of WSON with (a) hopanes (C_{27}-C_{32} hopanoid hydrocarbons) and (b) levoglucosan during campaign period (n = 21) and with (c) sucrose, (d) α-pinene-SOA tracers (sum of 3-hydroxyglutaric, pinonic, pinic and 3-methyl-1,2,3-butanetricarboxylic acids), and (e) MSA^- in spring and summer (n = 10) in Sapporo aerosols.

Fig. 6. Scatter plots between $\delta^{15}N_{TN}$ (and $\delta^{15}N_{WSTN}$) and mass fractions of nitrogenous components (NO_3^--N, NH_4^+-N, WSON and WION) in TN in Sapporo aerosols.

Fig. 7. Range or mean N isotope ratios in the particles emitted from point sources, source substance, and atmospheric aerosols from different sites in the world. *, **, and *** show gaseous NH_3, particulate NH_4^+ and WSTN, respectively. [a]Widory (2007); [b]Turekian et al. (1998); [c,g]Kundu et al. (2010a, 2010b); [d]Martinelli et al. (2002); [e]Pavuluri et al. (2010); [f]Aggarwal et al. (2013); [h,j]Miyazaki et al. (2011, 2014); [i]Hayasaka et al. (2004); [k]This study.

792 **Figure 1.**

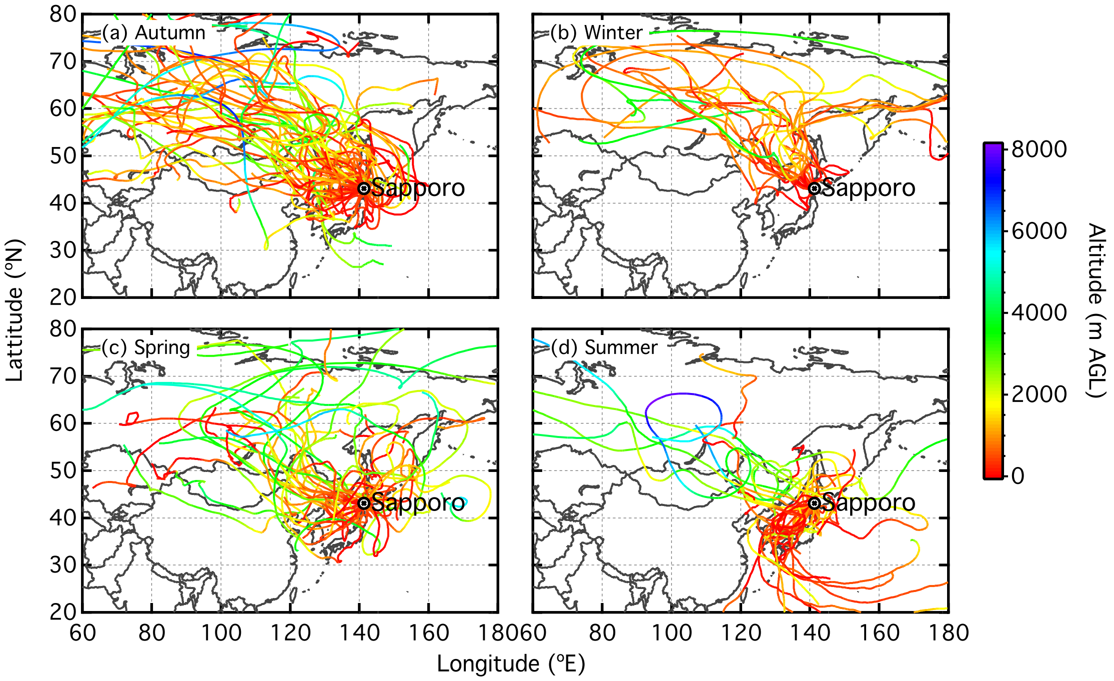

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Figure 2.

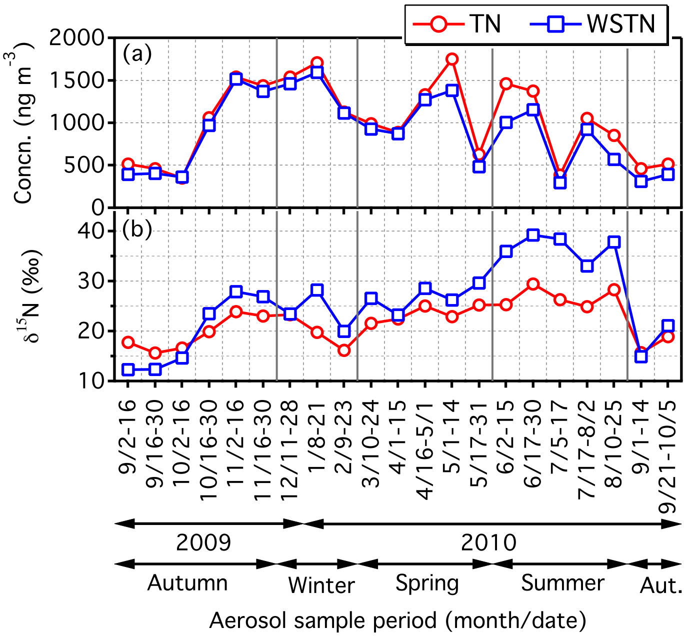
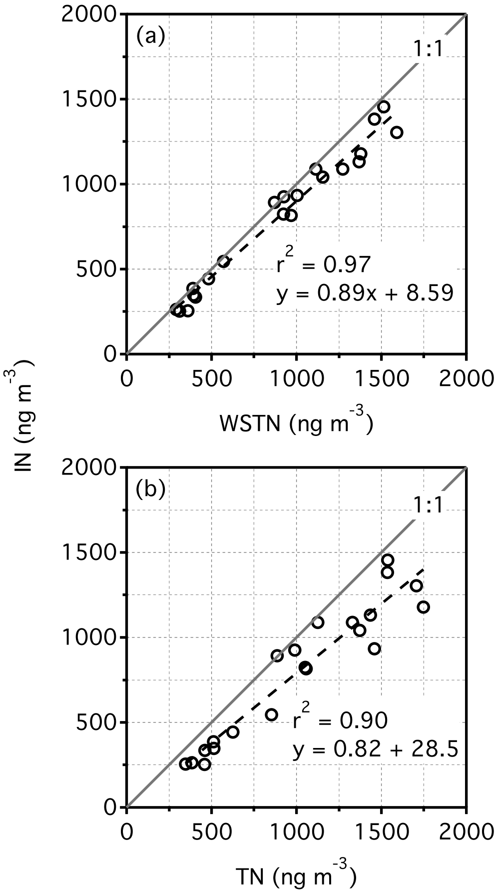

TN
WSTN
(a)
Concn. (ng m^{-3})
2000
1500
1000
500
0
(b)
δ^{15}N (‰)
40
30
20
10
9/2-16
9/16-30
10/2-16
10/16-30
11/2-16
11/16-30
12/11-28
1/8-21
2/9-23
3/10-24
4/1-15
4/16-5/1
5/1-14
5/17-31
6/2-15
6/17-30
7/5-17
7/17-8/2
8/10-25
9/1-14
9/21-10/5
2009
2010
Autumn
Winter
Spring
Summer
Aut.
Aerosol sample period (month/date)

Figure 3.


(a)
1:1
r^2 = 0.97
y = 0.89x + 8.59
0
500
1000
1500
2000
WSTN (ng m^{-3})
IN (ng m^{-3})
(b)
1:1
r^2 = 0.90
y = 0.82 + 28.5
TN (ng m^{-3})

801 **Figure 4.**

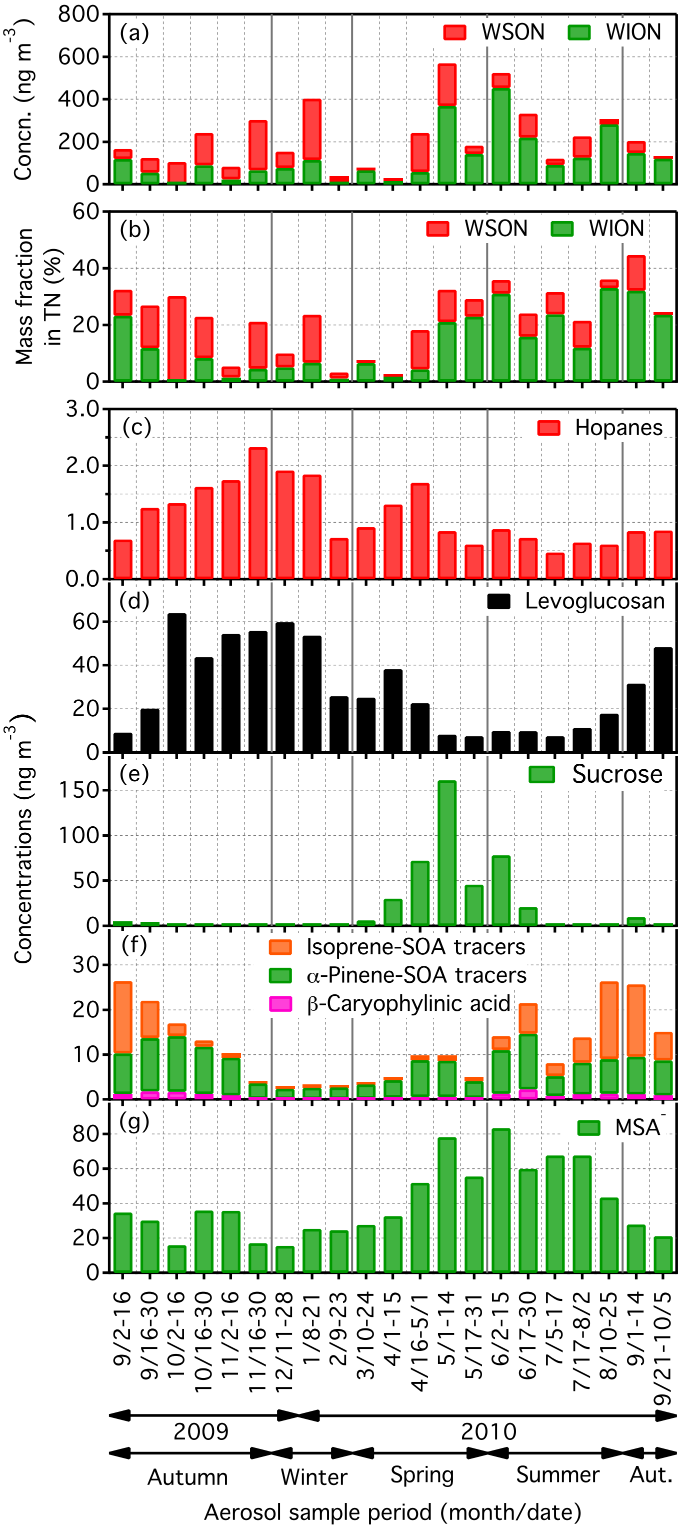


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Figure 5.

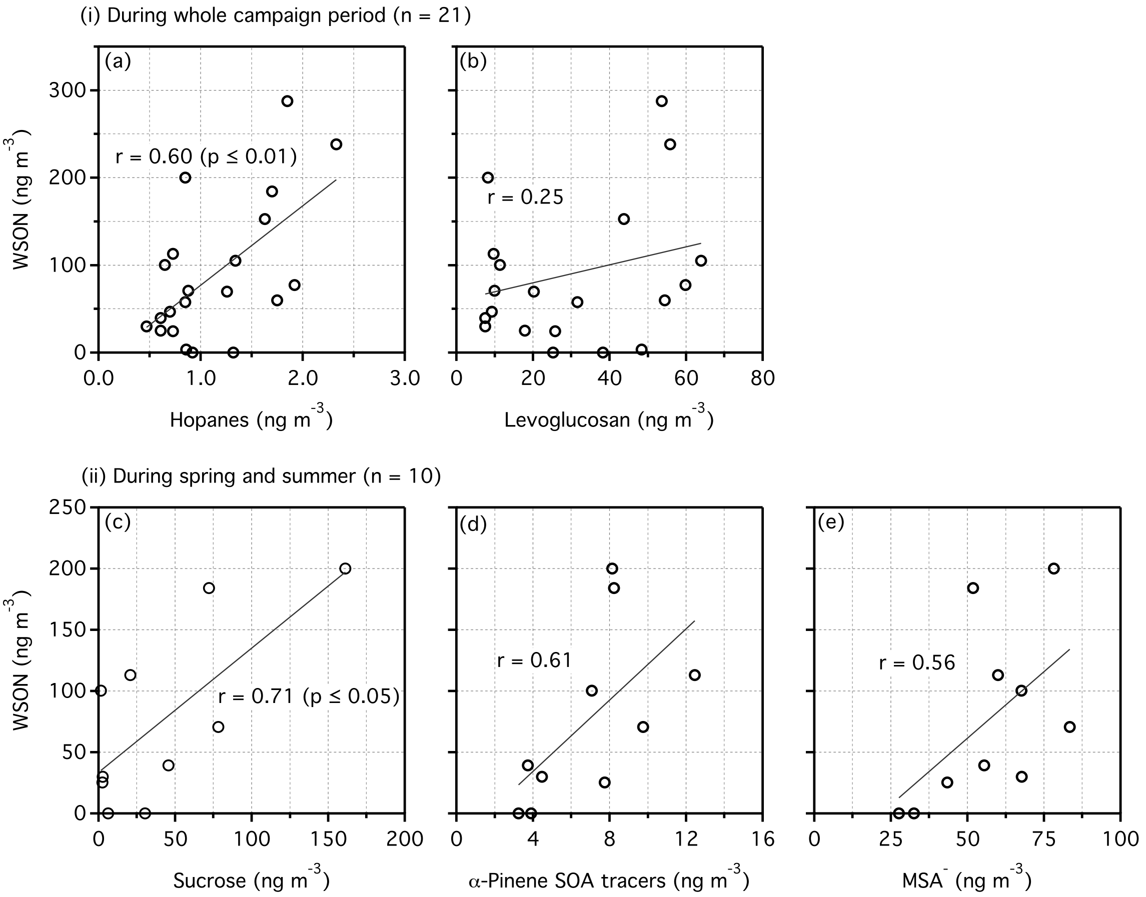

(i) During whole campaign period (n = 21)
(a)
r = 0.60 (p ≤ 0.01)
WSON (ng m^{-3})
300
200
100
0
0.0
1.0
2.0
3.0
Hopanes (ng m^{-3})
(b)
r = 0.25
0
20
40
60
80
Levoglucosan (ng m^{-3})
(ii) During spring and summer (n = 10)
(c)
r = 0.71 (p ≤ 0.05)
WSON (ng m^{-3})
250
200
150
100
50
0
0
50
100
150
200
Sucrose (ng m^{-3})
(d)
r = 0.61
0
4
8
12
16
α-Pinene SOA tracers (ng m^{-3})
(e)
r = 0.56
0
25
50
75
100
MSA$^-$ (ng m^{-3})

Figure 6.

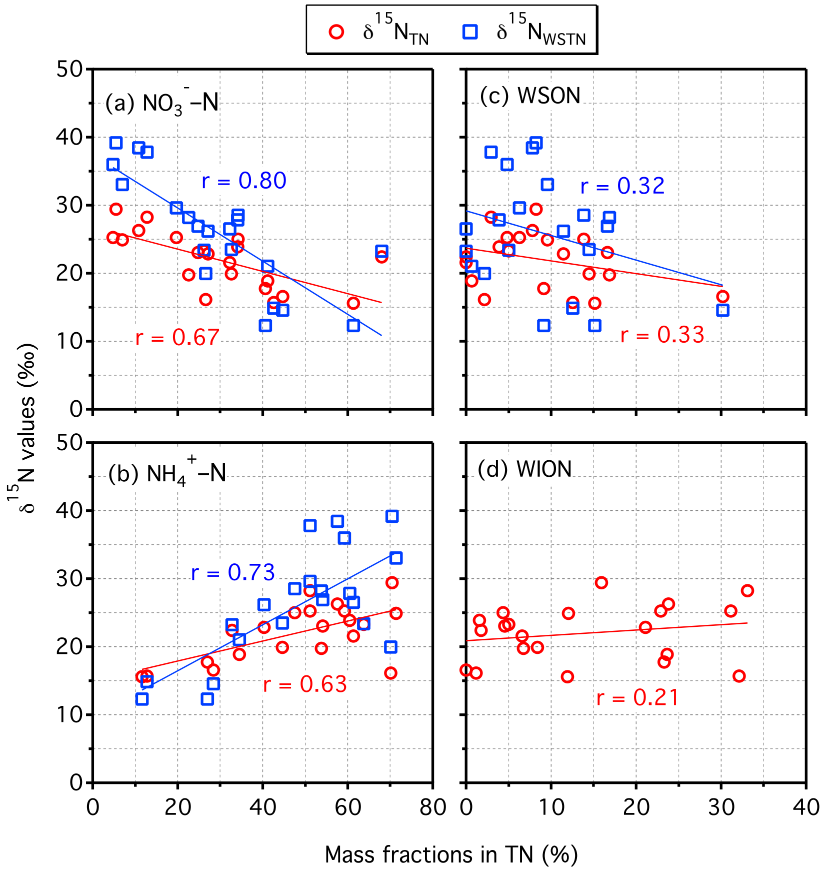
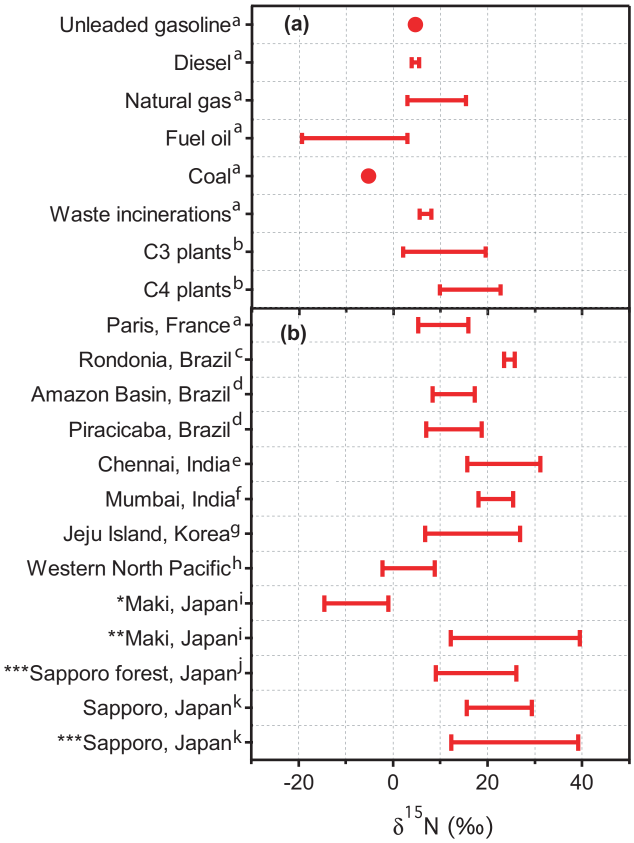

δ15NTN
δ15NWSTN
(a) NO3−–N
r = 0.80
r = 0.67
(b) NH4+–N
r = 0.73
r = 0.63
(c) WSON
r = 0.32
r = 0.33
(d) WION
r = 0.21
δ15N values (‰)
Mass fractions in TN (%)
0
10
20
30
40
50
0
20
40
60
80
0
10
20
30
40

Figure 7.


(a)
Unleaded gasoline[a]
Diesel[a]
Natural gas[a]
Fuel oil[a]
Coal[a]
Waste incinerations[a]
C3 plants[b]
C4 plants[b]
(b)
Paris, France[a]
Rondonia, Brazil[c]
Amazon Basin, Brazil[d]
Piracicaba, Brazil[d]
Chennai, India[e]
Mumbai, India[f]
Jeju Island, Korea[g]
Western North Pacific[h]
*Maki, Japan[i]
**Maki, Japan[i]
***Sapporo forest, Japan[j]
Sapporo, Japan[k]
***Sapporo, Japan[k]
-20
0
20
40
δ15N (‰)