Atmospheric
Chemistry
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Discussions

Year-round observations of water-soluble ionic species and trace metals in Sapporo aerosols: implication for significant contributions from terrestrial biological sources in Northeast Asia

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ACPD

13, 6589–6629, 2013

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Abstract

High aerosol loadings are prevalent in the atmosphere of East Asia, where the aerosols impact the Earth's climate system and human health; however, their sources and seasonal variations are not clearly understood. To better understand the sources of water-soluble ionic species and trace metals in Northeast Asia, we studied atmospheric aerosol samples collected in Sapporo, northern Japan for one-year period. SO_4^{2-} (average $3.47 \pm 1.03 \, \mu g \, m^{-3}$) was found as the most abundant ionic species, which accounted for on average $43 \pm 15\%$ of the measured total ionic mass followed by Cl^- ($13 \pm 12\%$) $\approx NO_3^- \approx Na^+ > NH_4^+ > Ca^{2+} > Mg^{2+} > K^+ > MSA^-$. Among the metals determined, Ca was found as the most abundant ($45 \pm 5.2\%$) followed by Fe ($27 \pm 4.5\%$), Al ($21 \pm 3.1\%$), Zn (3.2 ± 1.7), Ti, Mn, Ni, Pb, Cu, V, As, Cr and Cd. Based on factor analysis, linear relations of selected species with biomarkers, and backward air mass trajectories, we found that long-range atmospheric transport of soil dust ($\sim 33\%$) from arid regions of Mongolia and/or Northeast China is a major source for Sapporo aerosols as well as terrestrial biogenic emissions ($\geq 24\%$) including microbial activities and biomass burning mostly from distant source region(s) (e.g. Siberia). We also found that the contributions of soil dust to the aerosols maximized in early spring whereas those of vegetational emissions maximized in spring/summer. Contributions of microbial activities to aerosols peaked in autumn whereas forest fires/biomass burning peaked in autumn/winter. On the contrary, fossil fuel combustion/industrial activities and oceanic emissions to Sapporo aerosols are suggested to be rather minor. This study also suggests that fungal spores contribute to some trace metals (i.e. Ni, Cu, As) while pollen contributes to Zn in aerosols.

1 Introduction

Atmospheric aerosols have an impact on the Earth's climate system directly by absorbing and reflecting solar radiation and indirectly by acting as cloud condensation (CCN)

and ice nuclei (IN) and thus altering their hygroscopic properties on local, regional and global scales (Ramanathan et al., 2001; Pöschl et al., 2010). They also have an adverse effect on the human health (Nel, 2005). Such impacts of aerosols are largely depend on aerosol loading and chemical composition (Baustian et al., 2012; Déandreis et al., 2012; Dentener et al., 1996; Nel, 2005; Schaumann et al., 2004; Sciare et al., 2005; Zhang et al., 2012) that are spatially and seasonally highly variable in the lower atmosphere. Aerosol concentrations vary in the range of 1–100 μg m^{-3} and their dominant chemical components are characterized by sulfate, nitrate, ammonium, sea salt, minerals, organics and elemental carbon, each of which typically contribute about 10–30 % of the overall mass load (Pöschl, 2005).

Aerosol SO_4^{2-} could affect the radiation budget directly by reflecting solar radiation and indirectly by altering the physical properties of aerosols and the CCN activity (Déandreis et al., 2012). Inorganic salts are more water-soluble and their solubility is much higher than organics, enhancing CCN activity of the particles (Zhang et al., 2012). On the other hand, mineral dust adds complexity, because it can play a significant role in radiative forcing (Dentener et al., 1996) as well as in the uptake of acidic gases (Goodman et al., 2000). Trace elements are typically present in elevated concentrations, especially in urban aerosols, and can play an important role in the risk of human health due to their high bioreactivity (Moreno et al., 2011; Schaumann et al., 2004).

High aerosol loadings are commonly observed in East Asia due to anthropogenic activities (Carmichael et al., 2009). Radiative forcing and climatic effects over East Asia have been shown to be large (Nakajima et al., 2007) with significant seasonal variations due to the enhanced concentrations of dust in spring (Li-Xia and Zhi-Wei, 2011) and/or SO_4^{2-} in summer (Su et al., 2012). East Asian aerosols, including dusts from arid regions in Mongolia and North China, could be further transported across the Pacific Ocean (Alfaro et al., 2003; Kawamura et al., 2004; Uno et al., 2011) with an impact on the regional to global climate. However, the aerosol composition, sources and seasonal variations, which are crucial in reducing the uncertainty in modeling of the aerosol

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impacts, are still far from being fully understood, despite the extensive studies over the past decade (e.g. Huebert et al., 2003; Nakajima et al., 2007). For example, Huang et al. (2006) reported an underestimation of the annual averaged model-simulated aerosol optical depth (AOD) by $\sim 45\%$. They interpreted that the obtained negative intercept is due to the inclusion of only the anthropogenic aerosols (SO_4^{2-}, black carbon and organic carbon), suggesting that the contributions from natural sources might also be significant in this region.

It is generally believed that anthropogenic activities (largely coal combustion) and volcanic emissions are two major sources of particulate non-sea-salt (nss)-SO_4^{2-} (Andres and Kasgnoc, 1998; Moore et al., 2006; Smith et al., 2011). Biological production of dimethylsulfide (DMS) is also considered as a significant source of nss-SO_4^{2-} at least in marine regions (Moore et al., 2006; Oduro et al., 2012). Unlike nss-SO_4^{2-}, methanesulfonate (MSA^-) can only be produced by the oxidation of DMS that originates from the microbial activity in the ocean. Abundant levels of MSA^- and nss-SO_4^{2-} were reported in the ocean/coastal atmosphere (Bates et al., 1992; Gaston et al., 2010; Gondwe et al., 2004; Legrand and Pasteur, 1998; Yang et al., 2009; Kouvarakis et al., 2002; Mihalopoulos et al., 1997). Recently, Miyazaki et al. (2012) reported significant concentrations of MSA^- in forest aerosols and interpreted a pathway for the emissions of DMS from forest floor.

Other ionic species such as K^+, Na^+, Mg^{2+}, NH_4^+ and Cl^- are derived from biomass burning, oceanic and/or biogenic emissions (Andreae, 1983; Graham et al., 2003; Pöhlker et al., 2012). Graham et al. (2003) reported significant amounts of K, Na and Mg in the natural Amazonian aerosol and attributed to biogenic matter. Recently, Pöhlker et al. (2012) found K-rich particles along with substantial amounts of NH_4^+, Cl^- and SO_4^{2-} in the Amazon region and attributed to biogenic emissions. On the other hand, metalliferous particles are directly emitted from natural sources such as volcanic eruptions, dust storms, rock weathering, forest fires and biogenic emissions at significant levels (Nriagu, 1989). Based on chemical (organic and trace metal) composition of individual aerosol particles, Van Malderen et al. (1996) reported that the main part

of the particles above Lake Baikal, Siberia, could be related to natural sources. These studies suggest that the significant contributions of water-soluble ionic species and trace metals from the vegetation/biomass burning. However, less attention has been paid on terrestrial biogenic contribution of inorganic aerosols and such studies are lim-
5 ited to the forest regions (Graham et al., 2003; Maenhaut et al., 2002; Pauliquevis et al., 2012).

Sapporo is located in the west of Hokkaido Island, northern Japan (43.07° N, 141.36° E) and is an ideal site for the study of air masses delivered from Siberia, North China, and surrounding oceans (Aggarwal and Kawamura, 2008; Yamamoto
10 et al., 2011). Previous studies of Sapporo aerosols for chemical and stable carbon (δ^{13}C) isotopic compositions demonstrated that the spring and/or summer aerosols are largely influenced by the outflows from East Asia and Siberia and are character-ized by anthropogenic and biogenic (including biomass burning) contributions with the atmospheric processing during long-range transport (Agarwal et al., 2010; Aggarwal
15 and Kawamura, 2008, 2009; Pavuluri et al., 2012). Recently, Yamamoto et al. (2011) detected terrestrial biomarkers in the Sapporo snow samples, which were interpreted by the long-range transport from Siberia, Russian Far East and Northeast China based on stable carbon (δ^{13}C) and hydrogen (δD) isotope ratios of biomarkers together with backward trajectory analyses. However, the seasonality of biotic contributions is not
20 clearly understood due to the lack of year-round observations. To our knowledge, no study has been conducted for trace metal compositions in the aerosols from Northeast Asia.

To better understand the characteristics and sources of atmospheric aerosols and their seasonal variations over Northeast Asia, we conducted one-year observation of
25 total suspended particulate matter (TSP) collected from Sapporo, northern Japan for inorganic ions and trace metals. In this paper, we present a significant contribution of water-soluble ionic species and trace metals from terrestrial biological sources in Northeast Asia based on their seasonal variations and factor analysis. We also discuss

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the relations of selected trace metals (e.g. Ni, Cu, As) to specific organic tracers for pollen (sucrose) and fungal spores (mannitol).

2 Materials and methods

2.1 Aerosol sampling

Aerosol (TSP) sampling ($n = 21$) was performed from 2 September 2009 to 5 October 2010 on the rooftop (ca. 20 m above the ground level (a.g.l.)) of the Institute of Low Temperature Science (ILTS) building, Hokkaido University, Sapporo, northern Japan using a pre-combusted (450 °C, 4 h) quartz fiber filter and high-volume air sampler ($\sim$ 65 m^3 h^{-1}). The geographical details of the sampling site has been described elsewhere (Pavuluri et al., 2013). Briefly, the population of Sapporo, the capital of Hokkaido (the northernmost island of Japan), was 1.9 million in 2010 and the major industries include retail and tourism as well as manufacturing of foods, beverages, paper and pulp and machinery, from which the input of pollutants into the atmosphere is expected to be small. The climate in this region is strongly affected by the East Asian monsoon that controls the air mass source regions and compositions of atmospheric aerosols at the receptor site. Each sample was collected for ca. 2 consecutive weeks. Filter samples were placed in a pre-combusted glass jar with a Teflon-lined screw cap separately and stored in dark room at −20 °C prior to analysis.

2.2 Chemical analyses

2.2.1 Water-soluble ionic species

Water-soluble ionic species were measured by ion chromatograph (761 Compact IC, Metrohm, Switzerland). An aliquot of filter (1.2 cm in diameter disc) was extracted with 10 mL Milli Q water under ultrasonication for 20 min and filtered using a syringe filter (GL Sciences Chromatodisc Type A, 0.45 μm) and then injected into IC. For anion

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measurement, a column of SI-90 4E (Shodex, Showa Denko, Tokyo) equipped with a suppressor was used with an eluent of 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ solution at a flow rate of 1.2 mL min^{-1}. For cation analysis, we used a Metrosep C2-150 (Metrohm) column with 4 mM tartaric acid ($C_4H_6O_6$) + 1 mM dipicolinic acid ($C_7H_5NO_4$) solution with a flow rate of 1.0 mL min^{-1}. A calibration curve was evaluated by the analyses of a set of authentic standards along with a sequence of filter samples. The analytical errors in duplicate analysis of filter samples were within 14 % for MSA$^-$ and 4 % for the rest of the ionic species. The concentrations reported here are corrected for four field blanks that were collected every season.

2.2.2 Trace metals

Trace metals were measured using an inductively coupled plasma mass spectrometry (ICP-MS, Thermo Electron X Series) after the acid microwave digestion of samples as reported in Theodosi et al. (2010). Briefly, a filter disc (1.0 cm in diameter) was placed in Teflon vessel (DAP-60 K, 60 mL/40 bar), to which concentrated nitric acid was added and then digested using a microwave digestion system (Berghof MWS-2). Indium (CPI International, S4400-1000241) was used as internal standard, and a calibration curve was evaluated using standard certified solutions (CPI International). Recoveries obtained with the use of certified reference materials ranged from 90.0 to 104.1 %. The concentrations reported here are not corrected for field blanks because none of the trace metals measured were found to be significant in the field blanks.

2.2.3 Organic tracers

Details of the procedure for the determination of organic tracer compounds are described elsewhere (Fu et al., 2010). Briefly, the tracer compounds were extracted with dichloromethane/methanol (2 : 1; v/v) under ultrasonication and derivatized with 50 µL of N,O-bis-(trimethylsilyl)triflouroacetamide (BSTFA) with 1 % trimethylsilyl chloride and 10 µL of pyridine. The tracer compounds were then measured using a capillary

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gas chromatograph (Hewlett-Packard 6890) coupled to a mass spectrometer (Hewlett-Packard 5973 GC/MS).

2.3 Meteorology in Sapporo

24 h averaged meteorological data were obtained from Japan Meteorological Agency (http://www.data.jma.go.jp). The meteorological station of Sapporo is located ca. 2 km south of the sampling point. Averaged ambient temperature, relative humidity (RH), wind speed and precipitation for each sample period are presented in Fig. 1. During our campaign, the temperature, RH and wind speed ranged from $-3.30\,^{\circ}$C to $24.5\,^{\circ}$C, 59.7–80.3 % and 2.4–4.8 m s^{-1}, respectively, whereas the precipitation occurred occasionally with the highest amount (range 5.5–153 mm) in summer (June to August) during rainy season with the highest frequency (range 14.3–73.3 %) in winter (December–February) during snowfall season. September to November and March–May are classified as autumn and spring, respectively. The ground surfaces in Sapporo are covered with snow from late December to early April.

2.4 Air mass trajectories

Ten-day backward air mass trajectories arriving in Sapporo at 500 m a.g.l. were computed for every 48 h during each sample period using HYSPLIT model (Draxler and Rolph, 2012). Their three dimensional plots are presented in Pavuluri et al. (2013). Briefly, the air masses that arrived in Sapporo during autumn, winter and spring mostly originated from Siberia passing over Northeast Asia and the Japan Sea whereas in summer they mostly originated from the East China Sea and/or the western North Pacific passing over coastal region and/or the Japanese main island. The air parcels were mostly travelled at lower than 2000 m a.g.l. in all seasons.

3 Results and discussion

3.1 Concentrations and compositions

Table 1 presents statistical summaries of water-soluble ions (MSA$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Ca^{2+} and Mg^{2+}) and trace metals (Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb) in TSP samples ($n = 21$) measured in this study. TSP masses that were gravimetrically measured ranged from 13.5 µg m^{-3} to 73.8 µg m^{-3} with an average of 30.0 ± 12.7 µg m^{-3}.

3.1.1 Water-soluble ionic species

Concentrations of SO$_4^{2-}$ ranged from 1560 ng m^{-3} to 5710 ng m^{-3} (average 3470 ± 1020 ng m^{-3} in TSP samples ($n = 21$). SO$_4^{2-}$ was found as the most abundant ionic species throughout the campaign, accounting on average for 43 ± 15 % of the measured total ionic mass. Cl$^-$ (13 ± 12 %), NO$_3^-$ (13 ± 6 %) and Na$^+$ (13 ± 6 %) were found as the second most abundant group followed by NH$_4^+$ (8 ± 5 %), Ca^{2+} (6 ± 2 %), Mg^{2+} (1.8 ± 0.7 %), K$^+$ (1.7 ± 0.4 %) and MSA$^-$ (0.53 ± 0.35 %). It is noteworthy that the mass fraction of sum of inorganic ions in TSP ranged from 20 % to 51 % with an average of 31 ± 10 %, in which SO$_4^{2-}$ accounted for 12 ± 3.8 %.

The predominance of SO$_4^{2-}$ followed by NO$_3^-$ suggests an important contribution from anthropogenic activities to Sapporo aerosols. The second most abundant group of Cl$^-$ and Na$^+$ may suggest that marine emissions are also equally important. However, the contributions from these sources are rather minor as discussed in later sections. Similarly, the third and fourth dominant species NH$_4^+$ and Ca^{2+} indicate a significant contribution from biogenic and/or biomass burning emissions and soil dust, respectively. High concentrations of MSA$^-$ (Table 1), which are comparable to those (range ∼ 10–100 ng m^{-3}) reported in marine (Ayers and Gras, 1991; Mukai et al., 1995; Yang et al., 2009) and forest (Miyazaki et al., 2012) aerosols, further support the significant

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biological (phytoplankton, higher plants and/or soil organisms) contributions during the campaign. It is well known that non-sea-salt contents of ionic species are estimated using the Na^+ as reference for sea-salt, however, we did not estimate them in this study to avoid potential underestimation because Na^+ could be contributed from other sources than the ocean.

3.1.2 Trace metals

Ca was found as the most abundant metal ranging from $196\,ng\,m^{-3}$ to $2920\,ng\,m^{-3}$ (Table 1). Its relative abundance in all the metals detected is $45 \pm 5.2\%$ followed by Fe $(27 \pm 4.5\%)$. Al $(21 \pm 3.1\%)$ was found as the third most abundant followed by Zn $(3.2 \pm 1.7) > Ti > Mn > Ni > Pb > Cu > V > As > Cr > Cd$ (Table 1). The total mass of Al, Ca, Fe, Ti and Mn that mainly originate from the crust accounted for $95 \pm 2\%$ of all the trace metals determined in this study. On average, they accounted for $7.45 \pm 2.09\%$ (range 2.29–10.6%) of TSP. The amount of dust estimated from Al, whose mass ratio relative to the Asian dust is 7% (Zhang et al., 2003), accounted on average for $24 \pm 8\%$ (range 7–36%) of TSP, suggesting that the soil dust is one of the major sources of Sapporo aerosols. On the other hand, Ca concentrations obtained from ICP-MS measurements were always higher by a factor of 1.3–3.2 than water-soluble Ca^{2+} obtained from IC measurements (Table 1). The insoluble fraction accounted for 26–69% (average $51 \pm 11\%$) of total Ca, which may be attributed to the existence of insoluble minerals of Ca such as calcium oxide and feldspar. Similarly, the fourth most abundant Zn and high levels of Cu and Ni suggest that biogenic sources might be important. However, Pb was found to be almost equally abundant together with Ni, indicating that the contributions from anthropogenic activities might also be significant.

3.2 Seasonal variations of ionic species and trace metals

Seasonal variations of ionic species and trace metals are shown in Fig. 2. Seasonal variations of MSA^- and SO_4^{2-} are both characterized by a gradual increase from winter

to mid spring. They remained high until mid summer followed by a gradual decrease to winter, although the trend is not clear in autumn (Fig. 2a). This pattern is similar to that of volatile organic compounds (VOC) emission from vegetation; that is, their emissions are negligible in winter but increased toward the growing season (mid spring to mid summer) (Guenther, 1997). The ambient temperature, which is a key factor to control the BVOC emission, showed a distinct seasonal trend in Sapporo with winter minima and summer maxima (Fig. 1). A similar pattern should prevail in Northeast Asia. Interestingly, seasonal variation of SO_4^{2-} is characterized by an early summer maximum, being different from that of NO_3^- (Fig. 2a), whose concentrations are higher in autumn to spring but lower in summer. The air masses arriving over Sapporo originated from oceanic regions in summer (Pavuluri et al., 2013). These comparisons suggest that biogenic emissions might be a major source of SO_4^{2-} in Sapporo, although we could not preclude anthropogenic activities. Concentrations of Cl^- are higher in autumn to spring than in summer whereas Na^+ and Mg^{2+} peaked in autumn and early spring and minimized in winter as well as in summer (Fig. 2a). The seasonal variations of ions may be significantly influenced by biogenic sources and/or soil dust, in addition to marine contribution.

Concentrations of Ca^{2+} stayed low in autumn and summer and slightly decreased in winter, however peaked in early spring (Fig. 2a). Its concentrations may be associated with wet scavenging by snow in winter when snow precipitation frequency occurred (Fig. 1). Its peak in early spring may be due to the soil dust injection to the atmosphere from the arid regions of Mongolia and Northeast China (Wang et al., 2004; Zhang et al., 2003) followed by a long-range transport. In fact, two massive dust storms occurred in Mongolia and Northeast China in early spring on 20 and 31 March 2010, respectively (http://earthobservatory.nasa.gov). Liu et al. (2011) reported that the dust storm in Mongolia was blown in Beijing, China and the dust storm plume covered over the downwind regions including Hokkaido Island. Although NH_4^+ and K^+ showed seasonal variations, they significantly increased from mid- to late-autumn and stayed relatively high until mid winter. NH_4^+ then showed a gradual decrease toward early spring

whereas K^+ showed a decrease toward late winter followed by an increase in early spring (Fig. 2a). The higher levels of these species during mid autumn to mid winter might be due to significant contributions from forest fires and/or biomass burning on local and/or regional scale whereas the increase of K^+ from late winter to early spring might be associated with the long-range transport of soil dust.

Crustal metals such as Al, Ca, Fe, Ti and Mn did not show any significant seasonal variations, although their concentrations are relatively low in winter (Fig. 2b) probably due to wet scavenging (Fig. 1). They showed a very sharp increase in early spring (1–15 April) followed by a gradual decrease to late autumn (Fig. 2b). Being similar to Ca^{2+}, these trends indicate a significant contribution of soil dust particles that were probably transported from the arid regions in Mongolia and Northeast China. Ni showed a gradual decrease from autumn to mid winter and a gradual increase to early summer followed by a decrease in mid summer (Fig. 2b). This seasonal pattern is comparable to that of VOC emission from vegetation (Guenther, 1997). The seasonal trends of both Cu and As were also quite similar to that of Ni in autumn to mid spring and the rest of the period (Fig. 2b). In fact, Cu has often been considered to be of biological origin and found abundantly present in forest aerosols (Graham et al., 2003). These results suggest that Ni, Cu and even As may mainly be derived from biogenic sources (see Sect. 3.5.4 for further discussion), although they could partly be derived from anthropogenic sources.

Zn has also been considered as a biogenic metal derived from biomass burning (Graham et al., 2003; Pauliquevis et al., 2012). Its concentrations are rather constant in winter to late spring, although a high value was observed in early summer (Fig. 2b). Zn may be derived from biogenic sources at least in spring. V and Cr did not vary significantly in autumn but showed a gradual decrease to winter followed by a sharp increase in early spring. Thereafter V stayed relatively high until late summer whereas Cr decreased gradually to early summer (Fig. 2b). Cr and V may have been significantly contributed from soil dust in early spring and anthropogenic sources in the rest of the

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period. In contrast, Cd and Pb did not show any clear trend throughout the campaign (Fig. 2b), suggesting that they are mainly derived from anthropogenic activities.

3.3 Seasonality in ionic balance and correlations

The equivalent ratios of total cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) to anions (Cl^-, NO_3^- and SO_4^{2-}) ranged from 0.89 to 1.16 with an average of 1.00 ± 0.07 ($n = 21$) and seasonal averages of 1.03 ± 0.09 (autumn, $n = 8$), 0.95 ± 0.02 (winter, $n = 3$), 0.98 ± 0.05 (spring, $n = 5$) and 1.01 ± 0.07 (summer, $n = 5$). Although the overall slope of linear regression line for total cations and anions (Fig. 3) is 0.83 ± 0.03, the slopes for individual seasons are slightly different; 0.67 ± 0.07 in autumn, 0.86 ± 0.08 in winter, 0.86 ± 0.04 in spring and 0.85 ± 0.06 in summer. This result may be caused by a lack of measurements of H^+, HCO_3^-, CO_3^{2-}, PO_4^{3-} and organic acid anions. As discussed in previous section, the seasonal trends of most ionic species showed a distinct seasonal pattern (Fig. 2a), reflecting their source type/strength in each season. Therefore, it is reasonable to consider that the data sets should be grouped seasonally for the analyses of ionic species and their characteristics although the numbers of winter samples are small.

Average NH_4^+/SO_4^{2-} equivalent ratios were 0.36 ± 0.3 (autumn), 1.16 ± 0.09 (winter), 0.47 ± 0.19 (spring) and 0.47 ± 0.14 (summer). These results suggest that the atmospheric NH_3 was not abundant enough to neutralize H_2SO_4, except for winter. In addition, NH_4^+ showed a strong correlation with SO_4^{2-} in summer while the correlations are weak in other seasons (Fig. 4a). Similarly, NH_4^+ showed a good correlation with NO_3^- in autumn and winter (Fig. 4e) and a strong correlation with Cl^- in winter (Fig. 4j) although the correlations are insignificant in other seasons (Fig. 4e, j). Hence, it is likely that SO_4^{2-} and NH_4^+ are present in the forms of H_2SO_4 and/or NH_4HSO_4 in addition to $(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl. On the other hand, both SO_4^{2-} and NO_3^- showed a positive relation with metal species: K^+, Ca^{2+} and Mg^{2+}, except for autumn (they negatively correlate with Mg^{2+}), although the correlations are rather poor (Figs. 4b–d

and f–h). These positive relations suggest that SO_4^{2-} and NO_3^- are associated with metals such as Ca^{2+} and Mg^{2+}. A good correlation between SO_4^{2-} and K^+ in spring (Fig. 4b) may suggest that they were significantly contributed from biogenic emissions (see Sect. 3.5.4 for further discussion).

The equivalent ratios of Cl^-/Na^+ ranged from 0.14 to 1.17 (average 0.72 ± 0.39) in autumn, 1.05–1.54 (1.29 ± 0.25) in winter, 0.14–1.29 (0.76 ± 0.45) in spring and 0.01–0.09 (0.04 ± 0.03) in summer. Cl^- showed a good correlation with Na^+ in winter and spring whereas it was moderate in autumn (Fig. 4i). In summer, there was no relation due to negligible amounts of Cl^-, despite that the summer air masses arriving to Sapporo originated from oceanic regions (Pavuluri et al., 2013). The negligible amounts of Cl^- in summer can be explained by a significant depletion of Cl^- through HCl formation followed by its volatilization from the aerosols during the long-range transport. On the other hand, Cl^- showed a good correlation with NH_4^+ and K^+ in winter. Although the correlation is positive in autumn and spring, the plotted data points are somehow scattered (Fig. 4j, k). These results imply that Cl^- should have been significantly contributed from biomass burning at least in winter that is possibly present in the form of KCl in addition to NH_4Cl and NaCl.

3.4 Factor analysis and source identification

Factor analysis is widely used to identify and apportion the sources of particulate pollutants at receptor sites (Moreno et al., 2011; Pauliquevis et al., 2012). To better characterize the different sources of inorganic ions and trace metals in Sapporo aerosols, varimax rotated factor analysis was conducted here for all the data set using IBM SPSS statistics version 20 for Mac. Five factors were obtained with Eigen values greater than 1 that explain 88 % of the total variance of the data set (Table 2), representing four source categories: (i) soil dust emission, (ii) marine and biological source, (iii) anthropogenic source, and (iv) terrestrial biogenic emission.

3.4.1 Soil dust contributions

The first factor, which accounted for 32.5 % of the total variance, is strongly loaded with Ca^{2+}, Al, Ca, Ti, Mn, and Fe, which are typical crustal components, as well as Cr. Al and Ca/Al and Fe/Al ratios have been widely used as tracers for suspended soil and long-range transport of mineral aerosols (Alfaro et al., 2003). On the other hand, NO_3^-, SO_4^{2-}, Mg^{2+}, V, Ni and As showed moderate loadings (≥ 0.4) whereas MSA^-, Na^+, K^+ and Pb showed minor (≥ 0.2) loadings with factor 1 (Table 2). It is likely that V and Pb are mostly originated from anthropogenic activities whereas biogenic emissions and biomass burning are associated with MSA^-, K^+ and Ni, which should be adsorbed on soil dust particles (Moreno et al., 2011; Pauliquevis et al., 2012). NO_3^-, SO_4^{2-} and As are likely derived from mixed sources of anthropogenic and biogenic emissions (Graham et al., 2003; Nriagu, 1989; Yamasoe et al., 2000). Further, the association of Na^+ and Mg^{2+} with factor 1 can mostly be linked to their minor contributions from soil dust (Guo et al., 2007). Hence, this factor can mainly be attributed to soil dust but the mixed sources of anthropogenic and biogenic emissions may also be associated.

3.4.2 Marine and biological sources

The second factor is strongly loaded with Cl^-, Na^+ and Mg^{2+} that accounted for 19 % of total variance (Table 2). These ions are originated mostly from ocean because Na^+ is emitted from ocean surface; thus factor 2 should be associated with sea-salt emission. On the contrary, NO_3^- that can be produced from fossil fuel combustion and/or biomass burning showed a moderate loading (0.37) with factor 2. HNO_3 may react with alkaline particles such as NaCl, which are present in coarse mode. Seasonal variation of Cl^- is similar to that of NO_3^- (Fig. 2a), suggesting that Cl^- should have significantly been derived from biomass burning in addition to marine emissions. As noted earlier, soil dust might also be a minor source of Na^+ and Mg^{2+}. Na^+ showed a strong ($r = 0.97$ in winter) and good ($r = 0.60$ in spring) correlation with Al, a tracer for crustal origin. Mg^{2+} and Al also showed a correlation in winter ($r = 0.97$) and spring (0.83). These results

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suggest that the soil dust importantly contribute to Na^+ and Mg^{2+} at least in winter and spring. However, Na^+ and Mg^{2+} showed negative relations with Al in autumn ($r = 0.37$ and 0.43, respectively) and summer (0.60 and 0.19, respectively).

Interestingly, Na^+ is most abundant in autumn (Fig. 5), although the peak values in spring are comparable to those in autumn (Fig. 2a). The average and median values of Mg^{2+} in autumn and spring are the same ($0.19\,\mu g\,m^{-3}$), despite the enhanced soil dust contribution in early spring. The abundant Na^+ and Mg^{2+} in autumn suggest a significant contribution from season specific source(s), probably biogenic emissions such as fungi. Fungi can act as biological weathering agents through biomechanical and biochemical processes and play an important role in biogeochemical cycling of nutrients and metals (Burford et al., 2003). Fungal activities on soil surface and plants emit the spores and hyphae, which are enriched with several elements including Na and Mg at significant levels (Burford et al., 2003; Hammer et al., 2011). Their activities on fallen leaves may be increased during defoliation season. In fact, the concentrations of mannitol that is mainly produced by various fungi were found highest in the autumn aerosols ($20.3 \pm 13.3\,ng\,m^{-3}$): winter ($0.42 \pm 0.37\,ng\,m^{-3}$), spring ($2.27 \pm 1.13\,ng\,m^{-3}$) and summer ($7.07 \pm 3.38\,ng\,m^{-3}$) (Pavuluri et al., 2013).

In summer, the air masses that arrived in Sapporo mostly originated from oceanic region and passed over the coastal regions of Japanese Islands. Hence, it is likely that the contributions from marine emissions could be significant in summer. However, the concentrations of both Na^+ and Mg^{2+} were found to be lowest in summer (Fig. 5). This result implies that the biological contribution of these elements is more significant in autumn, winter and spring than summer. However, we cannot preclude some contribution of marine aerosol due to mixing of oceanic air masses with terrestrial air masses along the transport pathway.

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3.4.3 Anthropogenic sources

The fourth factor is found to associate with Cd and Pb, which are most likely derived from the anthropogenic activities. Factor 4 accounted for 13 % of the total variance (Table 2). NO_3^- that can originate from both fossil fuel combustion and biomass burning also showed a significant loading (0.58) with this factor. Hence, this factor can be interpreted as anthropogenic emissions. However, NO_3^- is well correlated with Cl^- as noted earlier, suggesting that these anions may have common origin; biomass burning. In addition, Cr, Zn and As as well as K^+ are all associated with factor 4. As discussed earlier, these elements might be contributed from biogenic/biomass burning emissions, although we could not preclude the input from industrial activities. Nriagu (1989) reported that the biogenic contributions can account for 30–50 % of the total As and several other trace metals. Therefore, factor 4 should be associated with a mixing of biogenic and/or biomass burning emissions as well, although the anthropogenic emissions are major.

3.4.4 Terrestrial biogenic emissions

Factor 3 is loaded with Cu, Ni and As whereas factor 5 is with K^+, Zn and SO_4^{2-} (Table 2). In addition, V showed a moderate loading with both factors whereas NH_4^+ showed a considerable loading with factor 5 (Table 2). It is of interest to note that MSA^-, which is likely produced by the oxidation of DMS originated from phytoplankton, higher plants and soil as well as biomass burning, showed a minor loading (0.24) with factor 5. Ni, Cu, As, Zn and SO_4^{2-} can originate from natural and/or anthropogenic sources (Graham et al., 2003; Moreno et al., 2011; Pauliquevis et al., 2012), whereas K^+ originates only from biomass burning and/or biogenic emissions (Andreae, 1983; Graham et al., 2003). Generally, V is considered as a tracer of oil and coal combustion, however, it has been detected in forest aerosols from the Amazonian atmosphere, which is quite pristine (Graham et al., 2003; Pauliquevis et al., 2012). NH_4^+ originates

mainly from biological sources and/or biomass burning (Graham et al., 2003; Pöhlker et al., 2012).

Ni, Cu and As showed a seasonal trends (Fig. 2a) similar to that of VOC emission from vegetation (Guenther, 1997) as noted earlier. Their seasonal trends are comparable to those of MSA^- (Fig. 2a) and similar to that of mannitol in Sapporo aerosols (Pavuluri et al., 2013), which is considered as a tracer for bioaerosol (Gilardoni et al., 2011). As shown in Fig. 6, Ni, Cu and As positively correlate with mannitol in Sapporo aerosols (r^2 = 0.33, 0.47 and 0.28, and p = 0.006, 0.001 and 0.013, respectively). In contrast, the tracers for combustion sources; (i) hopanes (C_{27}–C_{32} hopanoid hydrocarbons), specific biomarkers of petroleum and coal (Schauer et al., 2002 and references therein), (ii) levoglucosan, an excellent marker for biomass burning (Simoneit, 2002), and (iii) elemental carbon (EC) that is derived from combustion sources, did not show any significant seasonal trend in Sapporo aerosols (Pavuluri et al., 2013). It is also of interest to note that Ni, Cu and As showed negligible correlations with EC (r^2 = 0.03, 0.08 and 0.18, respectively) and even negative correlations with hopanes (r^2 = 0.22, 0.01 and 0.001, respectively) and levoglucosan (r^2 = 0.25, 0.03 and 0.03, respectively).

Zn also showed a gradual increase from winter minimum to late spring maximum although its level was relatively stable in summer and autumn, except for a sporadic peak in early summer (Fig. 2b). We found a positive correlation (r^2 = 0.60) between Zn and sucrose whereas weak or negligible correlations with hopanes (r^2 = 0.24), levoglucosan (r^2 = (−)0.001) and EC (r^2 = 0.12) in Sapporo spring aerosols (Pavuluri et al., 2013). Because sucrose is a tracer for pollens derived from terrestrial plants (Fu et al., 2012), this result suggests that Zn is emitted from the terrestrial biota to the atmosphere in spring although no relation was found in other seasons. Sucrose was abundantly detected in spring aerosols from Sapporo (Pavuluri et al., 2013). It is noteworthy that the association of Ni and Cu and Zn with different factors (Table 2) is similar to that reported in forest aerosols (Graham et al., 2003), in which both Cu and Zn are attributed for biological matter. These results and comparisons imply that Ni, Cu, As and Zn and

even V should have been derived from different types of biological sources rather than anthropogenic activities.

On the other hand, K^+ in winter showed a strong correlation ($r^2 = 0.97$) with levoglucosan but the correlation was weak ($r^2 = 0.22$) in autumn and no relation was found in other two seasons. The average concentration of K^+ (Table 1) is comparable to those in forest aerosols from Balbina, Central Amazonia (up to $140 \pm 88\,\mathrm{ng\,m^{-3}}$ in fine mode during dry season), where local biomass burning is insignificant and long-range transported biomass burning aerosol is not severe (Pauliquevis et al., 2012). Orsini et al. (1982) reported a strong correlation between S and K in fine particles from a remote site in the Amazon forest, which they interpreted by gas-to-particle conversion of gases emitted from higher plants. Pöhlker et al. (2012) detected K-rich particles in the Amazon forest and attributed to biogenic primary emissions particularly of fungal spores. In addition, SO_4^{2-} showed a linear relation with MSA^- (Fig. 7), which has been widely used as a tracer to estimate the biogenic $nss\text{-}SO_4^{2-}$ (Bates et al., 1992; Kouvarakis et al., 2002; Mihalopoulos et al., 1997; Yang et al., 2009). Although the correlation varies from season to season ($r^2 = 0.35$ in autumn, 0.05 in winter, 0.25 in spring and 0.12 in summer), these results suggest that the SO_4^{2-} is significantly derived from biological sources throughout the year.

3.5 Implication of sulfur species for terrestrial biogenic emissions

3.5.1 Enrichment of MSA^- and SO_4^{2-} in spring/summer

As shown in Fig. 8, both MSA^- and SO_4^{2-} were abundant in summer followed by spring. Their concentrations were lowest in winter. Average concentrations of MSA^- were 27.4 ± 8.3, 21.9 ± 5.5, 49.2 ± 20.2 and $64.4 \pm 14.5\,\mathrm{ng\,m^{-3}}$ in autumn, winter, spring and summer, respectively whereas those of SO_4^{2-} were 2.96 ± 0.77, 2.65 ± 0.09, 3.81 ± 0.50 and $4.45 \pm 1.26\,\mathrm{\mu g\,m^{-3}}$. Abundant MSA^- and biogenic SO_4^{2-} were reported in the marine and coastal atmospheres during summertime, which were attributed to the

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enhanced emission of DMS from phytoplankton bloom followed by the subsequent oxidation (Gaston et al., 2010; Legrand and Pasteur, 1998; Mihalopoulos et al., 1997). On the other hand, higher plants and soils as well as biomass burning could emit gaseous sulfur species including DMS (Geng and Mu, 2006; Meinardi et al., 2003; Yi et al., 2010) and may contribute to the atmospheric budget of MSA^- and SO_4^{2-}. VOC emission from vegetation is higher in growing season and lower in winter (Guenther, 1997). Recently, Miyazaki et al. (2012) reported significantly high levels of MSA^-, with a maximum during May and July, in the forest aerosols collected at two levels (~ 2 m and ~ 15 m) of the experimental forest in Sapporo, where the canopy height is ~ 20 m.

MSA^- was found to inversely correlate with Na^+ during the campaign ($n = 21$). A strong anti-correlation ($r^2 = 0.42$) was found in summer when the air masses arriving in Sapporo originated mostly from oceanic regions (Pavuluri et al., 2013). Interestingly, a negative correlation was found between MSA^- and levoglucosan during the whole campaign. A strong anti-correlation was found in autumn ($r^2 = 0.32$) and winter ($r^2 = 0.34$) when levoglucosan became more abundant (Pavuluri et al., 2013). Further, the concentration range of MSA^- (Table 1) is comparable to that ($9-95$ ng m^{-3}) in the forest aerosols in Sapporo (Miyazaki et al., 2012). As noted earlier, MSA^- showed a gradual increase from winter to growing season followed by a gradual decrease to autumn (Fig. 2a). In autumn, the microbial activities on surface soil and fallen leaves may be significant, while MSA^- did not show any seasonal trend (Fig. 2a). Hence, it is more likely that MSA^- in Sapporo aerosols should have been produced from DMS that mainly originated from higher plants and soil organisms rather than phytoplankton in the ocean and biomass burning in the continent.

Sulfate also showed a negative correlation with Na^+, being similar to the case of MSA^-. This result suggests that SO_4^{2-} should have same or similar origin with MSA^-: terrestrial biogenic emissions. No correlation ($r^2 = 0.03$) was found between SO_4^{2-} and levoglucosan although anti-correlations were found between MSA^- and levoglucosan ($r^2 = 0.32$) in autumn. The negative correlation between SO_4^{2-} and Na^+ become stronger ($r^2 = 0.75$) than that between MSA^- and Na^+ ($r^2 = 0.42$) in summer. The

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differences in season-specific relations further suggest that biomass burning emissions might be a minor source of SO_4^{2-} in autumn but significant in winter whereas marine emissions might be a minor source of MSA^- in summer.

3.5.2 Molar ratios of MSA^- and SO_4^{2-} and their relation with temperature

The molar ratios of MSA^- to SO_4^{2-} can provide an indication of the relative contributions of DMS and anthropogenic sources to SO_4^{2-} (Gondwe et al., 2004). The ratios ranged from 0.49 % to 2.47 % (average 1.16 ± 0.45 %) with seasonal averages of 0.95 ± 0.22 % (autumn), 0.84 ± 0.22 % (winter), 1.30 ± 0.46 % (spring) and 1.55 ± 0.56 % (summer). These values should be considered as lower ends because both the sea-salt SO_4^{2-} and a possible anthropogenic SO_4^{2-} are not excluded here. It is noteworthy that the average MSA^-/SO_4^{2-} molar ratio in Sapporo summer aerosols is thrice to that (0.55 %) reported in the summer aerosols from the North Yellow Sea, China (Yang et al., 2009), where the continental outflow of anthropogenic emissions is significant. The average concentration of MSA^- (64 $ng\,m^{-3}$) in Sapporo summer aerosols is also significantly higher than that (39 $ng\,m^{-3}$) in the Yellow Sea, China (Yang et al., 2009). These comparisons again support that SO_4^{2-} in Sapporo aerosols should have significantly been derived from terrestrial biological sources.

Finally, we examine the relationship of MSA^-/SO_4^{2-} molar ratios with the ambient temperatures. The ratios showed a linear relation during the campaign with a moderate correlation (Fig. 9), which is opposite to a general trend reported in the marine atmosphere: that is, the $MSA^-/nss\text{-}SO_4^{2-}$ molar ratio is inversely related with the temperature (Bates et al., 1992; Gondwe et al., 2004). It is well known that DMS oxidation can be initiated either by addition of OH radical to the sulfur atom or abstraction of a proton from the CH_3 group by OH that lead to produce MSA^- and SO_4^{2-}, respectively. The former is favored at lower temperatures whereas the later is favored at higher temperatures (Bates et al., 1992; Gondwe et al., 2004; Ravishankara et al., 1997). However, such temperature dependency is diminished when the atmospheric

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loading of NO_3 is significant because the NO_3 can also initiate the DMS oxidation that leads to the production of CH_3S intermediate, which eventually forms either MSA^- or SO_4^{2-} (Ravishankara et al., 1997).

In fact, NO_3^- concentrations were significant in Sapporo aerosols (Table 1) and hence, the NO_3-initiated oxidation of DMS and subsequent oxidation of intermediate compounds during the long-rang transport should have played a prominent role, resulting in a linear relation between MSA^-/SO_4^{2-} molar ratios and temperatures. Similar positive relation between $MSA^-/nss\text{-}SO_4^{2-}$ molar ratios and temperatures has been reported in several long-term aerosol studies in the Southern Hemisphere (Ayers et al., 1991; Legrand and Pastuer, 1998) and attributed to various parameters such as oxidant concentrations, relative humidity and aging during the long-range transport. It should also be noted that the MSA^-/SO_4^{2-} molar ratios are inversely related with temperatures in winter ($r^2 = 0.99$). Such a inverse relation may be driven by colder weather in winter (Fig. 1). Thus, this study implies that the sulfur species ($MSA^-/nss\text{-}SO_4^{2-}$) in Sapporo aerosols may be long-range transported in the atmosphere from terrestrial biological sources in Northeast Asia.

4 Summary and conclusions

Atmospheric aerosol (TSP) samples collected from Sapporo, northern Japan for one-year period, were studied for water-soluble ionic species and trace metals using ion chromatograph (IC) and inductively coupled plasma mass spectrometry (ICP-MS). SO_4^{2-} was found as the most abundant ion whereas Ca was the most abundant metal. The mass fraction of sum of inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) in TSP ranged from 20 % to 51 % with an average of 31 ± 10 %, in which SO_4^{2-} accounted for 12 ± 3.8 %. The group of crustal elements (Al, Ca, Fe, Ti and Mn) alone accounted for 95 ± 2 % of the total mass of the metals determined. The seasonal trends of MSA^- and SO_4^{2-} as well as Ni, Cu and even As showed maxima in growing season,

while crustal elements including Na^+, Ca^{2+} and Mg^{2+} peaked in early spring. On the other hand, Cl^- and NO_3^- became abundant from mid autumn to early spring whereas NH_4^+ and K^+ became abundant from mid autumn to mid winter. Na^+ and Mg^{2+} were abundant in autumn while Zn showed a gradual increase from winter to late spring. Cd and Pd did not show any clear seasonal trend, staying relatively constant throughout the year.

We found that Ni, Cu and As positively correlate with mannitol (a tracer for fungal spores), while Zn positively correlates with sucrose (tracer of pollen) in spring. Similarly, K^+ showed linear relation with levoglucosan (a tracer of biomass burning) in autumn and winter. MSA^- and SO_4^{2-}, which positively correlate, are inversely correlated with Na^+. These results together with air mass trajectories imply that the long-range atmospheric transport of soil dust, terrestrial biogenic emissions including microbial activities, and biomass burning are major sources of Sapporo aerosols although anthropogenic emissions and sea-salt emissions are minor sources of atmospheric aerosols in Northeast Asia. In addition, the seasonality of the source strength is significant, except for anthropogenic emissions. This study suggests the importance of terrestrial biological contributions to inorganic aerosols and their climatic impacts on regional to global scale.

References

Agarwal, S., Aggarwal, S. G., Okuzawa, K., and Kawamura, K.: Size distributions of dicarboxylic acids, ketoacids, α-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in atmospheric particles over Northern Japan: implication for long-range transport of Siberian biomass burning and East Asian polluted aerosols, Atmos. Chem. Phys., 10, 5839–5858, doi:10.5194/acp-10-5839-2010, 2010.

Aggarwal, S. G. and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: implications for photochemical aging during long-range atmospheric transport, J. Geophys. Res., 113, D14301, doi:10.1029/2007JD009365, 2008.

Aggarwal, S. G. and Kawamura, K.: Carbonaceous and inorganic composition in long-range transported aerosols over northern Japan: implication for aging of water-soluble organic fraction, Atmos. Environ., 43, 2532–2540, 2009.

Alfaro, S. C., Gomes, L., Rajot, J. L., Lafon, S., Gaudichet, A., Chaenet, B., Maille, M., Cautenet, G., Lasserre, F., Cachier, H., and Zhang, X. Y.: Chemical and optical characterization of aerosols measured in spring 2002 at the ACE-Asia supersite, Zhenbeitai, China, J. Geophys. Res., 108, 8641, doi:10.1029/2002JD003214, 2003.

Andreae, M. O.: Soot carbon and excess fine potassium: long-range transport of combustion-derived aerosols, Science, 220, 1148–1151, 1983.

Andres, R. J. and Kasgnoc, A. D.: A time-averaged inventory of subaerial volcanic sulfur emissions, J. Geophys. Res., 103, 25251–25261, 1998.

Ayers, G. P. and Gras, J. L.: Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air, Nature, 353, 834–835, 1991.

Ayers, G. P., Ivey, J. P., and Gillet, R. W.: Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulfate in marine air, Nature, 349, 404–406, 1991.

Bates, T. S., Calhoun, J. A., and Quinn, P. K.: Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosol particles over the South Pacific Ocean, J. Geophys. Res., 97, 9859–9865, 1992.

Baustian, K. J., Cziczo, D. J., Wise, M. E., Pratt, K. A., Kulkarni, G., Hallar, A. G., and Tolbert, M. A.: Importance of aerosol composition, mixing state, and morphology for heterogeneous ice nucleation: a combined field and laboratory approach, J. Geophys. Res., 117, D06217, doi:10.1029/2011JD016784, 2012.

Burford, E. P., Fomina, M., and Gadd, G. M.: Fungal involvement in bioweathering and biotransformation of rocks and minerals, Meneral. Mag., 67, 1127–1155, 2003.

Carmichael, G. R., Adhikary, B., Kulkarni, S., D'Allura, A., Tang, Y., Streets, D., Zhang, Q., Bond, T. C., Ramanathan, V., Jamroensan, A., and Marrapu, P.: Asian aerosols: current and year 2030 distributions and implications to human health and regional climate change, Environ. Sci. Technol., 43, 5811–5817, 2009.

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Déandreis, C., Balkanski, Y., Dufresne, J. L., and Cozic, A.: Radiative forcing estimates of sulfate aerosol in coupled climate-chemistry models with emphasis on the role of the temporal variability, Atmos. Chem. Phys., 12, 5583–5602, doi:10.5194/acp-12-5583-2012, 2012.

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J., and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869–26889, 1996.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL READY Website (http://ready.arl.noaa.gov/HYSPLIT.php), NOAA Air Resources Laboratory, Silver Spring, MD, 2012.

Fu, P. Q., Kawamura, K., Pavuluri, C. M., Swaminathan, T., and Chen, J.: Molecular characterization of urban organic aerosol in tropical India: contributions of primary emissions and secondary photooxidation, Atmos. Chem. Phys., 10, 2663–2689, doi:10.5194/acp-10-2663-2010, 2010.

Fu, P., Kawamura, K., Kobayashi, M., and Simoneit, B. R. T.: Seasonal variations of sugars in atmospheric particulate matter from Gosan, Jeju Island: significant contributions of airborne pollen and Asian dust in spring, Atmos. Environ., 55, 234–239, 2012.

Gaston, C. J., Pratt, K. A., Qin, X., and Prather, K. A.: Real-time detection and mixing state of methanesulfonate in single particles at an inland urban location during a phytoplankton bloom, Environ. Sci. Technol., 44, 1566–1572, 2010.

Geng, C. and Mu, Y.: Carbonyl sulfide and dimethyl sulfide exchange between trees and the atmosphere, Atmos. Environ., 40, 1373–1383, 2006.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenström, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined ^{14}C – macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685–5700, doi:10.5194/acp-11-5685-2011, 2011.

Gondwe, M., Krol, M., Klaassen, W., Gieskes, W., and de Baar, H.: Comparison of modeled versus measured MSA : nss-SO$_4^=$ ratios: a global analysis, Global Biogeochem. Cy., 18, GB2006, doi:10.1029/2003GB002144, 2004.

Goodman, A. L., Underwood, G. M., and Grassian, V. H.: A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles, J. Geophys. Res., 105, 29053–29064, 2000.

Graham, B., Guyon, P., Maenhaut, W., Taylor, P. E., Ebert, M., Matthias-Maser, S., Mayol-Bracero, O. L., Godoi, R. H. M., Artaxo, P., Meixner, F. X., Lima Moura, M. A., Eca D'Almeida

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Guenther, A.: Seasonal and spatial variations in natural volatile organic compound emissions, Ecol. Appl., 7, 34–45, 1997.

Guo, X.-Y., Zhao, W.-W., Huang, M., Zheng, H.-Y., Fang, L., and Zhang, W.-J.: Single particle analysis of soil dust by aerosol time-of-flight laser mass spectrometry, Opt. Appl., 37, 229–235, 2007.

Hammer, E. C., Nasr, H., Pallon, J., Olsson, P. A., and Wallander, H.: Elemental composition of arbuscular mycorrhizal fungi at high salinity, Mycorrhiza, 21, 117–129, 2011.

Huang, Y., Dickinson, R. E. and Chameides, W. L.: Impact of aerosol indirect effect on surface temperature over East Asia, P. Natl. Acad. Sci. USA, 103, 4371–4376, 2006.

Huebert, B. J., Bates, T., Russell, P. B., Shi, G., Kim, Y. J., Kawamura, K., Carmichael, G., and Nakajima, T.: An overview of ACE-Asia: strategies for quantifying the relationships between Asian aerosols and their climatic impacts, J. Geophys. Res., 108, 8633, doi:10.1029/2003JD003550, 2003.

Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in: Geochemical Investigations in Earth and Space Science: a Tribute to Isaac R. Kaplan, edited by: Hill, R. J., Leventhal, J., Aizenshtat, Z., Baedecker, M. J., Claypool, G., Eganhouse, R., Goldhaber, M., and Peters, K., The Geochemical Society, Publication No. 9, 243–265, 2004.

Kouvarakis, G., Bardouki, H., and Mihalopoulos, N.: Sulfur budget above the Eastern Mediterranean: relative contribution of anthropogenic and biogenic sources, Tellus B, 54, 201–212, 2002.

Legrand, M. and Pasteur, E. C.: Methane sulfonic acid to non-sea-salt sulfate ratio in coastal Antarctic aerosol and surface snow, J. Geophys. Res., 103, 10991–11006, 1998.

Li-Xia, J. and Zhi-Wei, H.: Direct radiative forcing and climatic effects of aerosols over East Asia by RegCM3, Atmos. Ocean. Sci. Lett., 4, 363–367, 2011.

Liu, Z., Liu, Q., Lin, H.-C., Schwartz, C. S., Lee, Y.-H., and Wang, T.: Three-dimensional variational assimilation of MODIS aerosol optical depth: implementation and application to a dust storm over East Asia, J. Geophys. Res., 116, D23206, doi:10.1029/2011JD016159, 2011.

Maenhaut, W., Fernández-Jiménez, M.-T., Rajta, I., and Artaxo P.: Two-year study of atmospheric aerosols in Alta Floresta, Brazil: multielemental composition and source apportionment, Nucl. Instrum. Meth. B, 189, 243–248, 2002.

Meinardi, S., Simpson, I. J., Blake, N. J., Blake, D. R., and Rowland, F. S.: Dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) emissions from biomass burning in Australia, Geophys. Res. Lett., 30, 1454, doi:10.1029/2003GL016967, 2003.

Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P.: Tropospheric aerosol ionic composition in the Eastern Mediterranean region, Tellus B, 49, 314–326, 1997.

Miyazaki, Y., Fu, P. Q., Kawamura, K., Mizoguchi, Y., and Yamanoi, K.: Seasonal variations of stable carbon isotopic composition and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, Atmos. Chem. Phys., 12, 1367–1376, doi:10.5194/acp-12-1367-2012, 2012.

Moore, J., Kekonen, T., Grinsted, A., and Isaksson, E.: Sulfate source inventories from a Svalbard ice core record spanning the Industrial Revolution, J. Geophys. Res., 111, D15307, doi:10.1029/2005JD006453, 2006.

Moreno, T., Querol, X., Alastuey, A., Reche, C., Cusack, M., Amato, F., Pandolfi, M., Pey, J., Richard, A., Prévôt, A. S. H., Furger, M., and Gibbons, W.: Variations in time and space of trace metal aerosol concentrations in urban areas and their surroundings, Atmos. Chem. Phys., 11, 9415–9430, doi:10.5194/acp-11-9415-2011, 2011.

Mukai, H., Yokouchi, Y. and Suzuki, M.: Seasonal variation of methanesulfonic acid in the atmosphere over the Oki Islands in the Sea of Japan, Atmos. Environ., 29, 1637–1648, 1995.

Nakajima, T., Yoon, S.-C., Ramanathan, V., Shi, G.-Y., Takemura, T., Higurashi, A., Takamura, T., Aoki, K., Sohn, B.-J., Kim, S.-W., Tsuruta, H., Sugimoto, N., Shimizu, A., Tanimoto, H., Sawa, Y., Lin, N.-H., Lee, C.-T., Goto, D., and Schutgens, N.: Overview of the atmospheric brown cloud East Asian regional experiment 2005 and a study of the aerosol direct radiative forcing in East Asia, J. Geophys. Res., 112, D24S91, doi:10.1029/2007JD009009, 2007.

Nel, A.: Air pollution-related illness: effects of particles, Science, 308, 804–806, 2005.

Nriagu, J. O.: A global assessment of natural sources of atmospheric trace metals, Nature, 338, 47–49, 1989.

Oduro, H., Van Alstyne, L. L., and Farquhar, J.: Sulfur isotope variability of oceanic DMSP generation and its contributions to marine biogenic sulfur emissions, P. Natl. Acad. Sci. USA, 109, 9012–9016, 2012.

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Orsini, C. Q., Netto, P. A., and Tabacniks, M. H.: Preliminary data on atmospheric aerosol of the Amazon Basin, Atmos. Environ., 16, 2177–2181, 1982.

Pauliquevis, T., Lara, L. L., Antunes, M. L., and Artaxo, P.: Aerosol and precipitation chemistry measurements in a remote site in Central Amazonia: the role of biogenic contribution, Atmos. Chem. Phys., 12, 4987–5015, doi:10.5194/acp-12-4987-2012, 2012.

Pavuluri, C. M., Kawamura, K., Kikuta, M., Tachibana, E., and Aggarwal, S. G.: Time-resolved variations in the distributions of inorganic ions, carbonaceous components, dicarboxylic acids and related compounds in atmospheric aerosols from Sapporo, northern Japan during summertime, Atmos. Environ., 62, 622–630, 2012.

Pavuluri, C. M., Kawamura, K., Uchida, M., Kondo, M., and Fu, P.: Enhanced modern carbon and biogenic organic tracers in Northeast Asian aerosols during spring/summer, J. Geophys. Res., doi:10.1002/jgrd.50244, in press, 2013.

Pöhlker, C., Wiedemann, K. T., Sinha, B., Shiraiwa, M., Gunthe, S. S., Smith, M., Su, H., Artaxo, P., Chen, Q., Cheng, Y., Elbert, W., Gills, M. K., Kilcoyne, A. L. D., Moffet, R. C., Weigand, M., Martin, S. T., Pöschl, U., and Andreae, M. O.: Biogenic potassium salt particles as seeds for secondary organic aerosol in the Amazon, Science, 337, 1075–1078, 2012.

Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects, Angew. Chem., 44, 7520–7540, 2005.

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhalov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., and Andreae, M. O.: Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, Science, 329, 1513–1516, 2010.

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Aerosols, climate, and hydrological cycle, Science, 294, 2119–2124, 2001.

Ravishankara, A. R., Rudich, Y., Talukdar, R. and Barone, S. B.: Oxidation of atmospheric reduced sulphur compounds: perspective from laboratory studies, Philos. T. Roy. Soc. London B, 352, 171–182, 1997.

Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N., Andreae, M. O., Maenhaut, W., and Sarda-Estève, R.: Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign, Atmos. Chem. Phys., 5, 2253–2265, doi:10.5194/acp-5-2253-2005, 2005.

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Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R.: Measurement of emissions from air pollution sources, 5. C_1–C_{32} organic compounds from gasoline-powered motor vehicles, Environ. Sci. Technol., 36, 1169–1180, 2002.

Schaumann, F., Born, P. J. A., Herbrich, A., Knoch, J., Pitz, M., Schins, P. F., Luettig, B., Hohfeld, J. M., Heinrich, J., and Krug, N.: Metal-rich ambient particles ($PM_{2.5}$) cause airway inflammation in healthy subjects, Am. J. Respir. Crit. Care Med., 170, 898–903, 2004.

Simoneit, B. R. T.: Biomass burning – a review of organic tracers for smoke from incomplete combustion, Appl. Geochem., 17, 129–162, 2002.

Smith, S. J., van Aardenne, J., Klimont, Z., Andres, R. J., Volke, A., and Delgado Arias, S.: Anthropogenic sulfur dioxide emissions: 1850–2005, Atmos. Chem. Phys., 11, 1101–1116, doi:10.5194/acp-11-1101-2011, 2011.

Su, X.-T., Wang, H.-J., and Zhang, Z.-B.: Radiative forcing and temperature response of dust aerosols over East Asia in the last decade, Sci. Cold Arid Reg., 4, 0351–0356, 2012.

Theodosi, C., Markaki, Z., Tselepides, A., and Mihalopoulos, N.: The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater, Mar. Chem., 120, 154–163, 2010.

Uno, I., Eguchi, K., Yumimoto, K., Liu, Z., Hara, Y., Sugimoto, N., Shimizu, A., and Takemura, T.: Large Asian dust layers continuously reached North America in April 2010, Atmos. Chem. Phys., 11, 7333–7341, doi:10.5194/acp-11-7333-2011, 2011.

Van Malderen, H., Van Grieken, R., Khodzher, T., Obolkin, V., and Potemkin, V.: Composition of individual aerosol particles above lake Baikal, Siberia, Atmos. Environ., 30, 1453–1465, 1996.

Wang, X., Dong, Z., Zhang, J., and Liu, L.: Modern dust storms in China: an overview, J. Arid Environ., 58, 559–574, 2004.

Yamamoto, S., Kawamura, K., and Seki, O.: Long-range atmospheric transport of terrestrial biomarkers by the Asian winter monsoon: evidence from fresh snow from Sapporo, northern Japan, Atmos. Environ., 45, 3553–3560, 2011.

Yamasoe, M. A., Artaxo, P., Miguel, A. H., and Allen, A. A.: Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements, Atmos. Environ., 34, 1641–1653, 2000.

Yang, G.-P., Zhang, H.-H., Su, L.-P., and Zhou, L.-M.: Biogenic emission of dimethylsulfide (DMS) from the North Yellow Sea, China and its contribution to sulfate in aerosol during summer, Atmos. Environ., 43, 2196–2203, 2009.

Yi, Z., Wang, X., Ouyang, M., Zhang, D., and Zhou, G.: Air-soil exchange of dimethyl sulfide, carbon disulfide, and dimethyl disulfide in three subtropical forests in south China, J. Geophys. Res., 115, D18302, doi:10.1029/2010JD014130, 2010.

Zhang, Q., Meng, J., Quan, J., Gao, Y., Zhao, D., Chen, P., and He, H.: Impact of aerosol composition on cloud condensation nuclei activity, Atmos. Chem. Phys., 12, 3783–3790, doi:10.5194/acp-12-3783-2012, 2012.

Zhang, X. Y., Gong, S. L., Shen, Z. X., Mei, F. M., Xi, X. X., Liu, L. C., Zhou, Z. J., Wang, D., Wang, Y. Q., and Cheng, Y.: Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 1. Network observations, J. Geophys. Res., 108, D94261, doi:10.1029/2002JD002632, 2003.

Table 1. Statistical summary for the concentrations ($ng\,m^{-3}$) of water-soluble ionic species and trace metals in atmospheric aerosol (TSP) samples ($n = 21$) collected from Sapporo, northern Japan during 2 September 2009 to 5 October 2010.

	Range	Median/Average	Standard Deviation
Water-soluble ionic species			
MSA^-	15.6–83.4	34.8/40.6	20.8
Cl^-	12.0–3850	929/1290	1250
NO_3^-	183–2670	1248/1200	728
SO_4^{2-}	1556–5710	3494/3470	1030
Na^+	294–2140	933/1070	547
NH_4^+	68.8–1260	78.1/68.6	42.3
K^+	94.5–233	139/144	40.6
Ca^{2+}	139–1564	471/507	295
Mg^{2+}	57.5–299	128/152	68.1
Trace metals			
Al	64.8–1830	475/532	372
Ca	196–2920	938/1070	578
Ti	4.03–82.8	30.6/31.7	16.3
V	0.39–9.40	3.15/3.42	2.12
Cr	0.18–4.35	2.41/2.36	0.88
Mn	3.61–51.8	19.8/19.9	10.3
Fe	40.7–1990	652/684	406
Ni	2.36–18.5	11.4/11.4	3.77
Cu	1.95–18.9	9.88/11.0	4.20
Zn	21.8–189	57.1/66.3	34.0
As	0.74–3.80	2.41/2.44	0.80
Cd	0.074–0.43	0.19/0.22	0.10
Pb	3.56–19.0	9.74/10.8	4.47

Table 2. Varimax rotated factor loadings for water-soluble ionic species and trace metals in the Sapporo TSP samples ($n = 21$) during the campaign.

Variable	Factor				
	1	2	3	4	5
MSA^-	0.23	−0.74	0.07	−0.26	0.24
Cl^-	0.19	0.87	−0.36	−0.01	0.13
NO_3^-	0.44	0.37	−0.45	0.58	−0.03
SO_4^{2-}	0.36	−0.65	0.01	−0.02	0.60
Na^+	0.23	0.96	0.15	0.02	0.03
NH_4^+	−0.15	−0.47	−0.66	0.27	0.36
K^+	0.22	0.14	−0.19	0.30	0.83
Ca^{2+}	0.95	0.13	−0.02	−0.02	0.18
Mg^{2+}	0.47	0.83	0.19	0.04	0.13
Al	0.98	0.01	0.11	0.03	0.10
Ca	0.94	0.10	0.21	0.06	0.06
Ti	0.95	−0.06	0.18	0.08	0.01
V	0.44	−0.57	0.35	−0.14	0.40
Cr	0.68	0.17	0.13	0.30	0.22
Mn	0.94	0.04	0.16	0.23	0.13
Fe	0.97	0.01	0.13	0.16	0.09
Ni	0.30	−0.09	0.80	−0.25	0.02
Cu	0.10	−0.12	0.89	0.28	−0.01
Zn	0.11	−0.20	0.29	0.40	0.63
As	0.31	0.04	0.75	0.34	0.18
Cd	0.10	0.18	0.01	0.90	0.23
Pb	0.22	−0.03	0.17	0.91	0.19
Eigenvalue	8.52	4.47	3.07	2.36	1.03
% of Variance	32.47	18.95	14.69	12.86	9.39
Cumulative %	32.47	51.42	66.11	78.97	88.36
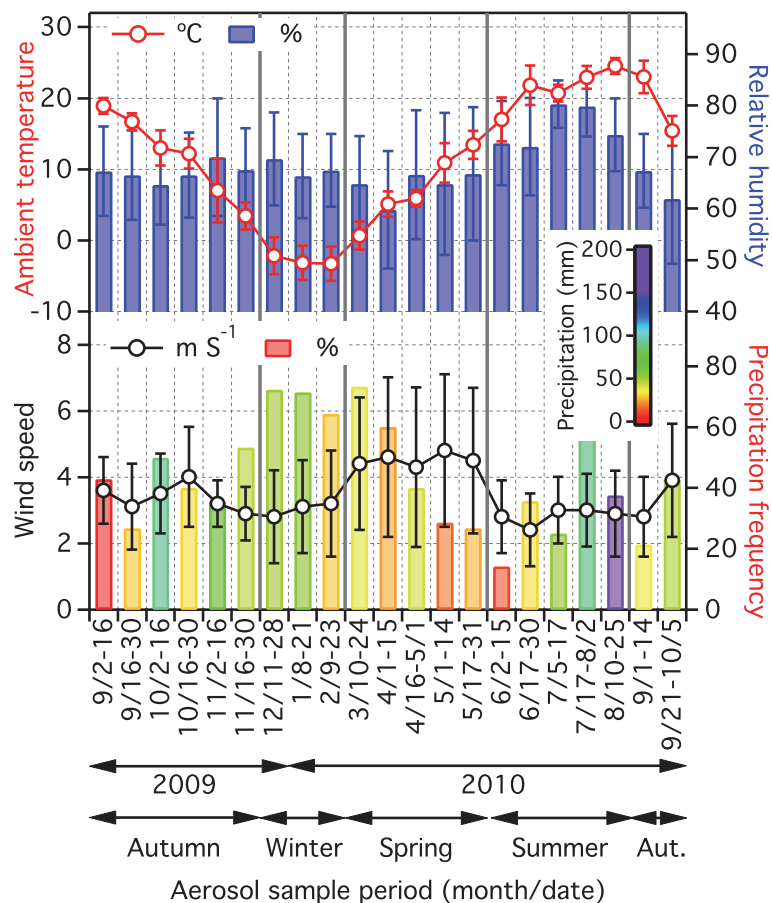
Fig. 1. Seasonal variations of meteorological parameters (ambient temperature, RH, wind speed and precipitation) in Sapporo, northern Japan.
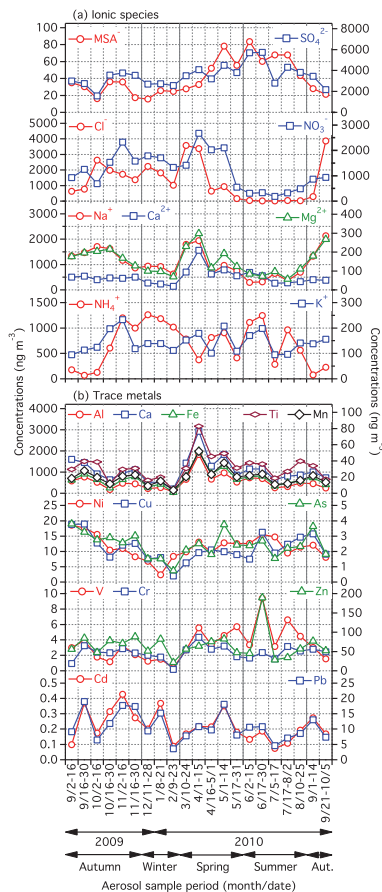
Fig. 2. Seasonal variations of **(a)** water-soluble ionic species (methanesulfonate (MSA$^-$); inorganic anions: SO_4^{2-}, Cl$^-$ and NO_3^-; inorganic cations: Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$ and K$^+$) and **(b)** trace metals (Al, Ca, Fe, Ti, Mn, Ni, Cu, As, V, Cr, Zn, Cd and Pb) in atmospheric aerosol (TSP) samples collected from Sapporo, northern Japan.

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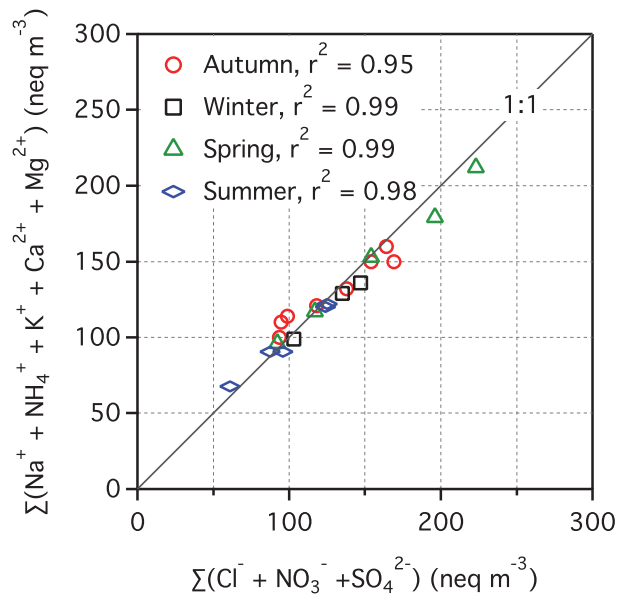
Fig. 3. Correlation plots for the summed equivalent concentrations of inorganic cations and anions in the Sapporo aerosols for autumn (September to November), winter (December–February), spring (March–May) and summer (June–August).
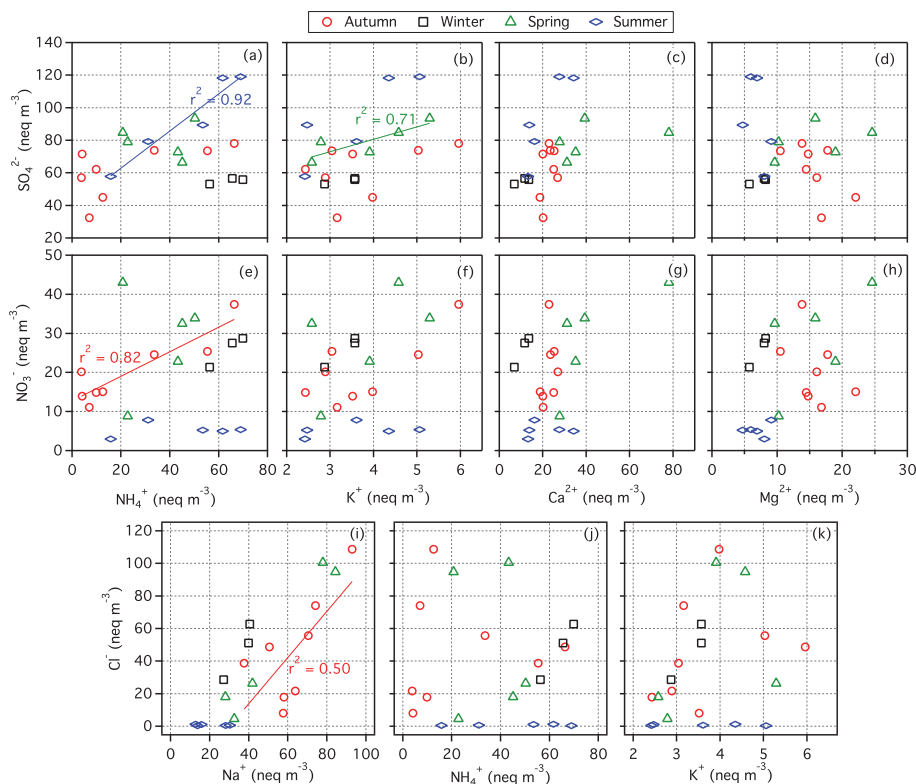
Fig. 4. Scatter plots for equivalent concentrations of individual cations (NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and anions (SO_4^{2-}, NO_3^- and Cl^-) in the Sapporo aerosols for autumn, winter, spring and summer.

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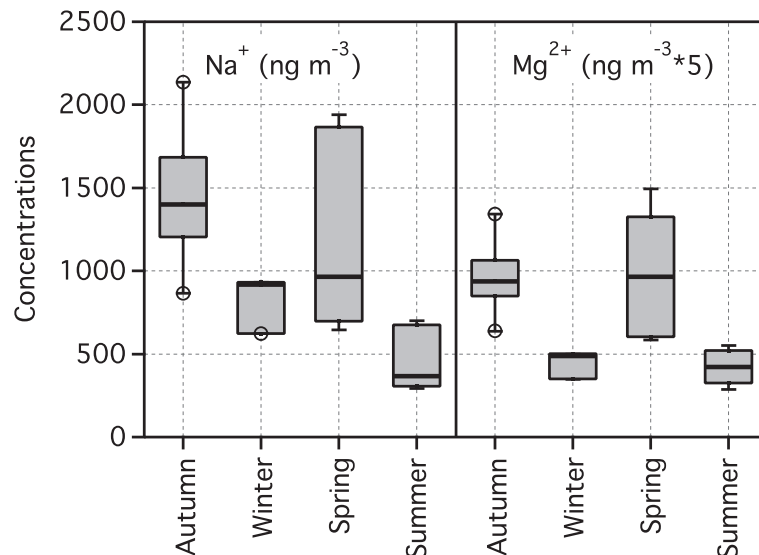
Fig. 5. Box-and-whisker plots of Na^+ and Mg^{2+} in autumn, winter, spring and summer. Lower and upper ends of the box show the quartiles at 25 % and 75 % whereas upper and lower bars of the whiskers present the quartiles at 10 % and 90 %. The cross bar in the box shows the median. Open circles mean outliers (1.25 × interquartile distance).
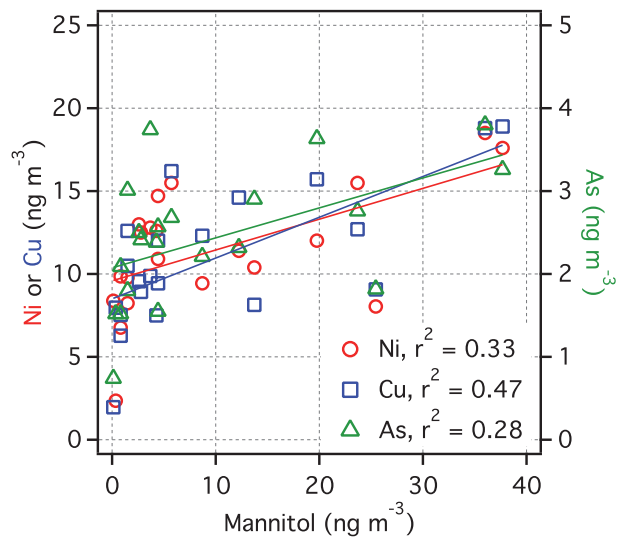
Fig. 6. Scatter plots of the concentrations of Ni, Cu and As as a function of the concentrations of mannitol in the Sapporo aerosols. The data of mannitol are from Pavuluri et al. (2013).
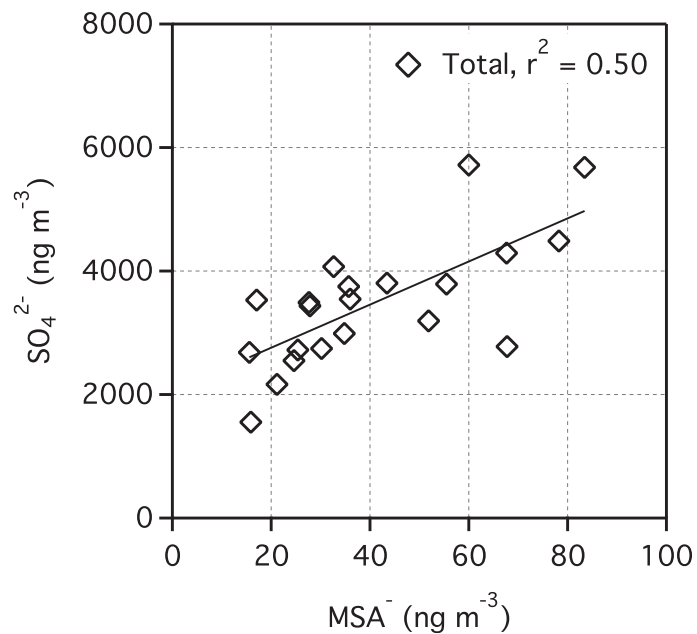
Fig. 7. Scatter plots of SO_4^{2-} and MSA^- in the Sapporo aerosols.

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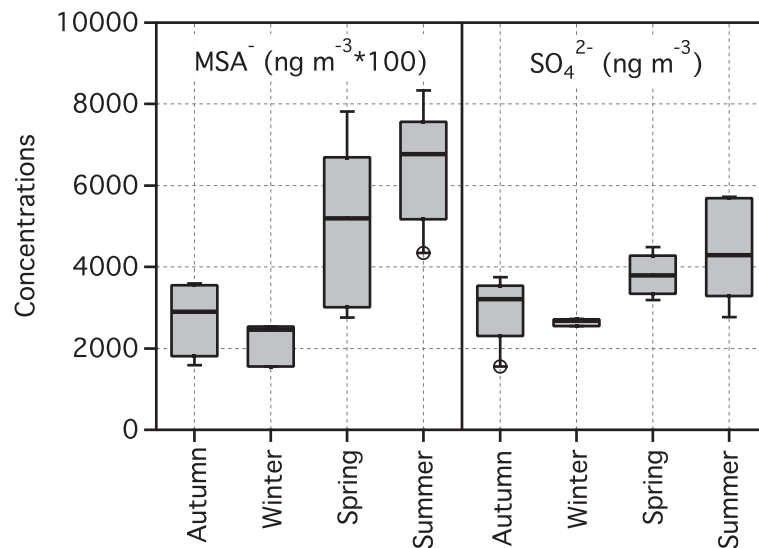
Fig. 8. Box-and-whisker plots of MSA^- and SO_4^{2-} in the Sapporo aerosols for autumn, winter, spring and summer. Lower and upper ends of box show the quartiles at 25 % and 75 %. Upper and lower bars of whiskers present the quartiles at 10 % and 90 %. The cross bar in the box shows the median value. Open circles indicate outliers (1.25 × interquartile distance).
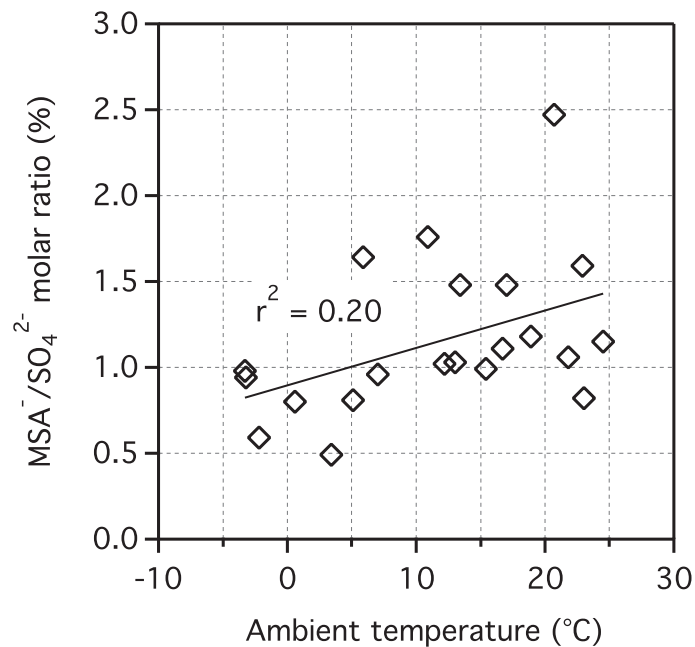
Fig. 9. Scatter plots of the MSA^-/SO_4^{2-} molar ratios against ambient temperatures in Sapporo, northern Japan.