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**Characteristics, seasonality and sources of inorganic ions and trace metals
in Northeast Asian aerosols**

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19 **Environmental context.** Atmospheric aerosols impact the Earth's climate system and cause
20 adverse effects on human health, depending on their loading and chemical composition. This
21 study presents the chemical characteristics and seasonality of inorganic ions and trace metals
22 in atmospheric aerosols from Sapporo, northern Japan and explores their possible sources
23 including the potential biological sources and secondary formation processes depending on
24 seasons over Northeast Asia. This work is relevant for atmospheric composition and climate
25 change.

Abstract. To better understand the characteristics, seasonality and sources of inorganic aerosols in Northeast Asia, we studied total suspended particulate samples collected in Sapporo, northern Japan for inorganic ions and trace metals over one-year period. SO_4^{2-} was found as the most abundant ionic species, which accounted for on average $43 \pm 15\%$ of the measured total ionic mass followed by $\text{Cl}^- \approx \text{NO}_3^- \approx \text{Na}^+$. Among the metals determined, Ca was found as the most abundant ($45 \pm 5.2\%$ of the measured total metals) followed by Fe. Temporal variations of methanesulfonate (MS^-) and SO_4^{2-} showed a clear seasonal pattern with maximum in summer followed by spring. Cl^- , NO_3^- , NH_4^+ and K^+ showed increasing trends from mid autumn to winter. Na^+ , Ca^{2+} and Mg^{2+} and crustal metals (Al, Ca, Fe, Ti and Mn) peaked in early spring. Na^+ and Mg^{2+} and Ni, Cu and As were abundant in autumn whereas Zn in spring. However, Cd and Pb did not show any seasonality. Based on comparisons of such seasonal trends with those of organic tracers as well as the air mass trajectories, we infer that the seasonality in inorganic aerosols in the northeast Asian atmosphere is mainly controlled by their season-specific source(s): soil dust in early spring, biogenic emissions in spring/summer, microbial activities in autumn and forest fires/biomass burning in autumn/winter. However, contributions from anthropogenic sources are significant in all seasons. This study also suggests that fungal spores partly contribute to some trace metals (i.e., Ni, Cu, As) while pollen contributes to Zn in aerosols.

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 nuclei (CCN) on local, regional and global scales.^[1] They also have an adverse effect on human health^[2]. Such impacts of aerosols are largely depend on aerosol loading and chemical composition that are spatially and seasonally variable in the lower atmosphere^[3]. Aerosol loading varies in the range of 1-100 $\mu\text{g m}^{-3}$ and dominant chemical components of the aerosols 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.^[3] On the other hand, trace metals are typically present in elevated concentrations, especially in urban aerosols, and their water-soluble contents are significant in atmospheric waters (e.g., cloud water).^[4-6]

Aerosol SO_4^{2-} affects the radiation budget directly by reflecting solar radiation and indirectly by altering the physical properties of aerosols.^[7] Inorganic salts are more water-soluble and their solubility is much higher than organics, enhancing CCN activity of the particles.^[8] Mineral dust adds complexity, because it can play a significant role in radiative forcing.^[9] Trace metals play an important role in the risk of human health due to their high bioreactivity.^[10,11] The water-soluble contents of trace metals can play a pivotal role in atmospheric chemistry through metal-catalyzed chemical reactions in atmospheric waters.^[12,13] Furthermore, long-range atmospheric transport and dry and wet deposition of trace metals can affect the ecosystem over continental and oceanic regions because of their biogeochemical accumulation and ecological toxicity.^[14,15]

High aerosol loadings are commonly observed in East Asia and have been attributed to anthropogenic activities.^[16,17] East Asian aerosols, including dusts from arid regions in Mongolia and North China, could be further transported across the Pacific Ocean^[18,19] with an impact on the regional to global climate. Radiative forcing and climatic effects over East

Asia have been shown to be large.^[20,21] However, the aerosol chemical characteristics, seasonal variations, and sources, which are crucial in reducing the uncertainty in modeling of the aerosol impacts, are still far from being fully understood in East Asia. For example, Huang et al.^[21] reported an underestimation of the annual averaged model-simulated aerosol optical depth (AOD) by ~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.

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.^[22] Previous studies of Sapporo aerosols demonstrated that the spring and/or summer aerosols are largely influenced by the outflows from East Asia and Siberia and are characterized by anthropogenic and biogenic (including biomass burning) contributions with the atmospheric processing during long-range transport.^[22-24] However, the seasonality of various source contributions is not clearly understood due to the lack of year-round observations. To the best of our knowledge, no study has been conducted for trace metal composition of aerosols from Northeast Asia.

Here, we present the chemical characteristics and seasonal variations of ionic species and trace metals in the total suspended particulate matter (TSP) collected from Sapporo, northern Japan over one-year period (2009-2010). Based on seasonal enrichment of selected ionic and metal species together with the backward air mass trajectories, we infer the possible season-specific sources of inorganic aerosols over Northeast Asian region. We also discuss the role of meteorology on the seasonality. Further, based on comparisons and linear relations of selected ionic species and trace metals with organic tracers,^[25] we discuss potential contributions from terrestrial biological sources to inorganic aerosols in this region.

Materials and Methods

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 (AGL)) 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 ($\sim 65 \text{ m}^3 \text{ h}^{-1}$). The geographical details of the sampling site has been described elsewhere.^[25] Each sample was collected for ca. 2 consecutive weeks, in order to obtain sufficient amount of carbon content for radiocarbon (^{14}C) analysis of organic molecular species, another objective of this research. 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.

It should be noted that aerosol samples collected on quartz fiber filters might have positive and negative sampling artifacts in the measurement of inorganic ions, in particular Cl^- , NO_3^- and NH_4^+ .^[26] In this study, the evaporative loss from the particles should be more significant than the adsorbed gases on quartz fiber filter for longer time of sampling and thus the reported concentrations may be underestimated. However, we consider that the negative bias should be minimal because the ambient temperatures encountered in Sapporo are very low even in summer (see Fig. 1) that would not cause a significant evaporative loss of ions.^[26]

Chemical analyses

Inorganic ions

Inorganic ions were measured using 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 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 ($\text{C}_4\text{H}_6\text{O}_6$) + 1 mM dipicolinic acid ($\text{C}_7\text{H}_5\text{NO}_4$) 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 MS^- and 4% for other ions. The concentrations reported here are corrected for four field blanks that were collected every season.

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 by Theodosi et al.^[27] 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.

Organic tracers

Details of the procedure for the determination of organic tracer compounds are described elsewhere.^[25,28] Briefly, organic tracer compounds were extracted with

dichloromethane/methanol (2:1; v/v) under ultrasonication and derivatized with 50 μ l of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10 μ l of pyridine. The tracer compounds were then measured using a capillary gas chromatograph (Hewlett-Packard 6890) coupled to a mass spectrometer (Hewlett-Packard 5973) (GC/MS).

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.

Results and Discussion

Source regions of Sapporo aerosols

As shown in Fig. 2, 10-day backward air mass trajectories arriving in Sapporo at 500 m AGL, which computed for every 48 h during each sample period using HYSPLIT model,^[29] originated from Siberia passing over Northeast Asia and the Sea of Japan during autumn, winter and spring whereas in summer they mostly originated from the East China Sea and/or western North Pacific passing over coastal region and/or the mainland of Japan.^[25] The air

parcels were mostly travelled at lower than 2000 m AGL in all seasons (Fig. 2) and hence, their advection from distant source regions to the receptor site should be significant.

As discussed in a later section (*seasonal variations*), the temporal variations of crustal metals (e.g., Ca^{2+} , Ca, Al and Fe) showed a peak in early spring (Fig. 3), indicating a significant long-range transport of Asian dust from arid regions in Mongolia and China. On the other hand, Pavuluri et al.^[25] reported that the percent modern carbon (pMC) of total carbon and water-soluble organic carbon in Sapporo aerosols started to increase from mid to late winter toward spring, although the growing season starts in May in Hokkaido when daily average temperatures are $\geq 10^\circ\text{C}$.^[30] They interpreted such earlier increase in pMC for the long-range atmospheric transport from Eurasia. Recently, Yamamoto and Kawamura^[31] reported that the terrestrial biomarkers are likely transported from Siberia, Russian Far East and Northeast China to northern Japan in winter, based on stable carbon ($\delta^{13}\text{C}$) and hydrogen isotope ratios of the biomarkers detected in Sapporo snow samples together with the air mass trajectories.

Further based on molecular distributions of dicarboxylic acids and their $\delta^{13}\text{C}$ in Sapporo aerosol samples collected during spring and summer as well as the air mass trajectories, Aggarwal and Kawamura^[32] reported that the Sapporo aerosols are mainly influenced by the photochemically processed air masses transported from distant source regions over Northeast Asia and surrounding oceans rather than local processes. Therefore, it is very likely that the characteristics, seasonality and sources of Sapporo aerosols should reflect the regional scenario, although we do not preclude a minor impact from the sources at local scale. It should also be noted that the air masses arrived in Sapporo during each sample period (~2 week) were mostly originated from the same source region (Fig. 2), suggesting that each sample might have been influenced by only the limited source regions, despite the long sampling interval.

Chemical characteristics

Statistical summaries of ionic species (methanesulfonate: MS^- (CH_3SO_3^-), 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) measured in TSP samples ($n = 21$) in this study are presented in Table 1. TSP masses, which were gravimetrically measured, ranged from $13.5 \mu\text{g m}^{-3}$ to $73.8 \mu\text{g m}^{-3}$ with an average of $30.0 \pm 12.7 \mu\text{g m}^{-3}$.

Ionic species

SO_4^{2-} was found as the most abundant ionic species throughout the campaign ($n = 21$), ranging from 1560 to 5710 ng m^{-3} and accounting for on average $43 \pm 15\%$ of the measured total ionic mass followed by $\text{Cl}^- > \text{Na}^+ > \text{NO}_3^- > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+ > \text{MS}^-$ in autumn, Cl^- , NO_3^- , NH_4^+ , Na^+ , Ca^{2+} , K^+ , Mg^{2+} and MS^- in winter, NO_3^- , Cl^- , Na^+ , Ca^{2+} , NH_4^+ , Mg^{2+} , K^+ and MS^- in spring and NH_4^+ , Na^+ , Ca^{2+} , NO_3^- , K^+ , Mg^{2+} , MS^- and Cl^- in summer (Fig. 4). However, Cl^- , NO_3^- and Na^+ were found as the second most abundant group ($\sim 13\%$ each) followed by NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ and MS^- during the study period ($n = 21$). It is noteworthy that the mass fraction of sum of inorganic ions in TSP ranged from 20% to 51% with an average of $31 \pm 10\%$, in which SO_4^{2-} accounted for $12 \pm 3.8\%$. The overall slope of linear regression line for measured total cations equivalents and anions equivalents is 0.83 ± 0.03 , although the slope value is slightly lower (0.67 ± 0.07) in autumn, and the correlation coefficient (r^2) is > 0.95 in each season. The deviation of the slope from 1:1 may be caused by a lack of measurements of HCO_3^- , PO_4^{3-} and organic acid anions. These results and comparisons indicate that the ion data obtained in this study is reasonable, despite long sampling time.

Trace metals

Ca was found as the most abundant metal ranging from 196 ng m⁻³ to 2920 ng m⁻³ during the campaign (n = 21) (Table 1). Its relative abundance in all the metals detected is 45±5.2% followed by Fe (27±4.5%). Al (21±3.1%) was found as the third most abundant metal followed by Zn > 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^[33] accounted for 95±2% of all the trace metals determined in this study. On average, they accounted for 7.45±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%,^[34] accounted on average for 24±8% (range 7-36%) of TSP. On the other hand, Ca concentrations obtained from ICP-MS measurements were always higher than water-soluble Ca²⁺ obtained from IC measurements by a factor of 1.3-3.2 (Table 1). The insoluble fraction accounted for 26-69% (average 51±11%) of total Ca, which may be attributed to the existence of insoluble minerals of Ca such as calcium oxide and feldspar. However, the association of such insoluble minerals either with fine particles or coarse particles is not clear from this study.

Seasonal variations: Possible sources and long-range atmospheric transport

MS⁻, SO₄²⁻ and NO₃⁻: Anthropogenic and/or biogenic origins and secondary formation processes

Seasonal variations of MS⁻, a tracer for biologically derived sulfur,^[35] and SO₄²⁻ are both characterized by a gradual increase from winter to growing season (mid spring to mid summer) by a factor of about 3 and 2, respectively, followed by a gradual decrease, although the trend is not clear in autumn (Fig. 3a). Further the MS⁻ and SO₄²⁻ were abundant in summer followed by spring (Fig. 5a). In addition, SO₄²⁻ showed a linear relationship with MS⁻ with a moderate correlation (r²=0.50) during the campaign (n = 21). The air parcels

arriving over Sapporo during autumn to spring originated from Siberia passing over Northeast Asia and the Sea of Japan (Fig. 2), which should have been enriched with SO_2 , a precursor for SO_4^{2-} , emitted from biomass burning and anthropogenic activities. In addition, they should have also been enriched with dimethyl sulfide (DMS), a precursor for both MS^- and SO_4^{2-} , whose emission from terrestrial higher plants (e.g., $0.42 \text{ pmol m}^{-2} \text{ s}^{-1}$ from *Platanus orientalis* L. on a single leaf area basis)^[36], soil in forests ($0.46 \pm 0.30 \text{ pmol m}^{-2} \text{ s}^{-1}$ to $1.27 \pm 1.40 \text{ pmol m}^{-2} \text{ s}^{-1}$, depending on forest type)^[37] and phytoplankton bloom in the ocean^[35] is significant and enhanced with increasing ambient (and soil) temperatures. In summer, the air masses originated from oceanic regions passing over coastal region and/or the mainland of Japan in summer (Fig. 2) should have mainly enriched with DMS rather than SO_2 .

In addition, ambient temperature, which promotes the photochemistry, showed a distinct seasonal trend in Sapporo with winter minima and summer maxima whereas the RH, which enhances the secondary processing of aerosols, showed a gradual increase from mid spring to late summer (Fig. 1). In contrast, precipitation that causes the wet scavenging of aerosols was relatively stable throughout the year, except in winter (high frequency) and summer (high amount) (Fig. 1). A similar pattern should prevail in Northeast Asia. Therefore, it is likely that the seasonal pattern of MS^- and SO_4^{2-} might have been driven mainly by enhanced emissions of their precursors from season-specific (source(s), potentially biogenic emissions in growing season, followed by intensive secondary formation processes whereas a potential removal by wet scavenging could have played a minor role.

Interestingly, the temporal trends of sum of hopanes ($\text{C}_{27}\text{-C}_{32}$ hopanoid hydrocarbons), specific biomarkers of petroleum and coal^[38] and elemental carbon that derives from fossil fuel combustion and biomass burning did not follow clear seasonal pattern during the campaign, except relatively high levels during late autumn to mid winter (Fig. 6), suggesting that the contributions from fossil fuel combustion to Sapporo aerosols are significant in all

seasons. Their high abundance during November to January (Fig. 6) is apparent because of increased consumption of fossil fuels in winter than in other seasons in East Asia^[39]. On the contrary, sums of lipid class compounds such as fatty acids (C₁₂-C₃₂) and fatty alcohols (C₁₈-C₃₂) present clear seasonal pattern with maxima in growing season. Their averaged molecular distributions are characterized by even-carbon-numbered predominance with a maximum at C₁₆, and C₂₆, respectively, suggesting that they were most likely derived from terrestrial higher plant waxes.(ref) In addition, tracers of biogenic secondary organic aerosols: sums of isoprene- and α -pinene-derived compounds and β -caryophyllenic acid, showed a clear seasonal pattern with maxima in spring to summer (Fig. 6), indicating that the contributions from biogenic emissions and subsequent secondary formation processes are significant in spring and summer.

In fact, the concentration range of MS⁻ in Sapporo aerosols (Table 1) is comparable to that reported for the marine aerosols from the North Yellow Sea (12-75 ng m⁻³),^[40] the Oki Islands in the Sea of Japan (3-95 ng m⁻³)^[41] and other oceanic regions (~10-100 ng m⁻³)^[35,42] and the forest aerosols (9-95 ng m⁻³) collected at two levels (~2 m and ~15 m) of the experimental forest in Sapporo, Japan, where the canopy height is ~20 m.^[43] The contributions of MS⁻ in the marine and forest aerosols were attributed to the emission of DMS from phytoplankton bloom and forest floor, respectively, followed by the subsequent photochemical oxidation. It is noteworthy that the averaged seasonal variations of MS⁻ in marine aerosols over Oki Islands in the Sea of Japan for a 9-year period showed a sharp increase from March to May followed by a gradual decrease to October.^[41] In contrast, in Sapporo aerosols, MS⁻ concentrations gradually increased from March to May and stayed high until late summer followed by a gradual decrease to autumn (Fig. 2a). The average concentration of MS⁻ (64 ng m⁻³) in Sapporo summer aerosols is significantly higher than that (39 ng m⁻³) reported in 2006 summer aerosols (July-August) from the North Yellow Sea.

In addition, the molar ratios of MS^- to SO_4^{2-} , which can be used as an indicator of the relative contributions of the SO_4^{2-} derived from biogenic DMS and anthropogenic SO_2 to measured SO_4^{2-} ,^[35] in Sapporo summer aerosols (average 1.55) is three times higher than that (0.55%) of the summer aerosols from the North Yellow Sea.^[40] Such differences might have occurred probably due to more continental outflow of anthropogenic emissions from China over the North Yellow Sea, compared to the Hokkaido region. Alternatively, additional contribution of MS^- originated from higher plant emissions is possible in Sapporo aerosols. Thus our results and their comparisons with organic tracers and with literature imply that the seasonality of MS^- and SO_4^{2-} in Sapporo aerosols should have been driven by the enhanced biogenic emissions of DMS and subsequent intensive secondary processes in spring and summer. On the other hand, the high frequency of precipitation should also lower the concentrations of SO_4^{2-} in winter, despite the enhanced contributions from the increased anthropogenic emissions.

The concentrations of NO_3^- , which is also produced by secondary processes in the atmosphere, are higher in autumn to spring and lower in summer, being different from the case of SO_4^{2-} (Fig. 2a). This discrepancy should be due to differences in mechanistic chains responsible for their formation and emission rates of their precursors, in addition to a potential loss of NO_3^- by dry deposition in summer (see next Sect.). In fact, the $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ molar ratios were <1.5 , except in winter, indicating the NH_4^+ -poor atmosphere^[26] during the campaign. Under such conditions, the production of $(\text{NH}_4)_2\text{SO}_4$ is favored over the formation of NH_4NO_3 through the homogeneous reaction between H_2SO_4 and NH_3 , which is intensive under high temperature and RH, rather than HNO_3 and NH_3 . Meanwhile, HNO_3 is more likely reacted with sea-salt (e.g., NaCl) and crustal particles (e.g., CaCO_3).^[26]

On the other hand, the origins of the air parcels that arrived in Sapporo in each season may have also influenced the different seasonality between SO_4^{2-} and NO_3^- . The air masses

that originated from Siberia passing over Northeast Asia during autumn to spring (Fig. 2) should have been enriched with NO_x (the precursors of NO_3^-) and SO_2 that are emitted from biomass burning and anthropogenic activities. In addition, the air masses may be enriched with DMS emitted from terrestrial vegetation in spring. In summer, the air masses originating from oceanic regions passing over coastal region and/or the mainland of Japan (Fig. 2) should contain abundant DMS emitted from both phytoplankton bloom and terrestrial higher plants rather than NO_x and SO_2 . Furthermore, it is likely that SO_4^{2-} is associated with fine particles whereas NO_3^- with coarse particles, and hence during long-range transport SO_4^{2-} should become more abundant than NO_3^- due to a preferential deposition of coarse particles over fine particles in summer (see the following sect.).

Cl^- , Na^+ , Mg^{2+} and Ca^{2+} : Emissions from natural sources including microbial 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. 3a). Those of Ca^{2+} stayed low in autumn and summer and slightly decreased in winter, however, they showed a peak in early spring (Fig. 3a). Cl^- and Na^+ are considered as typical components of sea-salt whereas Mg^{2+} and Ca^{2+} are crustal components. The higher concentrations of Mg^{2+} and Na^+ in autumn may be attributable to significant mixing of soil dust and sea-salt when the air masses passed over Northeast Asia and the Sea of Japan. On the contrary, the concentrations of Ca^{2+} and Cl^- in autumn were almost similar to those in winter (Fig. 3a), suggesting that Mg^{2+} and Na^+ are derived from other source(s) rather than soil dust and sea-salt in this season.

It is noteworthy that Na^+ is most abundant in autumn (Fig. 5b), although its peak values in spring are comparable to those in autumn and the average and median values of Mg^{2+} in autumn and spring are the same ($0.19 \mu\text{g m}^{-3}$) (Fig. 3a), despite a significant sea-salt

contribution in summer, and enhanced soil dust contribution in early spring as discussed below. In addition, Mg^{2+} showed insignificant but negative relations with Al, a tracer of crustal emission,^[34] in autumn ($r^2 = 0.19$), suggesting that soil dust may not be a major source. As noted earlier, sea-salt contribution to Na^+ may not be the major source in autumn. Therefore, it is likely that the abundant Mg^{2+} and Na^+ in autumn may be derived from other source, probably microbial activities. Fungal activities in soil surface emit the spores and hyphae, which are significantly enriched with several elements including Na and Mg.^[44] Their activities on fallen leaves may be increased during defoliation season. In fact, the concentration of mannitol that is mainly produced by fungi is highest in autumn ($20.3 \pm 13.3 \text{ ng m}^{-3}$) followed by summer ($7.07 \pm 3.38 \text{ ng m}^{-3}$) (Fig. 6).^[25] Therefore, we consider that the fungal activities are the potential sources of Na^+ and Mg^{2+} in autumn.

The relatively low concentrations of ions may be associated with wet scavenging in winter when snow precipitation frequently occurred (Fig. 1). Their peaks (e.g., Ca^{2+}) in early spring may be due to the soil dust injection to the atmosphere from the arid regions of Mongolia and Northeast China^[34] 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.^[45] reported that the dust storm in Mongolia was blown in Beijing, China and the dust plume covered over the downwind regions including Hokkaido Island.

In summer, the lowest concentrations of Cl^- , Na^+ , Mg^{2+} and Ca^{2+} as well as NO_3^- , which exist preferably in coarse mode, might be associated with the enhanced dry and wet deposition. Agarwal et al.^[23] reported that the concentrations of these ions (Na^+ is not reported) maximized in coarse ($>7.0 \text{ }\mu\text{m}$ in diameter) size particles collected in summer (8-11 August) 2005 from the same site. Dry deposition velocities are higher ($1.2\text{-}5 \text{ cm s}^{-1}$) for coarse mode particles than accumulation mode particles ($0.001\text{-}0.05 \text{ cm s}^{-1}$) and the

deposition rates are further influenced by surface thermal response to insolation on convective mixing in the boundary layer.^[46] The high temperature and low wind speed in summer (Fig. 1) might have caused boundary layer convective instability and reduction in convective mixing of pollutants, respectively, and hence, the dry deposition of coarse particles might be intensive in summer. In addition, the washout of pollutant should be more efficient in summer due to high amount of precipitation (Fig. 1). It is known that precipitation scavenges coarse particles more efficiently than fine ones.

NH₄⁺ and K⁺: Biomass burning emissions

NH₄⁺ and K⁺ significantly increased from mid- to late-autumn and stayed high until mid winter (Fig. 2a). NH₄⁺ then showed a gradual decrease toward early spring whereas K⁺ showed a decrease toward late winter followed by an increase in early spring and thereafter. They stayed relatively stable, except for few cases, from mid spring to summer (Fig. 3a). It is well recognized that NH₄⁺ and K⁺ are mainly originate from biomass burning and biogenic emissions.^[47-49] Higher levels of these species during mid autumn to mid winter may be associated with forest fires and/or biomass burning on a local and/or regional scale, whereas the increase of K⁺ from late winter to early spring may be caused by the long-range atmospheric transport of soil dust. Concentrations of levoglucosan, an excellent tracer of biomass burning^[50], were also high in mid autumn to mid winter (Fig. 6), further supporting the enhanced contributions from the biomass burning during this period.

In spring and summer, the temporal trends of K⁺ and NH₄⁺ (Fig. 3a) are not consistent with that of levoglucosan (Fig. 6). This discrepancy is probably due to significant decomposition of levoglucosan^[51] and (or) biogenic contributions of K⁺ and NH₄⁺ in during growing season. In fact, K⁺ in Sapporo aerosols showed a good correlation with SO₄²⁻ in spring ($r=0.71$), which is partly derived from biogenic emissions. However, MODIS fire

detections indicated that the forest fires/biomass burning events are significant over Siberia and northeast China in spring and over Japan mainland in summer 2010 (see Fig. S1). The air masses arriving over Sapporo in spring originated in Siberia and passed over Northeast China whereas in summer, they passed over Japan mainland (Fig. 2), which should have been enriched with biomass burning emissions. Therefore, we consider that the higher levels of NH_4^+ and K^+ from mid spring to late summer should have associated with enhanced biomass burning emissions, although we do not preclude a minor contribution from biogenic emissions.

Trace metals: Possible contributions from soil dust injection, anthropogenic emissions and biological sources

Crustal metals such as Al, Ca, Fe, Ti and Mn^[33] did not show any significant seasonal variations, although their concentrations are relatively low in winter (Fig. 3b) probably due to wet scavenging by snowfall (Fig. 1). They showed a very sharp increase in early spring (April 1-15) followed by a gradual decrease to late autumn (Fig. 3b). Being similar to Ca^{2+} , these trends indicate a significant contribution of soil dust particles that are transported from the arid regions in Mongolia and Northeast China,^[45] as discussed earlier.

Ni showed a gradual decrease from autumn to mid winter and a gradual increase toward early summer followed by a decrease in mid summer (Fig. 3b). The seasonal trends of both Cu and As are quite similar to that of Ni in autumn to mid spring and the rest of the period (Fig. 3b). The concentrations of Zn are rather constant during the campaign, except for spring: a gradual increase from winter to late spring followed by a decrease to summer, although a high value was observed in early summer (Fig. 3b). V and Cr did not vary significantly in autumn but showed a gradual decrease in winter followed by a sharp increase in early spring. Thereafter V stayed relatively high until late summer whereas Cr decreased gradually toward

early summer (Fig. 3b). In contrast, Cd and Pb did not show any clear trend throughout the campaign (Fig. 3b).

The trace metals: Ni, Cu, As, Zn, V, Cr, Cd and Pb, are considered to be emitted to the atmosphere by fossil fuel combustion, metallurgical industrial activity and traffic pollution.^[52] Therefore, it is likely that they originate from anthropogenic sources over the region. The lower values in winter might be associated with wet scavenging by snowfall (Fig. 1) whereas a sharp increase in early spring may be due to soil dust injection from arid regions of Mongolia and northeast China,^[45] where the soil surface could have been enriched with anthropogenic pollutants. However, the reason for a gradual decrease in autumn to winter and a gradual increase from winter to late spring of some trace metals (i.e., Ni, Cu, As, Zn) is unclear. In fact, the combustion tracers; (i) hopanes^[38] (ii) levoglucosan^[50] and (iii) EC, did not show such seasonal trends in Sapporo aerosols.^[25] Hence, it is possible that the seasonal trends of Ni, Cu, As and Zn should have been driven by other season-specific source(s).

Interestingly, Ni, Cu and As (Fig. 3b) showed a seasonal trend similar to that of mannitol (Fig. 5), which is considered as a tracer for bioaerosol (fungal species).^[53] On the other hand, seasonal pattern of Zn (Fig. 3b) is similar to that of sucrose (Fig. 5), which is a tracer of pollens emitted from terrestrial plants.^[54] Fungi uptake the trace metals from the substrate and the extent of their bioaccumulation is species-specific.^[55] As shown in Fig. 7, Ni, Cu and As positively correlate with mannitol ($r^2=0.33$, 0.47 and 0.28 , and $p = 0.006$, 0.001 and 0.013 , respectively). It is also noteworthy that these metals negligibly correlated with hopanes ($r^2=0.22$, 0.01 and 0.001), levoglucosan ($r^2=0.25$, 0.03 and 0.03) and EC ($r^2=0.03$, 0.08 and 0.18 , respectively). On the other hand, Zn showed a positive correlation ($r^2=0.60$) with sucrose whereas weak or no correlations with hopanes ($r^2=0.24$), levoglucosan ($r^2=(-)0.001$) and EC ($r^2=0.12$) in spring, although no relation was found in other seasons. In fact, Zn is present in pollen grains.^[56] Furthermore, we found that Cu and Zn, which are

considered to be emitted from metallurgical industrial activity,^[52] are associated with different factors obtained from Varimax rotated factor analysis of trace metals (see Table 3). Therefore, we consider that the terrestrial biological sources including microbial activities should have partly contributed to trace metals in Sapporo aerosols. Nriagu^[57] reported that biogenic sources could account for 30-50% of the global baseline emissions of trace metals, which again supports our assumption.

Factor analysis

Factor analysis (FA), which does not require a prior information on source composition,^[58] has been widely used to apportion the sources of chemical species in atmospheric aerosols.^[59] In this study, Varimax rotated FA was applied to inorganic ion and trace metal data sets (n = 21) to further examine the likely sources discussed in the previous section and the obtained results are presented in Tables 2 and 3, respectively. The FA resulted three factors each with Eigen values greater than 1 that explain 87% and 83% of the total variance of the data sets, respectively. The factor loadings: >0.75, 0.75-0.5 and 0.5-0.3, which can be classified as strong, moderate and weak, respectively,^[60] are used to infer the factors to distinguish possible sources. It should be noted that the sample size ($n = 30 + (V+3)/2$) of both ions and metals is relatively small for FA.^[58] However, the communalities obtained for all species are >0.6, except for V and Zn (0.5), suggesting that the obtained results from the FA of these data sets should be reasonable.^[61]

Inorganic ions

The first factor, which accounted for 31% of total variance, is strongly loaded with Mg^{2+} and Na^+ and moderately with Ca^{2+} and weakly with Cl^- (Table 2). Na^+ and Ca^{2+} are typical sea-salt and crustal components, respectively. Mg^{2+} originates mostly from soil dust

but oceanic emissions also could contribute at significant levels. In fact, Mg^{2+} showed a positive correlation ($r^2 = 0.24$) with Al, a tracer for crustal origin,^[34] during the campaign ($n = 21$). Hence, this factor can be attributed to a natural source: soil dust and sea-salt. It is noteworthy that both NO_3^- and K^+ are positively correlated with this factor, although the loading is very poor (Table 3), suggesting important heterogeneous reactions (mainly for NO_3) with dust and sea-salt and/or that biomass burning emissions may be associated with this factor.

The second factor, which accounted for 30% of total variance, strongly loaded with MS^- and SO_4^{2-} (Table 2). These ions are produced in the atmosphere by secondary transformations through photochemical reactions of their precursor compounds (DMS , SO_2) of biogenic and anthropogenic/biogenic origins, respectively, as discussed earlier. Therefore it is apparent that the second factor represents the secondary aerosols produced by homogeneous photochemical reactions. A weak positive correlation of K^+ and Ca^{2+} with this factor may be due to a possible association of SO_4^- with these metal ions.

The third factor, which accounted for 25% of total variance, is strongly associated with NO_3^- , NH_4^+ and K^+ and weakly with Cl^- and Ca^{2+} as well as SO_4^- (Table 2). NO_3^- and SO_4^- can be derived from fossil fuel combustion and/or biomass burning emissions whereas NH_4^+ and K^+ from biomass burning and/or biogenic emissions. Hence, this factor can mainly be interpreted as biomass burning mixed with other anthropogenic emissions but biogenic emissions may also be associated.

Trace metals

The first factor is strongly loaded with Al, Ca, Ti, Mn, and Fe, which are typical crustal components^[33,34] and with Cr, accounting for 41% of total variance. V is weakly loaded with this factor whereas Ni, As and Pb are also positively correlated, however, their loadings are

very poor (Table 3). Hence, this factor can mainly be attributed to soil dust. The second factor is strongly loaded with Ni and Cu, moderately with V and As, and weakly with Zn, accounting for 21% of total variance (Table 3). The metallurgical industrial activities have been considered as the major source of Cu, As and Zn whereas oil combustion is considered as a source of Ni and V.^[52] Therefore, this factor may be associated with industrial emissions mixed with other (fossil fuel combustion) anthropogenic sources. The third factor correlates strongly with Cd and Pb, moderately with Zn and weakly with Cr and As, accounting for 20% of total variance (Table 3). Mn, Fe and Cu also showed a positive correlation with this factor, although the coefficient is poor. All these trace metals are most likely derived from the anthropogenic activities, particularly fossil fuel combustion.^[52] Hence, this factor can be interpreted as emissions of fossil fuel combustion and road dust from the presence of Pb, Zn, Cu and crustal elements.

Summary and conclusions

Atmospheric aerosol (TSP) samples collected from Sapporo, northern Japan for one-year period, were studied for inorganic ions and trace metals using ion chromatograph (IC) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. 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 in TSP ranged from 20% to 51% with an average of $31 \pm 10\%$, in which SO_4^{2-} accounted for $12 \pm 3.8\%$. The group of crustal metals alone accounted for $95 \pm 2\%$ of the total metals determined. The seasonal trends of MS^- (a tracer for biologically derived sulfur) and SO_4^{2-} showed maxima in growing season, while crustal metals peaked in early spring, suggesting that biogenic emissions maximized in spring/summer whereas soil dust injection did in early spring. Na^+ and Mg^{2+} were abundant, despite insignificant contribution of both sea-salt and soil dust, in autumn. In addition, Ni, Cu and As showed maxima in autumn. Such

seasonal trends and their comparison with those of tracer species reported in our samples^[25] suggest the potential contribution of microbial activities in autumn. NH_4^+ and K^+ became more abundant from mid autumn to mid winter as well as from mid spring to late summer, indicating the enhanced contributions from biomass burning in these periods. The present results together with factor analysis of ionic species and trace metals, comparisons of the seasonality of specific ions and metals with the tracer species, and air mass trajectories, imply that the long-range atmospheric transport of soil dust, and anthropogenic emissions including biomass burning, biogenic emissions including microbial activities, and secondary production from both anthropogenic and biogenic emissions are the major sources of Northeast Asian aerosols, with the relative contributions being depending on seasons.

Supplementary material

Maps of monthly averages of active fires detected using MODIS data from the Terra satellite over the Asian region for the period of September 2009 and August 2010 are provided in Fig. S1. The global maps of active fire detections were obtained from MODIS Rapid Response website (<http://rapidfires.sci.gsfc.nasa.gov/>).

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Figure captions.

Fig. 1. Seasonal variations of meteorological parameters (ambient temperature, RH, wind speed and precipitation) in Sapporo, northern Japan.

Fig. 2. Plots of 10-day backward air mass trajectories arriving in Sapporo at 500 m AGL. Color scale shows the altitude of the air parcel AGL.

Fig. 3. Temporal variations of (a) ionic species and (b) trace metals.

Fig. 4. Relative abundances of ionic species to total ionic mass in (a) autumn, (b) winter, (c) spring and (d) summer.

Fig. 5. Box-and-whisker plots of (a) MS^- and SO_4^{2-} and (b) 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 ($1.25 \times$ interquartile distance).

Fig. 6. Temporal variations of concentrations of tracer species. Plant wax alkanes, fatty acids and fatty alcohols are sums of C_{23} to C_{37} , C_{12} - C_{32} and C_{18} - C_{32} compounds, respectively. Isoprene derived compounds are sums 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 α -pinene derived compounds are sums of 3-hydroxyglutaric, pinonic, pinic and 3-methyl-1,2,3-butanetricarboxylic acids. The data are from Pavuluri et al.

Fig. 7. Scatter plots of the concentrations of Ni, Cu and As as a function of the concentrations of mannitol. The data of mannitol are from Pavuluri et al.^[25]

745 **Table 1.** Statistical summary for the concentrations (ng m^{-3}) of methanesulfonate, major
746 inorganic ions and trace metals in atmospheric aerosol (TSP) samples ($n = 21$) collected from
747 Sapporo, northern Japan during September 2, 2009 to October 5, 2010.

	Range	Median/Average	Standard Deviation
<i>Ionic species</i>			
MS^-	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
<i>Trace metals</i>			
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

748

749 **Table 2.** Varimax rotated factor loadings for ionic species in the Sapporo TSP samples ($n =$
750 21) during the campaign^a.

Variable	Factor			Communality
	F1	F2	F3	
MS ⁻	-0.13	0.91	-0.09	0.85
Cl ⁻	0.46	-0.63	0.49	0.85
NO ₃ ⁻	0.18	-0.32	0.77	0.72
SO ₄ ²⁻	-0.13	0.89	0.34	0.92
Na ⁺	0.79	-0.55	0.18	0.96
NH ₄ ⁺	-0.76	0.16	0.60	0.96
K ⁺	0.14	0.24	0.81	0.73
Ca ²⁺	0.67	0.37	0.48	0.82
Mg ²⁺	0.91	-0.28	0.28	0.98
Eigenvalue	4.04	2.38	1.38	
% of Variance	31	30	26	
Source type	Natural	Photochemical	Biomass burning & Anthropogenic	

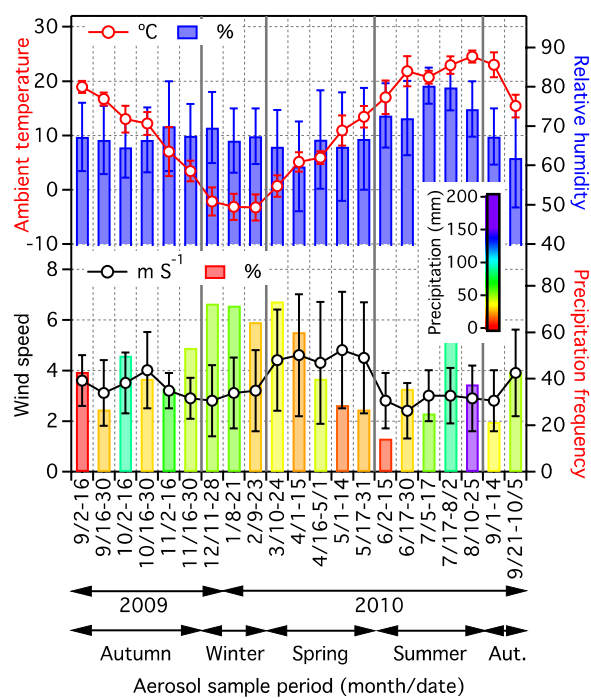
751 ^aFactor loadings ≥ 0.5 are in bold.

Table 3. Varimax rotated factor loadings for trace metals in the Sapporo TSP samples ($n = 21$) during the campaign^a.

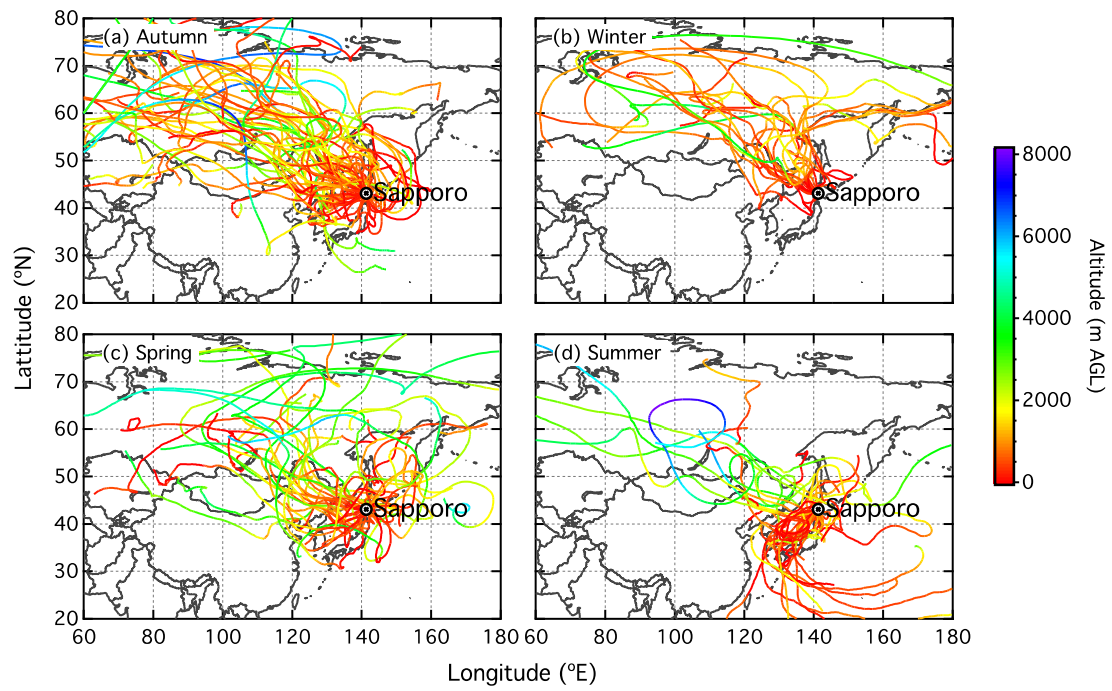
Variable	Factor			Communality
	F1	F2	F3	
Al	0.97	0.18	0.03	0.97
Ca	0.92	0.26	0.07	0.92
Ti	0.94	0.23	0.07	0.95
V	0.43	0.58	-0.07	0.52
Cr	0.72	0.08	0.40	0.68
Mn	0.93	0.20	0.26	0.97
Fe	0.96	0.18	0.17	0.99
Ni	0.24	0.83	-0.24	0.81
Cu	0.06	0.87	0.27	0.84
Zn	0.11	0.47	0.52	0.51
As	0.26	0.71	0.42	0.74
Cd	0.12	-0.08	0.96	0.94
Pb	0.21	0.14	0.92	0.92
Eigenvalue	6.81	2.14	1.81	
% of Variance	41	21	20	
Source type	Soil dust	Industrial	Fossil fuel combustion & road dust	

^aFactor loadings ≥ 0.5 are in bold.

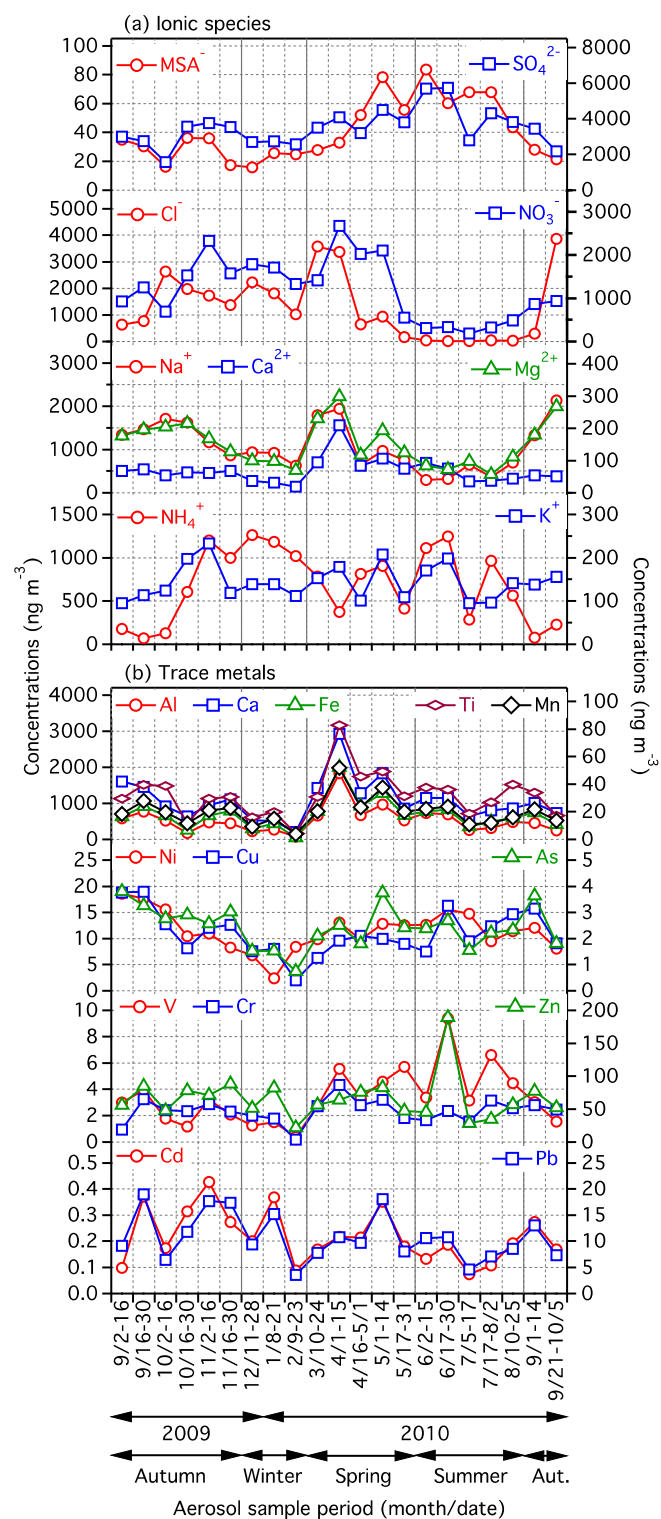
755 **Fig. 1.**

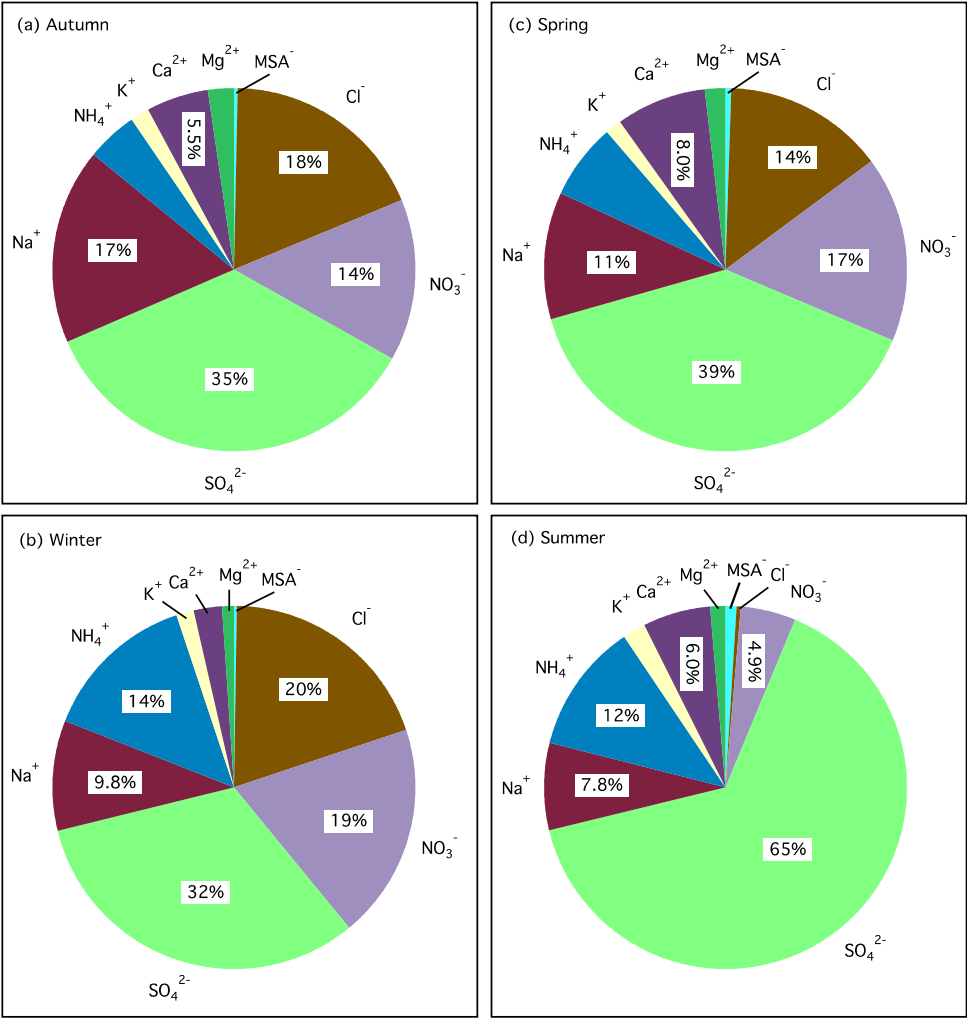


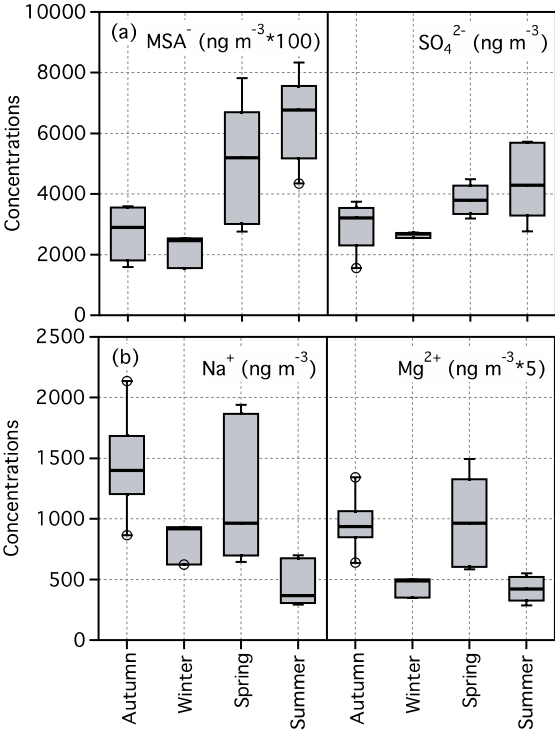
757 **Fig. 2.**

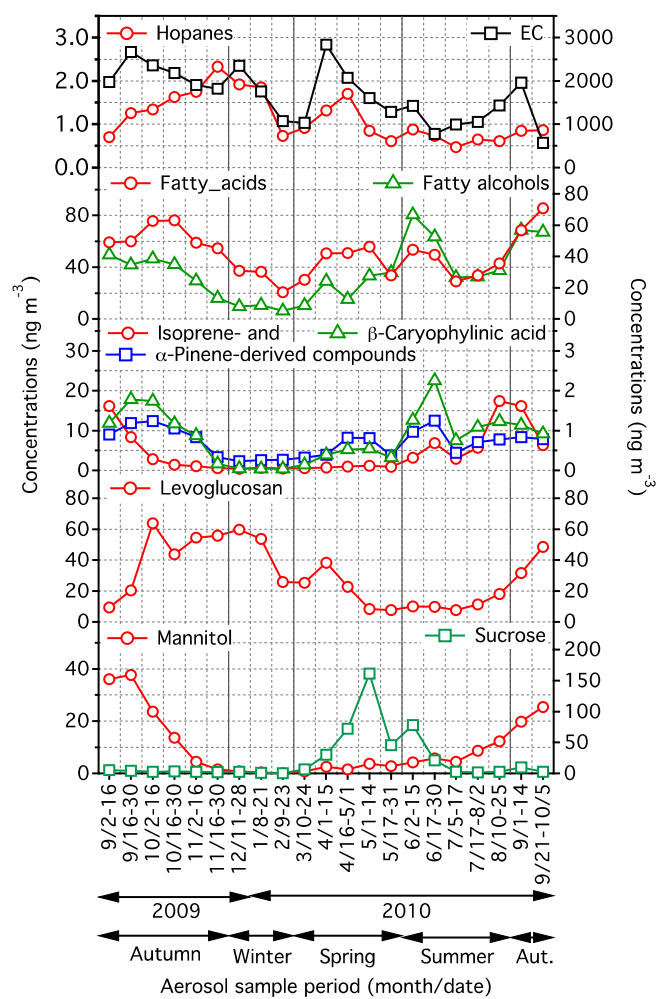


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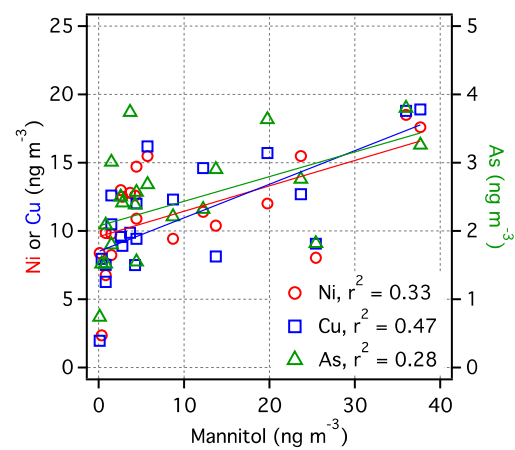








767 **Fig. 7.**



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