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Instructions for use

1 **Characteristics, seasonality and sources of inorganic ions and trace metals**

2 **in Northeast Asian aerosols**

3

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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.

26   **Abstract.** To better understand the characteristics, seasonality and sources of inorganic

27   aerosols in Northeast Asia, we studied total suspended particulate samples collected in

28   Sapporo, northern Japan for inorganic ions and trace metals over one-year period. SO_4^{2-} was

29   found as the most abundant ionic species, which accounted for on average 43±15% of the

30   measured total ionic mass followed by $Cl^- \approx NO_3^- \approx Na^+$. Among the metals determined, Ca was

31   found as the most abundant (45±5.2% of the measured total metals) followed by Fe.

32   Temporal variations of methanesulfonate (MS^-) and SO_4^{2-} showed a clear seasonal pattern

33   with maximum in summer followed by spring. Cl^-, NO_3^-, NH_4^+ and K^+ showed increasing

34   trends from mid autumn to winter. Na^+, Ca^{2+} and Mg^{2+} and crustal metals (Al, Ca, Fe, Ti and

35   Mn) peaked in early spring. Na^+ and Mg^{2+} and Ni, Cu and As were abundant in autumn

36   whereas Zn in spring. However, Cd and Pb did not show any seasonality. Based on

37   comparisons of such seasonal trends with those of organic tracers as well as the air mass

38   trajectories, we infer that the seasonality in inorganic aerosols in the northeast Asian

39   atmosphere is mainly controlled by their season-specific source(s): soil dust in early spring,

40   biogenic emissions in spring/summer, microbial activities in autumn and forest fires/biomass

41   burning in autumn/winter. However, contributions from anthropogenic sources are significant

42   in all seasons. This study also suggests that fungal spores partly contribute to some trace

43   metals (i.e., Ni, Cu, As) while pollen contributes to Zn in aerosols.

Introduction

44

45   Atmospheric aerosols have an impact on the Earth's climate system directly by absorbing and

46   reflecting solar radiation and indirectly by acting as cloud condensation nuclei (CCN) on

47   local, regional and global scales.[1] They also have an adverse effect on human health[2]. Such

48   impacts of aerosols are largely depend on aerosol loading and chemical composition that are

49   spatially and seasonally variable in the lower atmosphere[3]. Aerosol loading varies in the

50   range of 1-100 $\mu g\ m^{-3}$ and dominant chemical components of the aerosols are characterized

51   by sulfate, nitrate, ammonium, sea salt, minerals, organics and elemental carbon, each of

52   which typically contribute about 10-30% of the overall mass load.[3] On the other hand, trace

53   metals are typically present in elevated concentrations, especially in urban aerosols, and their

54   water-soluble contents are significant in atmospheric waters (e.g., cloud water).[4-6]

55   Aerosol SO_4^{2-} affects the radiation budget directly by reflecting solar radiation and

56   indirectly by altering the physical properties of aerosols.[7] Inorganic salts are more

57   water-soluble and their solubility is much higher than organics, enhancing CCN activity of

58   the particles.[8] Mineral dust adds complexity, because it can play a significant role in

59   radiative forcing.[9] Trace metals play an important role in the risk of human health due to

60   their high bioreactivity.[10,11] The water-soluble contents of trace metals can play a pivotal

61   role in atmospheric chemistry through metal-catalyzed chemical reactions in atmospheric

62   waters.[12,13] Furthermore, long-range atmospheric transport and dry and wet deposition of

63   trace metals can affect the ecosystem over continental and oceanic regions because of their

64   biogeochemical accumulation and ecological toxicity.[14,15]

65   High aerosol loadings are commonly observed in East Asia and have been attributed to

66   anthropogenic activities.[16,17] East Asian aerosols, including dusts from arid regions in

67   Mongolia and North China, could be further transported across the Pacific Ocean[18,19] with

68   an impact on the regional to global climate. Radiative forcing and climatic effects over East

69 Asia have been shown to be large.[20,21] However, the aerosol chemical characteristics,

70 seasonal variations, and sources, which are crucial in reducing the uncertainty in modeling of

71 the aerosol impacts, are still far from being fully understood in East Asia. For example,

72 Huang et al.[21] reported an underestimation of the annual averaged model-simulated aerosol

73 optical depth (AOD) by ~45%. They interpreted that the obtained negative intercept is due to

74 the inclusion of only the anthropogenic aerosols (SO_4^{2-}, black carbon and organic carbon),

75 suggesting that the contributions from natural sources might also be significant in this region.

76 Sapporo is located in the west of Hokkaido Island, northern Japan (43.07°N, 141.36°E)

77 and is an ideal site for the study of air masses delivered from Siberia, North China, and

78 surrounding oceans.[22] Previous studies of Sapporo aerosols demonstrated that the spring

79 and/or summer aerosols are largely influenced by the outflows from East Asia and Siberia

80 and are characterized by anthropogenic and biogenic (including biomass burning)

81 contributions with the atmospheric processing during long-range transport.[22-24] However, the

82 seasonality of various source contributions is not clearly understood due to the lack of

83 year-round observations. To the best of our knowledge, no study has been conducted for trace

84 metal composition of aerosols from Northeast Asia.

85 Here, we present the chemical characteristics and seasonal variations of ionic species

86 and trace metals in the total suspended particulate matter (TSP) collected from Sapporo,

87 northern Japan over one-year period (2009-2010). Based on seasonal enrichment of selected

88 ionic and metal species together with the backward air mass trajectories, we infer the possible

89 season-specific sources of inorganic aerosols over Northeast Asian region. We also discuss

90 the role of meteorology on the seasonality. Further, based on comparisons and linear relations

91 of selected ionic species and trace metals with organic tracers,[25] we discuss potential

92 contributions from terrestrial biological sources to inorganic aerosols in this region.

93

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 (~65 m^3 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

119   Chromatodisc Type A, 0.45 μm) and then injected into IC. For anion measurement, a column

120   of SI-90 4E (Shodex, Showa Denko, Tokyo) equipped with a suppressor was used with an

121   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

122   cation analysis, we used a Metrosep C2-150 (Metrohm) column with 4 mM tartaric acid

123    $(C_4H_6O_6)$ + 1 mM dipicolinic acid $(C_7H_5NO_4)$ solution with a flow rate of 1.0 ml min^{-1}. A

124   calibration curve was evaluated by the analyses of a set of authentic standards along with a

125   sequence of filter samples. The analytical errors in duplicate analysis of filter samples were

126   within 14% for MS$^-$ and 4% for other ions. The concentrations reported here are corrected for

127   four field blanks that were collected every season.

128

129   *Trace metals*

130   Trace metals were measured using an inductively coupled plasma mass spectrometry

131   (ICP-MS, Thermo Electron X Series) after the acid microwave digestion of samples as

132   reported by Theodosi et al.[27] Briefly, a filter disc (1.0 cm in diameter) was placed in Teflon

133   vessel (DAP-60 K, 60 ml/40 bar), to which concentrated nitric acid was added and then

134   digested using a microwave digestion system (Berghof MWS-2). Indium (CPI International,

135   S4400-1000241) was used as internal standard, and a calibration curve was evaluated using

136   standard certified solutions (CPI International). Recoveries obtained with the use of certified

137   reference materials ranged from 90.0 to 104.1%. The concentrations reported here are not

138   corrected for field blanks because none of the trace metals measured were found to be

139   significant in the field blanks.

140

141   *Organic tracers*

142   Details of the procedure for the determination of organic tracer compounds are

143   described elsewhere.[25,28] Briefly, organic tracer compounds were extracted with

144   dichloromethane/methanol (2:1; v/v) under ultrasonication and derivatized with 50 μl of

145   N,O-bis-(trimethylsilyl)triflouroacetamide (BSTFA) with 1% trimethylsilyl chloride and 10

146   μl of pyridine. The tracer compounds were then measured using a capillary gas

147   chromatograph (Hewlett-Packard 6890) coupled to a mass spectrometer (Hewlett-Packard

148   5973) (GC/MS).

149

150   *Meteorology in Sapporo*

151   24 h averaged meteorological data were obtained from Japan Meteorological Agency

152   (*http://www.data.jma.go.jp*). The meteorological station of Sapporo is located ca. 2 km south

153   of the sampling point. Averaged ambient temperature, relative humidity (RH), wind speed

154   and precipitation for each sample period are presented in Fig. 1. During our campaign, the

155   temperature, RH and wind speed ranged from -3.30 °C to 24.5 °C, 59.7-80.3% and 2.4-4.8 m

156   s^{-1}, respectively, whereas the precipitation occurred occasionally with the highest amount

157   (range 5.5-153 mm) in summer (June to August) during rainy season with the highest

158   frequency (range 14.3-73.3%) in winter (December-February) during snowfall season.

159   September to November and March-May are classified as autumn and spring, respectively.

160   The ground surfaces in Sapporo are covered with snow from late December to early April.

161

162   **Results and Discussion**

163   *Source regions of Sapporo aerosols*

164   As shown in Fig. 2, 10-day backward air mass trajectories arriving in Sapporo at 500 m AGL,

165   which computed for every 48 h during each sample period using HYSPLIT model,[29]

166   originated from Siberia passing over Northeast Asia and the Sea of Japan during autumn,

167   winter and spring whereas in summer they mostly originated from the East China Sea and/or

168   western North Pacific passing over coastal region and/or the mainland of Japan.[25] The air

169   parcels were mostly travelled at lower than 2000 m AGL in all seasons (Fig. 2) and hence,

170   their advection from distant source regions to the receptor site should be significant.

171   As discussed in a later section (*seasonal variations*), the temporal variations of crustal

172   metals (e.g., Ca^{2+}, Ca, Al and Fe) showed a peak in early spring (Fig. 3), indicating a

173   significant long-range transport of Asian dust from arid regions in Mongolia and China. On

174   the other hand, Pavuluri et al.[25] reported that the percent modern carbon (pMC) of total

175   carbon and water-soluble organic carbon in Sapporo aerosols started to increase from mid to

176   late winter toward spring, although the growing season starts in May in Hokkaido when daily

177   average temperatures are $\geq 10°C$.[30] They interpreted such earlier increase in pMC for the

178   long-range atmospheric transport from Eurasia. Recently, Yamamoto and Kawamura[31]

179   reported that the terrestrial biomarkers are likely transported from Siberia, Russian Far East

180   and Northeast China to northern Japan in winter, based on stable carbon ($\delta^{13}C$) and hydrogen

181   isotope ratios of the biomarkers detected in Sapporo snow samples together with the air mass

182   trajectories.

183   Further based on molecular distributions of dicarboxylic acids and their $\delta^{13}C$ in

184   Sapporo aerosol samples collected during spring and summer as well as the air mass

185   trajectories, Aggarwal and Kawamura[32] reported that the Sapporo aerosols are mainly

186   influenced by the photochemically processed air masses transported from distant source

187   regions over Northeast Asia and surrounding oceans rather than local processes. Therefore, it

188   is very likely that the characteristics, seasonality and sources of Sapporo aerosols should

189   reflect the regional scenario, although we do not preclude a minor impact from the sources at

190   local scale. It should also be noted that the air masses arrived in Sapporo during each sample

191   period (~2 week) were mostly originated from the same source region (Fig. 2), suggesting

192   that each sample might have been influenced by only the limited source regions, despite the

193   long sampling interval.

194

Chemical characteristics

196　Statistical summaries of ionic species (methanesulfonate: MS^- ($CH_3SO_3^-$), Cl^-, NO_3^-, SO_4^{2-},

197　Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) and trace metals (Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As,

198　Cd and Pb) measured in TSP samples ($n = 21$) in this study are presented in Table 1. TSP

199　masses, which were gravimetrically measured, ranged from 13.5 $\mu g\ m^{-3}$ to 73.8 $\mu g\ m^{-3}$ with

200　an average of 30.0±12.7 $\mu g\ m^{-3}$.

201

Ionic species

203　　　SO_4^{2-} was found as the most abundant ionic species throughout the campaign (n = 21),

204　ranging from 1560 to 5710 $ng\ m^{-3}$ and accounting for on average 43±15% of the measured

205　total ionic mass followed by $Cl^- > Na^+ > NO_3^- > Ca^{2+} > NH_4^+, > Mg^{2+} > K^+ > MS^-$ in autumn,

206　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+},

207　K^+ and MS^- in spring and NH_4^+, Na^+, Ca^{2+}, NO_3^-, K^+, Mg^{2+}, MS^- and Cl^- in summer (Fig. 4).

208　However, Cl^-, NO_3^- and Na^+ were found as the second most abundant group (~13% each)

209　followed by NH_4^+, Ca^{2+}, Mg^{2+}, K^+ and MS^- during the study period (n = 21). It is noteworthy

210　that the mass fraction of sum of inorganic ions in TSP ranged from 20% to 51% with an

211　average of 31±10%, in which SO_4^{2-} accounted for 12±3.8%. The overall slope of linear

212　regression line for measured total cations equivalents and anions equivalents is 0.83±0.03,

213　although the slope value is slightly lower (0.67±0.07) in autumn, and the correlation

214　coefficient (r^2) is >0.95 in each season. The deviation of the slope from 1:1 may be caused by

215　a lack of measurements of HCO_3^-, PO_4^{3-} and organic acid anions. These results and

216　comparisons indicate that the ion data obtained in this study is reasonable, despite long

217　sampling time.

218

Trace metals

220   Ca was found as the most abundant metal ranging from 196 ng m^{-3} to 2920 ng m^{-3}

221   during the campaign (n = 21) (Table 1). Its relative abundance in all the metals detected is

222   45±5.2% followed by Fe (27±4.5%). Al (21±3.1) was found as the third most abundant

223   metal followed by Zn > Ti > Mn > Ni > Pb > Cu > V > As > Cr > Cd (Table 1). The total

224   mass of Al, Ca, Fe, Ti and Mn that mainly originate from the crust[33] accounted for 95±2%

225   of all the trace metals determined in this study. On average, they accounted for 7.45±2.09%

226   (range 2.29-10.6%) of TSP. The amount of dust estimated from Al, whose mass ratio relative

227   to the Asian dust is 7%,[34] accounted on average for 24±8% (range 7-36%) of TSP. On the

228   other hand, Ca concentrations obtained from ICP-MS measurements were always higher than

229   water-soluble Ca^{2+} obtained from IC measurements by a factor of 1.3-3.2 (Table 1). The

230   insoluble fraction accounted for 26-69% (average 51±11%) of total Ca, which may be

231   attributed to the existence of insoluble minerals of Ca such as calcium oxide and feldspar.

232   However, the association of such insoluble minerals either with fine particles or coarse

233   particles is not clear from this study.

234

235   *Seasonal variations: Possible sources and long-range atmospheric transport*

236   *MS$^-$, SO$_4^{2-}$ and NO$_3^-$: Anthropogenic and/or biogenic origins and secondary formation*

237   *processes*

238   Seasonal variations of MS$^-$, a tracer for biologically derived sulfur,[35] and SO$_4^{2-}$ are

239   both characterized by a gradual increase from winter to growing season (mid spring to mid

240   summer) by a factor of about 3 and 2, respectively, followed by a gradual decrease, although

241   the trend is not clear in autumn (Fig. 3a). Further the MS$^-$ and SO$_4^{2-}$ were abundant in

242   summer followed by spring (Fig. 5a). In addition, SO$_4^{2-}$ showed a linear relationship with

243   MS$^-$ with a moderate correlation (r^2=0.50) during the campaign (n = 21). The air parcels

244   arriving over Sapporo during autumn to spring originated from Siberia passing over

245   Northeast Asia and the Sea of Japan (Fig. 2), which should have been enriched with SO_2, a

246   precursor for SO_4^{2-}, emitted from biomass burning and anthropogenic activities. In addition,

247   they should have also been enriched with dimethyl sulfide (DMS), a precursor for both MS^-

248   and SO_4^{2-}, whose emission from terrestrial higher plants (e.g., 0.42 pmol m^{-2} s^{-1} from

249   *Platanus orientalis L.* on a single leaf area basis)[36], soil in forests (0.46±0.30 pmol m^{-2} s^{-1} to

250   1.27±1.40 pmol m^{-2} s^{-1}, depending on forest type)[37] and phytoplankton bloom in the ocean[35]

251   is significant and enhanced with increasing ambient (and soil) temperatures. In summer, the

252   air masses originated from oceanic regions passing over coastal region and/or the mainland of

253   Japan in summer (Fig. 2) should have mainly enriched with DMS rather than SO_2.

254   In addition, ambient temperature, which promotes the photochemistry, showed a

255   distinct seasonal trend in Sapporo with winter minima and summer maxima whereas the RH,

256   which enhances the secondary processing of aerosols, showed a gradual increase from mid

257   spring to late summer (Fig. 1). In contrast, precipitation that causes the wet scavenging of

258   aerosols was relatively stable throughout the year, except in winter (high frequency) and

259   summer (high amount) (Fig. 1). A similar pattern should prevail in Northeast Asia. Therefore,

260   it is likely that the seasonal pattern of MS^- and SO_4^{2-} might have been driven mainly by

261   enhanced emissions of their precursors from season-specific (source(s), potentially biogenic

262   emissions in growing season, followed by intensive secondary formation processes whereas a

263   potential removal by wet scavenging could have played a minor role.

264   Interestingly, the temporal trends of sum of hopanes (C_{27}-C_{32} hopanoid hydrocarbons),

265   specific biomarkers of petroleum and coal[38] and elemental carbon that derives from fossil

266   fuel combustion and biomass burning did not follow clear seasonal pattern during the

267   campaign, except relatively high levels during late autumn to mid winter (Fig. 6), suggesting

268   that the contributions from fossil fuel combustion to Sapporo aerosols are significant in all

269   seasons. Their high abundance during November to January (Fig. 6) is apparent because of

270   increased consumption of fossil fuels in winter than in other seasons in East Asia[39]. On the

271   contrary, sums of lipid class compounds such as fatty acids (C_{12}-C_{32}) and fatty alcohols

272   (C_{18}-C_{32}) present clear seasonal pattern with maxima in growing season. Their averaged

273   molecular distributions are characterized by even-carbon-numbered predominance with a

274   maximum at C_{16}, and C_{26}, respectively, suggesting that they were most likely derived from

275   terrestrial higher plant waxes.(ref) In addition, tracers of biogenic secondary organic aerosols:

276   sums of isoprene- and α-pinene-derived compounds and β-caryophyllenic acid, showed a

277   clear seasonal pattern with maxima in spring to summer (Fig. 6), indicating that the

278   contributions from biogenic emissions and subsequent secondary formation processes are

279   significant in spring and summer.

280   In fact, the concentration range of MS^- in Sapporo aerosols (Table 1) is comparable to

281   that reported for the marine aerosols from the North Yellow Sea (12-75 ng m^{-3}),[40] the Oki

282   Islands in the Sea of Japan (3-95 ng m^{-3})[41] and other oceanic regions (~10-100 ng m^{-3})[35,42]

283   and the forest aerosols (9-95 ng m^{-3}) collected at two levels (~2 m and ~15 m) of the

284   experimental forest in Sapporo, Japan, where the canopy height is ~20 m.[43] The

285   contributions of MS^- in the marine and forest aerosols were attributed to the emission of

286   DMS from phytoplankton bloom and forest floor, respectively, followed by the subsequent

287   photochemical oxidation. It is noteworthy that the averaged seasonal variations of MS^- in

288   marine aerosols over Oki Islands in the Sea of Japan for a 9-year period showed a sharp

289   increase from March to May followed by a gradual decrease to October.[41] In contrast, in

290   Sapporo aerosols, MS^- concentrations gradually increased from March to May and stayed

291   high until late summer followed by a gradual decrease to autumn (Fig. 2a). The average

292   concentration of MS^- (64 ng m^{-3}) in Sapporo summer aerosols is significantly higher than that

293   (39 ng m^{-3}) reported in 2006 summer aerosols (July-August) from the North Yellow Sea.

294   In addition, the molar ratios of MS$^-$ to SO$_4^{2-}$, which can be used as an indicator of the

295   relative contributions of the SO$_4^{2-}$ derived from biogenic DMS and anthropogenic SO$_2$ to

296   measured SO$_4^{2-}$,[35] in Sapporo summer aerosols (average 1.55) is three times higher than that

297   (0.55%) of the summer aerosols from the North Yellow Sea.[40] Such differences might have

298   occurred probably due to more continental outflow of anthropogenic emissions from China

299   over the North Yellow Sea, compared to the Hokkaido region. Alternatively, additional

300   contribution of MS$^-$ originated from higher plant emissions is possible in Sapporo aerosols.

301   Thus our results and their comparisons with organic tracers and with literature imply that the

302   seasonality of MS$^-$ and SO$_4^{2-}$ in Sapporo aerosols should have been driven by the enhanced

303   biogenic emissions of DMS and subsequent intensive secondary processes in spring and

304   summer. On the other hand, the high frequency of precipitation should also lower the

305   concentrations of SO$_4^{2-}$ in winter, despite the enhanced contributions from the increased

306   anthropogenic emissions.

307   The concentrations of NO$_3^-$, which is also produced by secondary processes in the

308   atmosphere, are higher in autumn to spring and lower in summer, being different from the

309   case of SO$_4^{2-}$ (Fig. 2a). This discrepancy should be due to differences in mechanistic chains

310   responsible for their formation and emission rates of their precursors, in addition to a

311   potential loss of NO$_3^-$ by dry deposition in summer (see next Sect.). In fact, the [NH$_4^+$]/[SO$_4^{2-}$]

312   molar ratios were <1.5, except in winter, indicating the NH$_4^+$-poor atmosphere[26] during the

313   campaign. Under such conditions, the production of (NH$_4$)$_2$SO$_4$ is favored over the formation

314   of NH$_4$NO$_3$ through the homogeneous reaction between H$_2$SO$_4$ and NH$_3$, which is intensive

315   under high temperature and RH, rather than HNO$_3$ and NH$_3$. Meanwhile, HNO$_3$ is more

316   likely reacted with sea-salt (e.g., NaCl) and crustal particles (e.g., CaCO$_3$).[26]

317   On the other hand, the origins of the air parcels that arrived in Sapporo in each season

318   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 preferrential 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 μg m^{-3}) (Fig. 3a), despite a significant sea-salt

344   contribution in summer, and enhanced soil dust contribution in early spring as discussed

345   below. In addition, Mg^{2+} showed insignificant but negative relations with Al, a tracer of

346   crustal emission,[34] in autumn ($r^2 = 0.19$), suggesting that soil dust may not be a major source.

347   As noted earlier, sea-salt contribution to Na^+ may not be the major source in autumn.

348   Therefore, it is likely that the abundant Mg^{2+} and Na^+ in autumn may be derived from other

349   source, probably microbial activities. Fungal activities in soil surface emit the spores and

350   hyphae, which are significantly enriched with several elements including Na and Mg.[44]

351   Their activities on fallen leaves may be increased during defoliation season. In fact, the

352   concentration of mannitol that is mainly produced by fungi is highest in autumn (20.3±13.3

353   ng m^{-3}) followed by summer (7.07±3.38 ng m^{-3}) (Fig. 6).[25] Therefore, we consider that the

354   fungal activities are the potential sources of Na^+ and Mg^{2+} in autumn.

355   The relatively low concentrations of ions may be associated with wet scavenging in

356   winter when snow precipitation frequently occurred (Fig. 1). Their peaks (e.g., Ca^{2+}) in early

357   spring may be due to the soil dust injection to the atmosphere from the arid regions of

358   Mongolia and Northeast China[34] followed by a long-range transport. In fact, two massive

359   dust storms occurred in Mongolia and Northeast China in early spring on 20 and 31 March

360   2010, respectively (*http://earthobservatory.nasa.gov*). Liu et al.[45] reported that the dust

361   storm in Mongolia was blown in Beijing, China and the dust plume covered over the

362   downwind regions including Hokkaido Island.

363   In summer, the lowest concentrations of Cl^-, Na^+, Mg^{2+} and Ca^{2+} as well as NO_3^-, which

364   exist preferably in coarse mode, might be associated with the enhanced dry and wet

365   deposition. Agarwal et al.[23] reported that the concentrations of these ions (Na^+ is not

366   reported) maximized in coarse (>7.0 μm in diameter) size particles collected in summer (8-11

367   August) 2005 from the same site. Dry deposition velocities are higher (1.2-5 cm s^{-1}) for

368   coarse mode particles than accumulation mode particles (0.001-0.05 cm s^{-1}) and the

369   deposition rates are further influenced by surface thermal response to insolation on

370   convective mixing in the boundary layer.[46] The high temperature and low wind speed in

371   summer (Fig. 1) might have caused boundary layer convective instability and reduction in

372   convective mixing of pollutants, respectively, and hence, the dry deposition of coarse

373   particles might be intensive in summer. In addition, the washout of pollutant should be more

374   efficient in summer due to high amount of precipitation (Fig. 1). It is known that precipitation

375   scavenges coarse particles more efficiently than fine ones.

376

377   *NH_4^+ and K^+: Biomass burning emissions*

378   NH_4^+ and K^+ significantly increased from mid- to late-autumn and stayed high until

379   mid winter (Fig. 2a). NH_4^+ then showed a gradual decrease toward early spring whereas K^+

380   showed a decrease toward late winter followed by an increase in early spring and thereafter.

381   They stayed relatively stable, except for few cases, from mid spring to summer (Fig. 3a). It is

382   well recognized that NH_4^+ and K^+ are mainly originate from biomass burning and biogenic

383   emissions.[47-49] Higher levels of these species during mid autumn to mid winter may be

384   associated with forest fires and/or biomass burning on a local and/or regional scale, whereas

385   the increase of K^+ from late winter to early spring may be caused by the long-range

386   atmospheric transport of soil dust. Concentrations of levoglucosan, an excellent tracer of

387   biomass burning [50], were also high in mid autumn to mid winter (Fig. 6), further supporting

388   the enhanced contributions from the biomass burning during this period.

389   In spring and summer, the temporal trends of K^+ and NH_4^+ (Fig. 3a) are not consistent

390   with that of levoglucosan (Fig. 6). This discrepancy is probably due to significant

391   decomposition of levoglucosan[51] and (or) biogenic contributions of K^+ and NH_4^+ in during

392   growing season. In fact, K^+ in Sapporo aerosols showed a good correlation with SO_4^{2-} in

393   spring (r=0.71), which is partly derived from biogenic emissions. However, MODIS fire

394   detections indicated that the forest fires/biomass burning events are significant over Siberia

395   and northeast China in spring and over Japan mainland in summer 2010 (see Fig. S1). The air

396   masses arriving over Sapporo in spring originated in Siberia and passed over Northeast China

397   whereas in summer, they passed over Japan mainland (Fig. 2), which should have been

398   enriched with biomass burning emissions. Therefore, we consider that the higher levels of

399   NH_4^+ and K^+ from mid spring to late summer should have associated with enhanced biomass

400   burning emissions, although we do not preclude a minor contribution from biogenic

401   emissions.

402

403   *Trace metals: Possible contributions from soil dust injection, anthropogenic emissions*

404   *and biological sources*

405   Crustal metals such as Al, Ca, Fe, Ti and Mn[33] did not show any significant seasonal

406   variations, although their concentrations are relatively low in winter (Fig. 3b) probably due to

407   wet scavenging by snowfall (Fig. 1). They showed a very sharp increase in early spring

408   (April 1-15) followed by a gradual decrease to late autumn (Fig. 3b). Being similar to Ca^{2+},

409   these trends indicate a significant contribution of soil dust particles that are transported from

410   the arid regions in Mongolia and Northeast China,[45] as discussed earlier.

411   Ni showed a gradual decrease from autumn to mid winter and a gradual increase toward

412   early summer followed by a decrease in mid summer (Fig. 3b). The seasonal trends of both

413   Cu and As are quite similar to that of Ni in autumn to mid spring and the rest of the period

414   (Fig. 3b). The concentrations of Zn are rather constant during the campaign, except for spring:

415   a gradual increase from winter to late spring followed by a decrease to summer, although a

416   high value was observed in early summer (Fig. 3b). V and Cr did not vary significantly in

417   autumn but showed a gradual decrease in winter followed by a sharp increase in early spring.

418   Thereafter V stayed relatively high until late summer whereas Cr decreased gradually toward

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

420   campaign (Fig. 3b).

421   The trace metals: Ni, Cu, As, Zn, V, Cr, Cd and Pb, are considered to be emitted to the

422   atmosphere by fossil fuel combustion, metallurgical industrial activity and traffic pollution.[52]

423   Therefore, it is likely that they originate from anthropogenic sources over the region. The

424   lower values in winter might be associated with wet scavenging by snowfall (Fig. 1) whereas

425   a sharp increase in early spring may be due to soil dust injection from arid regions of

426   Mongolia and northeast China,[45] where the soil surface could have been enriched with

427   anthropogenic pollutants. However, the reason for a gradual decrease in autumn to winter and

428   a gradual increase from winter to late spring of some trace metals (i.e., Ni, Cu, As, Zn) is

429   unclear. In fact, the combustion tracers; (i) hopanes[38] (ii) levoglucosan [50] and (iii) EC, did

430   not show such seasonal trends in Sapporo aerosols.[25] Hence, it is possible that the seasonal

431   trends of Ni, Cu, As and Zn should have been driven by other season-specific source(s).

432   Interestingly, Ni, Cu and As (Fig. 3b) showed a seasonal trend similar to that of

433   mannitol (Fig. 5), which is considered as a tracer for bioaerosol (fungal species).[53] On the

434   other hand, seasonal pattern of Zn (Fig. 3b) is similar to that of sucrose (Fig. 5), which is a

435   tracer of pollens emitted from terrestrial plants.[54] Fungi uptake the trace metals from the

436   substrate and the extent of their bioaccumulation is species-specific.[55] As shown in Fig. 7,

437   Ni, Cu and As positively correlate with mannitol (r^2=0.33, 0.47 and 0.28, and p = 0.006,

438   0.001 and 0.013, respectively). It is also noteworthy that these metals negligibly correlated

439   with hopanes (r^2=0.22, 0.01 and 0.001), levoglucosan (r^2=0.25, 0.03 and 0.03) and EC

440   (r^2=0.03, 0.08 and 0.18, respectively). On the other hand, Zn showed a positive correlation

441   (r^2=0.60) with sucrose whereas weak or no correlations with hopanes (r^2=0.24), levoglucosan

442   (r^2=(-)0.001) and EC (r^2=0.12) in spring, although no relation was found in other seasons. In

443   fact, Zn is present in pollen grains.[56] Furthermore, we found that Cu and Zn, which are

444 considered to be emitted from metallurgical industrial activity,[52] are associated with

445 different factors obtained from Varimax rotated factor analysis of trace metals (see Table 3).

446 Therefore, we consider that the terrestrial biological sources including microbial activities

447 should have partly contributed to trace metals in Sapporo aerosols. Nriagu[57] reported that

448 biogenic sources could account for 30-50% of the global baseline emissions of trace metals,

449 which again supports our assumption.

450

451 *Factor analysis*

452 Factor analysis (FA), which does not require a prior information on source composition,[58]

453 has been widely used to apportion the sources of chemical species in atmospheric aerosols.[59]

454 In this study, Varimax rotated FA was applied to inorganic ion and trace metal data sets (n =

455 21) to further examine the likely sources discussed in the previous section and the obtained

456 results are presented in Tables 2 and 3, respectively. The FA resulted three factors each with

457 Eigen values greater than 1 that explain 87% and 83% of the total variance of the data sets,

458 respectively. The factor loadings: >0.75, 0.75-0.5 and 0.5-0.3, which can be classified as

459 strong, moderate and weak, respectively,[60] are used to infer the factors to distinguish

460 possible sources. It should be noted that the sample size (n = 30 + (V+3)/2) of both ions and

461 metals is relatively small for FA.[58] However, the communalities obtained for all species

462 are >0.6, except for V and Zn (0.5), suggesting that the obtained results from the FA of these

463 data sets should be reasonable.[61]

464

465 *Inorganic ions*

466 The first factor, which accounted for 31% of total variance, is strongly loaded with

467 Mg^{2+} and Na^+ and moderately with Ca^{2+} and weakly with Cl^- (Table 2). Na^+ and Ca^{2+} are

468 typical sea-salt and crustal components, respectively. Mg^{2+} originates mostly from soil dust

469 but oceanic emissions also could contribute at significant levels. In fact, Mg^{2+} showed a

470 positive correlation ($r^2 = 0.24$) with Al, a tracer for crustal origin,[34] during the campaign (n

471 $= 21$). Hence, this factor can be attributed to a natural source: soil dust and sea-salt. It is

472 noteworthy that both NO_3^- and K^+ are positively correlated with this factor, although the

473 loading is very poor (Table 3), suggesting important heterogeneous reactions (mainly for NO_3)

474 with dust and sea-salt and/or that biomass burning emissions may be associated with this

475 factor.

476   The second factor, which accounted for 30% of total variance, strongly loaded with

477 MS^- and SO_4^{2-} (Table 2). These ions are produced in the atmosphere by secondary

478 transformations through photochemical reactions of their precursor compounds (DMS, SO_2)

479 of biogenic and anthropogenic/biogenic origins, respectively, as discussed earlier. Therefore

480 it is apparent that the second factor represents the secondary aerosols produced by

481 homogeneous photochemical reactions. A weak positive correlation of K^+ and Ca^{2+} with this

482 factor may be due to a possible association of SO_4^- with these metal ions.

483   The third factor, which accounted for 25% of total variance, is strongly associated with

484 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^-

485 can be derived from fossil fuel combustion and/or biomass burning emissions whereas NH_4^+

486 and K^+ from biomass burning and/or biogenic emissions. Hence, this factor can mainly be

487 interpreted as biomass burning mixed with other anthropogenic emissions but biogenic

488 emissions may also be associated.

489

490   *Trace metals*

491   The first factor is strongly loaded with Al, Ca, Ti, Mn, and Fe, which are typical crustal

492 components[33,34] and with Cr, accounting for 41% of total variance. V is weakly loaded with

493 this factor whereas Ni, As and Pb are also positively correlated, however, their loadings are

494 very poor (Table 3). Hence, this factor can mainly be attributed to soil dust. The second

495 factor is strongly loaded with Ni and Cu, moderately with V and As, and weakly with Zn,

496 accounting for 21% of total variance (Table 3). The metallurgical industrial activities have

497 been considered as the major source of Cu, As and Zn whereas oil combustion is considered

498 as a source of Ni and V.[52] Therefore, this factor may be associated with industrial emissions

499 mixed with other (fossil fuel combustion) anthropogenic sources. The third factor correlates

500 strongly with Cd and Pb, moderately with Zn and weakly with Cr and As, accounting for

501 20% of total variance (Table 3). Mn, Fe and Cu also showed a positive correlation with this

502 factor, although the coefficient is poor. All these trace metals are most likely derived from the

503 anthropogenic activities, particularly fossil fuel combustion.[52] Hence, this factor can be

504 interpreted as emissions of fossil fuel combustion and road dust from the presence of Pb, Zn,

505 Cu and crustal elements.

506

507 **Summary and conclusions**

508 Atmospheric aerosol (TSP) samples collected from Sapporo, northern Japan for one-year

509 period, were studied for inorganic ions and trace metals using ion chromatograph (IC) and

510 inductively coupled plasma mass spectrometry (ICP-MS), respectively. SO_4^{2-} was found as

511 the most abundant ion whereas Ca was the most abundant metal. The mass fraction of sum of

512 inorganic ions in TSP ranged from 20% to 51% with an average of 31±10%, in which SO_4^{2-}

513 accounted for 12±3.8%. The group of crustal metals alone accounted for 95±2% of the total

514 metals determined. The seasonal trends of MS^- (a tracer for biologically derived sulfur) and

515 SO_4^{2-} showed maxima in growing season, while crustal metals peaked in early spring,

516 suggesting that biogenic emissions maximized in spring/summer whereas soil dust injection

517 did in early spring. Na^+ and Mg^{2+} were abundant, despite insignificant contribution of both

518 sea-salt and soil dust, in autumn. In addition, Ni, Cu and As showed maxima in autumn. Such

519   seasonal trends and their comparison with those of tracer species reported in our samples[25]

520   suggest the potential contribution of microbial activities in autumn. NH_4^+ and K^+ became

521   more abundant from mid autumn to mid winter as well as from mid spring to late summer,

522   indicating the enhanced contributions from biomass burning in these periods. The present

523   results together with factor analysis of ionic species and trace metals, comparisons of the

524   seasonality of specific ions and metals with the tracer species, and air mass trajectories, imply

525   that the long-range atmospheric transport of soil dust, and anthropogenic emissions including

526   biomass burning, biogenic emissions including microbial activities, and secondary production

527   from both anthropogenic and biogenic emissions are the major sources of Northeast Asian

528   aerosols, with the relative contributions being depending on seasons.

529

530 **Supplementary material**

531 Maps of monthly averages of active fires detected using MODIS data from the Terra satellite

532 over the Asian region for the period of September 2009 and August 2010 are provided in Fig.

533 S1. The global maps of active fire detections were obtained from MODIS Rapid Response

534 website (http://rapidfires.sci.gsfc.nasa.gov/).

535

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723 **Figure captions.**

724 **Fig. 1.** Seasonal variations of meteorological parameters (ambient temperature, RH, wind

725 speed and precipitation) in Sapporo, northern Japan.

726 **Fig. 2.** Plots of 10-day backward air mass trajectories arriving in Sapporo at 500 m AGL.

727 Color scale shows the altitude of the air parcel AGL.

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

729 **Fig. 4.** Relative abundances of ionic species to total ionic mass in (a) autumn, (b) winter, (c)

730 spring and (d) summer.

731 **Fig. 5.** Box-and-whisker plots of (a) MS^- and SO_4^{2-} and (b) Na^+ and Mg^{2+} in autumn, winter,

732 spring and summer. Lower and upper ends of the box show the quartiles at 25% and 75%

733 whereas upper and lower bars of the whiskers present the quartiles at 10% and 90%. The

734 cross bar in the box shows the median. Open circles mean outliers (1.25 × interquartile

735 distance).

736 **Fig. 6.** Temporal variations of concentrations of tracer species. Plant wax alkanes, fatty acids

737 and fatty alcohols are sums of C_{23} to C_{37}, C_{12}-C_{32} and C_{18}-C_{32} compounds, respectively.

738 Isoprene derived compounds are sums of 2-methylglyceric acid,

739 cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene

740 trans-2-methyl-1,3,4-trihydroxy-1-butene, 2-methylthreitol and 2-methylerythritol whereas

741 α-pinene derived compounds are sums of 3-hydroxyglutaric, pinonic, pinic and

742 3-methyl-1,2,3-butanetricarboxylic acids. The data are from Pavuluri et al.

743 **Fig. 7.** Scatter plots of the concentrations of Ni, Cu and As as a function of the concentrations

744 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
Ionic species			
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
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

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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 [a]Factor loadings ≥ 0.5 are in bold.

752   **Table 3.** Varimax rotated factor loadings for trace metals in the Sapporo TSP samples ($n = 21$)

753   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	

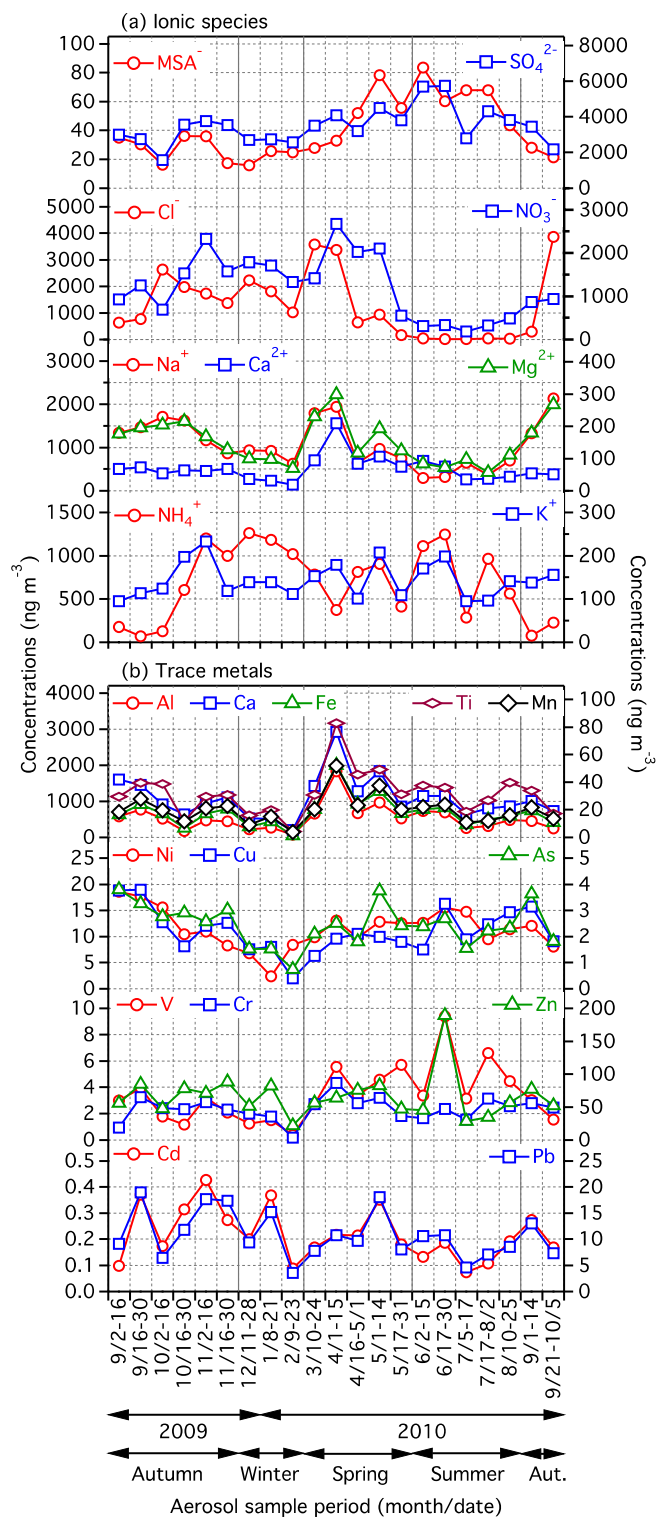754   [a]Factor loadings ≥0.5 are in bold.
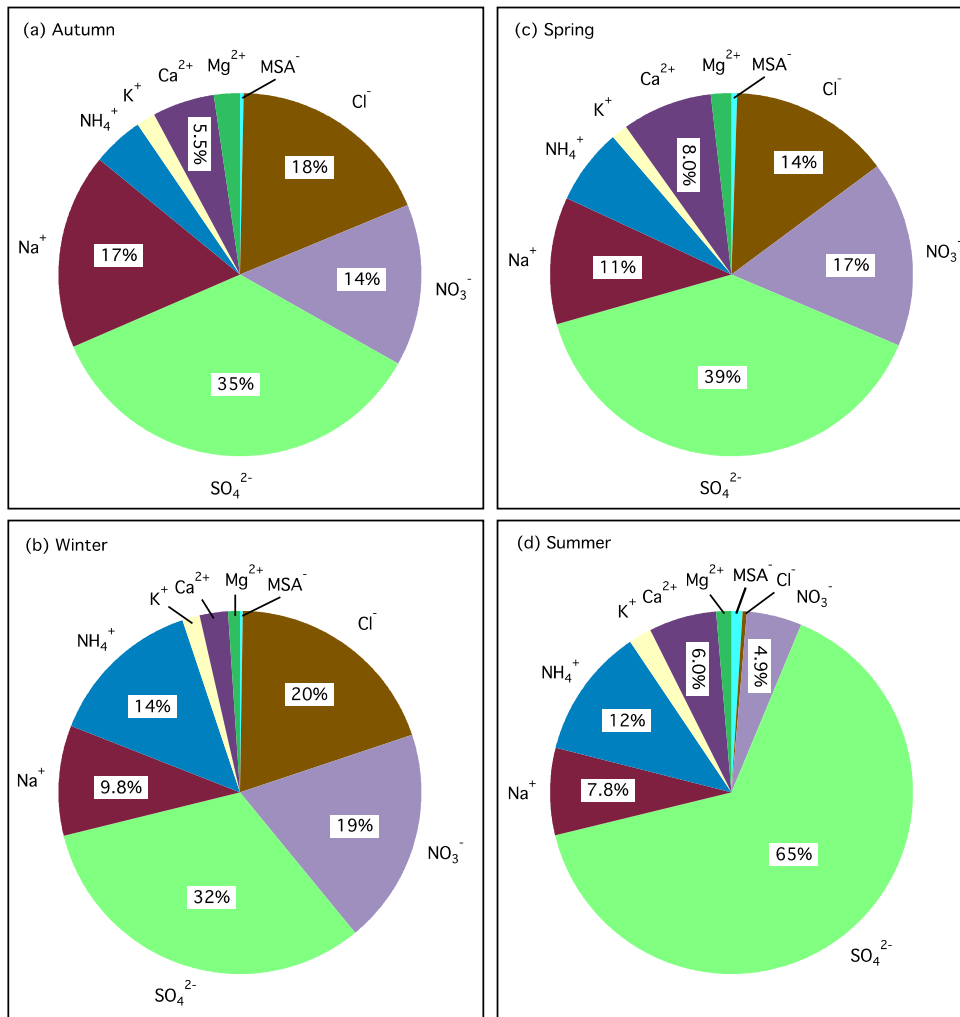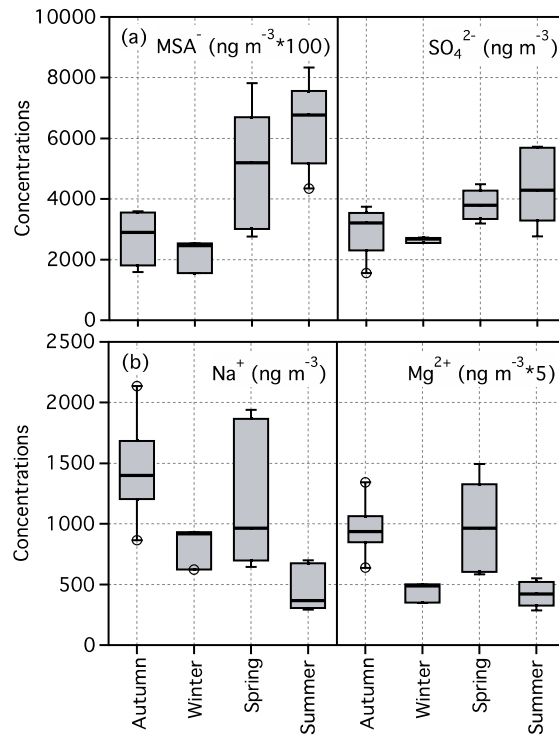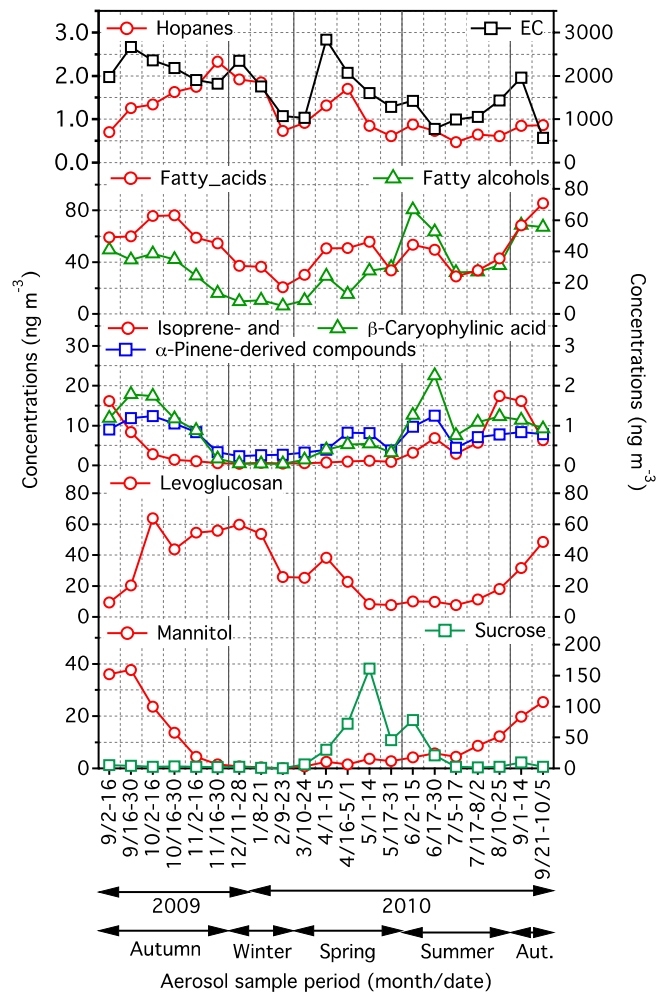
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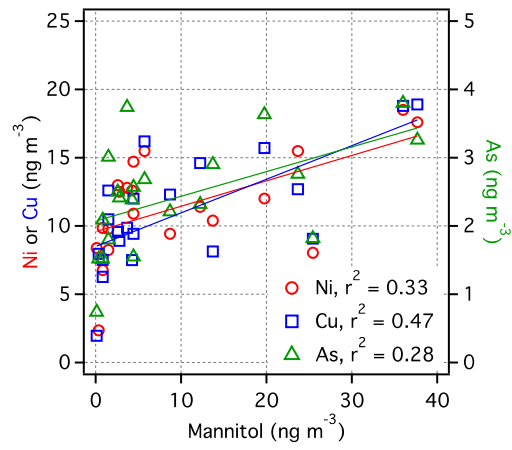757 **Fig. 2.**

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759   **Fig. 3.**

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761 **Fig. 4.**

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Fig. 6.

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