



# Water-soluble ions and trace elements in surface snow and their potential source regions across northeastern China



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## HIGHLIGHTS

- We collected 92 snow samples from 13 sites across northeastern China.
- The snow in the remote northeast on the border near Siberia was extremely clean.
- Al, and Fe were primarily derived from natural sources.
- Cu, Zn, As, V, and Cd in snow samples were likely derived from anthropogenic sources.

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## ABSTRACT

We collected 92 snow samples from 13 sites across northeastern China from January 7 to February 15, 2014. The surface snow samples were analyzed for the major water-soluble ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$ ) and trace element (Al, As, Mn, V, Cd, Cu, Pb, Zn, Fe, Cr, and Ni). The results indicated that the higher concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  and the trace elements Zn, Pb, Cd, Ni, and Cu were likely attributable to enhanced local industrial emissions in East Asia especially in China. In addition, snow samples characterized by higher enrichment factors of trace elements (Cu, Cd, As, Zn, Pb) were indicative of an anthropogenic source. Emissions from fossil fuel combustion and biomass burning were likely important contributors to the chemical elements in seasonal snow with long-range transport. On the other hand, the large attribution of  $\text{K}^+$  appeared in the higher latitude demonstrated that biomass burning was a dominated factor of the chemical species in seasonal snow in the higher latitude of China than that in the lower latitude. Finally, an interannual comparison with the 2010 China snow survey also confirmed the source attributions of chemical speciation in seasonal snow in these regions.

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## 1. Introduction

Trace elements and major water-soluble ions emitted into the atmosphere through natural and anthropogenic activities disperse (Nriagu et al., 1996), transported to the downwelling areas (Kyllonen et al., 2009), deposited onto snow surfaces via condensation (Gao et al., 2003; Steinhäuser et al., 2008). Water-soluble ions and the trace elements play key roles in many atmospheric processes, such as cloud formation, solar radiation, and haze formation because of their affinity with water (Cong et al., 2015; Deng et al., 2011; Cheng et al., 2012). Recent studies demonstrated that increasing industrial development has increased the anthropogenic

chemical species from various sources in East Asia, especially in the industrial areas across northern China (Wei and Yang, 2010; Duan and Tan, 2013; Lee et al., 2008; Liu et al., 2011).

The climate effects of chemical species in snow and ice in response to anthropogenic emissions have been investigated (Hong et al., 1996, 2009; Kang et al., 2004; Hegg et al., 2009, 2010; Dang and Hegg, 2014). Knowledge of the spatial and temporal distribution of trace elements in mid-latitude snow and ice areas is required to characterize the extent to which their sources are anthropogenic or natural. McConnell and Edwards (2008) indicated that the atmospheric wet deposition of numerous trace metals in snow has the potential to be toxic to human health and general ecosystems. Woodcock (1953) demonstrated that sea salt aerosols included higher concentrations of  $\text{Cl}^-$ ,  $\text{Na}^+$  are produced at the ocean surface through the bubble bursting mechanism. Water-soluble potassium is a good tracer for biomass burning (Andreae,

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1983), and elemental Al and Fe could be the good markers of crustal dust (Alfaro et al., 2004; Lafon et al., 2004; Wedepohl, 1995). Investigations of chemical species in snow and ice have allowed us to obtain important information to identify their source attributions in the Arctic, Greenland, Antarctic, North America, and Russia, and a great deal of attention has been focused on the Himalayas (Van de Velde et al., 2000; Rosman et al., 2000; Barbante et al., 2003; Schwikowski et al., 2004; Hong et al., 2004; Li et al., 2006, 2007; Hegg et al., 2009, 2010; Dang and Hegg, 2014).

Although widespread data obtained in recent decades have shown that trace elements and major water-soluble ions are distributed globally, little attention has been paid to the distribution and source attribution in seasonal snow in East Asia, especially in northern China. Furthermore, as the atmospheric lifetimes of most chemical contaminants are short and seasonal snowfall has a large spatial distribution each year, their mechanisms and potential source regions have not yet been fully determined. Zhang et al. (2013) identified three factors/sources that were responsible for the measured light absorption of snow: soil dust sources, industrial pollution sources, and biomass- or biofuel-burning sources. Recently, we focused on variations in the occurrences of trace elements and water-soluble ions in seasonal snow across northeastern China. This area is of special interest because of its rapid economic growth, which is dependent on industrialization; as a result, air pollutants, including high concentrations of chemical species, are generated, emitted into the atmosphere, and deposited on snow surfaces via dry and wet deposition. However, there were only a few studies in the experiments of measuring the trace elements and water-soluble ions in seasonal snow across northern China. The objectives of this study were to quantify the trace elements and major water-soluble ions in seasonal snow across northeastern China that can reflect their source attributions derived from the anthropogenic or natural emissions. Here, we present new data on 9 major ions and 11 trace elements in surface snow at 13 sites during the 2014 China snow survey from January 7 to February 15. Furthermore, an interannual comparison of the trace elements with the 2010 China survey was also performed. The results provide a better understanding of the chemical composition of the trace elements and water-soluble ions during the winter season across northern China.

## 2. Experiment and methods

### 2.1. Sample collection and handling

As there was less snowfall in January–February 2014 than in previous years, only 92 snow samples from 13 sites were collected. Photographs of some of the sampling conditions are shown in Fig. 1. Samples from sites 90–93 were collected from the surface of the Gobi Desert, located in Inner Mongolia (Fig. 1b). Sites 94–98 and sites 99–102 were located in Heilongjiang and Jilin provinces, respectively, which are the most polluted areas in northern China during the winter season. Farmland (Fig. 1c) and the Da Hinggan Mountains (Fig. 1d) were the other major land surface types during the 2014 China survey. We also noted that heavy industrial emissions were an important source of air pollutants (Fig. 1a) during the winter season in northern China (Sun et al., 2010; Wei and Yang, 2010; Duan and Tan, 2013; Li et al., 2013; Wang et al., 2014), and the dry deposition of chemical species was a dominant factor in variations in chemical properties of seasonal snow. To prevent contamination, the sampling sites were at least 50 km from villages and cities and at least 1 km upwind of the approach road, with the exception of site 101, which was downwind and close to the villages. The sampling site locations, shown in Fig. 1, were very similar to those of the previous China survey. The snow samples were kept

frozen until the filtration process. The mass concentration of black carbon (BC) was measured using an integrating sphere/integrating sandwich spectrophotometer (ISSW) as described by Doherty et al. (2010, 2014) and Grenfell et al. (2011).

### 2.2. Analytical procedures

In the laboratory, the snow samples were quickly melted in a microwave; the water samples were stored in clean low-density polyethylene (LDPE) bottles at  $-30\text{ }^{\circ}\text{C}$ . The major anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ , and  $\text{Cl}^-$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$ ) were analyzed with an ion chromatograph (Dionex 320; Dionex, Sunnyvale, CA) using a CS12 column (Dionex) for cations and an AS11 column (Dionex) for anions, with a detection limit of  $10\text{ ng g}^{-1}$ . The concentrations of 11 trace elements (Al, As, Mn, V, Cd, Cu, Pb, Zn, Fe, Cr, and Ni) were measured by inductively coupled plasma mass spectrometry (ICP-MS) in the laboratory, following the procedures described by Hegg et al. (2009, 2010) and Gao et al. (2003). Previous studies indicated that the concentrations of trace elements can varied significantly between filtered and unfiltered snow samples loaded with higher concentrations of mineral dust (Carling et al., 2012). Therefore, after snow samples were filtered, we placed each filter in 50 mL of 0.1 N Super pure nitric acid (EMD Millipore, Billerica, MA) and allowed them to leach for at least 2 days, after which the samples were analyzed by ICP-MS (Zhang et al., 2013).

### 2.3. Land cover and trajectory datasets

We use the Collection 5.1 MODIS global land cover type dataset (MCD12C1) to provide surface land cover type in Fig. 2. The dataset has 17 different surface vegetation types, which was developed by the International Geosphere-Biosphere Programme data (IGBP) (Loveland and Belward, 1997; Friedl et al., 2010). It provides the dominant land cover type as well as the sub-grid frequency distribution of land cover classes within  $0.05^{\circ}$  spatial resolution. To capture the long-range transport of air masses that arrive at our sampling sites, we chose the HYSPLIT model (Draxler and Rolph, 2003) at 500 m in the backward trajectory analysis, which was developed by NOAA/ARL (<http://ready.arl.noaa.gov/HYSPLIT.php>) during the experimental period in January–February 2014.

## 3. Results

### 3.1. Distribution of water-soluble ions in seasonal snow

As shown in Fig. 2, the sampling areas were located in the grassland, croplands and urban and built-up regions across northern China, where were probably influenced by human activities (Huang et al., 2015). We investigated the distribution of water-soluble ions in seasonal snow across northeastern China. Generally, the mass concentrations of the ionic abundances were much higher in the industrial area (sites 98–102) than that in the remote northeast on the Chinese border near Siberia, which were the cleanest sites (sites 92–94), and in Inner Mongolia at site 90. The results were consistent with previous studies by Wang et al. (2013) and Zhang et al. (2013). The average concentrations of ionic abundances in snow ( $\mu\text{g L}^{-1}$ ) exhibited a trend of  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{F}^-$  for anions, and  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+ > \text{NH}_4^+$  for cations at most of the sampling sites.  $\text{SO}_4^{2-}$  was the dominant anion, with concentrations ranging from 0.51 to  $12.38\text{ mg L}^{-1}$ . The next most abundant anion was  $\text{NO}_3^-$  with concentrations ranging from 0.11 to  $3.63\text{ mg L}^{-1}$  (median  $0.53\text{ mg L}^{-1}$ ), which were much higher than that in Qomolangma (Mt. Everest) station in Himalayas (Cong et al., 2015). The results indicated that  $\text{SO}_4^{2-}$  made the greatest contribution to the total ion mass in surface snow, accounting for



Fig. 1. Photographs of several snow sampling sites during 2014 China survey.

~24.4%–42.7% of the total ion mass and ~39.7%–68.0% of the total mass of measured anions. It is also worthy to note that the concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were much higher in site 96–102 than that in site 90–95, which reflect a significant anthropogenic source of fossil-fuel combustion in the heavy industrial areas. The results obtained in this study were very similar to those of the 2010 China survey shown in Table 2 (Zhang et al., 2013). Water-soluble  $\text{NH}_4^+$  predominantly originates from agricultural activities due to high levels of fertilizer usage, but the concentration of  $\text{NH}_4^+$  was the lowest of the water-soluble cation in the surface snow because all of the sampling sites were 50 km away from cities or villages, with the exception of site 101. We found significant higher concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  than that of  $\text{NH}_4^+$  throughout the 2014 China survey. However, the strong correlations of  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $R^2 = 0.91$ , and  $R^2 = 0.95$ ,  $n = 13$ ) reveals industrial emissions were also dominant in these areas, which were influenced by human activities. The most abundant cation of  $\text{Ca}^{2+}$ , a tracer for natural soil dust, ranged from 0.184 to 6.64  $\text{mg L}^{-1}$  with a median value of 0.83  $\text{mg L}^{-1}$  Xu and Han (2009) indicated that  $\text{Ca}^{2+}$  is emitted mainly from the dissolution of  $\text{CaCO}_3$  in soil dust transported from either local areas or desert areas in northern China. Previous studies also indicated that the crustal  $\text{Ca}^{2+}$  in snow and ice is present in higher concentrations during winter and spring due to strong dust input, and in lower concentrations during summer in response to heavy precipitation (Al-Khashman, 2005; Arimoto et al., 2004). Soluble potassium ( $\text{K}^+$ ), a good tracer of biomass burning is ranging from 0.19 to 1.47  $\text{mg L}^{-1}$ , with a medium value of 0.38  $\text{mg L}^{-1}$ . It presented much higher contribution to the total ion mass in Inner Mongolia and on the northern border of China near Siberia as a result of less industrial emissions and more biomass-burning emissions, such as cooking, open fires, and agricultural activities. This result corresponds with the open fires on the northeast border of China near Siberia detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) Fire Mapper. Concentrations of  $\text{Mg}^{2+}$  ranged from 0.02 to 0.87  $\text{mg L}^{-1}$  with a median value of 0.09  $\text{mg L}^{-1}$ . Contributions of marine ions ( $\text{Cl}^-$  and  $\text{Na}^+$ ) were much higher in surface snow at sites 91–93 and 95–96. The higher  $\text{Cl}^-/\text{Na}^+$  ratio of at most of the sampling sites also indicated that there

were other sources of  $\text{Cl}^-$  due to industrial emissions, such as coal combustion. This result was consistent with a previous study by Zhang et al. (2013), which indicated that industrial emissions were one of the most important sources of air pollutants in seasonal snow. As Table 2 indicated, sea salt ions of  $\text{Cl}^-$  and  $\text{Na}^+$  are found in the ranging from 0.18 to 3.4  $\text{mg L}^{-1}$  with a median value of 0.5  $\text{mg L}^{-1}$  and from 0.22 to 1.4  $\text{mg L}^{-1}$  with a median value of 0.48  $\text{mg L}^{-1}$ , respectively (see Table 2). The  $\text{Cl}^-/\text{Na}^+$  ratios in seasonal snow were ~1–2 times larger than that of seawater ( $\text{Cl}^-/\text{Na}^+ = 1.17$ ; Berner and Berner, 1987), also suggesting a significant anthropogenic  $\text{Cl}^-$  source. Previous studies indicated that  $\text{Cl}^-$  not from marine origins could originate from various sources of pollution, such as automobiles and coal combustion (Al-Khashman, 2009; Xu and Han, 2009).

### 3.2. Concentrations of chemical species

To better evaluate the current attributions of the emissions of trace elements to the seasonal snow across northern China, we compare our concentration levels with those observed in Himalayas snow, and the similar areas across northern China (Zhang et al., 2013; Lee et al., 2008; Kang et al., 2007). As shown in Table 1, the average concentrations of trace elements in snow samples exhibited the following trend:  $\text{Al} > \text{Fe} > \text{Zn} > \text{Mn} > \text{Pb} > \text{As} > \text{Cu} > \text{Ni} > \text{Cr} > \text{V} > \text{Cd}$ . 94–404  $\mu\text{g L}^{-1}$  for Al, 22–284  $\mu\text{g L}^{-1}$  for Fe, 14–110  $\mu\text{g L}^{-1}$  for Zn, 4–106  $\mu\text{g L}^{-1}$  for Mn, 1.3–10.5  $\mu\text{g L}^{-1}$  for Pb, 2–6  $\mu\text{g L}^{-1}$  for As, 0.8–16.7  $\mu\text{g L}^{-1}$  for Cu, 1.3–3.9  $\mu\text{g L}^{-1}$  for Ni, 0.6–1.6  $\mu\text{g L}^{-1}$  for Cr, 0.1–3.7  $\mu\text{g L}^{-1}$  for V, and 0.04–0.57  $\mu\text{g L}^{-1}$  for Cd. Among all trace elements, Mn, Cu, and Zn in our samples show comparable values than those during previous seasonal snow collection in 2010 (Zhang et al., 2013), but concentrations of Cu and Zn are one order of magnitude lower to those observed in Himalayas snow (Kang et al., 2007). It was estimated that anthropogenic emissions are dominant for Cu, Pb, and As in seasonal snow, while natural contribution of Fe form rock and soil dust. As indicated, mean concentration levels of crustal elements (Al, and Fe) are comparable to those at Himalayas region, indicating larger dust contributions in these areas. Wang et al. (2013)

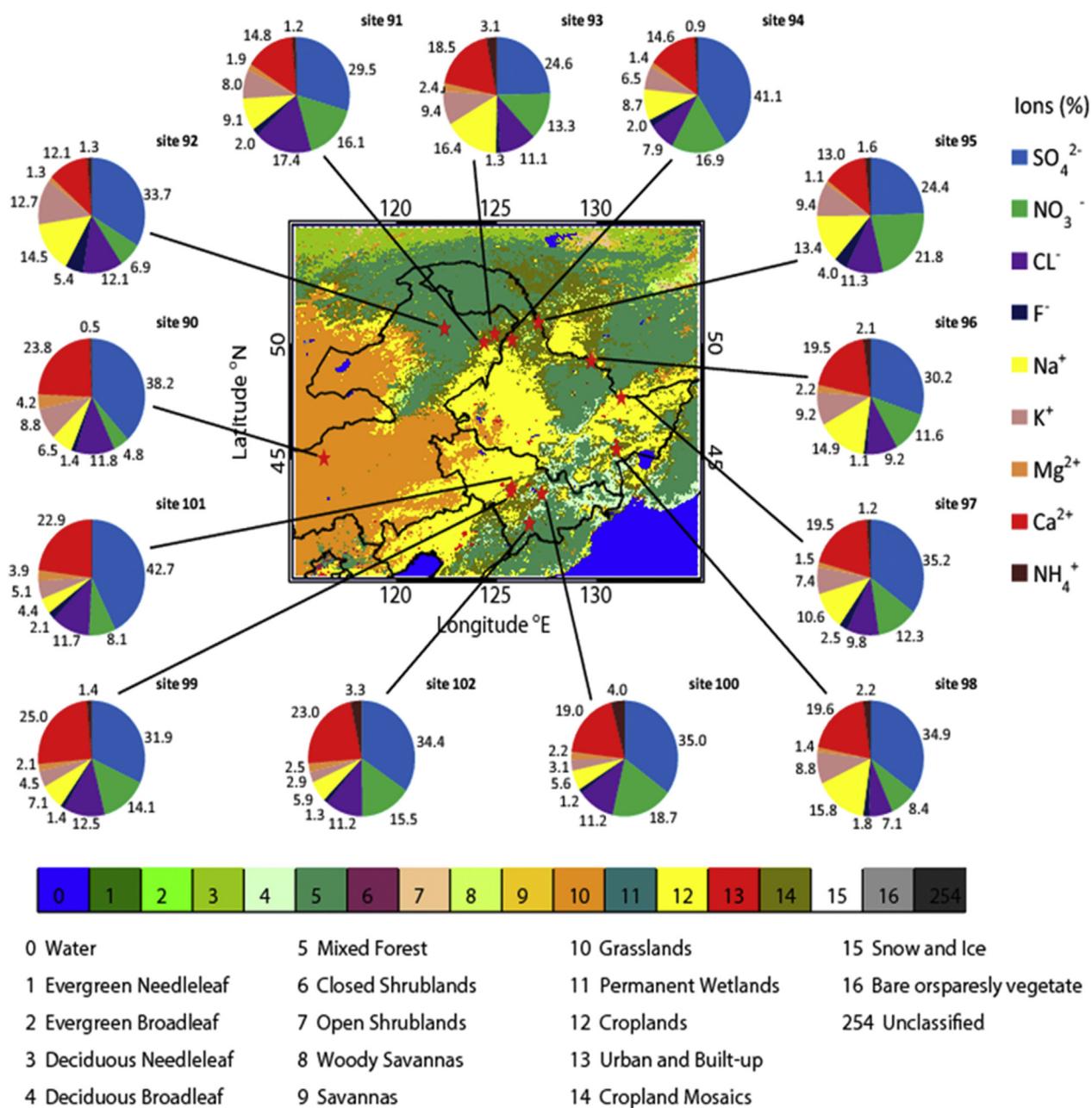


Fig. 2. The contributions of water-soluble ions to the total mass of ions in surface snow.

indicated that the seasonal snow was thin in this region, so most of the snow samples were drifted snow, and the wind-blown soil can be seen on top of the snowdrift. The concentrations of trace elements in snow from industrial areas (sites 98–102) were higher than those from the other sites. Fig. 3 shows the concentrations of trace elements and water-soluble ions in surface snow at different locations from the northern China surveys of January–February 2010 and 2014. Large interannual variability was seen for most chemical species, including SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, V, and Fe. The large differences in the V, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup> concentrations were possibly influenced by anthropogenic contributions. The median concentrations were relatively low, indicating that for these metals, the contribution from rock and soil dust was likely important (Table 2). Our Pb concentration is only two times lower than that reported for Himalayas snow (Kang et al., 2007), while they are comparable with those measured in Greenland (Barbante et al., 2003). The median

values of Pb and Zn concentrations are 2.470 µg L<sup>-1</sup> and 23 µg L<sup>-1</sup>, respectively. Several trace elements in recent snow samples, reported by Zhang et al. (2013), are not listed in Table 2, since no data were available during that experiment. The only data to which our values can be directly compared were published in 2011 for seasonal snow collected in 2010 across northern China (Zhang et al., 2013). A review by Galloway et al. (1982) reported Cd concentrations ranging from ~150 to 7000 pg g<sup>-1</sup> in snow in rural areas of North America and Europe, which is much higher than the value observed in the present study. For Ni, Pb, Cr, Mg, and Mn, the mean crustal enrichment factor (EF<sub>c</sub>) values ranged from 6.9 to 86.1, which is considered to be moderately to highly enriched, indicating an important contribution from anthropogenic or other natural sources. Overall, concentrations of trace elements in seasonal snow across northern China are much higher than those observed in Greenland and the Arctic (Boutron et al., 1991; Hegg et al., 2009,

**Table 1**  
The concentrations of trace elements and major ions in seasonal snow during the January–February 2014 China survey, all values in  $\mu\text{g L}^{-1}$ .

Site	90	91	92	93	94	95	96	97	98	99	100	101	102
Latitude N	45°02'44"	50°02'48"	50°39'07"	50°24'50"	50°09'05"	50°54'43"	49°14'21"	47°39'18"	45°25'38"	43°36'10"	43°30'45"	43°47'25"	42°12'34"
Longitude E	116°22'45"	124°22'41"	122°23'53"	124°54'20"	125°46'06"	127°04'50"	129°43'13"	131°13'10"	130°58'55"	125°42'04"	127°15'34"	125°46'08"	126°37'50"
F <sup>-</sup>	62	59	82	36	66	97	47	83	159	143	147	601	302
Cl <sup>-</sup>	518	503	183	325	256	271	391	323	624	1319	1350	3404	2628
NO <sub>3</sub> <sup>-</sup>	213	465	105	387	550	523	493	407	747	1492	2258	2364	3631
SO <sub>4</sub> <sup>2-</sup>	1685	718	511	1685	1335	587	1285	1163	3096	3379	4237	12382	8034
Na <sup>+</sup>	287	264	220	479	282	323	632	352	1398	755	672	1274	1373
K <sup>+</sup>	386	232	192	274	211	228	391	245	783	476	380	1472	684
Mg <sup>2+</sup>	184	56	20	68	47	25	93	50	127	222	265	865	589
Ca <sup>2+</sup>	1050	427	184	539	476	313	831	644	1731	2647	2299	6638	5367
NH <sub>4</sub> <sup>+</sup>	22	36	19	90	28	39	91	38	195	155	487	—	769
Al	136	120	94	119	231	143	162	165	272	211	264	242	404
V	0.70	0.14	0.15	0.23	1.17	0.17	0.22	0.43	1.00	1.01	0.94	3.68	1.73
Cr	0.64	0.67	0.62	0.82	0.71	1.08	0.92	0.76	1.25	1.13	1.03	1.34	1.62
Mn	46.9	20.2	10.9	4.0	17.0	4.1	24.7	14.0	22.0	31.8	33.9	106.1	56.2
Fe	41	50	22	32	284	52	91	62	105	100	153	59	187
Ni	1.6	1.8	1.3	1.4	1.7	1.9	1.7	1.4	1.9	2.6	2.5	3.9	2.6
Cu	1.17	0.89	0.79	1.20	2.42	1.25	1.22	1.25	1.50	3.00	4.74	16.73	3.34
Zn	14	23	15	19	20	19	23	33	31	40	46	110	58
As	3.1	2.4	1.6	2.3	10.3	2.1	2.4	2.2	3.0	7.0	4.1	15.7	4.9
Cd	0.04	0.05	0.07	0.04	0.06	0.06	0.10	0.26	0.26	0.27	0.30	0.24	0.57
Pb	1.3	1.5	1.4	2.3	2.3	2.5	2.1	3.6	3.3	4.1	10.5	9.2	7.6

**Table 2**

Statistical summaries of chemical species concentrations in seasonal snow across northeastern China in 2014 (this study) and 2010 (Zhang et al., 2013), all values in  $\mu\text{g L}^{-1}$ .

	2014			2010		
	Maximum	Median	Minimum	Maximum	Median	Minimum
F <sup>-</sup>	601	83	36	—	—	—
Cl <sup>-</sup>	3404	503	183	2116	397	65
NO <sub>3</sub> <sup>-</sup>	3631	523	105	11837	2096	564
SO <sub>4</sub> <sup>2-</sup>	12382	1335	511	13324	2518	274
Na <sup>+</sup>	1398	479	220	—	—	—
K <sup>+</sup>	1472	380	192	—	—	—
Mg <sup>2+</sup>	865	93	20	—	—	—
Ca <sup>2+</sup>	6638	831	184	—	—	—
NH <sub>4</sub> <sup>+</sup>	769	39	19	—	—	—
Al	404	165	94	1990	508	39
V	3.7	0.7	0.1	79.3	16.8	0.9
Cr	1.6	0.9	0.6	—	—	—
Mn	106.1	22.0	4.0	180.1	42.9	3.2
Fe	284	62	22	2477	434	31
Ni	3.9	1.8	1.3	—	—	—
Cu	16.7	1.3	0.8	6840.6	2.8	0.5
Zn	110	23	14	4449	17	1
As	16	3	2	—	—	—
Cd	0.57	0.1	0.04	—	—	—
Pb	10.5	2.5	1.3	—	—	—

2010). Our observations were in agreement with recent suggestion by Zhang et al. (2013) that anthropogenic contributions to the atmospheric environment were negligible across northern China in winter.

### 3.3. Estimates of natural versus anthropogenic contributions

To evaluate the relative contributions of trace elements from natural (e.g., mineral and soil dust) versus anthropogenic sources, an interannual comparison of  $EF_c$  values, which represent the enrichment of a given element relative to its concentration in the crust of the earth, was plotted against the concentration of Al for the surface snow samples from 2010 (triangles) and 2014 (dots). The primary uncertainty in these calculations is attributed to the differences between chemical compositions in the snow and the reference crustal composition. The  $EF_c$  is defined as the concentration ratio of a given metal to that of Al, which is a reliable measure of crustal dust, normalized to the same concentration ratio characteristic of the upper continental crust (Wedepohl, 1995), calculated with the following equation:

$$EF_c = \frac{(X/Al)_{\text{snow}}}{(X/Al)_{\text{crust}}}$$

Briefly,  $EF_c$  values ranging from ~0.1 to 10 suggest significant input from rock and soil dust as the dominant source. Conversely,  $EF_c$  values larger than ~10 indicate an important contribution from other natural sources or anthropogenic emissions. We use the  $EF_c$  values to consider potential anthropogenic and natural contributions affecting the concentrations of trace elements observed in our snow samples. Fig. 4 shows the  $EF_c$  values of the measured trace elements.  $EF_c$  values for Cr, Ni, and Mn indicate that they were moderately to highly enriched, suggesting an important contribution from other natural sources or anthropogenic sources. The mean  $EF_c$  values were relatively lower for Mg and Fe, indicating that the contribution from natural sources, such as soil and mineral dust, was likely important. Previous studies have also indicated that light-absorbing impurities in snow are dominated by local soil dust and mineral dust in the Inner Mongolia and Qilian Mountains regions, which have higher dust loading (Wang et al., 2013). Cu

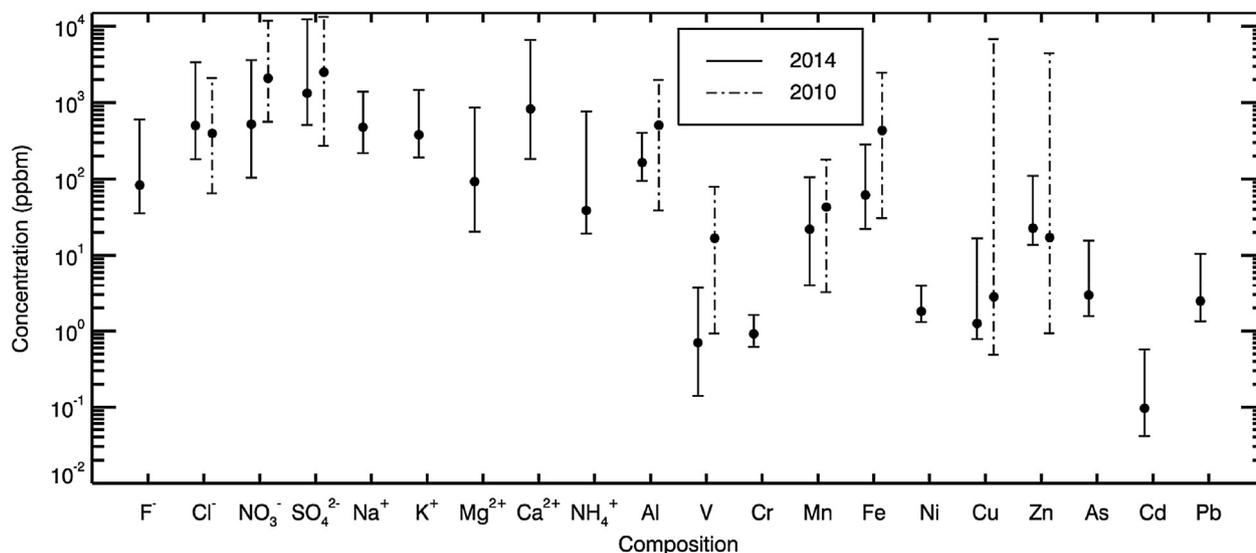


Fig. 3. The mass concentrations of major water-soluble ions and trace elements observed in seasonal snow.

primarily originates from emissions from fossil fuel combustion and industrial processes, while Zinc and Pb primarily originate from traffic-related activities (gasoline combustion) and coal burning. Among the enriched trace elements, As and Cd were highly enriched, indicating an important contribution of anthropogenic sources. Overall, the higher  $EF_c$  values for chemical species such as Cu, Zn, As, V, and Cd were likely the result of anthropogenic emissions. In most surface snow samples, Cr, Ni, and Pb had moderate  $EF_c$  values, indicating that both human activities and natural sources were important influences. For example, Pacyna and Pacyna (2001) reported that fossil fuel combustion is a major source of Cr and Ni. The  $EF_c$  values of trace elements V and Fe differed markedly between the 2010 and 2014 China surveys. We concluded that the chemical composition of seasonal snow has great temporal and spatial variation, and is also dependent on variations in atmospheric circulation. As shown in Fig. 4, most elements exhibited high  $EF_c$  values. Together with high  $EF_c$  values observed for Cu, Zn, As, V, and Cd in our snow samples clearly suggested that the seasonal snow has already been heavy polluted in the industrial areas than those in the border of northern China near Siberia.

### 3.4. Emission factors

Generally, the chemical species originated from different emission sources. For example,  $K^+$  is an important indicator of combustion sources and has a relatively long tropospheric lifetime, whereas  $NO_3^-$  was mainly produced by the combustion of diesel oil, gasoline, and coal.  $SO_4^{2-}$  was mainly a product of burning coal, which contains sulfur. Shen et al. (2007) indicate that the water-soluble ions were relatively more abundant during the pollution episodes in the Horqin sand land of northeastern China, such as  $SO_4^{2-}$  and  $NO_3^-$ . We compared the ratios of  $SO_4^{2-}/NO_3^-$  to the concentration of BC to identify the emission sources of chemical species in snow at mid-latitudes across northeastern China. An interannual comparison of the ratios of  $SO_4^{2-}$  and  $NO_3^-$  to the concentration of BC in seasonal snow during the 2010 and 2014 China surveys is shown in Fig. 5. The concentration of BC in snow was measured using an ISSW (Doherty et al., 2010; Grenfell et al., 2011). The  $SO_4^{2-}/NO_3^-$  ratios compared to the concentration of BC can indicate the relative impact of anthropogenic sources that are rich

in BC (Fig. 5). A low correlation coefficient of  $R^2 = 0.57$  between  $SO_4^{2-}$  and  $NO_3^-$  can partly be explained by the complicated air pollution emission sources in northeastern China in the winter season. Generally, lower  $SO_4^{2-}/NO_3^-$  ratios and lower concentration of BC were observed in the remote northeast on the border near Siberia from sites 91–95 in 2014 and sites 20–24 in 2010, in contrast to the high  $SO_4^{2-}/NO_3^-$  ratios observed in the industrial regions due to anthropogenic pollution.  $SO_4^{2-}$  concentration in seasonal snow across northern China indicates that the high concentration of  $SO_4^{2-}$  associated with anthropogenic emissions generally occur during winter in the heavy industrial areas, with much lower concentrations in the border of northern China near Siberia.

### 3.5. Back trajectory cluster analysis

To identify potential sources of the water-soluble ions and trace elements in the seasonal snow, cluster analysis was applied to track the transportation of air masses using a 60-h hybrid single particle Lagrangian integrated trajectory (HYSPLIT) model for 30 days prior to snow sampling at 500 m above ground level (AGL) (Fig. 6). We divided the trajectories into four clusters. An example of the cluster analysis for site 90 was located in the center of Inner Mongolia, and all of the trajectories were originated from the north path shown in Fig. 6a. The light-absorbing impurities deposited on the snow were likely dominant by soil dust in the remote area. Furthermore, the trace elements and water-soluble ions were probably from the Siberia region in winter, while sources for the substantial fire component were also obvious (Zhang et al., 2013). Fig. 6b shows that the northern path accounted for 92% of the total trajectories in the remote northeast on the border of China, while only 8% of the air mass was transported from the west, where there is little impact of human activities. As reported by Wang et al. (2013) and Warren (2013), snow does not completely cover the mid-latitude regions. Therefore, northern winds can carry a higher concentration of mineral or soil dust to the seasonal snow from other natural and anthropogenic sources. Zhang et al. (2013) also reported that soil dust can account for up to 53% of the insoluble light-absorbing impurities in seasonal snow across northern China. In contrast, an example of cluster analysis for an industrial area is shown in Fig. 6c. There was a significant cluster (30%) derived from the residential

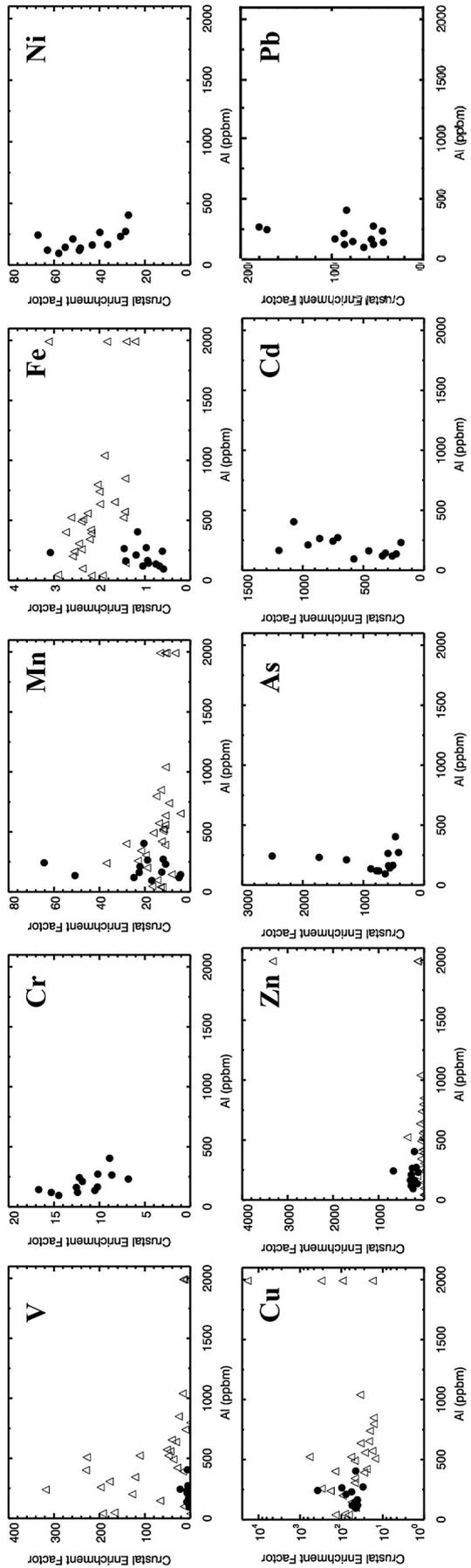


Fig. 4. Plots of crustal enrichment factors (EF<sub>c</sub>) versus Al concentrations for each heavy metal in seasonal snow in 2010 (Triangle) and 2014 (Dots).

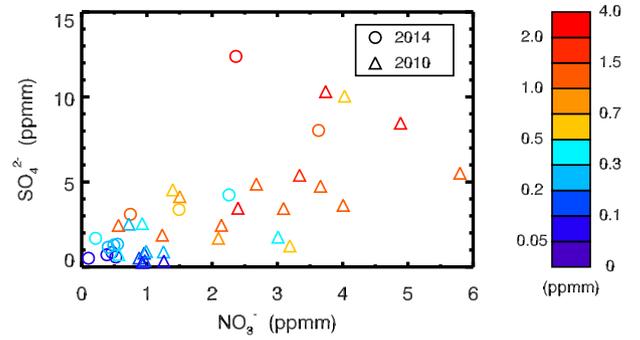


Fig. 5. Interannual comparison of the concentration of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> versus the mixing ratio of black carbon (BC) in seasonal snow.

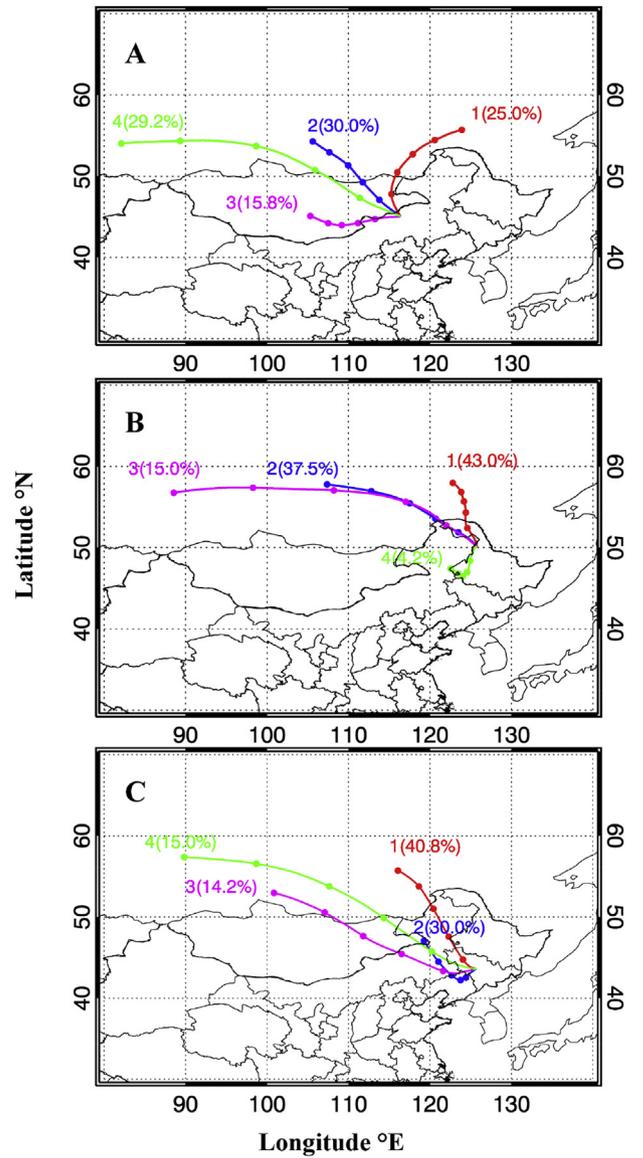


Fig. 6. Cluster analysis of 60-h air mass back trajectories with the initial positions in site 90, site 94 and site 99 at 500 m above ground level (AGL) for 30 days prior to the snow sampling (120 backward trajectories).

areas across northeastern China. During the winter season, the south wind is relatively low, and local air pollutants increase; therefore, urban and regional water-soluble ions and trace

elements can be deposited in surface snow via dry and wet deposition. Although the other three clusters were transported from the north, we note that the clean air mass could mix with the local air pollutants during transportation across the city and industrial factories. Hence, anthropogenic emissions are an important source of air pollutants in the industrial area.

#### 4. Discussion and conclusions

This report describes the distribution and source attributions of the trace elements and major water-soluble ions in seasonal snow across northeastern China in January–February 2014. Generally, there were large annual differences in the spatial and temporal distributions of trace elements in seasonal snow, based on the 2010 and 2014 China surveys. Compared to the chemical species in the industrial area, we found that the snow in the remote northeast on the border near Siberia was extremely clean, with very low concentrations of chemical species. In the north border of China, the contribution of  $K^+$  was much higher than those in the lower latitudes, indicating that biomass burning is an important source of the chemical species in seasonal snow. The strong correlations of  $NH_4^+$  with  $SO_4^{2-}$  and  $NO_3^-$  ( $R^2 = 0.91$ , and  $R^2 = 0.95$ ,  $n = 13$ ) reveals industrial emissions were also dominant in these areas, which were influenced by human activities. The high  $EF_c$  values of chemical species such as Cu, Zn, As, V, and Cd in our snow samples also suggested that they were likely derived from anthropogenic sources, including metal smelting, fossil fuel combustion, and combustion of gasoline. However, we note that major water-soluble ions and trace elements cannot absolutely characterize the various sources, and further studies of the chemical species in seasonal snow at different sites across northern China will be necessarily performed to reveal the contribution of anthropogenic pollution by human activities.

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