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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 (SO_4^{2-}, NO_3^-, F^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, and 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 NO_3^- and 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 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.

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; Steinhauser 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 Cl^-, 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 handing

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 °C. The major anions (SO_4^{2-}, NO_3^-, F^-, and Cl^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, and 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 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° 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 (μg L^{-1}) exhibited a trend of $SO_4^{2-} > NO_3^- > Cl^- > F^-$ for anions, and $Ca^{2+} > Mg^{2+} > Na^+ > K^+ > NH_4^+$ for cations at most of the sampling sites. SO_4^{2-} was the dominant anion, with concentrations ranging from 0.51 to 12.38 mg L^{-1}. The next most abundant anion was NO_3^- with concentrations ranging from 0.11 to 3.63 mg L^{-1} (median 0.53 mg L^{-1}), which were much higher than that in Qomolangma (Mt. Everest) station in Himalayas (Cong et al., 2015). The results indicated that SO_4^{2-} made the greatest contribution to the total ion mass in surface snow, accounting for