Distributions and impact factors of antimony in topsoils and moss in Ny-Ålesund, Arctic

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**Abstract**

The distribution of antimony (Sb) in topsoil and moss (*Dicranum angustum*) in disturbed and undisturbed areas, as well as coal and gangue, in Ny-Ålesund, Arctic was examined. Results show that the weathering of coal bed could not contribute to the increase of Sb concentrations in topsoil and moss in the study area. The distribution of Sb is partially associated with traffic and historical mining activities. The occurrence of the maximum Sb concentration is due to the contribution of human activities. In addition, the decrease of Sb content in topsoil near the coastline may be caused by the washing of seawater. Compared with topsoils, moss could be a useful tool for monitoring Sb in both highly and lightly polluted areas.

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1. Introduction

Antimony (Sb), a trace element, is ubiquitous in the environment because of natural processes and human activities (Filella et al., 2009). It has been found in both organic and inorganic species in soil and water systems, and the two dominant oxidation states in environmental materials are -3 and -5. Sb has been increasingly recognized as a toxic environmental pollutant and also implicated in cancer development (Gurnani et al., 1994; Gebel, 1997). Moreover, Sb and its compounds are considered as pollutants of high priority by the US Environmental Protection Agency (USEPA, 1979) and the European Union (Council of the European Communities, 1976). Recently, Sb has attracted increasing attention as being transported through the atmosphere (Filella et al., 2009). Many research efforts have been aimed at studying the distribution, speciation, biogeochemistry and ecotoxicity of Sb since 1990s (Reimann et al., 2010).

According to Nriagu (1989), 41% of Sb emission to the air can be attributed to natural sources (e.g., soil particles, volcanoes, sea-salt spray, forest fire, and biogenic sources); the remaining 59% is considered to be related to anthropogenic sources (e.g., mines, smelters, fertilizers, traffic). Mining and smelting are thought to be the greatest emission sources (Adriano, 1986); thus, research of the concentration and distribution of Sb in coals is urgently needed. The mean concentration of Sb in coals (3 mg/kg worldwide (Swaine, 1990; Valković, 1983)) seems to be much higher than that in the earth crust (0.3 mg/kg) (Wedepohl, 1995). However, Sb value in coals is quite variable, with the minimum concentration of about 0.007 mg/kg (Ren et al., 2006) and the maximum of about 17 000 mg/kg (Qi et al., 2008).

The distribution of Sb in topsoils and vegetation is easily affected by human activities. Various researches have been done, especially in characterizing distributional patterns in heavily polluted areas so as to investigate Sb transfer mechanism among different materials (Okkenhaug et al., 2011; He, 2007). Sternbeck et al. (2002) have shown that Sb was mainly released from the wearing of the brake lining around traffic, and the deposition of road dust and aerosol enriched in Sb would respond to the increase of Sb concentration in topsoils (Bukowiecki et al., 2009). The different forms of Sb in different materials from known contamination sources and their surroundings have been extensively studied. However, why the activity of coal mining can lead to an increase in Sb concentration is still poorly understood. Moreover, the distribution of Sb and impact factors that would possibly influence its concentration in topsoils and vegetation remains to be understood.

The Svalbard Archipelago in Arctic has a large reserve of coal and phosphorite (Yuan et al., 2006), where coal mining started in as early as 1899 AD (Sun et al., 2006). Ny-Ålesund, which is located in the northwest of Svalbard, once had a coal mine which was closed.
in 1960s because of a tragic accident (Hisdal, 1998). Separated from the European continent by the Barents Sea and with reduced human activities, Ny-Ålesund is considered to be an ideal location for scientific exploration, and many countries have set up research stations there. Studies on the heavy metal pollution in lake sediments and peat bogs from Ny-Ålesund have been reported (Jiang et al., 2010, 2011). However, previous work has paid limited attention to the distribution of pollutants (for example, Sb), especially in the surface environment (including the topsoils and vegetation). As a result, Sb concentration in local coals has been rarely studied.

In this paper, we investigate Sb contents in topsoils, Dicranum anauquastum (a typical tundra moss), coals and gangues collected from coal mine tailings in Ny-Ålesund. We discuss the biogeochemical process of Sb in different environmental materials, and explain the relationship between Sb distribution and anthropogenic activities.

2. Background of study area

The Svalbard Archipelago (74°N ~ 81°N, 10°E ~ 35°E), located between Barents Sea and Kara Sea, is one of the most northern places where humans live. It consists of the Spitsbergen Island, the Nordaustlandet, the Edgeoya, and dozens of small islands. With a total area of 62,700 km², about 60% of the Archipelago is covered by glaciers. Ever-frozen earth layer is up to 500 m thick; even in the summer time, only the 2–3 m surface layer is melt.

Ny-Ålesund is located at 78°55'N, 11°56'E, in the northwestern part of Svalbard Archipelago. Due to Atlantic warm waters, mean annual temperature of Ny-Ålesund is around 4 °C. Compared with areas with similar latitude in both hemispheres, Ny-Ålesund is populated with more plants, including 168 species of vascular plants, at least 373 species of bryophyte, 606 lichen species, 705 fungi, and over 1100 terrestrial, freshwater, and marine algae and Cyanobacteria (Rønnings, 1996). In Ny-Ålesund, there is a sparse and low-growing cover of Salix polaris, Cerastium arcticum, Saxifraga cemua, S. cespitosa, S. oppositifolia, S. hirculus, Luzula arcuata, L. arctica, and Poa arctica, as typical in the northern arctic (Biéks, 2001). The predominant flow here is from the east-southeast (Biéks et al., 2011).

After the coal mine was closed in 1960s, several countries have set up research stations in Ny-Ålesund (Fig. 1). To date, there are nearly 160 workers and researchers in Ny-Ålesund during summer time. The common transportation tools are motor vehicles and bicycles.

3. Materials and methods

3.1. Sample collection

As shown in Fig. 1, samples collected in Ny-Ålesund were divided into four series, A series (with 27 sampling sites) around the coal mine, B series (with 25 sampling sites) around the airport, C series (with 7 sampling sites) to the west of the human settlements, and D series (with 22 sampling sites) far away from the settlements. Moss and topsoil samples were collected in pairs within 0.5 m from each other. A series was designed to describe the possible influence made by the past coal mine activities and the traffic roads. B, C and D series were added to discuss other potential factors, such as the altitudes and the ocean waves.

Four coal samples and four coal gangue samples were collected from the coal tailings. Moreover, one moss sample collected in A series (Fig. 1) was divided into 2 parts. The top 1.5 cm green part was named A–G, and the yellow part was named A–Y. It is believed that the A–Y was much older than A–G.

3.2. Methods

Moss samples, cleaned by deionized water, were dried and powderized into small pieces. HNO3–H2SO4–HF is used to pretreat and dissolve grinded samples by using micro-wave oven (CEM MARS-5). Topsoil (<2 mm in size) samples, after dried and grinded, were pretreated in the same way as for moss samples. Coal and gangue samples were pretreated with H2SO4 and HNO3, and heated with electric board. All the reagents used are of extra pure grade. The concentration of Sb was determined with Ordinal Interaction Two-pass Atomic Fluorescence Spectrophotometer (AFS-930, Beijing Jitian Instrument Co., China). To validate the procedure, national standards GBW07403, GBW07404, GBW07603, GBW07605, and GBW07106 were used as quality control with a duplicate error of 5%. The experiment was performed in the Institute of Polar Environment at the University of Science and Technology of China.

4. Results and discussion

4.1. Sb concentrations in coals and gangues

Sb concentrations of coal and gangue samples from Ny-Ålesund and several coal producing countries of the world are presented in...
Fig. 2. The Sb contents in the world’s coals are between 0.007 and 17,000 mg/kg (Ren et al., 2006; Qi et al., 2008). The average Sb content is estimated to be 1.23 mg/kg (Ren et al., 2006) and 2.27 mg/kg (Qi et al., 2008) in coals from US and China respectively. The emission from the burning of coal and oil is one of the dominant sources of airborne Sb (Reimann et al., 2010), based on the fact that Sb is a common component of coal and petroleum (Filipello et al., 2002). Therefore, Sb level in coal mining surroundings is usually high. However, the mean Sb concentration of coals and gangues in Ny-Ålesund (in the current study), is only 0.1 mg/kg, much lower than what is seen in coals elsewhere and the earth crust. It is therefore speculated that the weathering of coal bed in Ny-Ålesund is unlikely to enhance the local surface environment. And there should be other factors responsible for the distributional difference in Sb concentration.

4.2. Distribution of Sb in topsoils

The Sb contents of the topsoils (Sbsoil for short) in the study area are shown in Fig. 3. The new EU risk assessment report for Dintimony Trioxide (EU, 2008) provides that the predicted baseline Sb concentration for soil is about 37 mg/kg, more than 100 times higher than what is seen in coals elsewhere and the earth crust. It is accordingly speculated that the Sbsoil is affected by Sb sources nearby. And this might be attributed to the anthropogenic activities.

As shown in Fig. 2, the mean value of Sbsoil in the study area (0.334 mg/kg) is higher than that in Northern Europe (0.22 mg/kg) (Salminen et al., 2005), and lower than those in Southern Europe (0.88 mg/kg) (Salminen et al., 2005), European Union (0.6 mg/kg) (Salminen et al., 2005), and the world (0.5 mg/kg) (Koljonen, 1992). Considering that Sb is stable in topsoils, and does not transfer easily over long distance (Hammel et al., 2000), this high variability across the Europe may simply reflect geographical separation. Since the D series in this study was far away from the human settlements, and likely not strongly affected by human activities, the mean value of Sbsoil from D series (about 0.310 mg/kg) was considered as the background Sbsoil in this study.

B and C series are near the airport (Fig. 1) and much closer to human settlements than the D series. Thus, the topsoil samples in B and C series might be influenced by human activities. However, the mean values of Sbsoil in B and C series were 0.310 mg/kg and 0.321 mg/kg, respectively, quite similar to that in BG series. Hence, anthropogenic factors (especially those related to airplane rising and landing) do not appear to affect the Sbsoil of B and C series significantly.

The mean value of Sbsoil from A series is 0.379 mg/kg, with the peak values appeared by the side of coal mine and traffic road (as seen in Fig. 3). Since the weathering of coal bed of Ny-Ålesund would not lead to the increase of Sbsoil in the study area, because of

Fig. 2. Sb concentrations (minimum, mean, and maximum are shown along each bar from top to bottom) in coals, gangues, topsoils, and moss from Ny-Ålesund and other places in the world. Different letters stand for the different sample materials. A, coal from Ny-Ålesund (N = 4, current study); B, coal gangue from Ny-Ålesund (N = 4, current study); C, coal of the world (Swaine, 1990; Qi et al., 2008; Valkovic, 1983; Ren et al., 2006); D, coal from China (N = 756) (Qi et al., 2008); E, coal from U.S. (N = 7599) (Ren et al., 2006); F, earth crust (Wedepohl, 1995); G, topsoil from Ny-Ålesund (<2 mm fraction, N = 81, current study); H, topsoil from A series (<2 mm fraction, N = 27, current study); I, topsoil from B series (<2 mm fraction, N = 25, current study); J, topsoil from C series (<2 mm fraction, N = 7, current study); K, topsoil from D series (<2 mm fraction, N = 22, current study); L, soil from the world (<2 mm fraction) (Koljonen, 1992); M, topsoil from European Union (<2 mm fraction, N = 840) (Salminen et al., 2005); N, topsoil from Northern European (<2 mm fraction, N = 172) (Salminen et al., 2005); O, topsoil from Southern European (<2 mm fraction, N = 216) (Salminen et al., 2005); P, Dicranum anagustatum from Ny-Ålesund (N = 75, current study); Q, Dicranum anagustatum from A series (N = 27, current study); R, Dicranum anagustatum from B series (N = 20, current study); S, Dicranum anagustatum from C series (N = 7, current study); T, Dicranum anagustatum from D series (N = 21, current study); U, Hylocomium splendens from Finnmark, Norway (Steinnes, 1995); V, Hylocomium splendens from European Arctic (Reimann et al., 2001); W, moss from Oslo (N = 40) (Reimann et al., 2006); X, moss from Germany (Siewers and Herpin, 1998); Y, moss from Czechia (N = 280) (Sucharová and Suchara, 2004); Z, reference plant of the world (Markert, 1992).
the low Sb concentration in coals and gangues, the appearance of Sb\textsubscript{soil} maximum value might be the result of the process of traffic and historical mining activity.

Numerous studies around mining sites have focused on minerals, which might have a high Sb component. However, the influence on the distribution of Sb made by the process of mining activities is poorly understood. It has been shown that Sb emitted from traffic road was probably dominated by brake-lining (Iijima et al., 2008; Bukowiecki et al., 2009). Considering the low contents of Sb in coal and gangue from Ny-Ålesund, the appearance of peak value of Sb\textsubscript{soil} in A series might be the result of activities including machine operations and car braking. In addition, According to Hammel et al. (2000) who suggested, Sb in contaminated soils is mostly immobile, which could explain why the peak values in Ny-Ålesund appeared only beside the coal mine and traffic road. However, Sb\textsubscript{soil} of other sampling sites in A series did not show significant statistical difference with the background value.

In addition to human activities, several natural factors may also affect Sb\textsubscript{soil}. Samples less than 400 m from the coastline (the sites at the side of the traffic road in A series are not included to avoid anthropogenic influences) were selected and the Sb\textsubscript{soil} of these sampling sites (as shown in Fig. 3) were determined. This allowed us to infer the influence of ocean waves. Results showed that the mean value of Sb\textsubscript{soil} of these 10 samples is 0.217 mg/kg, significantly less than the background value in Ny-Ålesund. Sb is slightly enriched in surface environment (Reimann et al., 2009), the loss of surface soil, caused by the ocean waves, might lead to the decrease of Sb\textsubscript{soil} near the coast and the significant difference between the Sb\textsubscript{soil} in these samples and the background value.

### 4.3. Distribution of Sb in moss

Sb is not an essential element for vegetations. The mechanism of Sb absorption is largely unknown. According to Markert (1992), Sb in vegetation is about 0.1 mg/kg. In Northern Europe, 0.05 mg/kg appears to be a more reliable estimate (Reimann et al., 2010). Sb is considered to be of higher concentration in moss than in other plants (Reimann et al., 2010). According to Yuan et al. (2006), Dicranum angustum, one species of moss, was considered a suitable bio-indicator for heavy metal pollution in Ny-Ålesund. Thus, we selected Dicranum angustum as a representative to study Sb distribution in vegetations in the study area.

The distribution pattern of Sb in moss samples (short for Sb\textsubscript{moss}) in the study area is shown in Figs. 2 and 4. The average of Sb\textsubscript{moss} in Ny-Ålesund is 0.133 mg/kg, much higher than those in Northern Europe (Steinnes, 1995; Reimann et al., 2001, 2006), but lower than those in other Europe countries (such as German (Siewers and Herpin, 1998) and Czechia (Sucharová and Suchara, 2004)). The mean value of Sb\textsubscript{moss} in A and B series is about 50% higher than that in C and D series. Considering that the content of Sb\textsubscript{moss} changed a lot (with a peak value of 0.384 mg/kg, nearly an order of magnitude higher than the lowest value of 0.047 mg/kg), the distribution of Sb\textsubscript{moss} might be influenced by Sb sources in the study area. However, there is no obvious correlation between Sb\textsubscript{moss} and Sb\textsubscript{soil} (with a square of relative coefficient $R^2 = 0.01$) at the same sites. Thus, moss and soil were likely to be influenced via different processes. It is believed that moss mainly absorbed elements from atmosphere rather than soil (Rühling and Tyler, 1968), the reason that moss is often used to estimate the atmospheric pollution. According to Berg et al. (1995), the distribution pattern of Sb in moss is as similar to the long-range transported elements (for example, Pb), showing that the absorption of Sb may be due to the atmospheric deposition. Therefore, the difference between the distributions of Sb\textsubscript{moss} and Sb\textsubscript{soil} in Ny-Ålesund is likely due to the Sb absorption mechanism of moss.

The mean value of Sb\textsubscript{moss} in D series (0.108 mg/kg) and C series (0.108 mg/kg) is much lower than that in B (0.149 mg/kg) and A series (0.148 mg/kg). Although Sb\textsubscript{moss} is highly influenced by the atmospheric environment and D series is at the downwind site of human settlements, considering the long distance between D series and the human settlements, Sb was unlikely to be transferred so far via atmosphere. In addition, C series is not at the downwind site of human settlements and is located at a much higher altitude, atmospheric Sb was unlikely to have an effect on moss in this series. Therefore, we could consider the mean value of D and C series as the reference background value of Sb\textsubscript{moss} of Ny-Ålesund.

Sb\textsubscript{moss} shows different patterns with Sb\textsubscript{soil} in B series. Interestingly, there is no clear relationship between Sb\textsubscript{moss} value and distance to the airport, indicating that the airport in Ny-Ålesund was unlikely to be the Sb source. The areas with high values of Sb\textsubscript{moss} in B series were located at lower altitudes than the other sample sites in B series (as shown in Fig. 1). Considering that B series is at the downwind site of human settlements in Ny-Ålesund, the increase of Sb\textsubscript{moss} in this series might be caused by the Sb pollution from upwind region, especially the human settlements.
The distribution pattern of Sb_{mos} in A series showed obvious influence by human activity. Sb_{mos} in A–G, the green part of moss sample is 0.088 mg/kg, and Sb_{mos} in A–Y, the yellow part of the same sample is 0.249 mg/kg. It suggested that older moss sample might accumulate more Sb than the younger moss. Accumulation of Sb in moss may provide a window to historical human activities. Coal mine activity in Ny-Ålesund began in 1898 AD and lasted until 1963 AD. Therefore moss, grown near the coal mine, would be affected by the mining activity for a much longer lasting-period than those collected in other places. This may lead to an increase of Sb_{mos} at the side of the coal mine. There were only dozens of people lived in Ny-Ålesund in the past, although the population in summers would be as large as 160. The local traffic activity is limited, and would not show significant influence on moss. This might explain why the peak value appeared by the side of the coal mine, but not the traffic road.

The distribution of Sb_{soil} and Sb_{mos} could provide information of Sb pollution in Ny-Ålesund. The characteristics of Sb_{soil} are related to the distribution of Sb deposited on the surface directly, whereas the characteristics of Sb_{mos} reflect the part of airborne Sb absorbed by moss. Both Sb_{soil} and Sb_{mos} seemed to be sensitive to human activities. However, considering that the reference value of Sb_{mos} in the study area was much lower than that of Sb_{soil}, the possible influence made by human activities to the Sb_{mos} would be much obvious. Sb_{mos} appeared to be more helpful for monitoring Sb pollution. Given its sensitivity, Sb_{mos} also has a high potential in places with low Sb contents.

5. Conclusions

Sb concentrations in coals and gangues from Ny-Ålesund are lower than the mean value of the world. The background value of Sb_{soil} in Ny-Ålesund is 0.310 mg/kg. The distribution pattern of Sb_{soil} is mainly affected by human activities. The peak values of Sb_{soil} appeared by the side of past coal mine and traffic road. Furthermore, seawaters could lead to the decrease of Sb_{soil} by the coastline.

We estimated the reference value of Sb_{mos} in Ny-Ålesund to be 0.108 mg/kg. There were differences between the distributions of Sb_{mos} and Sb_{soil}. The appearance of the peak value of Sb_{mos} was related to the human activities via the wind field in the study area. The distribution of Sb_{mos} was related to Sb absorbed by moss, and could reflect the accumulation of Sb pollution. Moss could be used to estimate Sb pollution in not only high pollution area, but also places with low Sb contents.

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