

## Article

## Natural and Anthropogenic Heavy Metal Deposition to the Snow in King George Island, Antarctic Peninsula

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**Abstract** : Successive 24 snow samples, collected from a 1.2 m snow pit at a site on the summit of Main Dome in King George Island, Antarctic Peninsula, were measured for heavy metals such as Pb, Cd, Cu, and Zn and other chemical species. The mean concentrations of heavy metals are 3.48 pg/g for Pb, 0.10 pg/g for Cd, 16.6 pg/g for Cu and 15.8 pg/g for Zn, respectively. Pb and Cd concentrations observed in our samples are very comparable to those reported for recent snow at other Antarctic sites, while Zn and Cu levels are much higher than those at other sites. The annual fallout fluxes of all heavy metals approximately calculated are, however, much greater in King George Island than at other sites. With respect to the estimates of natural contributions, sea salt spray is found to be a major contributor to Cd and Zn inputs to the snow and minor to Cu inputs. On the other hand, the anthropogenic input can account for a large part of Pb concentrations. A tentative estimate represents that local emissions could be responsible for more than half of the excess Pb flux to the snow in King George Island.

**Key words** : snow, heavy metals, natural sources, anthropogenic input.

### 1. Introduction

Considerable attentions have been paid to understand the perturbation of atmospheric heavy metal cycles in Antarctica over time due to anthropogenic contributions. At present, it is now well recognized that even the remote and isolated Antarctic atmosphere was contaminated by Pb and Cu because of anthropogenic emissions (Wolff and Suttie 1994; Rosman *et al.* 1994; Barbante *et al.* 1998; Wolff *et al.* 1999; Hong *et al.* 2000b). These results were provided from the concentration profiles in the successive well-preserved snow and firn layers collected at various sites where local influences such as manned stations and research activities were negligible. Such geographical situation of the sampling sites was selected to investigate

the large-scale environmental contamination caused by pollutant heavy metals entering Antarctica from mid-latitude source regions.

Although anthropogenic emissions from many stations within Antarctica can probably influence the atmospheric heavy metal cycles in local areas, on the other hand, the impact of this contribution remains very little studied (Boutron and Wolff 1989; Suttie and Wolff 1993). King George Island located at the northern tip of the Antarctic Peninsula is of special interest, because there are 8 permanent manned stations. According to the preliminary analysis of heavy metals in freshly fallen surface snow collected around King Sejong Station, it was suggested that most of Pb and some part of Cu in these snow samples were anthropogenic in origin and derived from local emissions (Hong *et al.* 2000a). Since these samples analyzed were collected at the sites very

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close to the station, however, the data could not be indeed regarded to be representative of the situation in King George Island.

We present here the new results obtained from a sequence of snow samples collected at a site in King George Island, which has the geographical location of minimizing a relatively significant contribution from a specific local source to heavy metal fluxes to the snow.

## 2. Experimental methods

### Sampling

Snow samples were collected on December 6, 2000, at a site (62°08'S, 58°40'W, elevation 620 m) close to the summit of Main Dome of Collins Ice Cap on King George Island, South Shetland Islands (Fig. 1). The sample collection was done as part of joint cooperation between Korea Ocean Research and Development Institute (KORDI) and Uruguayan Antarctic Institute (UAI). A snowmobile was used to approach to the sampling site. A snow pit was dug with acid-cleaned plastic shovels at a site 50 m upwind from a snowmobile. Great precautions were taken in the field to prevent the possibility of snow contamination. The operators wore full clean room clothing and polyethylene gloves. To remove any contamination introduced by the plastic shovels, about 10 cm of snow was then shaved away from

the upwind wall using ultraclean low-density polyethylene (LDPE) scrapers. A continuous series of 24 samples was collected at 5-cm intervals by horizontally pushing ultraclean cylindrical Teflon container (4.5 cm i.d., 35 cm length) and then pouring the snow into ultraclean 1 l LDPE bottle. Scrapers, Teflon containers and LDPE bottles have been extensively cleaned as described in detail in Hong *et al.* (2000a). The bottles were packed in double sealed acid-cleaned LDPE bags and brought back frozen to the laboratory. They were kept frozen until analysis.

When collected the samples, a series of 2-5 mm thick ice and 2-4 cm recrystallized snow layers were observed from the wall of a pit. The positions of ice layers were at the depths of 11.7-12.0 cm, 23.0-23.3 cm, 33.5-34.0 cm, 36.5-37.0 cm, 44.0-44.2 cm, 53.2-53.4 cm, 57.0-57.2 cm, and 82.5-83.0 cm and recrystallized snow layers at 16-19 cm, 62-64 cm, 71-75 cm, and 94-98 cm. Although these ice and recrystallized snow layers were present, it is likely that a glaciochemical record preserved in snow may not have been disturbed due to the large melting which takes place in King George Island during the summer.

### Analytical procedures

The samples were melted at room temperature in a class 100 laminar flow clean bench inside the clean room. Various aliquots were then taken in ultraclean LDPE bottles. The determination of Pb, Cd, Cu, Zn and Al was carried out by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin Elmer 4110ZL instrument equipped with a Zeeman background corrector, which is located inside a class 100 clean room. After preconcentration (by a factor of 30) by non-boiling evaporation (Görlach and Boutron 1990), Pb, Cd, Cu, and Zn were determined by GFAAS. Al was measured by direct injection GFAAS without preconcentration. The precision is estimated to range from  $\pm 5\%$  for the highest concentrations to  $\pm 20\%$  for the lowest (Hong *et al.* 2000a).

Na, Cl, methane sulphonic acid (MSA) and  $\text{SO}_4^{2-}$  were measured by ion chromatography (IC) with Dionex column AS 11 for anions and CS14 for cations. Analytical precision is in the range between 5 and 10% (Lee *et al.* 1999).

### Dating of the samples

The precise dating of the samples is not available, because no direct observation of snow accumulation, which varies from place to place with elevation, was made at the sampling site in 2000. According to the previous

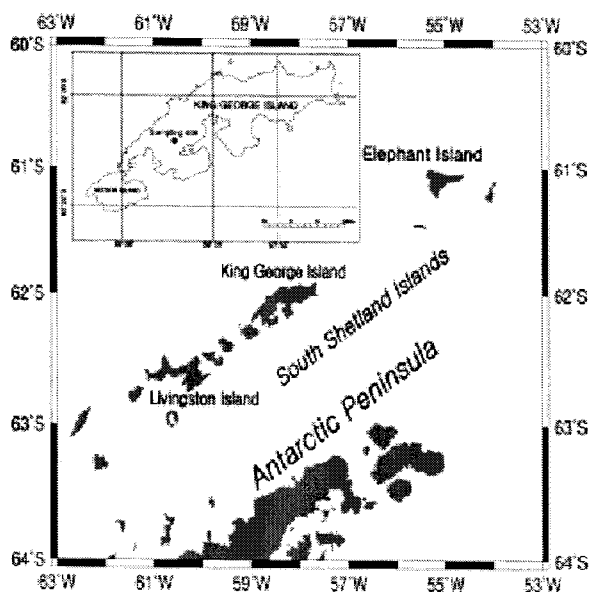


Fig. 1. Location of King George Island and the sampling site.

observation (Wen *et al.* 1998), an annual accumulation rate was found to amount to about  $250 \text{ g H}_2\text{O cm}^{-2} \text{ yr}^{-1}$  at the summit of Main Dome. When we use the mean snow density of approximately  $400 \text{ kg m}^{-3}$  at the summit of Main Dome (Wen *et al.* 1998), the accumulation of our samples corresponds to  $48 \text{ g H}_2\text{O cm}^{-2}$  which covers only part (~20%) of a full year of snow accumulation, assuming that year-to-year variation in accumulation rate is negligible at the summit of Main Dome. The data of precipitation at King Sejong Station in 2000 represent that about half of annual precipitation occurred during summer

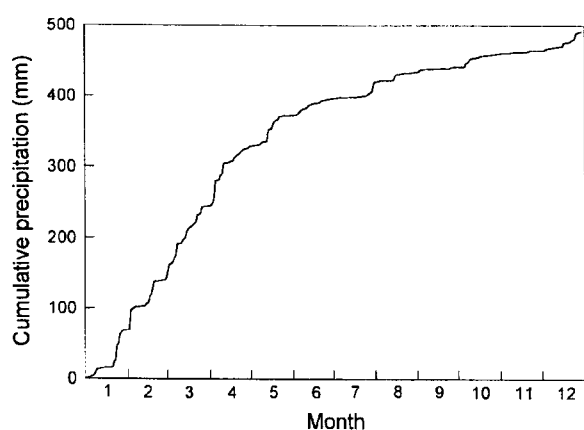


Fig. 2. Cumulative precipitation at King Sejong Station in 2000 (Lee *et al.* 2001).

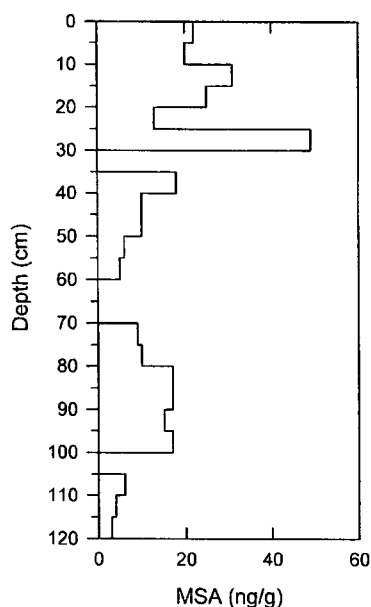


Fig. 3. Changes in MSA concentrations in the snow pit samples at Main Dome, King George Island.

(January-March) and, in particular, about 80% from January to June with relatively small precipitation in winter (Fig. 2). If we assume that the situation was also similar at the summit of Main Dome, the deepest part of our samples may represent winter (probably July 2000) snow layer.

An alternative approach for dating the snow pit samples is to use the chemical species, of which the concentrations have a pronounced seasonal cycle. MSA is exclusively derived from the oxidation of marine biogenic dimethyl sulphide (DMS) and its concentration in coastal Antarctic aerosol and surface snow exhibits a distinct annual cycle with the maximum during the austral summer period and minimum in winter (Minikin *et al.* 1998). The profile of MSA in the samples is shown in Fig. 3. The concentrations are much lower in the deepest part compared to the upper part, showing a more or less upward increase. Thus, this pattern may be ascribed to the seasonality of the MSA occurred during the winter-spring, corresponding to the dating estimated from the data of the precipitation.

### 3. Results and discussion

#### Description of the data

The results obtained in the snow samples are shown in Table 1 and Fig. 4. It is found that the heavy metal concentrations are very low. This is especially for Cd, of which concentrations are extremely low below the pg/g. The average concentrations are 3.48 pg/g for Pb, 0.10 pg/g for Cd, 16.6 pg/g for Cu and 15.8 pg/g for Zn, respectively.

The depth profiles of metals do not display a similar pattern, as illustrated in Fig. 4. The relationship between metals is also shown in Table 2. Except for a rather significant correlation between Zn and Al ( $r = 0.64$ ), the correlation coefficients are mostly insignificant. This implies that each metal measured in the samples has different transport way and/or input mechanism.

Here it must be considered that slight melting and percolation possibly lead to redistribution of elements in snow, because a series of thin ice and recrystallized snow layers were observed in the snow pit wall as shown in Fig. 4. In previous studies, higher concentrations of heavy metals such as Pb, Cu, Zn, and Cd were found in ice layers embedded in Greenland and Antarctic snow (Wolff and Peel 1988; Suttie and Wolff 1992). Since there existed only one or two ice layers in these snow pit samples, however, it is not evident whether redistribution of metals

Table 1. Element concentrations measured in the snow pit samples at the Main Dome, King George Island.

Depth (cm)	Pb	Cd	Cu	Zn	Al	Na	MSA	nssSO <sub>4</sub> <sup>2-</sup>
	pg/g			ng/g		μg/g		
0-5	0.77	0.053	18.9	21.2	5.21	1.11	0.022	0.144
5-10	0.94	0.029	4.31	14.2	1.02	0.07	0.020	0.083
10-15	0.89	0.056	14.4	18.4	5.75	0.87	0.031	0.137
15-20	2.46	0.062	30.5	34.4	17.4	0.71	0.025	0.452
20-25	1.23	0.034	15.1	21.5	4.86	0.52	0.013	0.056
25-30	1.26	0.064	21.0	27.1	3.35	1.38	0.049	0.208
30-35	6.54	0.134	14.6	17.5	2.58	0.66	ND	0.186
35-40	8.03	0.105	12.6	19.5	8.42	0.41	0.018	0.090
40-45	6.23	0.109	21.0	15.2	8.58	1.98	0.010	0.012
45-50	5.42	0.087	15.5	11.1	2.64	1.67	0.010	0.029
50-55	3.42	0.083	8.64	8.70	2.41	2.26	0.006	-0.226
55-60	2.42	0.065	10.7	7.00	6.00	1.30	0.005	0.092
60-65	6.04	0.070	16.2	12.8	4.83	1.76	ND	0.052
65-70	4.04	0.089	15.4	12.3	5.77	2.46	ND	0.043
70-75	5.10	0.068	16.4	10.1	2.67	3.56	0.009	0.010
75-80	6.23	0.127	13.1	18.7	4.78	6.97	0.010	0.370
80-85	5.77	0.098	24.7	17.4	6.93	6.51	0.017	0.417
85-90	5.94	0.171	29.4	23.1	5.87	8.48	0.017	0.135
90-95	0.83	0.181	18.2	13.3	3.63	10.8	0.015	0.005
95-100	2.05	0.179	39.4	14.4	2.08	9.62	0.017	0.409
100-105	4.05	0.333	10.3	18.4	1.67	0.04	ND	0.090
105-110	1.30	0.103	11.1	7.73	1.73	1.54	0.006	0.105
110-115	1.04	0.079	9.90	8.72	2.44	3.98	0.004	0.209
115-120	1.55	0.062	7.88	7.43	1.43	2.93	0.003	-0.036
Average	3.48	0.102	16.6	15.8	4.67	2.98	0.015	0.128

ND indicates not detectable MSA concentrations because of their values below the detection limit.

The nssSO<sub>4</sub><sup>2-</sup> concentrations were calculated as  $[\text{SO}_4^{2-}]_{\text{nss}} = [\text{SO}_4^{2-}]_{\text{total}} - 0.2517[\text{Na}^+]$ .

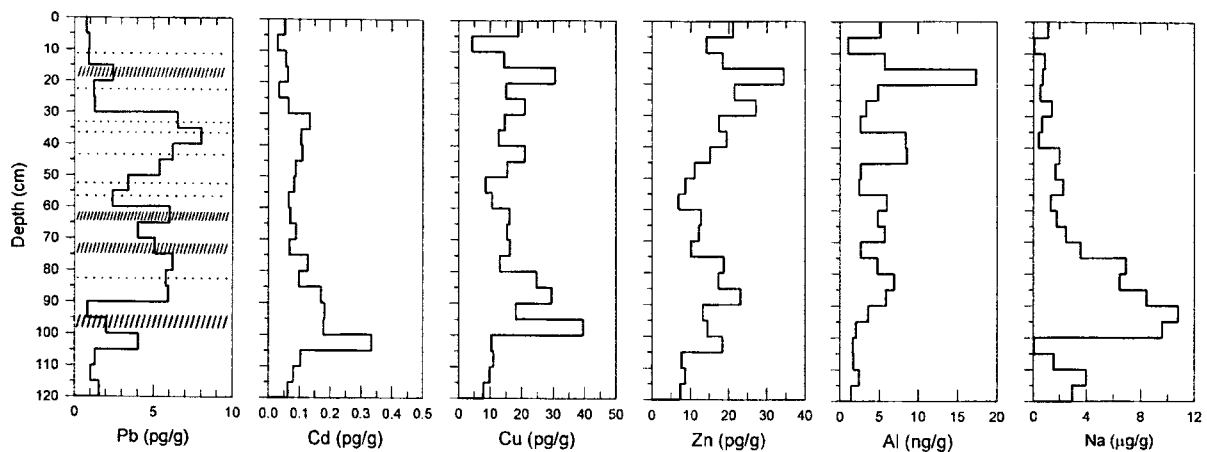


Fig. 4. Changes in Pb, Cd, Cu, Zn, Al and Na concentrations in the snow pit samples at Main Dome, King George Island. The positions of ice and recrystallized snow layers (see text) are represented as dotted and oblique lines, respectively, in the profile of Pb concentration.

**Table 2. Correlation coefficients determined for a continuous series of 24 samples collected in a snow pit.**

	Pb	Cd	Cu	Zn	Al	Na
Pb	1					
Cd	0.25	1				
Cu	0.11	0.20	1			
Zn	0.05	0.05	<u>0.52</u>	1		
Al	0.21	-0.19	0.44	<u>0.64</u>	1	
Na	0.04	0.35	<u>0.52</u>	-0.09	-0.11	1

The coefficients that are significant with 99% confidence levels are underlined.

**Table 3. Comparison of Pb, Cd, Cu and Zn concentrations in Antarctic snow and firn and their annual fallout fluxes (in  $\text{pg cm}^{-2} \text{yr}^{-1}$ ) in parentheses at various Antarctic sites (see text).**

Location	Year	Distance from coast (km)	Snow accumulation ( $\text{g H}_2\text{O cm}^{-2} \text{yr}^{-1}$ )	Pb	Cd	Cu	Zn
				(pg/g)			
This work	2000	Coastal	200	3.48 (696)	0.10 (20.0)	16.6 (3320)	15.8 (3160)
Livingston Island (62°37'S, 60°15'W)	1998	Coastal	60	4.97 (298)	-	-	-
Dolleman Island (70°35'S, 60°56'W)	1984-85	Coastal	39	4.0 (156)	0.08 (3.12)	4.0 (156)	0.4 (15.6)
Coats Land (77°34'S, 25°22'W)	1925-86	200	5.6	5.5 (30.8)	0.1 (0.56)	3.5 (19.6)	1.5 (8.4)
D55 Adélie Land (68°00'S, 137°46'E)	the late 1970s	180	8.0	5.4 (43.2)	0.31 (2.48)	5.3 (42.4)	4.2 (33.6)

had occurred. Moreover, the heavy metals observed from the samples showed different pattern of enhancement in concentration with relation to the ice layers. That is, the highest concentrations of Pb, Cu, and Zn but Cd occurred in ice layer in Greenland snow samples, while the highest concentration only for Cd in one of two ice layers in Antarctic snow.

In the case of our samples, it is likely that the variation of the heavy metal concentrations has no clear correlation with these ice and recrystallized snow layers (Fig. 4). Although we could not exclude a possibility that redistribution of metals due to slight melting and subsequent refreezing had occurred during snow accumulation, our concentration profiles indicate that this contribution to distribution of metals in snow can be neglected.

#### Comparison with previously reported data

Mean concentrations of heavy metals observed in our samples are compared with previous data obtained from recent snow and aged firn at different sites in Antarctica (Table 3). Note that the comparison of our data and mean Pb value in Livingston Island with those at other sites should be tentative, because the snow samples in King

George and Livingston Islands cover only part of a full year. Pb and Cd values are very comparable to those reported at various other Antarctic sites, despite the very large differences in location, snow accumulation rate, distance from the coast and even the time period covered. On the other hand, mean concentration of Zn in our samples is one to two orders of magnitude higher than those at other sites. For Cu, our mean value is higher by a factor of about 4 than those at other sites.

The concentration levels in snow could be influenced by snow accumulation rates, as higher accumulation rates seem to result in lower concentrations due to dilution effect during deposition. Therefore, it appears that the annual fallout fluxes could be a suitable index to provide detailed view of atmospheric deposition of elements of interest, assuming that wet deposition in falling snow is a dominant contributor to the annual fluxes of these elements (Wolff *et al.* 1998). The annual fallout fluxes of each heavy metal at our and other sites were calculated by combining mean concentration (pg/g) with an annual snow accumulation rate ( $\text{H}_2\text{O cm}^{-2} \text{year}^{-1}$ ). As presented in Table 3, the fallout fluxes so calculated are found to be much greater in King George Island than at the other sites.

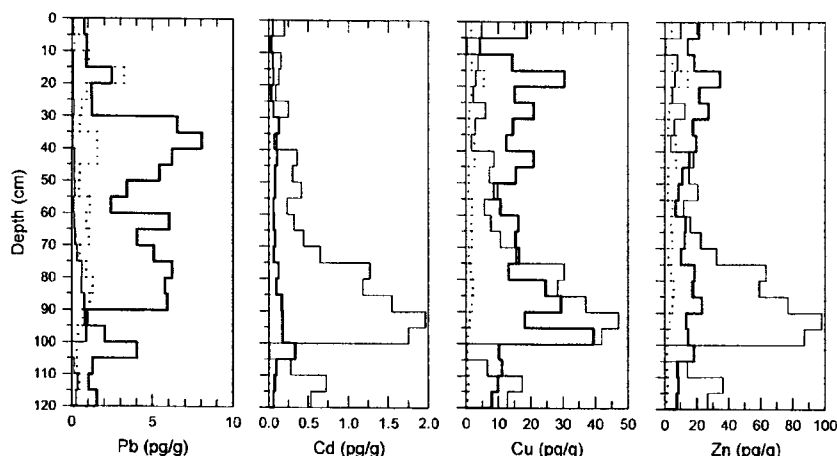


Fig. 5. Vertical profiles of Pb, Cd, Cu and Zn concentrations (thick solid lines) and estimated crustal (dotted lines) and marine inputs (thin solid lines) in the snow pit samples at Main Dome, King George Island.

This difference could result from different source strengths, which should affect atmospheric loading of heavy metals in various Antarctic sites. Another possibility is that the time interval covered by our samples could in part be a factor to make the annual fluxes very high, because a possible variability of heavy metal concentrations may take place through the year, as documented at different site (Suttie and Wolff 1992). More detailed temporal records, which provide information on the seasonal variations of heavy metal inputs to the snow, are required to confirm much higher fallout fluxes found in King George Island.

#### Estimated contributions from natural sources

Natural sources of various heavy metals in the atmosphere are rock and soil dust, sea salt spray, volcanoes, wild vegetation fires and continental and biogenic emissions (Nriagu 1989). We now evaluate the possible magnitude of natural contributions to the deposition of heavy metals to the snow.

Contribution from rock and soil dust can be estimated from Al concentrations in the samples and the mean heavy metals/Al ratios in crustal material as recently represented by Wedepohl (1995). The crustal contributions so calculated for each metal are shown in Fig. 5. The crustal inputs to the snow are on an average 0.87 pg/g for Pb, 0.01 pg/g for Cd, 1.47 pg/g for Cu and 3.81 pg/g for Zn, respectively. They represent about 40% for Pb, 7% for Cd, 10% for Cu and 25% for Zn of the measured concentrations.

Contribution from sea salt spray can be evaluated from sea-derived Na concentrations in the samples (after

correction for the contribution from rock and soil dust), mean heavy metal/Na ratios in surface bulk seawater, and the few available data on enrichments of metals in sea-derived aerosols relative to bulk seawater (Hong *et al.* 1998). It should be emphasized that an estimate of marine contribution is quite tentative, because enrichment factors available from various investigations were measured with very large uncertainties and mean concentrations of heavy metals in bulk seawater are highly variable in different oceans. In this study, we used the heavy metal/Na ratios in bulk seawater compiled by Duce *et al.* (1983). They were combined with the best estimates for enrichment factors of 100 for Pb, 10,000 for Cd, 800 for Cu, and 20,000 for Zn (Weisel *et al.* 1984; Boutron and Patterson 1986; Arimoto *et al.* 1987; Dick 1991). As shown in Fig. 5, this contribution is found to be very significant to Cd, Cu, and Zn with the averages of about 75% (Cu), 200% (Zn) and 500% (Cd) of the measured concentrations, while sea salt spray is a minor contributor to Pb (average: ~14%). The estimated marine contributions considerably overestimate the true Cd and Zn concentrations measured in the samples. This implies that either the enrichment factors used here or the bulk seawater Cd and Zn concentrations are too high by factors of 2 for Zn and 5 for Cd. In fact, the bulk seawater concentrations used are the levels previously reported for Central Pacific and North Atlantic surface waters. While surface Pb and Cu concentrations in Antarctic sea close to the Antarctic Peninsula, from which marine aerosols reaching the study area originate, are comparable to the levels in the Central Pacific and North Atlantic Oceans, the Cd and Zn concentrations in Antarctic sea are two orders of magnitude higher than those in other

regions of the Central Pacific and North Atlantic Oceans (Martin *et al.* 1990; Westerlund and Öhman 1991; Sañudo-Wilhelmy *et al.* 2002). Therefore, it is likely that the overestimates of marine contributions are mainly due to the large uncertainty in enrichment factors. Despite this overestimates, it appears that sea salt spray would be a dominant contributor to Cd and Zn deposition to our snow samples. Meanwhile, the estimated Pb contributions from sea salt spray are not likely to be totally natural in origin, taking into account the fact that a significant component of Pb present in Antarctic seawater could be anthropogenic as documented by Pb isotopic ratios (Flegal *et al.* 1993; Sañudo-Wilhelmy *et al.* 2002). However, it is suggested that the relatively higher levels of Cd, Cu and Zn in Antarctic seawater compared to other open oceans result from natural processes (Sañudo-Wilhelmy *et al.* 2002).

Contribution from volcanoes was tentatively estimated using the heavy metal/S ratios available from a few volcanic emission data combined with the assumption that on a global basis 13% of nss-sulfate is of volcanic origin (Boutron and Patterson 1986; Batifol *et al.* 1989). This approach for estimating volcanic inputs is, however, likely to be inappropriate for our samples, as the sampling site is located in coastal Antarctic regions where the marine biogenic source dominates the atmospheric sulfur budget (Minikin *et al.* 1998). The mean molar MSA/nss-sulfate ratio (0.37) in the samples is comparable to typical ratios (0.32-0.46) observed from Antarctic Peninsula ice cores (Mulvaney *et al.* 1992), indicating that nonbiogenic nss sulfate in the samples has little volcanic source. This leads to a crude conclusion that volcanic contribution may be negligible in our samples.

Other possible sources include wild vegetation fires and continental and marine biogenic sources (Nriagu 1989). Estimates of the mean contribution from wild vegetation fires can be tentatively obtained if we consider that wild vegetation fires were the unique source of black carbon (soot) in the atmosphere during the pre-industrial period. The average concentration of black carbon in Antarctic Holocene ice is 0.5 ng/g (Chýlek *et al.* 1992). When combined with the average heavy metal content in forest trees and foliage ash given by Nriagu (1979), the mean contribution from wild vegetation fires is estimated to be Pb 0.23 pg/g, Cd 0.004 pg/g, Cu 0.10 pg/g and Zn 0.73 pg/g, which account for very small portions (about 5% or less) of the measured mean heavy metal concentrations. Finally, the contribution from continental and marine biogenic emissions cannot be estimated from our data.

#### Possible anthropogenic contributions

While uncertainties still exist in estimating the natural contributions from various sources, it is evident that the natural crustal and marine contributions seem to account for most of the measured Cd concentrations (Fig. 5). For Zn and Cu, these natural inputs are found to contribute most of the measured concentrations observed in the snow layers below the depths of 40 cm for Zn and 50 cm for Cu, but they contribute only part (about 35% for Cu and 50% for Zn) of the total Cu and Zn contents in upper snow layers. For Pb, on the other hand, the estimated contributions from rock and soil dust and sea salt spray can explain only a small part of the measured concentrations, except for the layers, in which Pb concentrations are relatively low (Fig. 5).

The excess amount of Pb including some Cu and Zn which cannot be accounted for by the natural sources is likely to be attributed to the contribution from anthropogenic pollution. A significant part of these excess heavy metals should be of local origin, in the view of the fact that there are numerous local sources in King George Island. It is, however, possible that part of the excess metals in our samples could originate from South America, because King George Island is in close proximity to South America. In fact, various investigations have revealed that long-range transported anthropogenic aerosols from the countries of the Southern Hemisphere have already polluted the Antarctic atmosphere for Pb (Wolff and Suttie 1994; Rosman *et al.* 1994; Barbante *et al.* 1998; Hong *et al.* 2000b) and for Cu (Wolff *et al.* 1999), using snow profiles obtained at different geographical Antarctic sites where the influences of local sources were negligible. From our data, it is not possible to define the magnitude of local contribution to heavy metal inputs to the snow. Instead, using the mean Pb concentration (Table 3) found in Livingston Island which is in very close geographical situation and similar meteorological conditions with King George Island (Fig. 1), an attempt can be made to estimate the possible magnitudes of long-range transported and local emitted anthropogenic Pb inputs to the samples with large uncertainty. On average, about 16% of mean Pb content found in Livingston Island was estimated to be natural and the excess Pb to be probably anthropogenic pollutants transported from South America (Hong *et al.* 2000b). If we assume that this long-range transported anthropogenic Pb input to the snow in Livingston Island is the same magnitude as in King George Island, this contribution is found to give 1.25 pg/g of Pb to our samples after correction for the different accumulation

rates in both islands. When combined with the average Pb concentration in the 30-90 cm depth interval of the sample, in which the natural contributions are relatively small (Fig. 5), about 30% of the measured Pb concentrations is estimated to be long-range transported anthropogenic origin from the mid-latitude regions and 70% to be local in origin. Although there is a large uncertainty in estimating the geographical origin of anthropogenic Pb in our samples, it seems very likely that for Pb local emissions could contribute a significant portion of the flux to the snow in King George Island.

Various pollutant source indicators such as Pb isotopic signatures would greatly help the quantification of geographically different Pb sources contribution. The Pb isotopic evidence will be available soon from our samples.

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