

Variability of Pb, Mn, Al and Na Concentrations in Snow Deposited from Winter to Early Summer 1998 in Livingston Island, Antarctic Peninsula

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Abstract

The concentrations of Pb, Mn, Al and Na were measured from a total of 26 snow samples collected from a 1.5-m deep snow pit in Livingston Island, South Shetland Islands, at the northern tip of the Antarctic Peninsula. Our sampling location is of great concern, because of its proximity to the southern extremity of South America, a candidate for the source regions of pollutant aerosols entering Antarctica. The mean concentrations of Pb and Mn were found to be 4.97 pg g^{-1} and 20.6 pg g^{-1} , respectively. These concentrations levels are similar to those reported for recent snow at other Antarctic sites, with pronounced spring maxima for both metals. Contributions from natural sources are estimated to be minor ($\sim 16\%$) for Pb. For Mn, on the other hand, contribution from rock and soil dusts is found to be very important. Excess Pb over Pb from natural sources is likely to be anthropogenic, especially from South America. Our results show that yearly Pb fallout flux is much greater in Antarctic coastal areas than at other Antarctic locations far from the coast, indicating that the transport and deposition patterns of pollutant aerosols are not simple in Antarctica. It is also suggested that the recycling of anthropogenic Pb in seawater to the atmosphere could significantly contribute to the Pb fallout flux in the Antarctic coastal regions.

Key words : Snow, Lead, Manganese, Antarctica, Global pollution

1. INTRODUCTION

Polar snow and ice offer unique opportunities to

investigate the hemispheric scale of human impact on heavy metal cycle in the atmosphere. During the last two decades, great efforts have been devoted to unravel the signals of heavy metal pollution preserved in those frozen archives. In particular, atmospheric Pb pollution was of special concern, because this metal

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has been extensively exploited, produced and used by man from the antiquity, and thus could be a good tracer of man-induced changes in atmospheric composition. Comprehensive investigations of Pb in Greenland snow and ice have until now provided valuable indications of long-term atmospheric Pb pollution in the Northern Hemisphere (see, for example, Rosman *et al.*, 1997; Candelone *et al.*, 1995; Hong *et al.*, 1994; Rosman *et al.*, 1993; Boutron *et al.*, 1991; Murozumi *et al.*, 1969). Their works included source discrimination using Pb isotopes systematics as well as reconstruction of changing Pb deposition to the Greenland snow and ice over time.

For Antarctica, on the other hand, our understanding of the changing occurrence of anthropogenic Pb pollution is still very limited, even though many investigations have been performed to determine Pb variability in Antarctic snow and ice since the pioneering work of Murozumi *et al.* (1969) and Ng and Patterson (1981) (for example, Barbante *et al.*, 1998; Hong *et al.*, 1998; Wolff and Suttie, 1994; Gorlach and Boutron, 1992; Boutron and Patterson, 1983, 1987). This is mainly because Pb concentrations are extremely low in Antarctic snow and ice resulting into very severe contamination problems from field sampling to laboratory analysis. It is only recently that a continuous profile of Pb concentrations from the 1920s to the 1980s was obtained from an Antarctic snow pit in Coat Land, West Antarctica (Wolff and Suttie, 1994) and showed that the most remote areas in the Southern Hemisphere were already significantly polluted with Pb as early as in the beginning of the 20th century. It was also seen that Pb concentration values increased from about 2.5 pg g^{-1} to $8\text{--}12 \text{ pg g}^{-1}$ from the early 1950s to the late 1970s, before the concentrations decreased to about 5.5 pg g^{-1} in the mid 1980s. From a comprehensive inventory of Pb emissions to the atmosphere in the Southern Hemisphere, Wolff and Suttie (1994) showed that these variations largely paralleled the consumption patterns of Pb additives in gasoline in the countries of the Southern Hemisphere. The recent decrease in Pb concentrations in Antarctic snow was recently confirmed by Barbante *et*

al. (1998) from the analysis of a series of samples from Victoria Land in East Antarctica. In addition, Rosman *et al.* (1994) reported Pb isotope data from Antarctic recent snow, allowing to fingerprint the main source areas of anthropogenic Pb found in Antarctica.

Assessing geographical changes in Pb concentrations in present day Antarctic snow from one area to another would greatly help to understand the inputs of anthropogenic Pb pollutants into the remote southern hemispheric atmosphere. In this context, we present here for the first time data on short-term changes in Pb concentrations in shallow snow in Livingston Island, South Shetland Islands, i.e. a location close to South America, one of the possible source regions of anthropogenic Pb entering Antarctica. Short-term changes in Mn, Al and Na are also reported to help for the interpretation of the Pb data.

2. SAMPLE COLLECTION AND ANALYSIS

2.1 Field sampling

The snow samples were collected on December 18, 1998 at Livingston Island, South Shetland Islands, near the northern tip of the Antarctic Peninsula (Fig. 1). The sampling site ($62^{\circ} 37' \text{S}$, $60^{\circ} 15' \text{W}$) was at an altitude of 450 m, 5 km from the sea coast and 6 km and 8 km from the Bulgarian and Spanish summer stations, respectively (these stations were occupied only a few days before we collected our samples). A 1.5-m deep snow pit was hand dug by operators wearing full clean room garments and polyethylene gloves with acid cleaned plastic shovels. About 10 cm of snow were then shaved away from the upwind wall using acid cleaned low-density polyethylene (LDPE) scrapers. Three parallel series of 26 samples were then collected for subsequent determination of heavy metals, Pb isotopes and major ionic species, by horizontally pushing ultra-clean LDPE vials (160-ml vials with closure from Nalgene, Nalge Company). The vials used for the collection of the samples for heavy metals and Pb isotopes determination were acid cleaned in a clean room

at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) as described in detail elsewhere (Boutron, 1990).

A continuous series of 20 samples was first taken at a depth resolution of 5 cm from the surface down to a depth of 1 m. The following 6 samples were then collected from well preserved snow layers without recrystallized snow grains between the thin ice layers observed below 1 m. The depth intervals of the samples so collected were 105~110 cm, 110~115 cm, 118~123 cm, 125~130 cm, 130~135 cm and 139~144 cm.

The numerous rather thick ice layers observed below 150 cm did not allow to collect samples below that depth. A thick ice layer, which could not be penetrated by a steel probe, was found to be present at about 2~m depth. This ice layer may have been formed due to snow melting and freezing during the last summer.

In addition to snow sampling in a pit, two surface snow samples were collected on 16 December just after about 6 cm of accumulation of the fresh (not drifting by wind) snow to check the influence of local emissions from the Bulgarian station. The sampling sites were at 500 m and 1,000 m from the station, respectively. Samples were collected at each site by pushing wide mouth 1,000-ml LDPE bottles (acid cleaned at LGGE) horizontally into the snow at a depth of 2~3 cm from the surface. Surface snow collected at these sites is sure to correspond to the uppermost snow layer in a snow pit, because no precipitation event and drifting of snow by strong wind occurred during 16~18 December.

The vials and bottles containing the samples were sealed in double acid cleaned LDPE bags and kept frozen until laboratory analysis.

2.2 Laboratory analysis

The samples were melted at room temperature in a class 100 clean room. Aliquots were then taken for various analyses at Korea Ocean Research & Development Institute (KORDI) and different other laboratories. The clean laboratory facilities and procedures developed at KORDI for the determination of various heavy metals at or below the pg g^{-1} concentration level, are described in detail elsewhere (Hong *et al.*, 2000). We measured Pb, Mn, Al and Na concentrations by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using a Perkin Elmer 4110ZL instrument equipped with a Zeeman background corrector. This instrument is located inside a class 100 laminar flow clean bench. Mn, Al and Na were determined by direct GFAAS using multiple injections (up to $7 \times 50 \mu\text{l}$). Pb was determined by GFAAS after preconcentration (by a factor of 45) by non-boiling evaporation as describ-

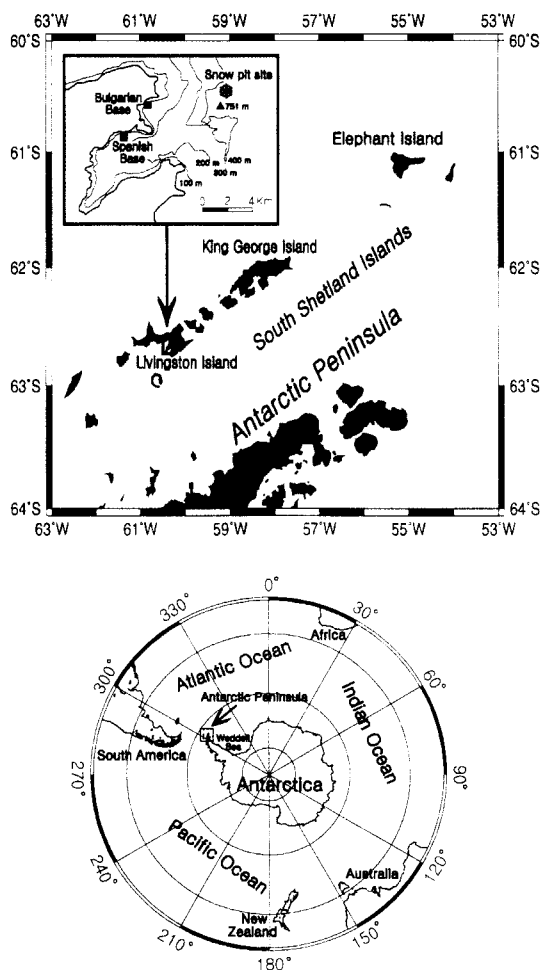


Fig. 1. Map of Antarctica and the Antarctic Peninsula region showing the sampling site of a 1.5-m snow pit in Livingston Island, South Shetland Islands.

ed in detail by Görlach and Boutron (1990). The precision is estimated to be better than 5% for the highest Pb and Mn concentrations. This decreases down to about 20% for concentrations close to the detection limit (Hong *et al.*, 2000).

2.3 Age assignment

Although no direct observations of snow accumulation rates are available for the sampling site, the samples could be tentatively dated from a vertical concentration profile of methane sulfonic acid (MSA) obtained in the same pit (Lee *et al.*, 1999). MSA shows strong seasonal patterns with pronounced maxima during the austral summer in coastal Antarctic aerosol and snow in relation to dimethylsulfide (DMS) emissions from the marine biota and its oxidation (Minikin *et al.*, 1998; Mulvaney *et al.*, 1992). As shown in Fig. 2, the concentration of MSA peaks at depths of about 20 and 60 cm. The maximum concentration is 66.9 ng g^{-1} at 20–25 cm. The mean concentration (29.8 ng g^{-1}) of MSA from the surface to 65 cm is about 3 times higher than that (9.3 ng g^{-1}) at depths of 65–144 cm. According to the chlorophyll data in 1998 available from the WWW site <http://seawifs.gsfc.nasa.gov>, a marked increase of the chlorophyll contents of seawater started in the middle of October 1998, especially in the Bellingshausen Sea, i.e. the ocean area, from which air masses reaching Livingston Island often originate (Kottmeier and Fay, 1998). Based on these chlorophyll data and the MSA profile of Fig. 2, it seems that the snow layers between the surface and 65 cm date from October to December 1998 (austral spring–early summer) and deeper layers from austral winter 1998. If we assume an approximate snow density of 0.3 g cm^{-3} , it gives an annual accumulation rate of about $60 \text{ g H}_2\text{O cm}^{-2} \text{ yr}^{-1}$, which is in a good agreement with an annual mean precipitation (ranging from 0.6 to $0.8 \text{ g H}_2\text{O cm}^{-2} \text{ yr}^{-1}$ with altitude) in Livingston Island for the period of 1979–1993 derived from a numerical weather prediction model (Turner *et al.*, 1998).

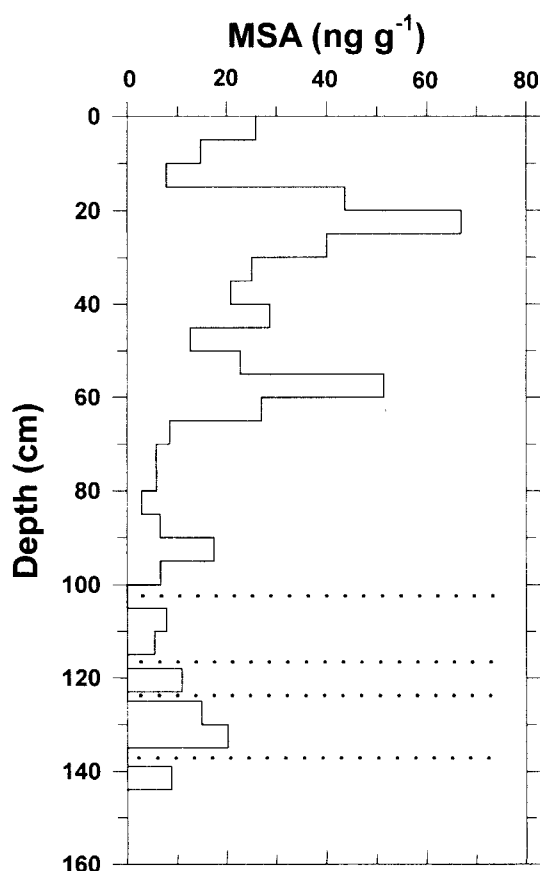


Fig. 2. Vertical profile of MSA concentrations measured by ion chromatography in snow samples collected from the same snow pit (Lee *et al.*, 1999) (dotted lines between 100 and 140 cm depth represent the position of thin ice layers).

3. RESULTS AND DISCUSSION

3.1 Presentation and characteristics of data

The concentrations of Pb, Mn, Al and Na determined by GFAAS in the snow samples are presented in Table 1 and in Fig. 3 as the depth profiles. For Pb, it is observed that the measured concentrations are highly variable, ranging from 0.16 to 17.6 pg g^{-1} , with an average of 4.97 pg g^{-1} and standard deviation of 4.02 pg g^{-1} . The maximum concentration is found at 40–45 cm with more or less upward increase pattern in concentration between 35 and 144 cm. The mean concen-

tration of Pb is similar with those obtained in recent snow at various other Antarctic sites, Table 3.

The Mn profile shows two peaks at 40~45 and 125~130 cm (Fig. 3). The maximum concentration is 150 pg g^{-1} , with an average of 20.6 pg g^{-1} and standard deviation of 31 pg g^{-1} . The above mean value of 20.6 pg g^{-1} is also in good agreement with the various Mn concentration data published by Boutron and Lorius (1977, 1979) and Boutron (1980, 1981, 1982) for shallow snow collected at various locations in East and West Antarctica, especially at the Geographic South Pole and Dome C and along traverses in Adelie Land and in the areas of New Byrd Station.

Al concentrations show peaks at the 40~45 and 50~55 cm depth intervals with the maximum concentration of 8.80 ng g^{-1} at 40~45 cm (Fig. 3). As like Pb and Mn, the mean concentration of 1.82 ng g^{-1} is similar in magnitude to those measured in snow at much more remote locations in Antarctica (for example, the East Coast of the Antarctic Peninsula, Dome C and South Pole) (Suttie and Wolff, 1992; Boutron, 1982; Boutron and Lorius, 1979).

For Na, the profile shows three peaks at 20~25, 45~50 and 130~135 cm (Fig. 3). As expected from our

coastal sampling site, Na concentrations are found to be usually high above the $\mu\text{g g}^{-1}$ level, indicating very strong influence of sea salt aerosol (Table 1). These concentrations at the $\mu\text{g g}^{-1}$ level in our samples are higher by about two or three orders of magnitude than those at the ng g^{-1} level found in central Antarctic snow (see, for example, Legrand and Delmas, 1985; Boutron, 1982; Boutron and Lorius, 1979).

Although our data do not cover one full year of snow accumulation, it is interesting to compare the observed changes in Pb and Mn with those of Al (a good tracer of rock and dust soils) and Na (a good tracer of sea salt spray), Fig. 3. Interestingly, elevated Pb and Mn concentrations are observed in snow which is likely to have been deposited in spring (see section 2.3), Fig. 3. Spring maxima for Pb and Al were also observed by Suttie and Wolff (1992) at a site on the East Coast of Antarctic Peninsula. The correlation coefficient ($p < 0.05$), r , is shown in Table 2. The correlation coefficient between Pb and Al indicates a rather significant relationship between these two metals ($r = 0.61$). On the other hand, no correlation is observed between Pb and Na ($r = 0.10$), indicating a different input mechanism for Pb and Na in our coastal area. Changes in Mn concen-

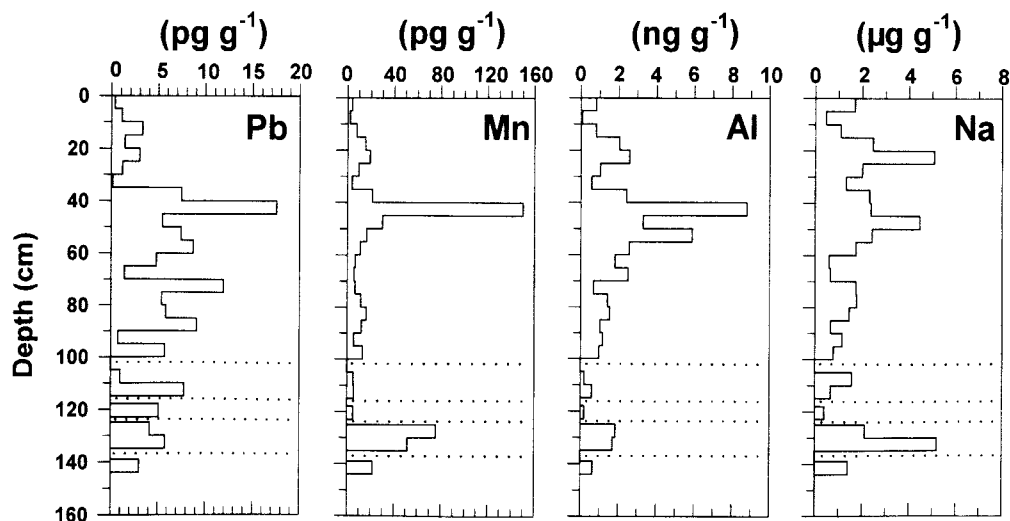


Fig. 3. Vertical profiles of Pb, Mn, Al and Na concentrations in the snow samples from a 1.5-m snow pit in Livingston Island (dotted lines between 100 and 140 cm depth represent the position of thin ice layers).

Table 1. The concentrations of Pb, Mn, Al and Na determined from the samples collected in a snow pit. Source contributions were estimated from rock and soil dust (Pb_{crustal} and Mn_{crustal}) and from sea salt spray (Pb_{marine} and Mn_{marine}) based on Al and sea salt Na concentrations (see the text).

Depth (cm)	Measured concentrations				Estimated contribution			
	Pb (pg g^{-1})	Mn (pg g^{-1})	Al (ng g^{-1})	Na ($\mu\text{g g}^{-1}$)	Pb_{crustal} (pg g^{-1})	Mn_{crustal} (pg g^{-1})	Pb_{marine} (pg g^{-1})	Mn_{marine} (pg g^{-1})
0~ 5	0.41	3.98	0.82	1.69	0.18	5.58	0.062	2.00
5~ 10	1.15	2.12	0.07	0.46	0.02	0.48	0.017	0.54
10~ 15	3.32	7.82	0.80	1.09	0.18	5.45	0.039	1.28
15~ 20	1.45	15.2	2.06	2.47	0.45	14.0	0.090	2.92
20~ 25	3.00	19.3	2.58	5.09	0.57	17.6	0.185	6.01
25~ 30	1.20	9.62	1.05	2.01	0.23	7.15	0.073	2.38
30~ 35	0.16	3.95	0.58	1.34	0.13	3.95	0.049	1.58
35~ 40	7.50	21.3	2.45	2.33	0.54	16.7	0.085	2.75
40~ 45	17.6	150.3	8.80	2.38	1.94	59.9	0.087	2.81
45~ 50	5.48	30.0	3.30	4.46	0.73	22.5	0.162	5.27
50~ 55	7.44	16.6	5.90	2.43	1.30	40.2	0.088	2.87
55~ 60	8.73	11.3	2.58	1.75	0.57	17.6	0.064	2.07
60~ 65	4.85	6.73	1.83	0.60	0.40	12.5	0.022	0.71
65~ 70	1.43	5.88	2.52	0.66	0.55	17.2	0.024	0.78
70~ 75	11.9	6.73	0.69	1.75	0.15	4.70	0.064	2.07
75~ 80	5.39	11.6	1.44	1.77	0.32	9.81	0.064	2.09
80~ 85	5.83	16.3	1.56	1.47	0.34	10.6	0.053	1.73
85~ 90	9.09	12.2	1.03	0.68	0.23	7.01	0.025	0.80
90~ 95	0.76	5.63	1.17	1.16	0.26	7.97	0.042	1.38
95~ 100	5.76	13.6	0.98	0.80	0.22	6.67	0.029	0.94
105~ 110	0.98	5.45	0.20	1.57	0.04	1.36	0.057	1.86
110~ 115	7.77	5.98	0.60	0.68	0.13	4.09	0.025	0.80
118~ 123	5.09	5.25	0.19	0.39	0.04	1.29	0.014	0.47
125~ 130	4.15	76.0	1.87	2.12	0.41	12.7	0.077	2.51
130~ 135	5.79	51.8	1.71	5.22	0.38	11.7	0.190	6.17
139~ 144	3.02	22.1	0.65	1.40	0.14	4.43	0.051	1.66

trations are found to rather well parallel those of Al ($r=0.74$) (Fig. 3). For both metals, elevated concentrations are observed in the 40~60 cm depth interval which corresponds to the spring period. This is consistent with the observation that Mn concentrations in the aerosols at Neumayer station on the Ekström Ice Shelf, Weddell Sea, were found to be enhanced during spring to summer (Wagenbach *et al.*, 1988). As like Pb, Mn is much less correlated with Na ($r=0.35$). Finally, the relationship ($r=0.60$) between Pb and Mn may reflect that part of them is transported from the same source regions and deposited to the snow in a similar manner.

3. 2 Contributions from natural sources

Pb and Mn in the atmosphere originate from various natural sources such as rock and soil dusts, sea salt

spray, volcanoes, wild forest fires, and continental and marine biogenic sources (Nriagu, 1989). The contribution from rock and soil dusts can be evaluated from the Al concentrations measured in the samples and the mean Pb/Al and Mn/Al ratios in crustal material (Wedepohl, 1995). The crustal contributions so calculated for each metal are shown in Table 1 and Fig. 4. On the average, they represent about 8% and 89% of measured Pb and Mn concentrations, respectively.

Contribution from sea salt spray can be calculated from Na concentrations measured in the samples (after correction for the contribution from rock and soil dust), combined with the Pb/Na and Mn/Na ratios in surface bulk seawater and the few available data on metal enrichments in sea-derived aerosols relative to bulk seawater. As previously discussed by Hong *et al.*

(1998), metal concentrations in bulk seawater vary from one oceanic area to the different oceanic area. In addition, the atmospheric input of industrial aerosols to the ocean is known to have already significantly modified the trace metal content of surface seawater (Duce *et al.*, 1991). This is even the case for Pb in the Antarctic seawater (Flegal *et al.*, 1993). We have used the concentration values reported for seawater adjacent to the study area: 4 pg g^{-1} for Pb (based on the assumption that 50% of mean Pb concentration in the seawater near the Antarctic Peninsula is anthropogenic, Flegal *et al.*, 1993) and 13 pg g^{-1} for Mn (Martin *et al.*, 1990). They were then combined with metal enrichment fac-

tors documented for sea-derived aerosols: 100 for Pb and 1,000 for Mn (Boutron and Patterson, 1986; Weisel *et al.*, 1984). Sea salt contribution so evaluated is found to represent, on the average, 4% and 18% of measured Pb and Mn concentrations, respectively (Table 1 and Fig. 4).

Volcanic contribution has been estimated by several authors from non-sea-salt (nss) sulfate and mean metal/sulfur ratios in volcanic emissions (see, for example, Boutron and Patterson, 1986). However, sulfate is dominated by the marine biogenic source in the coastal Antarctic atmosphere and nonbiogenic nss sulfate, being a small fraction of the total nss sulfate, is

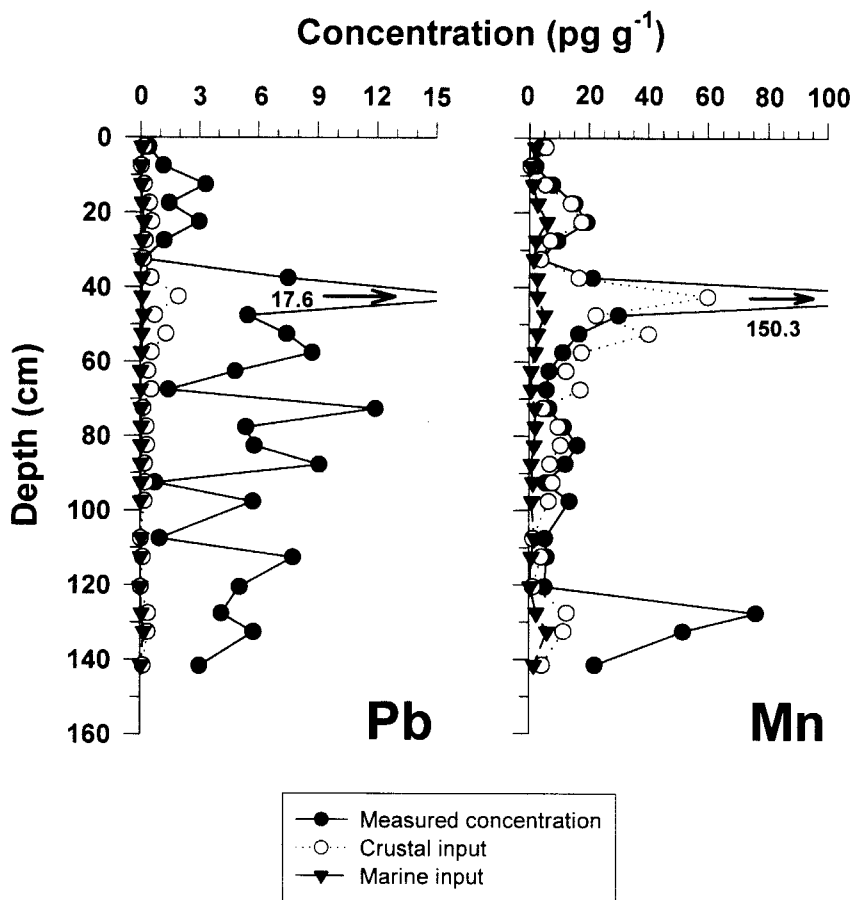


Fig. 4. Vertical profiles of Pb and Mn concentrations in the snow samples from a 1.5-m snow pit in Livingston Island and estimated crustal and marine inputs based on Al and sea salt Na concentrations. The profiles are simply shown as interconnected data points without the position of thin ice layers.

suggested to be long-range transported from continental areas where anthropogenic sulfur dominates the atmospheric sulfur cycle (Minikin *et al.*, 1998). This makes it not possible to evaluate the volcanic contribution for Pb and Mn in our samples using a sulfate-based calculation. We can only surmise that volcanic contribution might be insignificant, based on the fact that nss sulfate level in our samples does not indicate large volcanic perturbation (Lee *et al.*, 1999). Zreda-Gostynska *et al.* (1997) noted that Mount Erebus (77° 55'S, 167° 17'E, 3,794 m above sea level), the world's southernmost active volcano, could be a source of volcano-derived heavy metals for the Antarctic environment. It is, however, still uncertain to what extent volcanic emissions from Mount Erebus influence heavy metals fallout to the snow (Palais *et al.*, 1994).

Other possible sources include wild forest fires and continental and marine biogenic sources (Nriagu, 1989). When considering the fact that forest fires were the only known natural source of black carbon (soot) in the atmosphere during the pre-industrial period, their contribution can be tentatively evaluated from the concentration of black carbon in Antarctic Holocene ice. We used a mean Holocene black carbon concentration of 0.5 ng g⁻¹ (Chýlek *et al.*, 1992). When combined with the averaged Pb content of forest trees and foliage ash given by Nriagu (1979), the contribution of forest fires amounts to about 0.23 pg g⁻¹ for Pb, which is relatively minor with an average of less than 5%. For Mn, no estimate can be made, because of the lack of data of the average Mn content in forest trees and foliage ashes. It is however likely that the corresponding contribution is negligible, since Mn emitted from biomass burning is present mainly in the coarse fraction, which makes the long-range transport of Mn particulate hampered (Gaudichet *et al.*, 1995). Finally, the contribution from continental and marine biogenic emissions cannot be evaluated from our data.

3.3 Anthropogenic Pb and comparative Pb fallout flux

From the previous section, it appears that only about

16% of total Pb concentrations measured in our snow pit samples can be explained by natural contributions, while most of Mn is found to originate mainly from rock and soil dusts. The remaining ("excess") Pb, which cannot be explained by the crustal or marine input (Fig. 4), is likely to be anthropogenic, as in various other sites in Antarctica (Barbante *et al.*, 1998; Wolff and Suttie, 1994; Suttie and Wolff, 1992; Görlach and Boutron, 1992; Boutron and Patterson, 1987).

There are various arguments to rule out any influence from scientific stations both in Livingston Island and especially King George Island where numerous permanent stations are located. Firstly, we exclude the possibility of local emissions in Livingston Island, because the Bulgarian and Spanish summer stations were occupied only a few days before we collected our snow pit samples. The 16 December surface snow samples collected near the Bulgarian station can be used to assess the influence of local emissions. The concentrations of Pb measured in surface snow are 0.33 and 0.62 pg g⁻¹ at 500 m and 1,000 m, respectively. The concentration level is lower at 500 m than at 1,000 m from the station, which may result from a slight difference of sample depth at each site. In addition, the concentrations are very close to that (0.41 pg g⁻¹) obtained in the 0~5 cm depth interval (corresponding to the same precipitation event as mentioned in section 2.1.) in a pit. These findings indicate that the influence of local emissions from the station is certainly negligible. Secondly, the concentrations of Pb in our samples may not have been affected by emissions of pollutants from the stations in King George Island. The sampling site in Livingston Island is over 100 km from King George Island. At this distance, it was found that the influence of local emissions could not be detected (Suttie and Wolff, 1993). Moreover, the South Shetland Islands are within the circumpolar westerly wind zone where frequent pass of cyclones takes place: inverse transport of air pollutants from King George to Livingston Island is then unlikely.

Instead South America is considered to be a candidate as the source region, as hypothesized by Barbante

et al. (1998) for anthropogenic Pb reaching the Atlantic sector of Antarctica (Fig. 1). Their hypothesis is based on the comparison of Pb concentration profiles in Coats Land snow, West Antarctica (Wolff and Suttie, 1994) and in Victoria Land snow, East Antarctica (Barbante *et al.*, 1998) with the inventories of Pb emissions in South America and Oceania, respectively. On the other hand, Rosman *et al.* (1994) suggest South America as a likely source of anthropogenic Pb in Antarctica, based on the Pb isotope abundance in recent snow of East Antarctica. As shown in Fig. 1, Livingston Island is close to the southern edge of South America and thus the eastward-moving low-pressure systems could drive an occasional intrusion of lower latitude air masses containing the aerosols transported from South America, although its probability is predicted to be small (Kottmeier and Fay, 1998). The rela-

tionships between Pb, Mn and Al changes in concentration as discussed in section 3.1 and observed in Fig. 3 may be also used to estimate the origin and pathway of excess Pb in our samples. The Pb profile follows to some extent those of both Mn and Al, well-known tracers for crustal aerosol, with marked peak in the spring period. A rather significant correlation associates Pb with Mn and Al (Table 2). This implies that part of Pb, Mn and Al is probably transported from the same source regions and deposited to the snow in a similar manner. Flegal *et al.* (1993) suggest South America as the source of crustal aerosol entering the Antarctic Peninsula surface seawater.

When compared with Pb levels in Antarctic recent snow at a few locations (Table 3), our averaged Pb concentration tends to be at an apparently similar level, even though large differences in geographic features such as distance from the coast, altitude and snow accumulation rate exist. Since the concentrations in snow could be dependent upon the snow accumulation rate, we here compare the Pb fallout flux (expressed as $\text{pg cm}^{-2} \text{ year}^{-1}$) at each site, calculated by combining an annual mean concentration (pg g^{-1}) of Pb with an annual snow accumulation rate of $\text{H}_2\text{O cm}^{-2} \text{ year}^{-1}$. The annual Pb fallout fluxes to various sites so calculated are given in Table 3. The results clearly show

Table 2. Correlation coefficient ($p < 0.05$) determined for 26 samples collected in a snow pit.

	Pb	Mn	Al	ssNa ^a
Pb	1			
Mn	0.60	1		
Al	0.61	0.74	1	
Na	0.10	0.35	0.37	1

^a sea salt (ss) Na: Na concentrations in the samples after being corrected for the contribution from rock and soil dust.

Table 3. Comparison of Pb concentration values in recent Antarctic snow and annual fallout flux at various sites.

Location	Year	Distance from coast (km)	Elevation a.s.l. (m)	Annual accumulation rate ($\text{g H}_2\text{O cm}^{-2} \text{ yr}^{-1}$)	Mean measured Pb concentration (pg g^{-1})	Pb fallout flux ($\text{pg cm}^{-2} \text{ yr}^{-1}$)
This work (62° 37' S, 60° 15' W)	1998	Coastal	450	60	4.97 ^e	298 ^c
Hercules Névé ^a (73° 06' S, 165° 28' E)	1986~91	90	2,960	17	5.6	95
Dolleman Island ^b (70° 35' S, 60° 56' W)	1984~85	Coastal	398	39	4	156
Coats Land ^c (77° 34' S, 25° 22' W)	1980~86	200	1,420	5.6	5.5	31
Stake D55 ^d (68° 00' S, 137° 46' E)	the late 1970s	180	2,000	8.0	5.2	42

^a Barbante *et al.* (1998).

^b Suttie and Wolff (1992).

^c Wolff and Suttie (1994).

^d Görlach and Boutron (1992). Pb concentration presented is a mean value for the depth interval of 0.07~0.72 m.

^e This value is tentative only, because our samples do not cover a full year of accumulation and ice layers present below 1 m depth in a snow pit were not analyzed (see the text)

first that the Pb fallout flux is much greater in Livingston Island than in other sites, as expected from its locality close to South America. Second, it is of interest to observe that the Pb flux is greater in the coastal areas with relatively high snow accumulation rates than in the interior of the Antarctic continent. This may indicate that the pathway of pollutant aerosols entering Antarctica from the source regions, dispersion pattern in the Antarctic and even deposition mechanisms are not simple. An alternative explanation is that the actual marine contribution from sea salt spray may be much greater, because of the recycling of anthropogenic Pb in seawater to the atmosphere. To estimate sea-salt-derived Pb concentrations in our snow pit samples, we used enrichment factor of 100, which was suggested by Boutron and Patterson (1986) for Pb using the pre-industrial natural Pb concentration in surface seawater (Flegal and Patterson, 1983). The magnitude of the Pb enrichments in sea salt aerosols must be increased with anthropogenic Pb input into ocean surface waters, however, because enrichments of Pb result from the scavenging of Pb by rising bubbles and from the fractionation of the sea surface microlayer (Boutron and Patterson, 1986). Pb isotope tracers have shown that a significant part of Pb in Antarctic surface waters was anthropogenic in origin (Flegal *et al.*, 1993). It is therefore suggested that the recycling of anthropogenic Pb in seawater could significantly contribute to the Pb fallout flux in the Antarctic coastal regions.

Further investigations of heavy metals concentrations in present-day Antarctic snow at various sites will be very helpful to expand our understanding on the input mechanisms of air pollutants to the snow and their dispersion pattern in Antarctica. In addition to such a work, the isotopic composition of Pb obtained in snow will be also helpful to characterize the origin of Pb derived from different sources as already shown in the previous studies (see, for example, Rosman *et al.*, 1994). Pb isotopes are currently being analyzed in our samples and should provide valuable information on source regions of Pb found in snow at the northern tip of the Antarctic Peninsula.

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REFERENCES

- Barbante, C., C. Turetta, A. Gambaro, G. Capodaglio, and G. Scarponi (1998) Sources and origins of aerosols reaching Antarctica as revealed by lead concentration profiles in shallow snow. *Annals of Glaciology*, 27, 674–678.
- Boutron, C.F. (1980) Respective influence of global pollution and volcanic eruptions on the past variations of the trace metals content of Antarctic snow since 1880's. *Journal of Geophysical Research*, 85, 7426–7432.
- Boutron, C.F. (1981) Nouvelles données sur le contenu en métaux traces des neiges de l'Antarctique, du Greenland et de l'île de Devon. *Zeitschrift für Gletscherkunde und Glazialgeologie*, 17, 79–113.
- Boutron, C.F. (1982) Atmospheric trace metals in the snow layers deposited at the South Pole from 1928 to 1977. *Atmospheric Environment*, 16, 2451–2459.
- Boutron, C.F. (1990) A clean laboratory for ultralow concentration heavy metal analysis. *Fresenius Journal of Analytical Chemistry*, 337, 482–491.
- Boutron, C.F. and C. Lorius (1977) Trace elements content in East Antarctica snow samples. *International Association of Scientific Hydrology Publication*, 118, 164–171.
- Boutron, C.F. and C. Lorius (1979) Trace metals in Antarctic snows since 1914. *Nature*, 277, 551–554.
- Boutron, C.F. and C.C. Patterson (1983) The occurrence of lead in Antarctic recent snow, firn deposited over the last two centuries and prehistoric ice. *Geochimica et Cosmochimica Acta*, 47, 1355–1368.
- Boutron, C.F. and C.C. Patterson (1986) Lead concentration changes in Antarctic ice during the Wisconsin/Holocene transition. *Nature*, 323, 222–225.
- Boutron, C.F. and C.C. Patterson (1987) Relative levels of na-

- tural and anthropogenic lead in recent Antarctic snow. *Journal of Geophysical Research*, 92, 8454–8464.
- Boutron, C.F., U. Görlach, J.P. Candelone, M.A. Bolshov, and R.J. Delmas (1991) Decrease in anthropogenic lead, cadmium and zinc in Greenland snows since the late 1960s. *Nature*, 353, 153–156.
- Candelone, J.P., S. Hong, C. Pellone, and C.F. Boutron (1995) Post industrial revolution changes in large scale atmospheric pollution of the Northern Hemisphere by heavy metals as documented in central Greenland snow and ice. *Journal of Geophysical Research*, 100, 16605–16615.
- Chýlek, P., B. Johnson, and H. Wu (1992) Black carbon concentration in Byrd Station ice core: from 13,000 to 700 years before present. *Annales Geophysicae*, 10, 625–629.
- Duce, R.A., P.S. Liss, J.T. Merrill, E.L. Atlas, P. Buat-Menard, B.B. Hicks, J.M. Miller, J.M. Prospero, R. Arimoto, T.M. Church, W. Ellis, J.N. Galloway, L. Hansen, T.D. Jickells, A.H. Knap, K.H. Reinhardt, B. Schneider, A. Soudine, J.J. Tokos, S. Tsunogai, R. Wollast, and M. Zhou (1991) The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles*, 5, 193–259.
- Flegal, A.R. and C.C. Patterson (1983) Vertical concentration profiles of lead in the Central Pacific at 15° N and 20° S. *Earth and Planetary Science Letters*, 64, 19–32.
- Flegal, A.R., H. Maring, and S. Niemeier (1993) Anthropogenic lead in Antarctic sea water. *Nature*, 365, 242–244.
- Gaudichet, A., F. Echalar, B. Chatenet, J.P. Quisefit, G. Malingre, H. Cachier, P. Buat-Menard, P. Artaxo, and W. Maenhaut (1995) Trace elements in tropical African Savanna biomass burning aerosols. *Journal of Atmospheric Chemistry*, 22, 19–39.
- Görlach, U. and C.F. Boutron (1990) Preconcentration of lead, cadmium, copper and zinc in water at the $\mu\text{g g}^{-1}$ level by non-boiling evaporation. *Analytica Chimica Acta* 236, 391–398.
- Görlach, U. and C.F. Boutron (1992) Variations in heavy metals concentrations in Antarctic snows from 1940 to 1980. *Journal of Atmospheric Chemistry*, 14, 205–222.
- Hong, S., J.P. Candelone, C.C. Patterson, and C.F. Boutron (1994) Greenland ice evidence of hemispheric scale pollution for lead two millennia ago by Greek and Roman civilizations. *Science*, 265, 1841–1843.
- Hong, S., C.F. Boutron, R. Edwards, and V.I. Morgan (1998) Heavy metals in Antarctic ice from Law Dome: Initial results. *Environmental Research*, A78, 94–103.
- Hong, S., A. Lluberas, and F. Rodriguez (2000) A clean protocol for determining ultralow heavy metal concentrations: its application to the analysis of Pb, Cd, Cu, Zn and Mn in Antarctic snow. *Korean Journal of Polar Research*, 11, 35–47.
- Kottmeier, C. and B. Fay (1998) Trajectories in the Antarctic lower troposphere. *Journal of Geophysical Research*, 103, 10947–10959.
- Lee, G., J. Park, and S. Hong (1999) Major ionic species in a snow pit in Livingston Island. *Korean Journal of Polar Research*, 10, 59–65.
- Legrand, M. and J.R. Delmas (1985) Spatial and temporal variations of snow chemistry in Terre Adélie (East Antarctica). *Annals of Glaciology*, 7, 20–25.
- Martin, J.H., R.M. Gordon, and S.E. Fitzwater (1990) Iron in Antarctic waters. *Nature*, 345, 156–158.
- Minikin, A., M. Legrand, J. Hall, D. Wagenbach, C. Kleefeld, E. Wolff, E.C. Pasteur, and F. Ducroz (1998) Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation. *Journal of Geophysical Research*, 103, 10975–10990.
- Mulvaney, R., E.C. Pasteur, and D.A. Peel (1992) The ratio of MSA to non-sea-salt sulfate in Antarctic Peninsula ice cores. *Tellus*, 44B, 295–303.
- Murozumi, M., T.J. Chow, and C.C. Patterson (1969) Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. *Geochimica et Cosmochimica Acta*, 33, 1247–1294.
- Ng, A. and C.C. Patterson (1981) Natural concentrations of lead in ancient Arctic and Antarctic ice. *Geochimica et Cosmochimica Acta*, 45, 2109–2121.
- Nriagu, J.O. (1979) Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature*, 279, 409–411.
- Nriagu, J.O. (1989) A global assessment of natural sources of atmospheric trace metals. *Nature*, 338, 47–49.
- Palais, J.M., B.W. Mosher, and D. Lowenthal (1994) Elemental tracers of volcanic emissions from Mount Erebus in Antarctic snow samples, in *Volcanological*

- and Environmental Studies of Mount Erebus, Antarctica, Antarct. Res. Ser.*, vol. 66, edited by P.R. Kyle, pp. 103–113, AGU, Washington, D.C.
- Rosman, K.J.R., W. Chisholm, C.F. Boutron, J.P. Candelone, and U. Görlach, U (1993) Isotopic evidence for the sources of lead in Greenland snows since the late 1960s. *Nature*, 362, 333–335.
- Rosman, K.J.R., W. Chisholm, C.F. Boutron, J.P. Candelone, and C.C. Patterson (1994) Anthropogenic lead isotopes in Antarctica. *Geophysical Research Letters*, 21, 2669–2672.
- Rosman, K.J.R., W. Chisholm, S. Hong, J.P. Candelone, and C.F. Boutron (1997) Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D. *Environmental Science & Technology*, 31, 3413–3416.
- Suttie, E.D. and E.W. Wolff (1992) Seasonal input of heavy metals to Antarctic snow. *Tellus*, 44B, 351–357.
- Suttie, E.D. and E.F. Wolff (1993) The local deposition of heavy metal emissions from point sources in Antarctica. *Atmospheric Environment*, 27A, 1833–1841.
- Turner, J., S. Leonard, T. Lachlan-Cope, and G.J. Marshall (1998) Understanding Antarctic Peninsula precipitation distribution and variability using a numerical weather prediction model. *Annals of Glaciology*, 27, 591–596.
- Wagenbach, D., U. Görlach, K. Moser, and K.O. Münnich (1988) Coastal Antarctic aerosol: the seasonal pattern of its chemical composition and radionuclide content. *Tellus*, 40B, 426–436.
- Wedepohl, K.H. (1995) The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59, 1217–1232.
- Weisel, C.P., R.A. Duce, J.L. Fasching, and R.W. Heaton (1984) Estimates of the transport of trace metals from the ocean to the atmosphere. *Journal of Geophysical Research*, 89, 11607–11618.
- Wolff, E.W. and E.D. Suttie (1994) Antarctic snow record of southern hemisphere lead pollution. *Geophysical Research Letters*, 21, 781–784.
- Zreda-Gostynska, G., P.R. Kyle, D. Finnegan, and K.M. Prestbo (1997) Volcanic gas emissions from Mount Erebus and their impact on the Antarctic environment. *Journal of Geophysical Research*, 102, 15039–15055.