# Lichen Biomonitoring for the Detection of Local Heavy Metal Pollution around King Sejong Station, King George Island, Antarctica

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ABSTRACT. Epilithic macrolichens, Usnea antarctica, were sampled at 37 sites with distance in a radial direction around King Sejong Station on King George Island, Antarctica, in January 1998. They were analyzed to investigate the local pollution for heavy metals caused by the station and to assess the spatial distribution of these atmospheric pollutants. No geographical pattern in concentration was observed for most of the heavy metals analyzed, whereas Pb levels showed a prominent decrease with distance from the station. From the distribution pattern of Pb in lichens, it is estimated that the atmospheric Pb influx has been nearly 50 times higher within ~200 m from the station than in remote areas (~1 km) during the past 10 years, indicating that the bioaccumulation of Pb has significantly been influenced by the anthropogenic Pb released from the station. The pattern of elevated Pb levels in lichens is in good agreement with the predominant downwind direction (southeast). The major local sources of Pb pollution are likely to be the burning of diesel oil and, particularly, leaded gasoline at the station.

Key Words: lichens, heavy metals, bioaccumulation, geographical pattern, anthropogenic lead

#### Introduction

Long-range transport of atmospheric heavy metal pollutants released from the industrial activities in populated areas clearly affects the quality of air in remote regions of the Antarctic, which is an unique clean compartment on the earth. Pb is indeed the case; the large scale air pollution for Pb was detected in Antarctic sea water (Flegal et al., 1993) and recent snow deposits (Görlach and Boutron, 1992; Suttie and Wolff, 1992; Wolff and Suttie, 1994). So far, the main efforts have been devoted to the investigation of a hemispheric scale air pollution in Antarctica (Hong et al., 1998). However, considerable concerns on the local pollution, arising from the stationary scientific stations within Antarctica, need to be made, because these stations could be the potential sources of severe contamination in the local and sometimes regional environments (Boutron and Wolff, 1989). This is especially the case for King George Island where there are eight overwintering stations.

Aerosol particles of heavy metals emitted from the Antarctic stations are readily deposited and accumulated in soils, plants and snow. Thus the atmospheric pollutions for heavy metals can be monitored by the extensive investigation of these materials. Among them, lichens have a high cation exchange and retention capacity of elements which enter the thallus by wet or dry deposition of airborne particles. This results in the binding of metal ions to cell wall exchange sites (Longton, 1988). Because of the remarkable metabolic and physiological properties of lichens, they have been used as an indicator for assessing the atmospheric pollution for various trace elements (Olmez et al., 1985; Walther et al., 1990; Sloof and Wolterbeek, 1991). An assessment of the atmospheric pollution is mainly based on the geographical difference in concentration level with distance from a point source.

The aim of this study is to determine the geographical patterns of heavy metals concentrations in

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lichens around King Sejong Station and to evaluate the extent of local atmospheric pollution for heavy metals, which may have occurred since construction of the station in February 1988.

### Materials and Methods

Epilithic macrolichen, *Usnea antarctica*, is common through continental and maritime subantarctic regions as well as continental Antarctica. As in other areas, this fruticose *Usnea antarctica* communities are widespread and extensive from sea level to altitudes of several hundred meters, principally on boulders, cliff and scree slopes and other rocky substratum around King Sejong Station. Lichen thalli were sampled at 37 sites with distance in a radial direction as a part of the environmental monitoring program during the 1997/98 Korean summer expedition (Fig. 1).

Due to the exceedingly slow rate of growth, mature thalli (more than 0.5 g dry weight) of Usnea antarctica growing in the maritime subantarctic regions would be estimated to be more than 70 years old (Hooker, 1980). This indicates that the aged mature thalli can attenuate the signals of anthropogenic changes in inorganic composition which may have been accumulated since the construction of the station on February, 1988. Thus a composite of several juvenile thalli (less than 0.5 g dry weight) were collected at each of 37 sites to possibly detect an influence of local pollution caused by the station activities on the heavy metals accumulation in lichens. They were carefully taken into acidcleaned low density polyethylene bags by hands wearing wrist length polyethylene gloves.

After returning to the laboratory at Polar Research Center, Korea Ocean Research & Development Institute, the samples were thoroughly washed with Milli-Q Plus deionized water and then dried in an oven at 65°C for a week. In order to obtain relatively comparable data that minimize the difference of growth age as described previously, a sample weighted between 0.2 and 0.3 g at each site was sorted to be analyzed. However, lichen thalli having

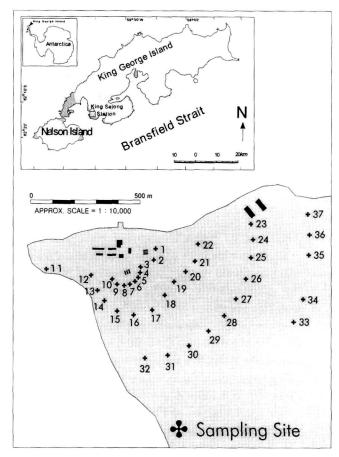


Fig. 1. Map area showing lichen sampling sites around King Sejong Station.

**Table 1.** Measured and certified values (ppm d.w.) of heavy metals analyzed from National Institute of Standards and Technology peach leaves standard reference material #1547. The concentration values are the mean and standard deviation

Element	Measured value	Certified value
Cr	$0.7 \pm 0.1$	(1)*
Cu	$3.50 \pm 0.06$	$3.7 \pm 0.4$
Fe	$162.0 \pm 1.3$	$218 \pm 14$
Mn	$85.0 \pm 0.4$	$98 \pm 3$
Mo	$0.09 \pm 0.03$	$0.06 \pm 0.008$
Ni	$0.72 \pm 0.10$	$0.69 \pm 0.09$
Pb	$0.86 \pm 0.29$	$0.87 \pm 0.03$
Zn	$16.60 \pm 0.07$	$17.9 \pm 1.2$

<sup>\*</sup>Determined but not certified.

a dry weight between 0.2 and 0.3 g were absent at sites of 1, 7, 11, 21, 27 and 33. For this case, we selected two samples which gave a mean weight of 0.2 - 0.3 g at sites 1, 11 and 33. In the case of sites 7,

Table 2. Heavy metals concentrations (ppm d.w.) measured in lichens around King Sejong Station

Site	Dry wt (g)	Cr	Cu	Fe	Mn	Мо	Ni	Pb	Zn
1	0.2396	1.55	5.04	656	8.33	0.42	4.01	22.7	13.3
2	0.2207	0.80	5.18	608	11.71	0.21	2.86	53.1	12.9
3	0.2195	0.93	3.04	120	4.84	0.42	3.32	31.2	11.0
4	0.2431	0.57	1.21	49	2.28	0.25	2.79	22.3	9.33
5	0.2766	0.38	1.75	78	3.62	0.20	2.90	32.5	9.90
6	0.2323	0.54	2.28	90	4.07	0.11	2.73	107	12.5
7	0.1980	0.81	3.10	150	7.72	0.27	2.62	146	15.5
8	0.2221	0.61	1.98	94	6.27	0.23	3.53	38.8	22.5
9	0.2572	1.20	2.59	138	5.14	0.23	3.16	70.4	11.6
10	0.2303	0.94	3.90	112	5.98	0.25	2.24	44.0	12.5
11	0.2762	0.51	2.49	55	4.91	0.22	2.47	2.10	11.7
12	0.2543	0.55	2.85	284	5.98	0.21	2.65	17.0	10.3
13	0.2142	0.57	1.71	94	6.67	0.22	3.20	10.4	8.41
14	0.2474	0.72	1.56	81	3.49	0.25	2.80	8.29	8.97
15	0.2292	1.00	1.51	42	4.29	0.37	2.25	14.8	9.22
16	0.2759	0.52	2.82	243	5.63	0.24	2.37	31.4	18.4
17	0.2101	0.69	3.53	122	3.57	0.31	3.19	40.4	9.86
18	0.2691	0.51	2.53	167	4.74	0.16	2.61	47.6	9.52
19	0.2047	0.63	2.11	192	4.79	0.22	3.56	23.1	11.4
20	0.2154	0.59	1.85	169	8.60	0.23	3.68	10.7	19.2
21	0.1347	0.75	1.81	91	3.86	0.28	3.73	4.86	11.3
22	0.2320	0.56	1.46	138	4.34	0.16	3.09	2.64	8.95
23	0.2413	0.71	1.32	47	3.31	0.27	3.27	23.8	17.0
24	0.2117	0.59	2.48	251	4.48	0.26	2.76	5.78	9.12
25	0.2297	0.47	1.31	62	3.26	0.22	3.06	3.65	7.63
26	0.2637	0.52	3.06	370	4.31	0.23	2.48	5.42	9.67
27	0.1755	0.84	2.83	230	6.22	0.23	3.79	6.23	15.2
28	0.2770	0.45	2.05	79	3.75	0.19	2.77	0.35	5.51
29	0.2503	0.41	1.38	99	3.74	0.22	2.76	1.27	5.22
30	0.2720	0.93	1.49	53	3.09	0.28	1.41	3.23	11.6
31	0.2057	0.91	1.21	55	2.83	0.20	4.29	8.41	10.1
32	0.2166	0.65	1.34	75	2.66	0.30	3.51	3.94	2.83
33	0.2585	0.57	1.18	65	3.61	0.22	3.55	1.26	6.33
34	0.2416	0.46	0.96	35	2.63	0.24	2.50	0.58	6.25
35	0.2008	0.72	7.57	1141	9.93	0.38	4.60	1.47	13.2
36	0.2381	0.71	5.59	237	6.90	0.22	3.12	0.85	21.9
37	0.2042	0.72	4.69	135	4.89	0.13	3.58	21.5	12.1

21 and 27, we used a sample less than 0.2 g, because of no suitable sample (Table 2).

The samples selected were first cut into small chips using ceramic scissors already extensively cleaned by nitric acid. They were then digested overnight with 15 mL of concentrated HNO₃ in acid-cleaned teflon bombs. The solution was heated at

 $40^{\circ}\text{C}$  for 2 h. And 1 mL of  $H_2O_2$  was added to complete oxidation of the organic matter. The solution was evaporated to dryness at  $80^{\circ}\text{C}$  and then the residue was diluted by 10 mL of  $1 \% \text{ HNO}_3$ .

To avoid a possible contamination incurred from suspended dusts in the laboratory, all the procedures for sample preparation were made in a laminar flow clean bench (class 100) and for dryness in a specially designed fume hood which has a prefilter. All the digestions were carried out with Merck suprapur acids. The measurement of heavy metals (Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn) was performed by ICP-AES (Perkin Elmer Optima 3000Sc). Quality of metal analyses was checked by National Institute of Standards and Technology peach leaves standard reference material #1547 and the blanks. The values measured for the analyses of Cu, Ni, Pb, and Zn did not differ more than 10% from the certified values (Table 1). The concentrations of Cr and Fe analyzed represent to differ up to 25-30% from the certified values. For Mo, the difference between the measured and certified values is the largest (50%), which is due surely to too low concentration in the standard material. The precision assessed by the duplicate measurement ranges from ± 5 to 10%, increasing as the concentrations approach to the detection limit. The total blank contributions from the whole analytical procedures were found to be negligible for each metal.

## Results and Discussion

# Character of the data and bioaccumulation pattern in lichens

Table 2 summarizes the measured concentrations of heavy metals in lichens. Fe and Pb concentrations are shown to be highly variable depending on the sampling site. In contrast, the concentrations of Mo and Ni are considerably homogeneous. Mean values and standard deviation calculated for all the sites are  $181 \pm 214$  and  $23.5 \pm 30.8$  ppm for Fe and Pb and  $0.24 \pm 0.07$  and  $3.06 \pm 0.63$  ppm for Mo and Ni, respectively (Table 3).

In general, a geographical distribution pattern in concentration is used as an effective method to have an insight into an influence of anthropogenic pollutants released from a point source. From the mean concentrations in four groups separated according to the distance between the station and sampling sites (Table 3), an apparent geographical gradient is not found for most of the elements except for Pb.

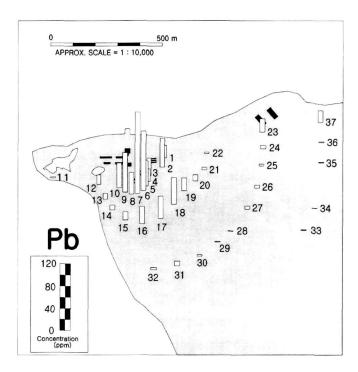
The highest mean concentration values of Cr, Mn, Mo and Zn are shown at sites 1-10, whereas the highest Cu, Fe, and Ni values at 33-37. Here we cannot draw a firm conclusion that anthropogenic pollutants released from the station have influence on slightly higher Cr, Mn, Mo and Zn values in lichens close to the station. This is because an approximation of the growth rate in lichens at each of 37 sites remains uncertain as explained in section 2. Although the same quantity of metals may be actually deposited from the atmosphere, it is plausible that the difference in age of lichens could control the occurrence of heavy metals between the sites. Moreover, although uptake processes of inorganic composition in lichens is not clearly understood, it is probable that few lichens are fully independent of their substratum (Longton, 1988). In fact, the metal levels in volcano-plutonic rocks present on the Barton Peninsula was found to be quite variable at even small area according to the rock composition such as basaltic, andesitic, dacitic, and rhyodacitic rocks (Jin and Jwa, 1990). A general conclusion is that when the changes in concentration between the sites are relatively large by, at least, a factor of two, the pattern in heavy metals concentrations in lichens could allow an exclusive biomonitoring in the small region.

Whereas most of the elements do not show any distinct geographical pattern in concentration, a gradual drop in Pb levels with distance from the station is particularly apparent (Table 3). The average values of Pb levels decrease from  $56.8 \pm 40.5$  to  $5.13 \pm 9.16$  ppm. Although various unpredictable factors affecting the changes in concentration are considered as mentioned above, this comparative relationship between Pb levels in lichens and distance from the station should result from the atmospheric Pb concentration gradients and eventually from the anthropogenic Pb pollutants emitted from the station.

The geographical concentration pattern of Pb is quite well defined in the plot of Fig. 2. While much lower values (less than 1 ppm) are present at the remote areas, Pb levels are extremely elevated at sites close to the station. Here we can make a tenta-

Table 3. Average and range of the measured heavy metals concentrations (ppm d.w. ± SD) in all the lichen samples and
four groups approximately separated with distance between the sampling sites and station.

Site	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
All the sites	$0.69 \pm 0.23$	2.56 ± 1.47	181 ± 214	5.04 ± 2.11	$0.24 \pm 0.07$	$3.06 \pm 0.63$	$23.5 \pm 30.8$	$11.40 \pm 4.34$
Groups with								
distance								
1-10	$0.83 \pm 0.35$	$3.01 \pm 1.34$	$210 \pm 225$	$6.00 \pm 2.72$	$0.26 \pm 0.10$	$3.01 \pm 0.50$	$56.8 \pm 40.5$	$13.10 \pm 3.74$
11-22	$0.63 \pm 0.14$	$2.19 \pm 0.66$	$140 \pm 74$	$5.07 \pm 1.47$	$0.24 \pm 0.06$	$2.97 \pm 0.52$	$17.8 \pm 15.0$	$11.44 \pm 3.60$
23-32	$0.65 \pm 0.19$	$1.85 \pm 0.70$	$132 \pm 111$	$3.77 \pm 1.05$	$0.24 \pm 0.04$	$3.01 \pm 0.79$	$6.21 \pm 6.62$	$9.39 \pm 4.42$
33-37	$0.64 \pm 0.12$	$4.00 \pm 2.87$	$323 \pm 64$	$5.59 \pm 2.90$	$0.24 \pm 0.09$	$3.47 \pm 0.77$	$5.13 \pm 9.16$	$11.96 \pm 6.42$



**Fig. 2.** Geographical distribution pattern of Pb in lichens around King Sejong station.

tively quantitative comparison of the relative atmospheric Pb influx between at the closest and the most remote areas since construction of the station in February 1988. At sites 1-10 and 33-36, the average Pb concentrations and dry weight of samples are 56.8 and 1.0 ppm and 0.2339 and 0.2348 g, respectively (Table 2). The site 37 was excluded in calculating the average values of concentration and dry weight. This is because the Pb level at this site is very highly elevated in comparison with sites 33-36 and thus suspected to be significantly influenced by

anthropogenic Pb resulting from local activities around the warehouses (see also the Pb levels at sites 23 and 24). According to the age-dry weight relationship of Usnea antarctica grown on Signy Island (lat. 60°45' S, long. 43°38' W), South Orkney Islands, presented by Hooker (1980), the net annual production of a thallus 0.2 g dry weight is about 70 mg g-1 dry weight per year. This relationship yields the ages of lichen thalli at sites 1-10 and 33-36 to be about 17 years old. Of course, it appears that the growth rate of lichens growing on King George Island would be different from that on Signy Island, because of the difference of micro-habitats such as wind speed, properties of substratum, moist contents, and so on. In addition, there exists a difference in altitude at even two groups of the sites 1-10 and 33-36 (~10-20 and ~25-110 m above sea level, respectively), indicating that the net annual productivity may be to some extent different between two groups. In spite of these facts, it is believed that lichen thalli collected at sites 1-10 have been extensively affected by the Pb pollutants emitted since construction of the station. With this estimate, atmospheric Pb influx is calculated to have been more than 50 times higher at sites 1-10 than at 33-36 during the past 10 years.

From the plot of Fig. 2, the anthropogenic Pb emitted from the station is shown to have been deposited at sites very close to the source. This is in good agreement with the previous study on the local pollution from the scientific stations in Antarctica (Suttie and Wolff, 1993). The prevailing

direction of the transport of Pb pollutants seems to be south and southeast as revealed by the elevated Pb levels in lichens (Fig. 2). This phenomenon corresponds to the fact that the predominant wind direction at King Sejong Station for the period of 1988-1996 was northwest (Lee *et al.*, 1997).

In conclusion, the results obtained from lichens demonstrate that local pollution for Pb has occurred due to atmospheric emission of Pb from human activities at King Sejong Station, but indicate that the fallout of Pb pollutants is still limited in the areas near the station (within ~500 m). In addition, lichens are found to be very effectively used as indicators and monitors of the atmospheric pollution caused by the stationary scientific stations in even remote regions of the Antarctic as well as near the heavily industrialized zones.

## Possible source of anthropogenic Pb in lichens

With the pattern of elevated Pb levels in lichens near the station, it is impossible to discriminate a source and/or sources of anthropogenic Pb pollutants accumulated in lichens. Since the limited sources exist at the Antarctic stationary stations unlike the heavily industrialized regions, however, we can assume that the diesel oil combustion for the electric power generation, use of leaded gasoline for the vehicles, pigments used in paints and waste incineration may be possible sources which could emit Pb pollutants.

The approximate discrimination of possible sources could be deduced from the occurrence of heavy metals in soils collected just beneath the exhaust of the electric power generators in January 1997 (Table 4) (Hong et al., 1997). As shown in Table 4, it is evidently found that the enhancement of Cr, Mo, Pb and Sn contents at the surface soil in the depth profiles are 3.4, 5.2, 16.0 and 1.4, respectively. The site of soil sampling is expected to be easily contaminated by various elements emitted from the combustion of diesel oil in electric power generators. In fact, high-temperature processes in oil-fired electric power plants could release a significant amount of all the heavy metals determined in the soil samples (Pacyna, 1986, 1987; Nriagu and

**Table 4.** Depth profile of the heavy metals concentrations (ppm) measured in soils collected just beneath the exhaust of the electric power generators at King Sejong Station. From Hong *et al.* (1997)

Depth (cr	n) Cr	Cu	Mo	Ni	Pb	Sn	Zn
0-1	48.3	65.7	8.17	6.61	224	16.1	80.5
1-2	18.5	76.2	2.62	6.31	37.8	16.6	72.1
3-4	15.5	82.7	1.86	6.52	14.7	12.7	81.0
7-8	14.2	92.4	1.57	6.68	14.0	11.2	84.2

Pacyna, 1988). The actual contamination at the surface soil, however, occurs only for Cr, Mo, Pb and Sn, suggesting that the amount of Cu and Zn contaminants arising from this source was negligible at the station or that the soil contamination for these metals was masked due to their high background level in soils.

Taking into account the fact that pigments containing the compounds of PbCrO<sub>4</sub>, PbMoO<sub>4</sub> and PbSO<sub>4</sub> have been used as colorants in paints at the station (Jae Il Color Ind. Co., Ltd., personal communication), on the other hand, the fine particles of paint-spray is believed to have been a dominant contributor of Cr, Mo and Pb accumulated at the surface soil. At present, it is difficult to assess to what extent Cr, Mo and Pb accumulated at the surface soil have been derived from each of two sources, oil combustion and paint-spray. Despite that, our geographical distribution patterns of heavy metals in lichens represent that the fine particles of paint-spray is likely to be negligible contributor to the bioaccumulation of Pb in lichens, in view of the finding that Cr and Mo, being main ingredients of pigments in paints, do not show particularly increased levels in lichens near the station. This indicates that the fine particles of paint-spray might be deposited just in the vicinity of the buildings of the station.

According to the inventory of Pb emission from different industrial sources presented by Nriagu and Pacyna (1988), a large quantity of Pb is also emitted from the waste incineration. Of course, the emission rates are very dependent on the type and amount of waste as well as its chemical composition. At King

Sejong Station, the waste incineration would not be a significant contributor to anthropogenic Pb accumulated in lichens, because the wastes to be incinerated have been strictly limited to the combustible materials such as woods, papers and leftover foods.

Another possible source which can be attributed to anthropogenic Pb emission at the station is the use of leaded gasoline for the vehicles such as amphibious, zodiac, fork-lift, skidoo. Since a large amount of Pb is emitted from leaded gasoline due to Pb anti-knock additives, it seems likely that the use of leaded gasoline at the station could be a dominant source of the bioaccumulation of Pb. According to the data compiled, the quantities of Pb emitted from the burning of leaded gasoline and diesel oil within Antarctica by various stations were estimated to be about 460 and 45 kg per year, respectively (Boutron and Wolff, 1989), indicating that Pb emission in Antarctica is dominated by the combustion of gasoline. This may be the case at King Sejong Station. For comparison, we can make an approximate amount of Pb released from oil and leaded gasoline combustion at the station, using the data available for the consumption rates of fuels and Pb emission factors (defined as the mass of Pb emitted by the combustion of a unit volume of fuels). Total amount of diesel oil and leaded gasoline consumed during the period from 1988 to 1997 was compiled from Korean overwintering reports to reach roughly 2 million and 25,500 liters, respectively. For Pb emission factors, we have used the representative values  $(4 \times 10^{-4} \text{ and } 2 \times 10^{-6} \text{ kg } l^{-1} \text{ for leaded gasoline and})$ diesel) for fuels in Antarctica suggested by Boutron and Wolff (1989). The calculation using the above total amounts of fuel consumption rates and emission factors gives the values of about 10 and 4 kg for Pb emission from leaded gasoline and diesel. It should be noted that, due to wide ranges of Pb contents in diesel oil and even leaded gasoline depending on the manufacturer, these figures calculated from the averaged values within Antarctica are believed to be to some extent erroneous. However, it seems reasonable to assume that at King Sejong Station a significant amount of Pb emission can be attributed to the use of leaded gasoline during the

past 10 years.

In summary, the combustion of leaded gasoline and diesel oil is likely to be major sources for anthropogenic Pb accumulation in lichens distributed at the surrounding area of the station. The paint-spray particles is shown to have significant influence on the excess accumulation of Cr, Mo and Pb in soils, but insignificant on Pb in lichens, because of their relatively large size not to be transported over large areas around the station. It must be emphasized that the transport of heavy metal pollutants from the neighboring other stations could occur, even though this cannot be confirmed by the present study. In the future, the studies detailed are needed to verify the major contributor to local pollution for Pb observed from our lichen samples. One of these studies is to measure stable Pb isotopes in lichens and aerosols with distance from the point sources.

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