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Article

Heavy Metal Concentrations in the Fruticose Lichen *Usnea aurantiacoatra* from King George Island, South Shetland Islands, West Antarctica

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The accumulation of selected heavy metals in the fruticose lichen *Usnea aurantiacoatra* is reported in the vicinity of the Korean research station on Barton Peninsula, King George Island, West Antarctica. To assess the impact of human activities in the study area, all samples were divided into five groups according to distance from the research station. The corresponding heavy metal levels in samples near the station were relatively higher than those collected far from the station. In particular, a very high level of Pb near the station strongly suggests the anthropogenic release of this pollutant. The relationship between trace metal content and age of the lichen was investigated, but no significant difference was found. When evaluating the vertical distribution of heavy metals in lichen thalli, most elements, particularly Pb, accumulated preferentially in the upper parts, probably due to the morphology of *U. aurantiacoatra*. Therefore, the vertical distribution of heavy metals in fruticose lichens should be considered to enhance data quality in biomonitoring studies.

Key words: *Antarctica, biomonitoring, heavy metal, human impact, lichen,* Usnea aurantiacoatra

Antarctica, especially the Antarctic Peninsula, has been exposed to contamination through increasing human activity at research stations and increased tourism. Recent studies have reported heavy metal concentrations in different components of King George Island, including snow-ice [Hong *et al.*, 2002], soil [Santos *et al.*, 2005], sediments [Andrade *et al.*, 2001; Santos *et al.*, 2005], and vegetation [Poblet *et al.*, 1997; Hong *et al.*, 1999; Osyczka *et al.*, 2007]. King George Island, on which ten research stations are located, is the largest of the South Shetland Islands in West Antarctica. Most of the ice-free area on King George Island is covered by relatively abundant vegetation, dominated by lower plants such as mosses and lichens [Kim *et al.*, 2006]. Lichens are perennial, slow-growing organisms that maintain a uniform morphology over time, and do not shed parts as readily as vascular plants. The lack of a waxy cuticle and stomata allows many contaminants to be absorbed over the whole lichen surface [Hale, 1983]. Because the concentrations of heavy metals in lichen thalli appear to be directly correlated to contamination levels, lichens have been used extensively for biomonitoring of airborne trace elements [Garty, 2001]. Although there are many papers on this subject, little is known regarding the relationship between heavy metal content and age of thalli or the vertical distribution of heavy metals in fruticose lichens. As shown in previous studies on foliose lichens [Hale Jr and Lawrey, 1985; Bargagli *et al.*, 1987], older thalli are likely to contain higher concentrations of heavy metals due to increased exposure time. In addition, the vertical distribution of heavy metals in thalli is important to understand physiological processes in lichens. Although many studies have examined the preferential accumulation of heavy metals in different thallial zones, this relationship remains unclear in fruticose lichens.

The objectives of this study were to test the following hypotheses: 1) whether the fruticose lichen *Usnea aurantiacoatra* on Barton Peninsula of King George Island has been influenced by pollutants released from the Korean research station; 2) whether the concentrations of

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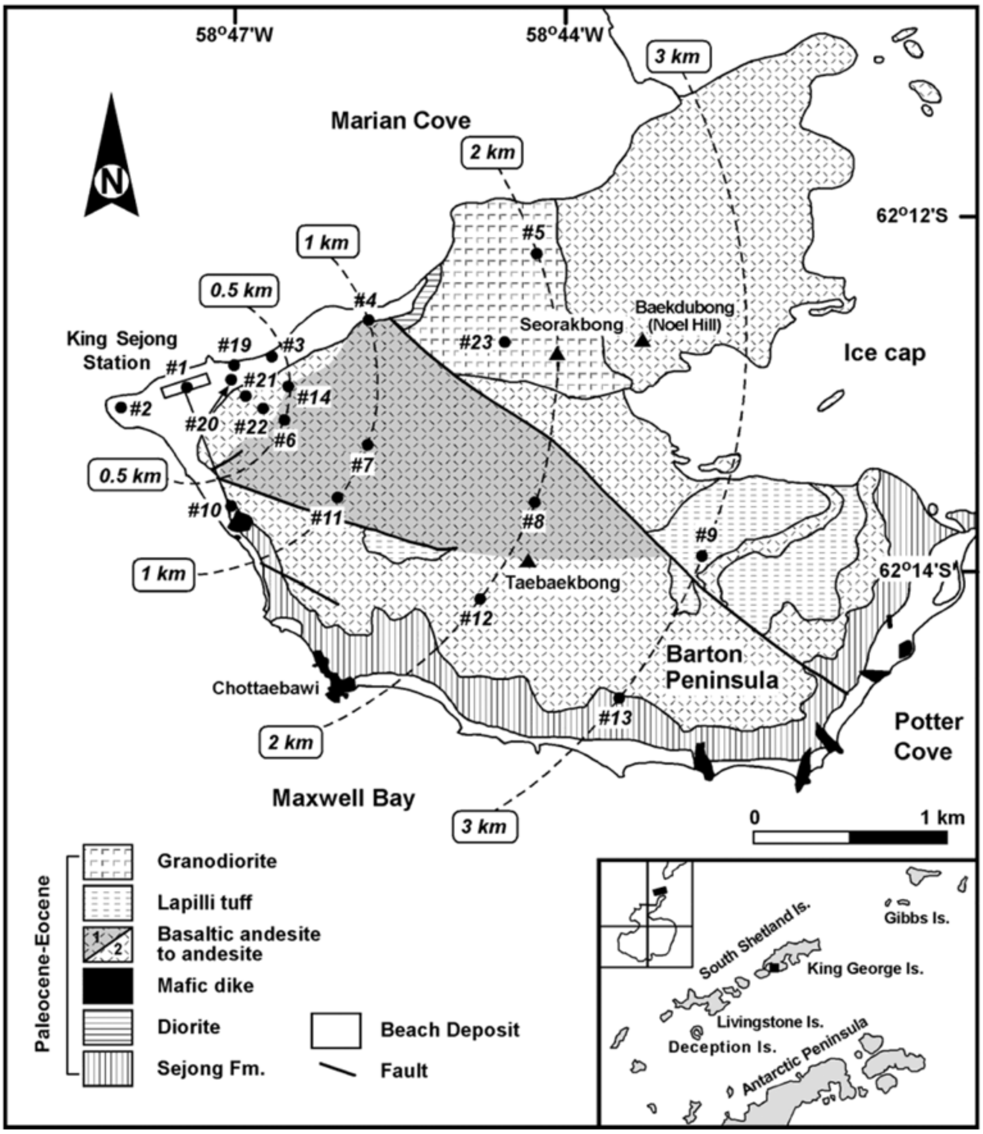

Fig. 1. Geologic map of the Barton Peninsula, King George Island, West Antarctica (after [Lee *et al.*, 2001]. Sampling locations of vegetation are marked with solid circles.

heavy metals increase with lichen size; and 3) whether individual heavy metals accumulate preferentially either in the upper or basal parts of the lichen. Heavy metal concentrations in *U. aurantiacoatra*, which is widespread in Antarctic habitats, are expected to provide useful information for comparison other lichens of the same genus from other areas.

Material and Methods

King George Island, the largest island of the South Shetland Islands, has a cold, oceanic climate characteristic of maritime Antarctica. Meteorological data for the study area, recorded at King Sejong Station, show a mean annual temperature of −1.8 to −1.6°C, relative humidity of 89%, annual precipitation of 437.6 mm, and wind velocity of 7.9 m/s, predominantly from the northwest and southwest [Lee *et al.*, 1997; Chung *et al.*, 2004]. Most of the ice-free area is covered by relatively abundant vegetation, dominated by cryptogamic species [Kim *et al.*, 2007]. The flora comprises two flowering plants, 33 bryophytes, and 62 lichens [Lee, 1992; Kim *et al.*, 2006]. The Chottaebawi area on the southern coast of the peninsula contains one of the most important penguin colonies (*Pygoscelis papua* and *Pygoscelis antarctica*) in the maritime Antarctic region (Fig. 1). The cape area near King Sejong Station is populated by flying seabirds, such as skuas.

This study focuses on the epilithic, fruticose lichen, *U. aurantiacoatra*, which grows on rock surfaces on Barton Peninsula of King George Island. It is generally abundant in most habitats, from sheltered to very exposed and

Table 1. Classification of lichen samples by size and weight, which are indicative of thallus age

Group	Height (cm) mean (range)	Width (cm) mean (range)	Dry weight (g) mean (range)
Young	1.91 (1.5–2.0)	2.14 (1.5–2.3)	0.106 (0.05–0.14)
Mid-aged	3.72 (3.4–3.9)	5.62 (4.6–5.0)	0.751 (0.69–0.84)
Old	5.62 (5.2–6.5)	8.23 (7.6–8.5)	5.553 (5.31–5.93)

Table 2. Geographic distribution of heavy metals (mg/g d.w.) in *Usnea aurantiacoatra*. Samples were divided into five groups based on distance between the station and sampling location

Group	Site	Cr	Cu	Zn	Al	Mn	Fe	V	Ni	Pb
Group 1* (near the station)	# 1	1.00	0.88	7.21	38.24	2.24	381.9	0.14	0.62	4.20
	# 19	1.31	1.17	4.45	39.09	1.68	508.1	0.18	0.75	13.53
	# 20	0.84	0.88	4.97	28.01	1.46	365.7	0.11	0.56	13.24
	# 21	0.60	1.18	4.50	24.07	1.32	312.3	0.09	0.38	5.96
	# 22	3.08	1.59	3.44	56.50	2.06	880.0	0.35	1.79	4.84
	# 2	0.55	1.07	3.88	30.93	1.67	480.9	0.11	0.41	0.95
	Mean	1.37	1.14	4.91	37.18	1.75	489.6	0.18	0.82	8.36
	SD	0.99	0.29	1.40	12.59	0.39	229.8	0.10	0.56	4.63
Group 2 (~0.5 km)	# 3	1.56	0.94	4.01	40.85	1.69	519.2	0.16	0.95	2.70
	# 6	1.58	1.09	4.54	40.14	1.75	470.8	0.17	0.93	2.56
	# 10	1.21	0.75	3.31	58.49	1.99	594.3	0.23	0.79	1.36
	# 14	0.53	0.53	1.77	30.76	1.43	270.5	0.12	0.34	0.44
	Mean	1.22	0.83	3.41	42.56	1.72	463.7	0.17	0.75	1.76
	SD	0.49	0.24	1.20	11.57	0.23	138.5	0.05	0.28	1.07
Group 3 (~1 km)	# 4	1.15	1.42	4.99	61.83	2.12	633.6	0.25	0.72	1.58
	# 7	0.92	0.56	3.27	16.18	1.15	259.8	0.06	0.56	0.59
	# 11	0.78	0.65	3.51	35.27	1.81	340.3	0.14	2.26	1.01
	Mean	0.95	0.88	3.92	37.76	1.69	411.2	0.15	1.18	1.06
	SD	0.19	0.47	0.93	22.93	0.50	196.7	0.10	0.94	0.49
Group 4 (~2 km)	# 5	0.57	0.57	3.08	15.20	1.06	272.9	0.05	0.38	0.87
	# 8	1.09	0.47	2.02	16.83	1.22	273.4	0.07	0.66	0.51
	# 12	0.90	0.80	2.31	25.60	1.07	334.1	0.10	0.52	0.84
	# 23	0.22	0.88	3.72	15.03	1.04	211.6	0.05	0.21	0.84
	Mean	0.69	0.68	2.78	18.16	1.10	273.0	0.07	0.44	0.77
	SD	0.38	0.19	0.77	5.03	0.08	50.0	0.02	0.19	0.17
Group 5 (~3 km)	# 9	1.91	0.80	3.68	37.14	1.67	440.7	0.16	1.12	4.29
	# 13	0.79	1.04	3.18	41.10	1.55	381.7	0.13	0.48	0.72
Total	Mean	1.08	0.91	3.78	34.28	1.58	417.5	0.14	0.76	3.21
	SD	0.64	0.30	1.23	14.18	0.37	162.9	0.08	0.51	3.95

*Site 2 was excluded in calculation of mean values.

moist to dry areas, often in association with other lichen species (*Usnea antarctica* and *Himantormia lugubris*) and mosses (*Chorisodontium aciphyllum, Polytrichum strictum,* and *Andreaea* spp.) [Kim *et al.*, 2006]. A field survey was conducted in January and February 2007 during the 2006/2007 Korea Antarctic Research Programme (KARP) expedition. Lichen samples were collected from 19 sites in snow-free areas of the peninsula (Fig. 1). Sample sites were divided into five groups according to distance from the research station (Fig. 1, Table 2). Because of snow cover, however, only two samples in group 5 (~3 km) were collected at (sites 9 and 13). Among the sampling sites, sites 19 and 20 were very close to the fuel storage tanks of the station, and sites 21 and 22 were 100 and 150 m from the station, respectively (Fig. 1). At each site, at least 20 thalli of *U. aurantiacoatra* of different sizes were collected. Based on size and weight, samples collected at each site were divided into three age groups: young, mid-aged, and old (Table 1). Old thalli were subdivided into three parts: upper, middle, and basal segments. Samples were always handled with plastic gloves and clean plastic or ceramic tools. Lichen samples were cleaned in distilled water, oven-dried at 70ºC for 72 h, and then homogenised to a fine powder in an agate mortar.

Lichen samples were cleaned in distilled water and oven-dried at 70ºC for 72 h. The samples were cut into small chips using ceramic scissors, and then 1 g of samples was digested overnight at 50ºC with 5 mL of concentrated HNO_3 (Merck Suprapur) in acid-cleaned teflon bombs. The digested samples were added with 0.5 mL of H_2O_2 (Merck Suprapur) and then incubated for additional 2 hr at 100ºC to complete oxidation of the organic matter. Before analyzing, ddH_20 was added up to 20 mL of total volume and then samples were filtered using Whatman filter paper No. 2 to remove the debris. Concentrations of heavy metals were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500, Santa Clara, CA).

Metal content was assayed in triplicate and measurements were repeated three times; all concentrations were expressed on a dry weight (d.w.) basis. Data quality was checked by concurrent digestion and analysis of a standard reference material (SRM 1547 peach leaves) obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD). The values of most elements in lichens did not differ by more than 10% from the standard values, except for Cr and Zn, which differed by up to 14% from the standard.

Results and Discussion

To assess the impact of human activities in the area, the data from all sample sites were divided into five groups according to distance from the research station (Fig. 1), and the mean concentration of each group was shown in Table 2. Although Site 9 is very far from the station, most metal concentrations in this sample were extremely high in comparison to other sites, suggesting unexpected contamination from an anthropogenic source. Therefore, site 9 was excluded from the calculation of mean values, and the remaining samples in group 5 were omitted because of a lack of statistical validity. The lichen samples collected from site 2, west of the station, had very low metal concentrations in comparison with other samples from group 1 (near the station). This is consistent with previous work on local pollution from King Sejong Station [Hong *et al.*, 1999]. Because the wind blows predominantly from the northwest at King Sejong Station [Lee *et al.*, 1997], site 2 does not seem to have been influenced by anthropogenic pollutants released from the station. Thus, site 2 was also excluded from the calculation of the mean value of group 1.

The results show that most heavy metals were relatively more concentrated (1.6- to 2.6-fold higher) in group 1 than in group 4 samples, which were collected approximately 2 km away (Table 2), suggesting that the bioaccumulation of trace metals was significantly influenced by anthropogenic pollutants released from the station. Moreover, a dramatic decrease in Pb concentrations was observed with increasing distance from the station. The mean Pb content of group 1 samples was 8.36±4.6 μg/g, which is more than 10-fold higher than in group 4 (0.77± 0.17 μg/g). Overall, the mean Pb concentration (3.21± 3.95 μg/g) in this study was relatively high, although the mean values of group 3 (1.06±0.49 μg/g) and Group 4 (0.77±0.17 μg/g) were within the same range or slightly lower than those previously reported (1.15±1.03 μg/g) from Potter Peninsula on King George Island [Poblet *et al.*, 1997]. As suggested by [Hong *et al.*, 1999], the use of leaded gasoline and diesel oil in King Sejong Station are likely sources of Pb.

However, additional environmental factors, such as geological characteristics of substrata and distance from the seashore, should also be considered to precisely assess the human influence on heavy metal concentrations in lichens. As shown in Fig. 1, most samples were collected from the basaltic andesite region, but some were from granodiorite (sites 5 and 23), Sejong Formation (site 13), and lapilli tuff (site 9) areas. According to a study on soil geochemistry on King George Island, most soils on Barton Peninsula developed *in situ* and primarily reflect the bedrock composition [Lee *et al.*, 2004]. The mean concentrations of most heavy metals in soils developed on volcanic parent material were similar, whereas soils developed on granodiorite showed significantly different heavy metal values. For example, the mean content of Cr, Al, Fe, V, and Ni in volcanic soil was relatively higher than in soils derived from granodiorite. When soil heavy metal concentrations were compared with those of lichen samples, a significant relationship was found between lichen and substrate. Lichen samples collected from the granodiorite region (sites 5 and 23) had relatively low levels of Cr, Al, Fe, V, and Ni (Table 2), clearly indicating the presence of adsorbed or entrapped soil particles in the lichen thalli [Bargagli, 1995; Bargagli *et al.*, 1999]. The high correlation coefficients (r^2>0.7) between lithophilic elements such as Al, Fe, Mn, and V also support this interpretation. Nonetheless, the effects of different substrata were outweighed by those of anthropogenic pollutants. In addition to the relationships between substrata and lichen, the influence of seawater on the heavy metal composition

Table 3. Mean concentration of heavy metals (mg/g d.w.±SD) in young, mid-aged, and old thalli of *Usnea aurantiacoatra*

	Young	Mid-aged	Old
Cr	0.909±0.378	1.056±0.608	0.951±0.628
Cu	1.060±0.384	0.795±0.278	0.757±0.321
Zn	3.912±1.374	3.757±1.397	3.727±1.722
Al	24.36±8.15	28.13±10.16	50.24±32.07
Mn	1.545±0.362	1.443±0.372	1.664±0.761
Fe	407.0±112.6	343.6±111.6	424.6±257.5
V	0.110±0.047	0.106±0.052	0.170±0.133
Ni	0.579±0.225	0.947±1.267	0.580±0.353
Pb	3.360±4.720	3.263±4.260	2.744±3.384

Table 4. Mean concentration of heavy metals (mg/g d.w.±SD) in terms of their vertical distribution within *Usnea aurantiacoatra*

	Basal segment	Middle segment	Upper segment
Cr	0.045±0.018	0.034±0.015	0.031±0.011
Cu	0.408±0.155	0.310±0.077	0.591±0.224
Zn	2.223±1.075	2.063±1.024	2.722±1.106
Al	22.31±21.62	16.21±10.59	16.97±10.60
Mn	0.865±0.384	0.819±0.325	1.109±0.502
Fe	143.0±123.4	181.0±98.5	314.7±184.9
V	0.107±0.123	0.073±0.056	0.078±0.053
Ni	0.040±0.014	0.060±0.018	0.085±0.025
Pb	0.659±0.998	2.094±3.101	3.769±5.083

of lichens should be considered. The marine environment is known to affect the element composition of lichens through aerosols, as well as through the melting of snow and dissolution of salt encrustations [Bargagli *et al.*, 1999]. According to previous work in northern Victoria Land, the mean concentrations of P, K, and Na increased significantly with proximity to the coast, indicating a significant influence of seawater and seabird nests [Bargagli *et al.*, 1999]. Because the study area (Barton Peninsula) is surrounded by sea on three sides and all samples were collected within 3 km of the seashore, however, it is difficult to evaluate such impacts in this study. Therefore, the marine effect on heavy metal accumulation in lichens was ignored in this study.

The relationship between heavy metal content and age of the lichen is summarised in Table 3. The amounts of Al and V increased in older thalli, whereas Cu and Pb were relatively more concentrated in younger thalli. However, thalli of different sizes did not show statistically significant differences in other heavy metal concentrations (less than 8%). According to previous studies on foliose lichens [Hale Jr and Lawrey, 1985; Loppi *et al.*, 1997; Nimis *et al.*, 2001], large, old thalli generally contain higher quantities of metals, probably due to increased exposure time. However, Bargagli *et al.* [1999] reported no significant differences between element concentrations in the different size classes of the foliose lichen *Umbilicaria decussata* in Antarctica. Our results suggest that the size effect is not significant in *U. aurantiacoatra*.

Lichen morphology plays an important role in the determination of trapped [Chiarenzelli *et al.*, 1997]. In general, foliose lichens contain greater amounts of metals than fruticose lichens in the same site [Garty, 2001, and references therein] and surface characteristics of the thallus may determine the efficiency of particle entrapment [Puckett and Finegan, 1980]. In this study, the vertical distribution pattern of heavy metals in *U. aurantiacoatra* was also examined. The concentrations of metals such as Cr, Al, and V were relatively high in basal segments (ca. 30-40%; Table 4), but most heavy metals were enriched in upper lichen parts. In particular, the mean content of Pb in the upper segment was 5.7-fold higher than that in the basal segment. The upper segments of *U. aurantiacoatra* are thought to have a greater affinity for particulate matter than basal segments due to the finely divided thallus (*i.e.*, relatively greater surface area). However, further study is required to determine why some elements preferentially accumulate in basal parts.

Many studies have examined the concentrations of heavy metals in different thallial zones, but most studies have focused on foliose and crustose lichens [Garty, 2001, and references therein]. In general, central (older) parts of the organism contain higher amounts of heavy metals than peripheral (younger) parts [Hale Jr and Lawrey, 1985; Bargagli *et al.*, 1987], but the opposite has also been reported [Seaward, 1980; Armstrong, 1997]. Previous studies on the vertical distribution of heavy metals also suggest that some elements are preferentially accumulated either in the basal or upper segments [Pakarinen *et al.*, 1978; Pakarinen, 1981; Pakarinen, 1985]. Thus, an assumption that heavy metals are likely to be concentrated in the older parts of a thallus cannot be generalised. In the case of *U. aurantiacoatra*, our results indicate that most heavy metals are preferentially concentrated in the upper parts of thalli, but some metals were found in lower parts. These findings have important implications for defining sampling protocols and enhancing data quality. Specifically, heavy metal quantification may be biased by selective sampling of specific segments of thalli for biomonitoring purposes.

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