Analysis of mercury and other heavy metals accumulated in lichen *Usnea antarctica* from James Ross Island, Antarctica

Ondřej Zvěřina · Kamil Láska · Rostislav Červenka · Jan Kuta · Pavel Coufalík · Josef Komárek

Abstract The study was designed to investigate the content and distribution of selected heavy metals (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Fe, Pb and Zn) in samples of fruticose macrolichen *Usnea antarctica* from James Ross Island. A special emphasis was devoted to mercury and its species (elemental mercury and methylmercury). It was found that mercury contents were relatively high (up to 2.73 mg kg^{-1} dry weight) compared to other parts of the Antarctic Peninsula region, while the concentrations of most other elements were within reported ranges. Mercury contents in lichens originating from the interior were higher than those from the coast, which is probably the result of local microclimate conditions. Similar trends were observed for Hg^0 and MeHg$^+$, whose contents were up to 0.14 and 0.098 mg kg^{-1} dry weight, respectively. While mercury did not show a significant correlation with any other element, the mutual correlation of some litophile elements probably refers to the influence on thalli of resuspended weathered material. The influence of habitat and environmental conditions could play an essential role in the bioaccumulation of contaminants rather than just the simple presence of sources. Thus, the study of the thalli of this species can bring a new perspective on the interpretation of contaminant accumulation in lichens of the polar region.

Keywords Antarctica · Heavy metal · Mercury · Lichen

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Introduction

Due to its remote location, Antarctica presents a unique opportunity to study the long distance transport and allocation of chemicals generated naturally or produced by humans on other continents. Although it is protected from the entry of lower latitude air masses by natural atmospheric circulation, Antarctica represents a potential sink for the deposition of long-range transported pollutants including mercury (Bargagli 2008). The atmospheric transport of pollutants is considered to be a significant pathway of Antarctic environment contamination (Montone et al. 2003; Bargagli 2008; Cipro et al. 2011). Therefore, studies on the amounts of particular chemicals

in different compartments of Antarctic ecosystems are of great importance.

Mercury is an atmospheric pollutant of global concern. Its biogeochemical cycle includes various physical, chemical and photochemical interactions, both wet and dry deposition, and reemission from environmental surfaces (Schroeder and Munthe 1998; Wängberg et al. 2001). In the atmosphere, mercury occurs mainly as Hg^0 (elemental mercury vapour), along with reactive gaseous mercury ((RGM)—Hg^{2+} divalent mercury compounds) and mercury associated with particulate matter. The presence of methylated mercury species has also been reported (Slemr et al. 1981, 1985; Fitzgerald et al. 1991; Lin and Pehkonen 1999). Hg^0 is stable and its residence time of 6–24 months allows its transport over large distances on a global scale (Schroeder and Munthe 1998; William et al. 1998; Wängberg et al. 2001). The rate of deposition is largely affected by Hg^0 to Hg^{2+} conversion, since RGM includes highly surface-reactive species and is rapidly deposited through both wet and dry deposition (Lindberg and Stratton 1998). It is known that, in polar regions, intensive Hg deposition occurs during and after the polar sunrise during mercury depletion events (MDEs). Elemental mercury undergoes photochemical oxidation to RGM by reactive halogens, and thereafter is rapidly deposited on the Earth's surface. MDE is considered to be a critical factor for mercury input in coastal polar ecosystems.

Concerns have been raised about the possible environmental effects of changes in the regional climate on the role of Antarctica as a "cold trap". The warming of both land and ocean causes increased outgassing and also changes in sea-ice cover and in precipitation patterns (Lindberg et al. 2002; Bargagli 2005; Bargagli et al. 2005). The west side of the Antarctic Peninsula has experienced the largest increase in annual surface air warming over the last few decades. An annual temperature growth of +0.56 °C per decade was reported at the Faraday/Vernadsky station between 1951 and 2001 (Turner et al. 2005), while warming in the northwest Antarctic Peninsula was considerably greater than the mean Antarctic trend (Vaughan et al. 2001). The mean annual air temperatures also rose substantially along the eastern coast of the Antarctic Peninsula, accelerating glacier retreat and an increase in permafrost temperature (Strelin et al. 2006; Cook and Vaughan 2010). The recent breakup of the Prince Gustav shelf in 1995 (Rott et al. 1996) is one of the consequences of this temperature increase. It can also be assumed that open water connected with sea aerosol input may additionally increase the deposition of Hg and other metals into the surveyed area.

As the retreating ice is uncovering bedrock in coastal areas, new terrestrial ecosystems are being established. Lichens are among the first colonisers of exposed rock and snow-free ground (Bargagli et al. 1999). Along with mosses, they are able to tolerate extreme temperatures together with long periods of desiccation and are the main components of Antarctic terrestrial flora (Bargagli et al. 1998; Wojtuń et al. 2013).

Lichens are known for their ability to capture and accumulate gaseous atmospheric pollutants and are commonly used as biomonitors of airborne metals including Hg (Bargagli and Barghigiani 1991; Loppi and Bonini 2000; Conti and Cecchetti 2001; Pisani et al. 2011; Mlakar et al. 2011; Lodenius 2013; Mão de Ferro et al. 2014). Five processes by which both nutrients and contaminants are deposited onto lichens are described. These are wet deposition (including snowfall), occult precipitation (fog, dew and mist), sedimentation (particles >1–4 mm), impaction (particles <1–4 mm carried by wind) and direct uptake (particularly when wetted) (Knops et al. 1991). Unlike higher plants, lichens have neither roots nor stomata, and a weak or absent cuticle enables easy exchange between the environment and their cell walls. Owing to their high cation exchange capacity, lichens have the ability to accumulate available ions of all gaseous, dissolved and particulate elements in air, snow and melting water (Bargagli et al. 1998). In addition, due to the lichens having a complicated surface structure, contaminants are absorbed over the whole thallus surface (Lupsina et al. 1992; Lodenius 2013). Different lichen morphotypes vary in their active surface for ion uptake. From this perspective, the fruticose type of thallus represents an ideal material with a large surface area. The fruticose macrolichen *Usnea antarctica* has already been utilised for monitoring the levels of heavy metals (Bargagli et al. 1993; Poblet et al. 1997; Osyczka et al. 2007; Cansaran-Duman 2011; Wojtuń et al. 2013).

There is a continuous need to monitor pollutants in the polar environment. In contrast to numerous studies on the Arctic, information on the levels of heavy metals in Antarctic lichens is still scarce. Moreover, most of the studies concerning this topic are focused on the South Shetland Islands and no similar report has been published on mercury levels in the Antarctic Peninsula and on James Ross Island in particular. The small amount of

available data from the Antarctic hinders the assessment of mercury (and other heavy metal) concentrations and the complex comparison of such concentrations and their trends between different geographical locations. James Ross Island represents an ideal area for the investigation of heavy metal concentrations and their geographical distribution, as it is one of the largest deglaciated areas along the eastern coast of the Antarctic Peninsula with only small glaciers remaining in the present landscape (Engel et al. 2012).

The objectives of this research were to determine the contents of Hg (including MeHg$^+$ and Hg^0 species) and some other heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Fe, Pb and Zn) and to investigate their distribution in lichen samples originating from the northern part of James Ross Island. The geographical distribution of sampling points affected by local factors and climatic conditions (distance from the seashore, snow accumulation and fog occurrence) was expected to be the most influential factor.

Materials and methods

Sample origin and treatment

James Ross Island (JRI, 64° 10′ S, 57° 45′ W) is situated on the east side of the Antarctic Peninsula tip (Fig. 1). About 20 % of its total area of 2500 km^2 is recently deglaciated (Rabassa et al. 1982). The Ulu Peninsula, the northern part of JRI, represents the largest deglaciated area, with several lava-fed deltas, abundant outcrops of glacial sedimentary rock and exposures of Cretaceous marine sediments (Crame et al. 1991; Kristjánsson et al. 2005; Nývlt et al. 2014). The area of the Abernethy Flats was selected for sampling considering the articulation of the recently deglaciated terrain, which is characterised by a gradual increase in altitude from 0 to 134 m at San Jose Pass. The morphology of the valley is relatively flat and formed mostly by less resistant Cretaceous marine deposits. Local and small elevations in the central part of the valley are mostly formed by exhumed volcanic dykes. Monolith Stream, one of the largest watercourses in the area, is dewatering the vicinity of Monolith Lake towards the broad and shallow Brandy Bay. The river is located in the western and southern part of the asymmetric depression Abernethy Flats.

Climatic conditions of the Ulu Peninsula are characterised by a short summer (December–February) with positive air temperatures up to 10 °C and an annual mean air temperature of around −7 °C (Láska et al. 2011a). Total precipitation is estimated at between 300 and 500 mm water equivalent per year, with snowfall occurring even in the summer period (Bromwich et al. 2004; Dethloff et al. 2010). The snow-free period can vary from 1 to 3 months with large year-to-year variations. The daily mean incoming solar radiation is around 250 W m^{-2} in summer, which significantly reduces snow cover (Láska et al. 2011b). In order to describe local wind conditions, 30-min surface wind observations from the nearby meteorological station at Johnson Mesa were used. The flat surface of Johnson Mesa at an elevation of 320 m a.s.l. was found as a representative site for evaluation of the prevailing wind direction. In the study, the relative frequency of wind direction measured at 6 m above ground was estimated for the period 2008–2010.

Samples were collected from the gravel plain Abernethy Flats and also in the area of the continuous and stable slope of Keller Stream and Monolith Lake during the 2012 Czech Antarctic expedition. Fruticose macrolichens *U. antarctica* were sampled along a 6-km transect beginning inland and running down across the Abernethy Flats to the seashore (Fig. 1). In the laboratory, the lichens were washed in deionised water in order to remove dust and any unwanted particles and dried for 48 h at 30 °C. Then, the thalli were homogenised in a ball mill and stored at −20 °C until analysis.

Analytical procedures

Total mercury concentrations in the samples were determined by means of an AMA-254 analyser (Altec, Czech Republic). Determination is based on dry decomposition followed by preconcetration by amalgamation and AAS detection (Száková et al. 2004).

Elemental mercury was determined by means of thermal desorption. Aliquots of samples were heated at 105 °C for 48 h and the mercury concentrations subsequently measured. The contents of elemental mercury were calculated as the differences between total concentrations and those measured in treated aliquots. The pyrolytical determination of Hg^0 was first suggested by Biester and Scholz (1997) and applied as a single-step analysis by Nóvoa-Muñoz et al. (2008). This method was also conducted for Hg^0 determination
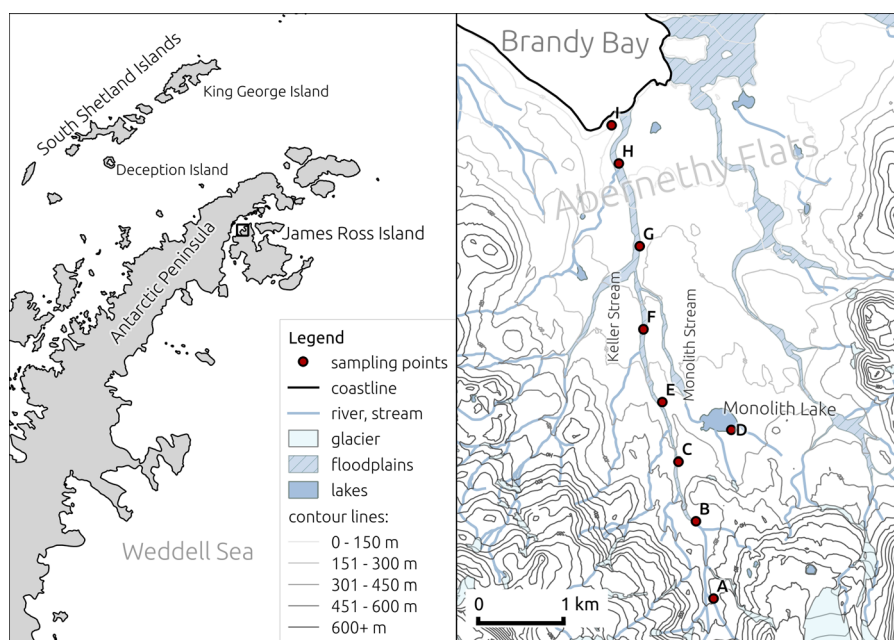
Fig. 1 Maps of the Antarctic Peninsula region (*left*) and the Abernethy Flats sampling locality on James Ross Island (*right*). Modified map of James Ross Island-Northern part (Czech Geological Survey 2009)

in samples with a high content of organic carbon (Coufalík et al. 2013a).

For methylmercury determination, 300-mg samples were extracted with 10 mL of 6 mol L^{-1} HCl (Sigma-Aldrich, Germany). The extraction was conducted for 2 h in an ultrasound bath and then for another 18 h on an end-over-end shaker (150 RPM). The obtained extracts were filtered through glass microfibre filters (Whatman) and the pH of the solution was adjusted to 5 with acetate buffer. The contained polar methylmercury was then converted to nonpolar volatile ethylated methylmercury using NaBEt$_4$ (Sigma-Aldrich, Germany), and the resulting solution was extracted with hexane (Sigma-Aldrich, Germany). Finally, an aliquot of 2 μl was injected into an Agilent 6890N gas chromatograph with a PSA 10.750 atomic fluorescence detector (Cai et al. 2000; Leermakers et al. 2005; Kuballa et al. 2008; Nevado et al. 2011; Červenka et al. 2011).

For the determination of selected metal contents (As, Cd, Co, Cr, Cu, Mn, Ni, Fe, Pb and Zn), the homogenised lichen thalli were digested in an HNO$_3$/H$_2$O$_2$ (both Sigma-Aldrich, Germany) mixture in a microwave digester (Berghof MSW3+ speedwave) according to EPA 3052 method. The contents of elements in digestions were subsequently measured using an Agilent 7500 CE quadrupole ICP-MS spectrometer (Agilent, Japan) according to the EPA 6020A method.

The spectrometer was equipped with an octopole reaction cell to avoid isobaric interferences, a Babington nebuliser and a double-pass Scott chamber. The conditions were optimised to obtain maximum sensitivity and minimum CeO$^+$/Ce$^+$ and Ce^{++}/Ce$^+$ ratios.

All analyses were performed in an ultra-clean laboratory equipped with HEPA filters. The used chemicals were ACS reagent grade, especially pure for mercury. Prior to use, all glassware was cleaned by two-stage decontamination in an HNO$_3$ bath and heated to 250 °C for 2 h.

The accuracy of the methods was verified by means of the following reference materials: IRMM BCR-482 Lichen (for elements As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and IAEA-336 Lichen (for elements As, Co, Cu, Hg, Fe, Mn, Zn). Recoveries of all elements were consistently within the ranges of certified values. Typical relative standard deviations for triplicate analysis of reference materials and lichen samples were within the order of units of percents. Contents of particular elements in samples were at least one order of magnitude higher than the method detection limits.

Statistical analysis

To summarise the collected data, general descriptive statistics including Spearman rank order correlation

and Bartels' rank test (investigation of trend occurrence) (Bartels 1982) were performed using R version 3.0.2 (R Development Core Team 2013). Nonparametric tests were used due to the non-normality of the data.

Results and discussion

Surface wind conditions

Figure 2 shows the relative frequency of the wind direction at the Johnson Mesa in the period 2008–2010. The prevailing wind directions were observed in the south-western sector. Southerly and westerly winds were the most common, with a frequency of occurrence of 18.8 and 14.4 % of all cases, respectively. On average, the summertime and wintertime wind directions were slightly different, but were observed within the same sector. Northerly, northwesterly and southeasterly winds had the lowest frequency of occurrence. From the observed wind pattern, it is evident that the orography of the Antarctic Peninsula affects the airflow along the eastern side of the Peninsula and the northern coast of James Ross Island.

Total mercury contents

Figure 3 shows the total Hg contents in lichen samples. Hg concentrations ranged from 0.72 to 2.73 $mg\,kg^{-1}$ dry weight (d.w.) with a median value of 1.59 $mg\,kg^{-1}$ d.w. Bartels' test for randomness was used to examine the probability of trend occurrence (Bartels 1982). A p
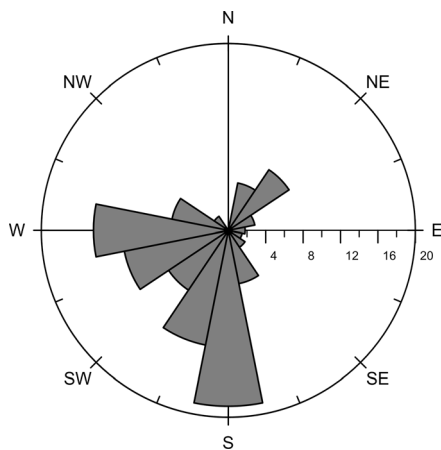

Fig. 2 Relative wind frequency at the Johnson Mesa in the period 2008–2010

value of 0.82 indicates a gradual mercury content increase in the direction from the coast to the interior.

Marine aerosol has been suggested as the main contributor of mercury contamination in lichens together with volcanic emissions (Mão de Ferro et al. 2014). The lowest mercury content determined in coastal sample I, together with the above mentioned trend, indicates that sea spray does not represent a significant Hg source in this case. This fact can be partly attributed to the prevailing winds blowing towards the sea (Fig. 2). Moreover, lichens growing in localities further inland may be more affected by moisture at higher elevations. An increase in relative air humidity of 5 % from seashore to higher-elevated plateaus was observed in a previous study (Láska et al. 2011a). Increased mercury input into lichens caused by the effect of fog was already observed (Evans and Hutchinson 1996).

Abernethy Flats is a valley with suitable conditions for snow accumulation and subsequent melting. At the beginning of the sampling transect (in the vicinity of sampling points A and partially in the vicinity of B), there is the probability of increased accumulation of wind-blown snow from the glaciers south of the sampling area (e.g. Whisky Glacier). Dissolved Hg^{2+} compounds are known to be readily absorbed by lichens when snow melts (Skov et al. 2004; Bargagli et al. 2005).

In fact, the concentrations of mercury in lichens are two to three orders of magnitude higher than those determined in soils from the same sampling localities (0.0073–0.011 $mg\,kg^{-1}$) (Coufalík et al. 2013b). The enrichment factor between lichens and the underlying soil would reach a value of several hundred. This ratio excludes crustal aerosols as a strongly influential factor (Carignan et al. 2009). Therefore, atmospheric deposition could be considered the main source of mercury in lichens.

In comparison with mercury contents reported in lichens from the Antarctic Peninsula region, the values obtained in this work are substantially higher. Table 1 summarises published Hg levels for lichen samples originating from the South Shetland Islands, the closest area for which similar information has been published. The likely explanation is the fact that the environments of JRI and the South Shetlands are influenced by the circulation of different air masses. The climate of the South Shetlands is mainly affected by relatively warm (oceanic) air masses associated with synoptic-scale systems moving across the Bellingshausen Sea (Martin and

Fig. 3 Total mercury concentrations in samples of *Usnea antarctica* (*n*=5, ±SD) from inland site (*A*) towards the seashore (*I*)
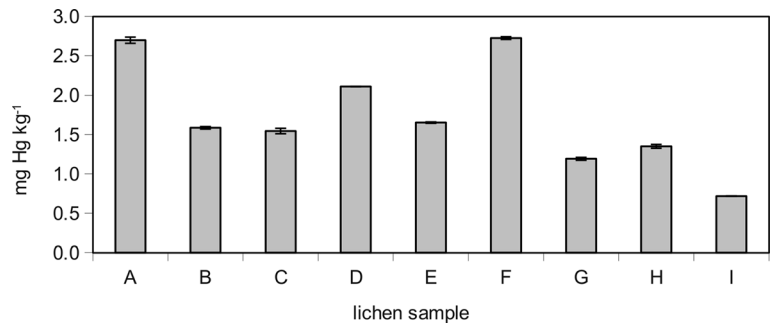
Peel 1978). JRI, however, is moderated by cold air masses of continental origin coming from the south and southwest, along the eastern coast of the Antarctic Peninsula. The advection of oceanic air masses towards James Ross Island is reduced by the pronounced orographic effect of the Peninsula (King 2003). Therefore, the frequency of the occurrence of continental and oceanic air masses determines the climate of the study site. These factors are assumed to play a crucial role in the distribution of long-range transported pollutants such as mercury.

Elemental mercury

An amount of up to 0.14 mg Hg kg^{-1} d.w. was released by thermal desorption experiments, which presents less than 5 % of the total mercury in the samples (Fig. 4). The amounts of the desorbed portions correlate closely with total mercury contents (Spearman's correlation coefficient r_s=0.93, $p<0.001$). Similarly to the total Hg concentration, the desorbed fraction also increased along the sampling transect from the coast to the interior (*p* value of Bartels' test is 0.78).

Recently, laboratory experiments have shown the ability of some plants to take up Hg^0 directly from the atmosphere and bond it strongly with almost no losses from evaporation or leaching (Lodenius et al. 2003). It has been demonstrated that, on the lichen surface, elemental mercury is converted into a strongly held form or diffuses into the lichen cells and is released less readily; possibly, it is converted into an inorganic form—Hg^{2+} (Krishna et al. 2003, 2004). The high concentration of mercury in some plants could be created by an irreversible accumulation process determined by oxidation of the adsorbed Hg^0 followed by complexation of Hg^{2+} by -SH groups of amino acids (Bacci et al. 1994). Some authors suggest that Hg is captured by lichens mainly after its atmospheric oxidation to the more soluble Hg^{2+} (Krishna et al. 2003). The above-described processes are probably the reason for the small proportion of total mercury that was desorbed at 105 °C, although Hg^0, the main mercury form in the atmosphere, is readily released under these conditions.

Table 1 Reported mercury levels in lichens of *Usnea* species originating from the South Shetland Islands

Study, location	Lichen specie	Hg [mg kg^{-1}]	MeHg [mg kg^{-1}]
(Mão de Ferro et al. 2014)			
Deception Island	*Usnea sphacelata*	0.14–0.24	0.021–0.026
(Bargagli et al. 1993)			
King George Island	*Usnea antarctica*	0.026–0.061	–
Deception Island	*Usnea antarctica*	0.190–0.253	–
(Wojtuń et al. 2013)			
King George Island	Several lichen species including *Usnea antarctica*	0.18	–
(dos Santos et al. 2006)			
King George Island	*Usnea spp.*	0.0363	–

"–" means that methylmercury was not determined in this study

Fig. 4 Elemental mercury and methylmercury contents in samples of *Usnea antarctica* (*n*= 3, ±SD) from inland site (*A*) towards the seashore (*I*)
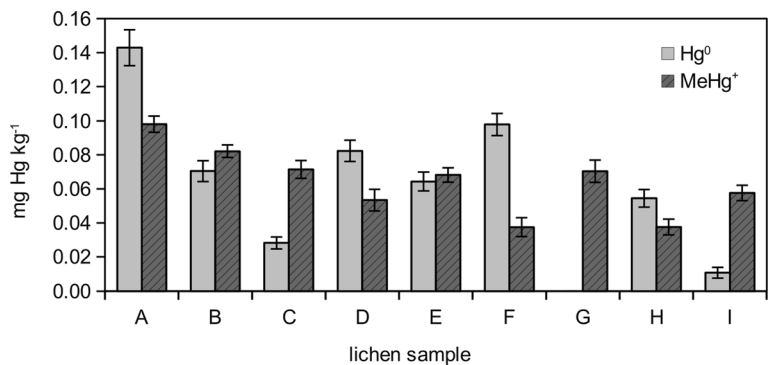
Locally, Hg vapours can be evaporated from the top soil layer. According to literature, the Hg evaporation rate from bare uncontaminated soils increases linearly from 10 °C (the lowest measured temperature) to 15–20 °C and then exponentially to 35 °C, while the volatile species (such as Hg^0 and $(CH_3)_2Hg$) are supposed to dominate Hg evaporation from soil (Schlüter 2000). However, previously reported results suggest that Hg content in Abernethy Flats soils is stable at temperatures up to 50 °C (Coufalík et al. 2013b). Moreover, a recent study showed that the mean monthly surface temperature on the Ulu Peninsula ranges from −11 to 6 °C (Láska et al. 2011a), which implies a low rate of Hg evaporation. Furthermore, a surface temperature higher than 10 °C is exceeded only for several days in the summer (December–February).

Methylmercury

The methylmercury concentration in samples ranged from 0.037 to 0.098 mg kg^{-1} d.w. with a median of 0.068 mg kg^{-1} d.w., which represents a portion of 1.4 to 8.1 % of total Hg. A trend of increasing MeHg$^+$ content from the cost to the interior was observed (Bartels' test *p* value is 0.82).

So far, little data has been published on the occurrence of methylmercury in lichens. It was reported for lichen (*Usnea sphacelata* from Deception Island) to have a higher capacity for Hg and MeHg bioaccumulation than that observed for moss (*Polytrichum strictum* Brid. and *Sanionia georgico-uncinata*), while published MeHg$^+$ levels (Tab. 1) were slightly lower than those observed in this work (Mão de Ferro et al. 2014). Similar concentrations of MeHg$^+$ were also determined in *Hypogymnia physodes* lichens from Slovenia: 5–106 μg kg^{-1} (0.06–3.70 % of total Hg). In addition, a good statistical correlation with total Hg was found

(Lupsina et al. 1992). In contrast, our data shows no correlation between total Hg and MeHg$^+$ (r_s=−0.05, p= 0.9). Moreover, MeHg$^+$ contents were in anti-correlation with contents of most of the measured elements (Fig. 5).

Several processes of MeHg$^+$ production in the polar environment have been suggested, but the pathways and methylation/demethylation processes which occur are still not fully understood (Steffen et al. 2008). Snowmelt water has been identified as a significant source of MeHg$^+$ in the High Arctic, and elevated levels of bio-available Hg were found in snow after the MDE (Loseto et al. 2004; Steffen et al. 2008).
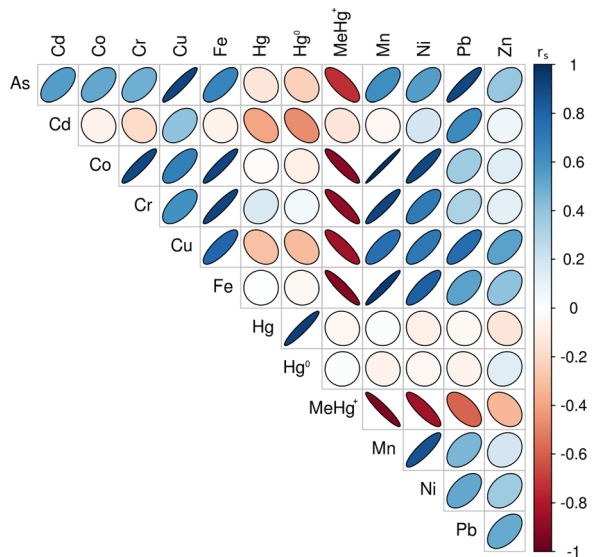

Fig. 5 Matrix of Spearman rank correlations between measured elements. The r_s coefficients are denoted both by *different shapes of ellipse and different colours* (Murdoch and Chow 1996). *Thin and deeply coloured ellipses* refer to the strongest correlations, *the inclination of an ellipse* indicates the sign of the correlation. (*Thin blue ellipses* refer to the strongest positive correlations, *thin red* to the negative.)

Table 2 Contents of heavy metals in samples and reported contents for *Usnea antarctica* [mg kg^{-1} d.w.]

Element	As	Cd	Co	Cr	Cu	Mn	Ni	Fe	Pb	Zn
Range	0.9–2.3	0.03–0.05	0.3–1.6	1.9–4.6	1.8–6.7	10–47	1–5.1	1800–6400	0.9–3	12–27
Median	1.5	0.04	0.8	2.7	3.9	26	2.5	3900	2.0	20
Bartels' negative rank[a]	0.97	0.47	0.77	0.85	0.98	0.80	0.39	0.82	0.59	0.55
(Olech 1991)[b]	–	–	–	5.6	2.9	–	2	170	2	7
(Poblet et al. 1997)	–	0–0.03	–	–	–	16–56	2.2–9.5	283–1115	0–2.9	–
(Osyczka et al. 2007)[b]	–	<1.8	–	<1.7	6±1	25±5	–	–	<0.9	26±5

[a] *p* value of Bartels' negative rank test indicates the probability of a decreasing trend of element content from seashore to the interior

[b] reference samples of *Usnea antarctica* originating from areas remote to polar stations on the South Shetland Islands

"–" means that the element was not determined in this work

Ocean evasion of volatile Hg compounds (including dimethylmercury) was postulated as a source of these compounds in glacial meltwater streams (Vandal et al. 1998). The MeHg levels reported for Antarctic waters were some of the highest observed in the open ocean (Cossa et al. 2011). Unique conditions enable the oxidation of atmospheric Hg by halogens followed by its deposition into the sea. Subsequently, it is scavenged by organic particles and together with organic matter it presents a substrate for methylating bacteria in the hypoxic zone. The upwelling water is low in oxygen and rich in MeHg (Cossa et al. 2011). The sampling area is adjacent to Brandy Bay; therefore, the sea may represent a potential source of MeHg for lichens. However, no elevated MeHg levels were found in samples originating from the Brandy Bay seashore (Fig. 4).

In situ methylation in sediment, followed by diffusion into overlaying water, is another suggested cause of the presence of MeHg in the polar environment (Vandal et al. 1998). In the investigated area, conditions for methylation are expected in Monolith Lake and its close vicinity. The bottom of the lake is covered by a thick cyanobacterial mat accumulated on sediment, which allows particularly suitable conditions for microbial methylation. However, no elevated MeHg$^+$ level was observed in sample D. The highest level of MeHg$^+$ (0.098 mg kg^{-1} d.w.) was detected in sample A, originating from the headwater area of Keller Stream with thicker snow accumulation. Lichens in this locality are frequently wetted by meltwater from both the glacial Keller Stream and also snow, which is brought by wind from the south-western sector, where the higher-located glaciers occur.

The methylation abilities of lichens themselves are not well explored. The methylation of arsenic compounds was confirmed for *Hypogymnia* lichen as a part of the detoxification process (Mrak et al. 2008). It was suggested that lichens do not act as simple passive biomonitors, but are actively involved in the uptake, accumulation and/or biotransformation of arsenic, and possibly other elements as well (Machado et al. 2006). Nevertheless, little is known about the transformation of mercury in lichens. Further research has to be undertaken to investigate the applicability of lichens as bioindicators of organometallic compounds.

Selected heavy metals

The concentrations of selected heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Fe, Pb and Zn) are presented in Table 2. Generally, the contents of most metals were similar to those already reported for *U. antarctica* in other studies (Table 2). The only exception is Fe, which content is slightly higher than published values; however, it is still of the same order of magnitude. The significant correlation of lithophile elements (Co, Cr, Fe, Mn and Ni) indicate that lichen thalli may be affected by absorbed soil particles. Elevated Fe levels are likely caused by dust particles deposited onto lichen by impaction. A significant relationship has been reported to exist between the concentration of lithophile elements (including Fe and particularly Cu) in Antarctic soils and lichens (Bargagli et al. 1999). Therefore, bedrock composition is supposed to be an influencing factor, since most other metal levels are within the

ranges reported for *U. antarctica* from reference areas.

As follows from the Bartels' test *p* values (Table 2), the contents of As and Cu decrease with distance from the ocean. This indicates sea spray as a potential source of these metals. In contrast, no significant trend was observed for Cd, Ni, Pb or Zn.

There was no significant correlation found between the content of Hg and that of any other metal (Spearman's correlation coefficient $r_s < 0.4$, $p > 0.3$, Fig. 5). The same lack of correlation between Hg and some other heavy metals (Pb, Cd) has been reported (Carignan et al. 2009), suggesting decoupling between these elements during emission and/or transport.

Conclusion

Local climate and microclimate conditions are key determinants with respect to total mercury content and its variability in the Antarctic Peninsula region. While the levels of most monitored metals were within already published ranges, total Hg levels determined in the samples of *U. antarctica* originating from the area of Brandy Bay were some of the highest reported in Antarctica. According to the results of this research, elemental mercury and methyl-mercury accounted for up to 5.0 and 8.1 % of total mercury, respectively. It remains unclear whether these species were accumulated from the environment or whether they are products of lichen metabolism. The effects of atmospheric deposition and sea spray are most likely overlapped by the different abilities of individual thalli to effectively capture pollutants from their immediate surroundings. Nevertheless, lichen species selected for this purpose appeared to be suitable for the monitoring of heavy metals and their deposition patterns in the polar environment. Mercury speciation and the clarification of undergoing biotransformation in lichens should be important tasks for future studies.

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