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The value of the terricolous lichen *Cetrariella delisei* in the biomonitoring of heavy-metal levels in Svalbard

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Abstract: The aim of this study was to identify a suitable lichen species for the long-term monitoring of heavy-metal atmospheric pollution in Svalbard. *Cladonia* and *Cetraria* s.l. species that have been widely used until now for assessing heavy-metal deposition in the Arctic are in decline over extensive areas of Svalbard, mainly due to climate change and over-grazing by reindeer. *Cetrariella delisei*, rarely used for biomonitoring, is still common and widespread in this area. Levels of Cr, Ni, Fe, Cu, Pb, Zn, Cd and Mn were measured in three lichen species: *Cetrariella delisei*, *Cladonia uncialis*, *Flavocetraria nivalis* and in a moss *Racomitrium lanuginosum* from Sørkapp Land, South Spitsbergen. The results imply that *Cetrariella delisei* can be safely compared to *Cladonia uncialis* for identifying the levels of heavy metals, but direct comparison between *Cetrariella delisei* and other species studied is more difficult owing to differences in levels of heavy metals even in samples from the same site.

Key words: Arctic, Spitsbergen, lichenized fungi, heavy metals, air pollution monitoring.

Introduction

Lichens and bryophytes are effective biomonitors of heavy metals derived from pollution. Since these cryptogams constitute a major component of the High Arctic tundra flora, they have frequently been used for this purpose (*e.g.* Riget *et al*. 2000; Allen-Gil *et al*. 2003; AMAP 2005; Naeth and Wilkinson 2008; Søndergaard *et al*. 2011; Zhulidov *et al*. 2011). In Svalbard, Jóźwik (1990, 2000) conducted long-term and extensive studies on heavy metal concentrations in numerous lichens and bryophytes from the Bellsund area, Grodzińska and Godzik (1991) employed several moss species to assess heavy metal and sulphur pollution in South Spitsbergen, and Samecka-Cymerman *et al*. (2010) investigated heavy-metal contents in a moss *Sanionia uncinata* (Hedw.) Loeske from Hornsund area.

Monitoring surveys require the use of species that have broad geographical ranges and are abundant in the study area. In regard to lichens, the most popular indicator species of heavy metal levels in the Arctic have been terricolous fruticose *Cetraria* s. l. and *Cladonia* spp. (AMAP 2005).

Climate changes observed in the Arctic during recent decades have triggered significant changes in tundra vegetation. Those changes, coupled with the increased impact of herbivores, have led to a serious decline in terricolous species of *Cladonia* and *Cetraria* s.l. (van der Wal *et al*. 2001; Joly *et al*. 2009). This trend is clear over extensive areas of Svalbard, where after a long absence reindeer (*Rangifer tarandus platyrhynchus*) was reintroduced (Øritsland 1987; Elvebakk 1997), or recovered naturally (Elvebakk 1997; Węgrzyn *et al*. 2011). *Cetraria islandica* (L.) Ach., *Flavocetraria nivalis* (L.) Kärnefelt *et* A. Thell and various species of *Cladonia*, which previously dominated the vegetation in open, dry habitats, have declined significantly (Elvebakk 1997; Węgrzyn *et al*. 2011), such that monitoring of heavy-metal pollution using those common lichen indicators has become difficult.

While certain lichen species have been retreating, others have started expanding. *Cetrariella delisei* (Bory ex Schaer.) Kärnefelt *et* A. Thell, another terricolous lichen with a fruticose thallus, seems to be an expansive species in tundra communities of SW Spitsbergen, where *Cladonia* spp. and *Flavocetraria nivalis* have undergone a serious decline due to reindeer grazing (Węgrzyn *et al*. 2011). This lichen has rarely been used for monitoring purposes, but the results of Jóźwik (1990, 2000) show its potential as an indicator species. Moreover, *C. delisei* is a circumpolar Arctic-alpine lichen, and is widespread in various parts of the Arctic (Thomson 1984).

This paper presents the results of preliminary research to assess whether *Cetrariella delisei* can be used for monitoring heavy-metal atmospheric pollution in Svalbard, whether *C. delisei* can successfully replace *Cladonia* and *Flavocetraria* species used in the past, and if it is possible to compare directly the data on heavy metal concentrations obtained from these species.

Materials and methods

Fieldwork was undertaken in July and August 2008 at a *c*. 3 km^2 study area located in NW Sørkapp Land, South Spitsbergen, Svalbard. The climate is Arctic and oceanic with relatively mild winters; average annual temperatures oscillate between -9°C and -3°C, average summer (July–August) temperature is 3–5°C, and annual precipitation, concentrated in the summer, is *c*. 300–500 mm (Ziaja 2011a). Climate changes, mainly a temperature increase, are noticeable in this area (Ziaja 2011b).

Sørkapp Land has been a national park with no hunting pressure since 1973. Protection of this area led to a recovery of the reindeer population. Their number increased from the 1980s to *c*. 100 individuals in 2000 (Ziaja 2002) and *c*. 170 in-

Table 1

List of sampling sites with names of collected species, GPS coordinates (WGS 84) and altitude.

No.	Species	GPS coordinates	Altitude m a.s.l.
1	*Racomitrium lanuginosum*	N 76°52’56.1” / E 15°30’31.3”	4
2	*Racomitrium lanuginosum*, *Cetrariella delisei*	N 76°53’42.4” / E 15°32’35.29”	15
3	*Cetrariella delisei*	N 76°53’36.1” / E 15°34’07.4”	30
4	*Racomitrium lanuginosum*	N 76°53’40.9” / E 15°35’20.6”	76
5	*Cladonia uncialis*	N 76°54’09.3” / E 15°36’01.1”	129
6	*Flavocetraria nivalis*	N 76°54’08.8” / E 15°36’12.9”	160

dividuals in 2008 (Węgrzyn *et al*. 2011). Extensive reindeer grazing and trampling have caused severe degradation of tundra lichen communities and a significant decline of epigeic macrolichens from the genera *Cetraria*, *Flavocetraria* and *Cladonia*. Conversely, *Cetrariella delisei* has expanded in the area (Węgrzyn *et al*. 2011).

Three terricolous fruticose lichen species, *C. delisei*, *Cladonia uncialis* (L.) F.H. Wigg. and *Flavocetraria nivalis* were investigated (Table 1), together with the moss *Racomitrium lanuginosum* (Hedwig) Bridel, Muscol., in order to provide comparative data on heavy metal levels in non-lichen cryptogams in this area. The sampling sites were located on marine terraces and mountain slopes, within the following plant communities (phytosociological nomenclature after Dubiel and Olech 1990, 1991): the mosaic of *Cetrariella delisei* and *Gymnomitrion corallo-ides* communities, *Racomitrium lanuginosum* community, and the mosaic of *Candelariella arctica* and *Tetraplodon mnioides* communities. Location of the sites depended on distribution of the studied species, *C. uncialis* and *F. nivalis* were collected from steep places, inaccessible to reindeer. Healthy and undamaged specimens were collected and cleaned in the field, then air-dried and transported to Poland.

Two replicates of 3 g from each lichen and moss sample were homogenized and dried at 105°C, then mineralized and extracted in *aqua regia* for 16 hours, according to the method described by Sastre *et al*. (2002). After extraction, the samples were digested at 130°C for 2 hours, filtered, and put into 0.5 mol HNO_3 in 100 ml flasks. Levels of Cr, Mn, Fe, Ni, Cu, Zn, Pb and Cd were detected using the Perkin Elmer Optima 7300DV optical emission spectrometer, using inductively coupled plasma-optical emission. Plasma gas-flow was 15 $dm^3 \cdot min^{-1}$, external gas flow – 0.2 $dm^3 \cdot min^{-1}$, nebulizing gas flow – 0.6 $dm^3 \cdot min^{-1}$. Calibration was carried out using certified reference material ERM®-CD 281.

To test differences between concentrations of an element in different species, Mann-Whitney U tests were employed. Statistical analyses were performed using STATISTICA 10.0 software (StatSoft, Inc. 2011).

Results

Levels of heavy metals in *Cetrariella delisei* were similar to those in *Cladonia uncialis* (Table 2, Figs 1, 2), the differences being statistically insignificant, (Figs 1, 2). Whereas, concentrations of most elements (Fe, Cr, Ni, Pb, Zn) were higher in *C. delisei* than in *Flavocetraria nivalis* (Table 2, Figs 1, 2), with the exceptions of Cd which was highest in *F. nivalis,* and Mn, which was highest in *F. nivalis* and *Racomitrium lanuginosum* (Table 2, Fig. 2). The levels of Cu in *C. delisei* and *F. nivalis* were very similar (Fig. 1). The differences were statistically significant ($p < 0.05$) only for Cr and Ni (Fig. 1) for *Cetrariella delisei* and *F. nivalis*.

Cetrariella delisei accumulated similar amounts of Cr, Ni, Cu and Cd to *R. lanuginosum* (Figs 1, 2). Regarding Mn, Zn and, to a lesser extent, Fe and Cd, some differences between these two species were noted but they were statistically insignificant (Figs 1, 2). When comparing *R. lanuginosum* to *C. uncialis*, the difference was significant only in case of Mn (Fig. 2). Differences in levels of Cr, Ni, Fe (Fig. 1), Pb, and Cd (Fig. 2) between *R. lanuginosum* and *F. nivalis* were significant.

Table 2

Element concentrations (µg/g dry wt.) in lichens *Cetrariella delisei*, *Cladonia uncialis*, *Flavocetraria nivalis*, and a moss *Racomitrium lanuginosum* from NW Sørkapp Land (Spitsbergen).

Species		*Cetraria delisei*	*Cladonia uncialis*	*Flavocetraria nivalis*	*Racomitrium lanuginosum*
n		4	5	4	8
Cr	mean±SD	13.50±1.32	13.17±0.84	0.51±0.07	14.11±1.20
	min-max	11.95–14.6	12.7–14.5	0.44–0.59	12.7–15.75
Ni	mean±SD	8.84±0.77	8.18±0.62	0.37±0.11	9.21±1.11
	min-max	8.05–9.5	7.6–9.1	0.25–0.5	7.6–10.6
Fe	mean±SD	290.53±198.37	247.44±72.28	147.94±25.99	659.03±390.36
	min-max	59.55–461.85	161.65–323.45	122.23–172.03	206.8–1141.5
Cu	mean±SD	2.35±1.91	4.34±2.93	1.72±1.54	3.79±2.20
	min-max	0.7–5.1	1.55–8.55	0–3.63	1.6–7.15
Pb	mean±SD	4.70±4.66	3.46±4.08	0.63±0.49	2.86±1.40
	min-max	0.95–11.5	0.5–10.5	0–1.19	1–4.7
Zn	mean±SD	24.41±18.08	9.72±2.58	7.53±1.31	11.01±5.20
	min-max	3.6–47.75	5.6–12	6.60–9.43	4.85–18.4
Cd	mean±SD	0.03±0.03	0.01±0.02	0.22±0.17	0.03±0.04
	min-max	0–0.05	0–0.05	0.05–0.43	0–0.1
Mn	mean±SD	5.48±3.32	4.89±1.16	11.76±8.16	10.31±4.47
	min-max	1–8.5	3.25–6.2	4.69–19.51	4.35–14.7

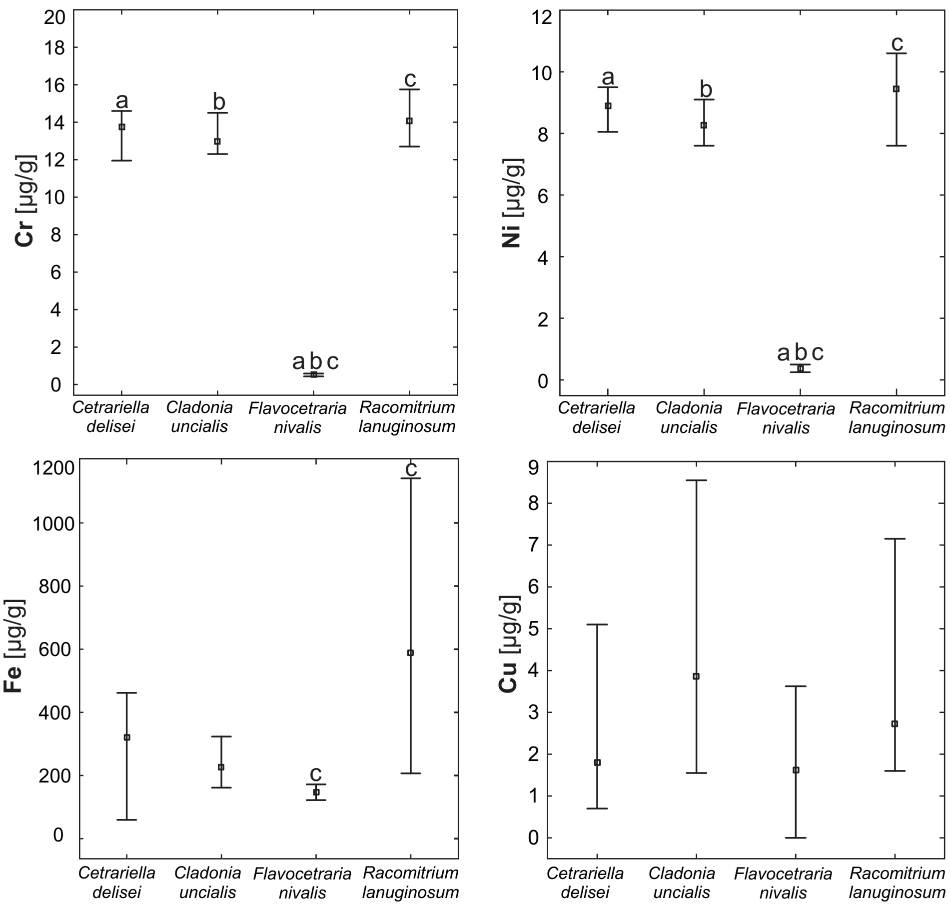

Fig. 1. Medians (points) and ranges (lines) of concentrations of Cr, Ni, Fe, and Cu in lichens *Cetrariella delisei*, *Cladonia uncialis*, *Flavocetraria nivalis* and a moss *Racomitrium lanuginosum* from NW Sørkapp Land (Spitsbergen); a, b, c – pairs of significantly different values (Mann-Whitney U test, $p < 0.05$).

Discussion

The results obtained from analyses of *Cetrariella delisei* were in general similar to those in *Cladonia uncialis*. They were also comparable to the levels in *C. delisei* and *Cladonia mitis* Sandst. from Bellsund, SW Spitsbergen (Jóźwik 2000). Therefore, the use of *C. delisei* as an indicator species of heavy metal levels and comparison of results with *Cladonia* spp. appears promising.

In all cases except Cu, the elemental levels differed between *C. delisei* and *Flavocetraria nivalis*, but the differences were only statistically different for Cr and Ni. In the studies of Jóźwik (2000), mean levels of Mn and Pb in *F. nivalis* proved lower than those in *C. delisei*, and levels of Cu and Cd were higher, and of Zn similar. (Levels of Cr and Ni were not tested by this author). Our data, sup-

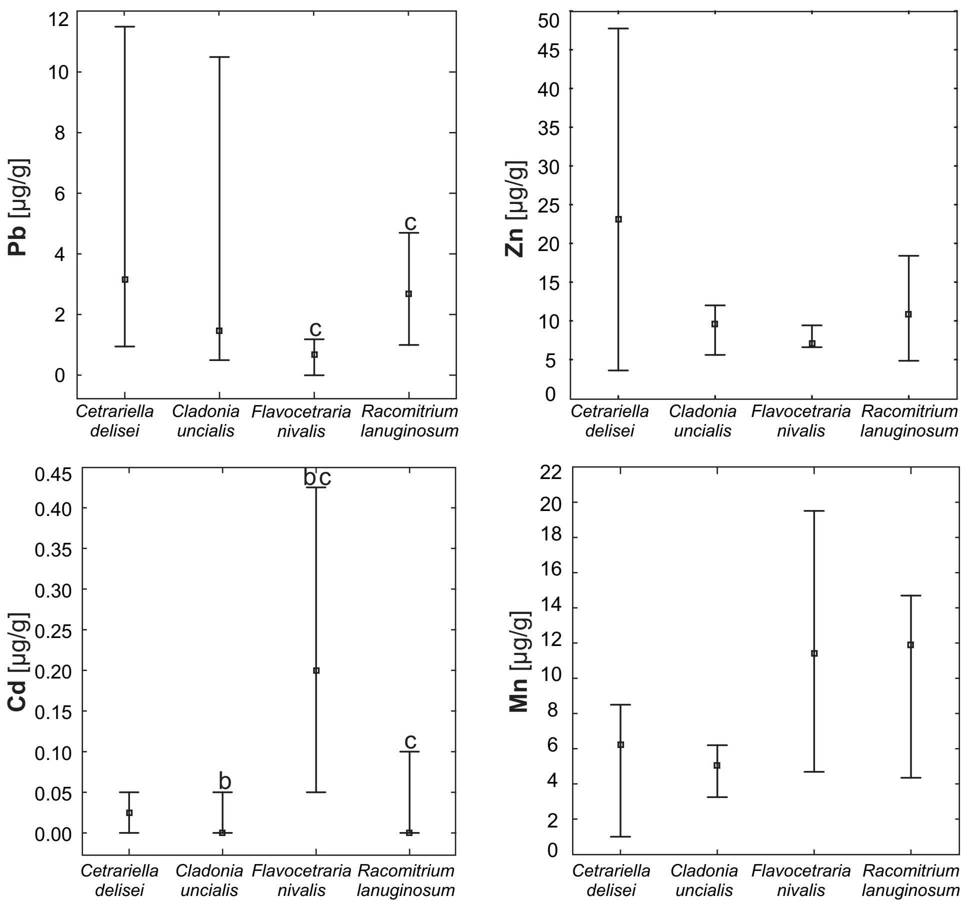

Fig. 2. Medians (points) and ranges (lines) of concentrations of Pb, Zn, Cd and Mn in lichens *Cetrariella delisei*, *Cladonia uncialis*, *Flavocetraria nivalis* and a moss *Racomitrium lanuginosum* from NW Sørkapp Land (Spitsbergen); b, c – pairs of significantly different values (Mann-Whitney U test, $p < 0.05$).

ported by the results of Jóźwik (2000), suggest that comparison of *C. delisei* and *F. nivalis* in terms of heavy metal accumulation has to be carried out with caution.

There can be various reasons for the different behaviour of *F. nivalis* in comparison to *C. delisei* and *C. uncialis*, such as anatomical features, specifically the composition of the cortex: gelatinized hyphae present in the *Flavocetraria* cortex may act as a mechanical barrier for big particles and prevent them from entering the interior of the thallus; such hyphae are absent in the cortex of *Cetraria*, *Cetrariella* and *Cladonia* (Bargagli and Mikhailova 2002; Smith *et al*. 2009). Another factor may involve differences in the binding mechanisms of different metals in the studied species (Bargagli and Mikhailova 2002). Secondary metabolites present in *Flavocetraria*, such as usnic acid, may be partly responsible for a lower accumulation capacity of some elements.

Direct comparison of heavy metal levels in lichens *vs.* bryophytes is difficult owing to the different accumulation properties of various elements (Jóźwik 2000; Riget *et al*. 2000) but assessing an order of magnitude is possible. The moss *Racomitrium lanuginosum* showed generally similar levels of heavy metals to *Cetrariella delisei* and *Cladonia uncialis*, as noted by Jóźwik (2000). The differences between *Racomitrium lanuginosum* and *Flavocetraria nivalis* noticeable in our results are also similar to those obtained by Jóźwik (2000) from Svalbard and by Riget *et al*. (2000) from Greenland.

Intraspecies variability of metal content in the studied species may result from the random sampling effect or the accuracy of the analyses adopted; it may also be due to the fact that the collected thalli were of different ages.

The measured concentrations of heavy metals, with the exceptions of Cr and Ni, did not exceed background levels for the Arctic (Bargagli and Mikhailova 2002). The low levels of most of the elements in spite of the proximity to the Polish Polar Station Hornsund (*c.* 10 km to the north of the study area) suggest that its influence on the environment is only local, as noted by Grodzińska and Godzik (1991) who analysed heavy metals and sulphur contents in mosses in the vicinity of this station.

In general, *C. delisei* proved to be a useful indicator of heavy metal pollution in the study area, the data obtained are favourably comparable to those from popular indicator species, such as *C. uncialis*. *C. delisei* has a broad geographical range (Thomson 1984), and appears not to be negatively affected by reindeer grazing (Elvebakk 1997; Węgrzyn *et al*. 2011). Therefore it will be possible to conduct comparative studies from different parts of the Arctic where herbivore pressure is strong, but further detailed studies are necessary to support this recommendation.

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