Environ Monit Assess (2013) 185:1367–1376
DOI 10.1007/s10661-012-2638-5

Atmospheric deposition studies of heavy metals in Arctic by comparative analysis of lichens and cryoconite

Shiv Mohan Singh · Jagdev Sharma · Puja Gawas-Sakhalkar · Ajay K. Upadhyay · Simantini Naik · Shailesh M. Pedneker · Rasik Ravindra

Received: 30 May 2011 / Accepted: 2 April 2012 / Published online: 25 May 2012

Abstract Lichens and cryoconite (rounded or granular, brownish-black debris occurring in holes on the glacier surface) from Ny-Ålesund were used for understanding the elemental deposition pattern in the area. Lichen samples collected from low-lying coastal region and cryoconite samples from high altitudinal glacier area were processed and analysed for elements such as aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), cesium (Cs), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) through inductively coupled plasma mass spectrometry. Results showed that heavy metals, Al and Fe, are present in high concentration in the cryoconite samples. Al was also present in high amounts in seven of the eight lichen samples studied. The general scheme of elements in the decreasing order of their concentrations for most of the cryoconite samples was Al>Fe>Mn>Zn>V>Pb>Cr>Ni>Cu>Co>As>Cs>Cd while that for the lichen samples was Al>Fe>Zn>Mn>Pb>Cu>Cs>Cr>Ni>V>Co>As>Cd. Similarity in trends in the two sample types confirms that the environment indeed contains these elements in that order of concentration which overtime got accumulated in the samples. Overall comparison showed most elements to be present in high concentrations in the cryoconite samples as compared to the lichen samples. Within the lichens, elemental accumulation data suggests that the low-lying site (L-2) from where *Cladonia mediterranea* sample was collected was the most polluted accumulating a number of elements at high concentrations. The probable reasons for such deposition patterns in the region could be natural (crustal contribution and sea salt spray) and anthropogenic (local and long-distance transmission of dust particles). In the future, this data can form a baseline for monitoring quantum of atmospheric heavy metal deposition in lichens and cryoconite of Svalbard, Arctic.

Keywords ICPMS · Elemental deposition · Biomonitoring · Glacier · Crustal contribution

Introduction

The Arctic is one of the least disturbed habitats on earth. Increased human activities including industrial and mining processes however, have affected the process of biogeochemical cycling of heavy metals in the region (Naeth and Wilkinson 2008). The impact of such activities on environment can be determined through

S. M. Singh (✉) · P. Gawas-Sakhalkar · S. Naik · S. M. Pedneker · R. Ravindra
National Centre for Antarctic and Ocean Research, Vasco da Gama, Goa 403804, India
e-mail: drsmsingh@yahoo.com

J. Sharma · A. K. Upadhyay
National Research Centre for Grapes, Pune 412307, India

elemental analysis of the sediments and vegetation collected from the area.

Biomonitoring of the environment for assessing environmental pollution by phytotoxic substances and heavy metal deposition has been carried out previously in the Arctic (Riget et al. 2000; Shevchenko et al. 2010; Søndergaard et al. 2011) as well as Antarctic regions (Olech et al. 2000; Osyczka et al. 2007; Lim et al. 2009; Cabrerizo et al. 2012) using lichens. Lichens are capable of absorbing elements directly from the atmosphere and accumulating them in their tissues. The concentrations present in the thalli reflect the environmental levels of these elements (Loppi et al. 2002; Paoli et al. 2012). Direct environmental monitoring of major, minor as well as trace metals has been done using water samples in the Antarctic (Abollino et al. 2004).

The present study was undertaken to examine and comparatively analyse the heavy metal levels existing on the land habitats and glaciers around Ny-Ålesund, Arctic. Ny-Ålesund, one of the busy areas of Svalbard, although appears less polluted than down the latitudes may have been certainly exposed to local and transboundary pollution. It was therefore of interest to measure the concentration of elements accumulated in the ice-free and ice-covered areas of the region. For this, the lichens were collected from the low-lying ice-free areas while the cryoconite samples from the glacier valleys where no lichens or mosses could be located. 'Cryoconite' is the rounded or granular, brownish-black debris occurring in holes on the glacier surface containing a wide array of microorganisms including bacteria, fungi, cyanobacteria, green algae, diatoms, rotifers, tardigrades and ciliates (Xu et al. 2010). The level of metals in these samples is of particular importance in environmental and geochemical studies as these data reflect the levels of local metals in soil, rocks and glaciers.

Materials and methods

Study area Ny-Ålesund (78°55′N, 11°56′E) is on the west coast of Spitsbergen, the largest island of Svalbard archipelago. Topographical features of Ny-Ålesund include East and West glaciers, terminal moraines, glacial streams and rivers flowing northwards to Kongsfjord. The mean temperature in the coldest month (February) is −14°C while the warmest month (July) has a mean temperature of +5°C. The lichen sampling sites are situated at various lowland habitats such as wetland and plains (Fig. 1).

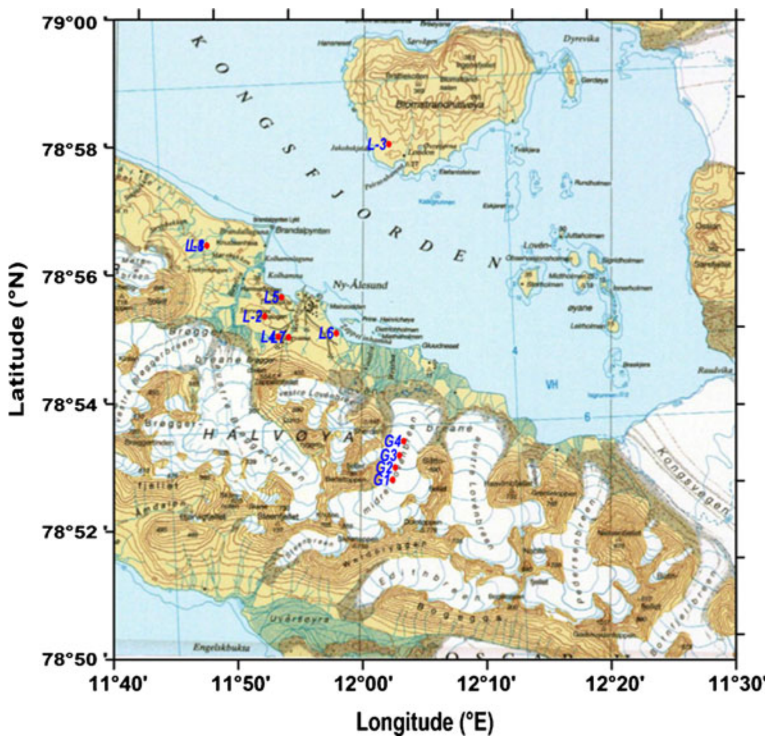

Fig. 1 Sampling sites of lichen (L1–L8) and cryoconite (G1–G4)

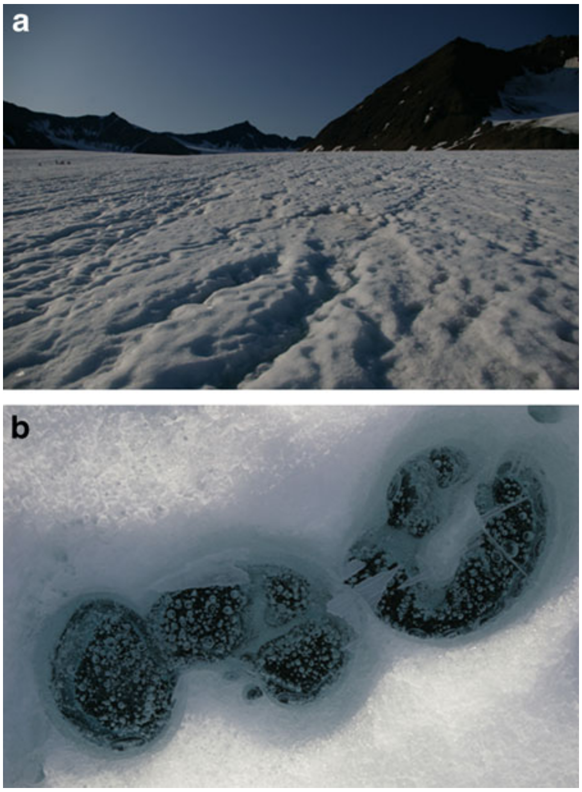

Fig. 2 **a** Midre Lovénbreen glacier **b** Cryoconite holes

Cryoconite samples were collected from Midre Lovénbreen, a well-known polythermal valley glacier (Fig. 2a), located in Ny-Ålesund. Cryoconite holes (Fig. 2b) represent about 6 % of the glacier surface. Typically, the holes are about 8–30 cm deep and 5–50 cm in diameter. The mean temperature of the water in the cryoconite hole was +0.2 to −1.9°C and pH 7.1 to 8.6 (measured using Thermo Orion 4Star, USA).

Specimen collection All collections were done during Indian Arctic Expedition 2007 and 2009, in the Arctic summer months of July–August. Natural thalli of lichen species chosen for the study (Table 1) were collected from different low-lying localities (L1 to L7) in Ny-Ålesund, Arctic. These were identified on the basis of their morphology following Thomson (1984) and Olech and Alstrup (1989). At each sampling site, a minimum of six lichen samples (~2.0 g) for each species were collected. The specimens were stored in sterile perforated plastic bags, transported to laboratory with dry ice and maintained at −5°C till used. A part of the material of each species has been preserved as dried herbarium specimen in Polar Herbarium at NCAOR, Goa, India. Cryoconite sediments were collected from four sampling sites at different altitudes over the glacier. The sampling locations were designated as G1, G2, G3 and G4. The collection ranged from an altitude of 273 m (G1) to 164 m (G4) (Table 1). Samples were collected from the cryoconite holes using a sterile syringe and stored in sterile ampules at low temperature (−20°C) until studied.

Analytical procedure The oven-dried lichen and cryoconite samples were powdered and 0.5 g each was digested in HNO_3 and HCl and in HNO_3 and H_2O_2, respectively. The digestion was carried out in a Teflon vessel at 180°C (Milestone, 'Ethos' advanced digestion system). Lithophiles (Al, Cr, Cs and V), siderophiles (Co, Fe Mn and Ni) and chalcophiles (As, Cd, Cu, Pb and Zn) were determined through inductively coupled plasma mass spectrometry (ICPMS; Thermo Scientific ICPMS-X series II) using Merck CertiPUR ICP multi-element standard solution XXI

Table 1 List of lichen species used for the study

Acc. No.	Name	Thallus type	GPS location		Altitude (m)
			Latitude	Longitude	
L-1	*Cladonia amaurocraea*	Fruticose	78°56′0.466″N	11°47′0.464″E	39
L-2	*Cladonia mediterranea*	Fruticose	78°55′0.360″N	11°52′0.113″E	3
L-3	*Cetraria fastigata*	Fruticose	78°58′0.053″N	12°02′0.095″E	40
L-4	*Flavocetraria nivalis*	Fruticose	78°55′0.042″N	11°53′0.202″E	40
L-5	*Physcia caesia*	Foliose	78°55′0.659″N	11°53′0.472″E	47
L-6	*Pseudophebe pubescence*	Fruticose	78°55′0.097″N	11°57′0.871″E	19
L-7	*Umbilicaria hyperborea*	Foliose	78°55′0.033″N	11°54′0.033″E	39
L-8	*Xanthoria elegans*	Foliose	78°56′0.466″N	11°47′0.464″E	38

Table 2 Elemental concentration in Arctic lichen and cryoconite samples compared with the baseline values laid down for lichens from remote areas of North Canada (Chiarenzelli et al. 2001, as reported by Bergamaschi et al. 2004) and crustal values of Western Europe and Canada (Shaw et al. 1967, 1976, Wedepohl 1995)

	Lichen samples								Cryoconite samples				Baseline value	Crustal composition
	L-1	L-2	L-3	L-4	L-5	L-6	L-7	L-8	G1	G2	G3	G4		
Al	1,076±1.53a	1,937±11.6b	88.6±0.71c	652.5±1.36ad	251.9±2.97cd	501.1±2.57cd	207.6±2.39c	335.2±1.18cd	38,603±405e	42,633±194f	41,763±172g	42,870±154f	–	79,600
As	1.46±0.11a	1.76±0.23a	0.11±0.01b	0.47±0.11b	0.18±0.09b	0.74±0.03b	0.12±0.13b	0.12±0.01b	14.22±0.32c	13.73±0.51c	12.05±0.19d	11.01±0.35e	0.2	1.7
Cd	145.6±9.1a	286.3±23.7b	583.8±15.0c	253.0±19.9b	191.3±16.4a	125.9±12.5ae	556.1±13.7c	242.6±18.5b	60.31±14.6d	80.07±15.1ed	144.81±17.2a	43.33±7.6d	70	100
Co	0.65±0.01a	7.50±0.03b	0.08±0.01c	0.30±0.01c	0.14±0.01c	0.30±0.01c	0.11±0.01c	0.12±0.01c	15.76±0.26d	16.73±0.10e	17.94±0.06f	16.82±0.13e	0.2	24
Cr	0.88±0.03 a	6.90±0.06b	15.25±0.14c	3.68±0.02d	2.18±0.06e	6.82±0.03b	1.63±0.11ae	0.75±0.03a	52.37±1.27f	58.76±0.23g	60.68±0.50h	59.57±0.26gh	1.3	126
Cs	4.93±0.01 a	7.61±0.02b	12.72±0.07c	3.67±0.03d	16.59±0.12e	1.96±0.01f	5.76±0.04g	3.17±0.01h	6.03±0.02i	6.45±0.04j	6.50±0.02j	6.42±0.04j	0.1	3.4
Cu	5.59±0.10 a	19.86±0.1b	2.08±0.07c	10.20±0.03d	3.54±0.06e	7.32±0.14f	9.38±0.05d	2.32±0.03c	38.99±0.7g	42.83±0.21h	43.98±0.58i	40.06±0.33j	1.4	25
Fe	849.2±1.12a	1,566±8.74b	74.15±2.44c	803.7±1.90a	231.1±3.18c	459.6±0.46ac	173.5±2.04c	208.1±0.42c	28,186±437d	30,400±97.1e	32,413±55.7f	31,496±155g	553	43,200
Mn	22.17±0.06a	80.15±0.57b	11.63±0.07dc	13.03±0.09dc	10.08±0.18dce	14.26±0.04c	8.29±0.09de	6.28±0.02e	320±5.17f	362±1.86g	374±0.45h	381±1.20i	–	716
Ni	1.99±0.05a	22.02±0.17b	0.35±0.01cd	0.64±0.02cd	0.97±0.06c	1.87±0.04a	0.50±0.04cd	0.16±0.05d	38.56±0.72e	68.56±0.21f	42.17±0.06g	40.89±0.5h	–	56
Pb	9.19±0.06a	79.69±0.49b	5.66±0.05c	18.65±0.03d	4.91±0.03c	2.09±0.02e	8.02±0.04a	2.14±0.02e	73.88±1.38f	85.08±0.09g	57.18±0.11h	49.87±0.4i	0.7	14.8
V	2.43±0.03ab	4.35±0.02a	0.32±0.01b	1.27±0.03b	1.06±0.03b	1.84±0.01b	0.62±0.02b	0.60±0.02b	79.99±2.67c	90.42±0.59d	84.23±0.5e	87.88±0.71f	1.1	98
Zn	38.26±0.33a	64.01±0.36b	28.57±0.18ad	48.52±0.18c	28.50±0.46d	52.65±0.3c	93.14±0.21e	26.39±0.18d	150±11.11fh	138±0.12gh	146±2.26h	132±1.15g	16	65

For each experimental set, data in the same row followed by a different alphabet are significantly different according to the one-way ANOVA ($P<0.01$). All values are in ppm except Cd which is in ppb for MS. Elemental concentrations were recorded in ppm and in ppb. Variance in the data sets was tested for statistical significance through one-way ANOVA based on triplicate readings. A multivariate ordination analysis based on elemental concentration for each set was performed using principal coordinates (PAST software ver. 2.01, Hammer et al. 2001). Linear regression model of the Microsoft Excel Data Analysis package was used to determine the relation between the various elements.

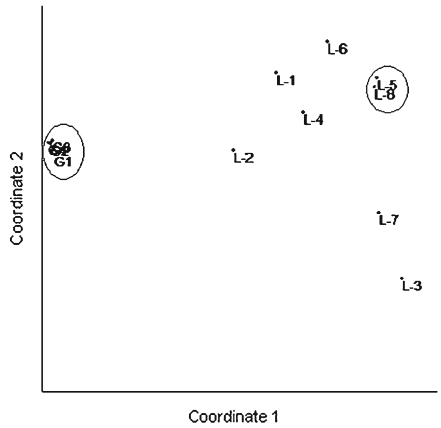

Fig. 3 Principal coordinate analysis based on elemental concentration of the samples

Results and discussion

The elemental analysis illustrates that amongst the elements analysed, heavy metals Al and Fe were present in high concentration in all the four cryoconite samples while in lichens, Al was high in seven of the eight samples studied (L-1, L-2, L-3 L-5, L-6, L-7 and L-8) and Fe in L-4. The general scheme of elements in the decreasing order of their concentration for most of the cryoconite samples was Al>Fe>Mn>Zn>V>Pb>Cr>Ni>Cu>Co>As>Cs>Cd while that for the lichen samples was Al>Fe>Zn>Mn>Pb>Cu>Cs>Cr>Ni>V>Co>As>Cd. Similarity in trends in the two sample types confirms that the environment indeed contain these elements in that order of concentration which overtime got accumulated in these samples.

Concentrations of the various elements analysed (Table 2) illustrate that in case of lichens as well as cryoconite, minor variations do exist within the individual samples, collected in triplicates. Variations between samples collected from different locations, however, remained statistically significant at $P<0.01$ for most elements, as computed through one-way ANOVA. Variability in the chemical parameters within and between the cryoconite holes has been reported previously by Fountain et al. (2008).

Principal coordinates ordination analysis (Fig. 3) using Bray–Curtis similarity index based on the elemental concentration in the samples groups the four high altitude sites G-1, G-2, G-3 and G-4 in a single cluster confirming their alike elemental concentration. Amongst the low altitude lichen samples, L-5 and L-8 were grouped together, segregated from the rest. The elements that are responsible for such a grouping are As, Co, Cr, Cs, Cu, Li, Mn, Ni, V and Zn in case of cryoconite samples and Al, As, Cd, Co, Cu, Fe, Pb and Zn in the case of lichens.

Although it is well-known that lichens growing in the area frequently accumulate variety of air-borne particles by virtue of their large surface area, wide intercellular spaces, thin or no upper cortex, long life span, high cell permeability and high ion exchange capacity (Scerbo et al. 2002; Aslan et al. 2004; Naeth and Wilkinson 2008), the overall comparison showed that most elements were present in high concentrations in the cryoconite samples (collected from high altitude glacier regions) as compared to the lichen samples (collected from low altitudinal areas) (Table 2). The difference in the two groups was found to be statistically significant at $P<0.01$, except in the case of Cd and Cs.

Amongst the eight lichens studied, highest amount of elemental accumulation occurred in L-2 (*Cladonia mediterranea*) followed by L-1 (*Cladonia amaurocraea*), L-4 (*Flavocetraria nivalis*), L-6 (*Pseudophebe pubescence*), L-7 (*Umbilicaria hyperborea*), L-8 (*Xanthoria elegans*), L-5 (*Physcia caesia*) and L-3 (*Cetraria fastigata*). The element concentration data of lichen samples was compared for 10 elements (As, Cd, Co, Cr, Cs, Cu, Fe, Pb, V and Zn) with the baseline data from remote areas of North Canada as proposed by Bergamaschi et al. (2004) from Chiarenzelli et al. (2001). The baseline data indicated as *B* values in the lichen elemental accumulation plots (Fig. 4a–d) suggest that location from where L-2 sample was collected was the most polluted accumulating all the 10 elements at concentrations higher than the

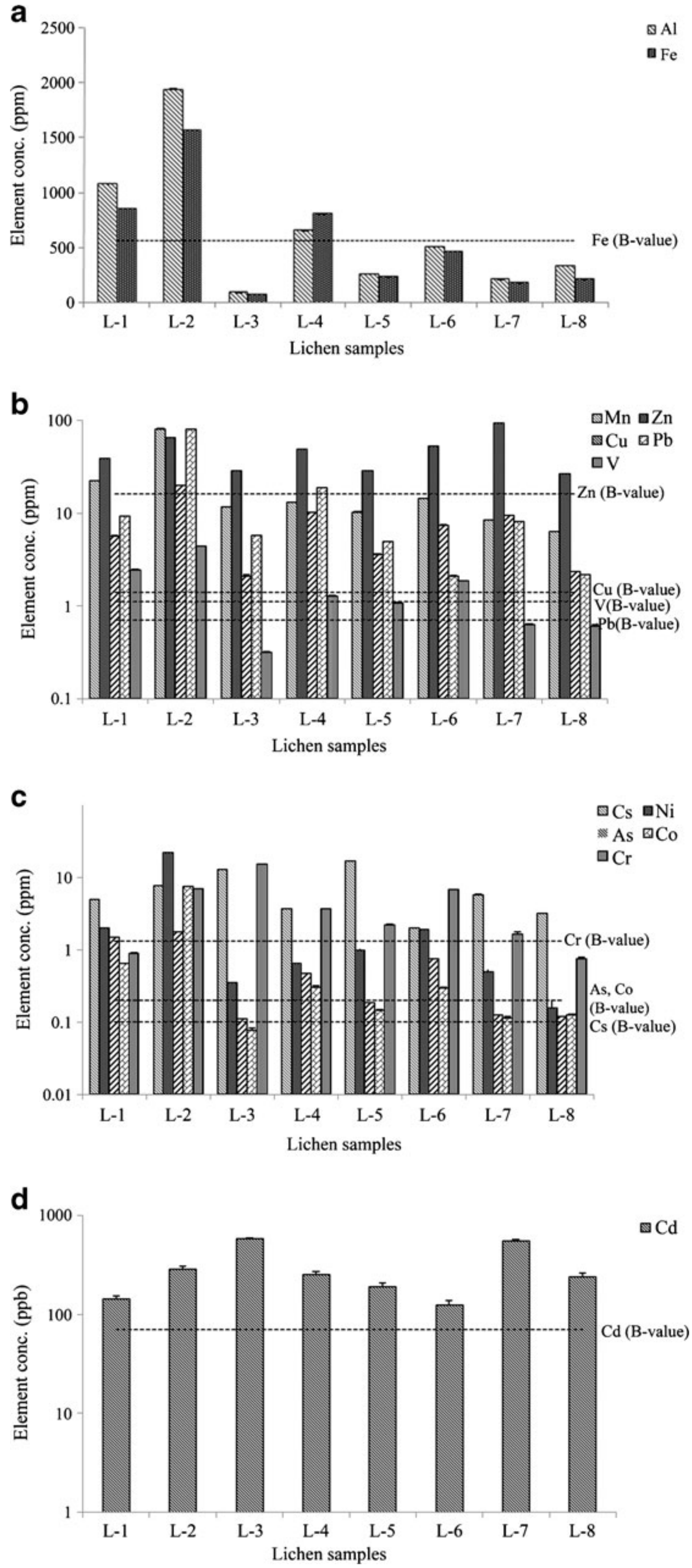

Fig. 4 a–d Elemental accumulation in lichen samples. *B* values represent the baseline values for lichens as proposed by Bergamaschi et al. (2004) from Chiarenzelli et al. (2001)

baseline values. Next, most polluted regions were those from where L-1 and L-6 samples were collected. L-8 was the least polluted region amongst those tested, accumulating only four elements (Cu, Pb, Zn and Cd) at concentrations higher than baseline value.

The lichens were grouped into two groups based on their thalli type—foliose and fruticose. The possibility of the effect of lichen thalli on the accumulation levels of elements was eliminated by significance tests of the two groups. The variation in the two groups was found to be statistically insignificant.

Based on their tolerance to physiological toxicity, threshold values of various heavy metals have been laid down of lichens in general. According to Nieboer et al. (1978), lichen species can tolerate Cd and Cu between 1–30 and 1–50 ppm, respectively. Threshold values for Pb in lichens are from 5 to 100 ppm, although above 15 ppm, the values are considered enhanced (Nieboer and Richardson 1981). For Zn, enhanced levels in lichens are above 500 ppm (Nieboer et al. 1978). Taking these values into account, the results of the present study indicate that a further increase in Pb concentration, in areas from which L-2 and L-4 lichen samples were collected, may threat the existence of lichen species.

When linear regression model was used to determine the relation between different elements, it was observed that except for Cd, Cs, Pb and Zn and to some extent Ni, most other elements showed correlation with one another ($R^2 \geq 0.9$, Table 3) in terms of concentration. Presence of Cd, Pb, Cs, Ni and Zn in high concentration and their non-correlation with others indicates that these disturbing elements in all probability are sourced from anthropogenic activities.

Probable sources of heavy metals

Crustal contribution Atmospheric occurrence of various heavy metals is a contribution of rock and soil dust, sea salt spray and continental and biogenic emissions (Nriagu 1979). Factors such as precipitation, wind and air stability of an area determines the deposition patterns of air-borne dust particles (DiGiovanni and Fellin 2006). In order to evaluate the possible crustal contributions to the deposition of heavy metals in the cryoconite samples, the data was compared with crustal composition of refraction seismic profile of Western Europe and Canada (Shaw et al. 1967, 1976; Wedepohl 1995) [Table 2, Fig. 5a–d (indicated as *C* values)]. Comparison shows that the value of elements such as Co, V, Cr, Al, Ni, Mn, Cd and Fe were well below the levels found in the continental crust implying these elements to likely be the crustal contributions from rocks and soils of the region. In each one of the cryoconite samples, however, Ni and Cd were present in concentration higher than the continental crust levels. Elements such as As, Cs, Cu, Pb and Zn were present at elevated levels in all the four cryoconite samples examined. Further, comparison with lichen data suggests that the elements accumulated in lichens are generally well below the crustal values. Some exceptions to this were Zn in L-7, Pb and As in L-2 and Pb in L-4. Cd was present in high concentration in all the lichen samples while Cs

Table 3 R^2 values indicating correlation between the various elements measured

	As	Cd	Co	Cr	Cs	Cu	Fe	Mn	Ni	Pb	V	Zn
Al	0.97	0.36	0.94	0.98	0.01	0.93	0.99	0.99	0.86	0.56	0.99	0.85
As		0.39	0.93	0.94	0.01	0.93	0.96	0.95	0.88	0.64	0.97	0.86
Cd			0.34	0.28	0.08	0.33	0.36	0.36	0.32	0.20	0.37	0.20
Co				0.92	0.01	0.98	0.94	0.98	0.90	0.75	0.94	0.85
Cr					0.00	0.91	0.98	0.97	0.84	0.54	0.97	0.81
Cs						0.02	0.01	0.01	0.00	0.00	0.01	0.04
Cu							0.94	0.96	0.90	0.75	0.93	0.91
Fe								0.99	0.85	0.55	0.99	0.86
Mn									0.88	0.63	0.99	0.85
Ni										0.79	0.87	0.75
Pb											0.57	0.59
V												0.85

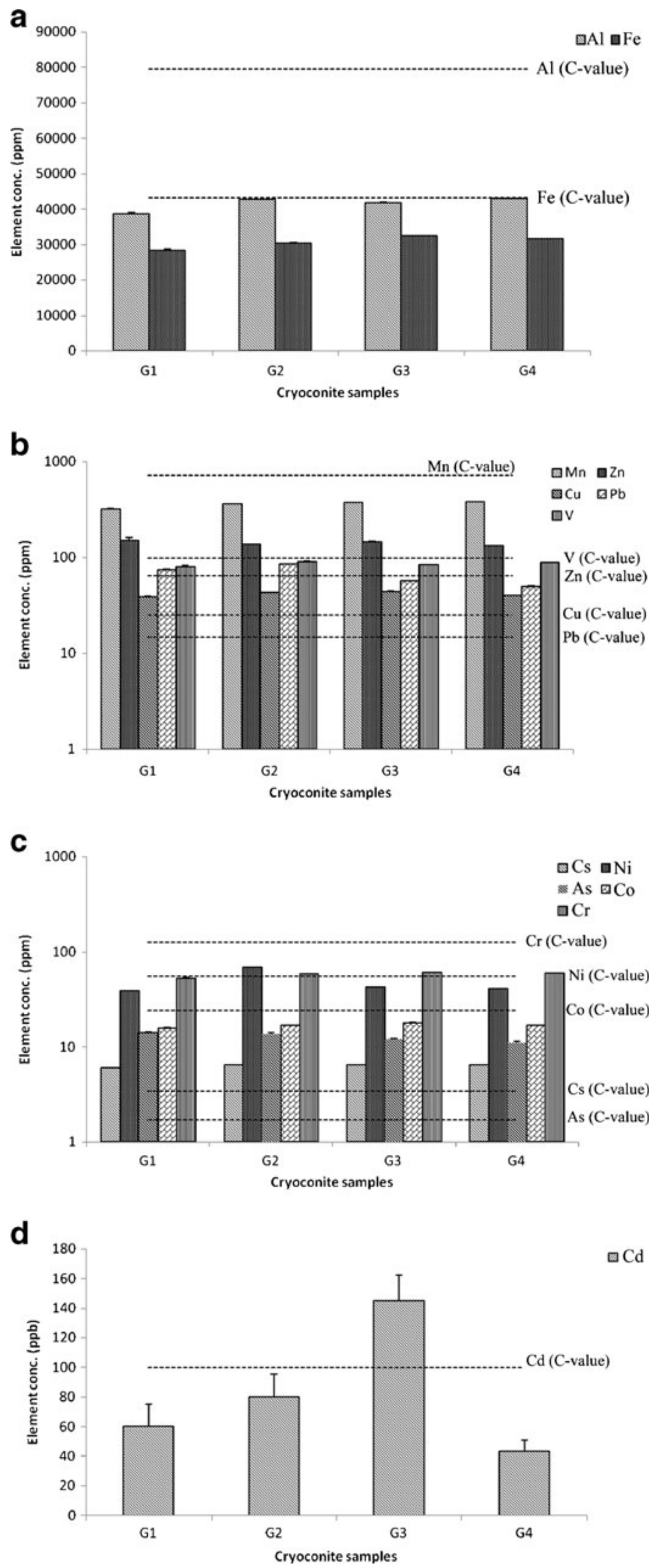

Fig. 5 **a–d** Elemental accumulation in cryoconite holes. *C* values represent the standard crustal contributions according to Shaw et al. (1967, 1976), Wedepohl (1995)

accumulated in high concentration in six of eight samples tested.

Other natural and anthropogenic contribution High concentration of heavy metals, especially Pb, Cu and Zn present in the cryoconite samples, which cannot be accounted for by crustal source, is likely a contribution from other natural and/or anthropogenic sources. The source of pollution could either be local deposition or long-distance transmission of heavy metal dust particles as reported in previous studies (DiGiovanni and Fellin 2006). In sheltered valleys, such as the glacier valley in the study area, the lower air layers become stable and prone to pollution (Benson 1987). High-velocity winds blowing from sea to land that collapses in the valley after striking against the mountainous terrain could bring about high-level deposition of heavy metal dust. Subsequent deposition of heavy metals and their accumulation in the cryoconite holes due to freeze–thaw cycles in the summer months year after year is likely the reason of extreme high levels of heavy metal presence in the cryoconite samples. Another factor that is likely to influence the elemental concentration in cryoconite is the presence of an abandoned mine in the region. Presence of an industrial city, Norilsk at about 2,270 km away in Russia could be a source of long-distance transmission of heavy metal pollution at higher altitudes of the region. The Siberian city of Norilsk is one of the ten most polluted industrial cities of the world and houses the world's largest heavy metals smelting complex. It disperses in air over 4 million tons of Cd, Cu, Pb, Ni, As and Zn, annually (Blacksmith Institute Project 2006).

The airport area and adjacent vehicular traffic may act as the local source of pollution in the low-lying areas thereby leading to contamination of the area (L-2 and L-4 sampling area) with Pb, as it is known that vehicular exhaust is one of the common sources of Pb pollution. The increase in cadmium concentration in most of the lichen samples could be likely due to the influence of sea salt spray (Hong et al. 2002), traffic in the area, coal burning activities (Scerbo et al. 2002) or even long-distance atmospheric transport by virtue of its highly volatile nature (Bergamaschi et al. 2004).

A multi-element study of biological samples along with baseline data comparison is an effective tool for environmental monitoring of pollution. Baseline data helps identify the elements that are sourced through anthropogenic activities. The present study holds significance as it compares the elemental data from high altitude cryoconite samples with the low-lying lichens and observes that the cryoconite samples accumulate higher concentrations of elements than the lichens. The study also points out to the fact that although the pollution levels at lower altitudes is not very high, further increase in the levels of Pb can affect the survival of lichen species in the region.

The higher altitudes glacier valleys even though less disturbed than the lowlands, are muddled up with high concentrations of elemental dust. Although too early to speculate, there occurs a possibility that if the dust continues to settle over these glaciers at this or higher rate, the albedos of snow would reduce, resulting in thinning of the glacier, thereby contributing to the anthropogenically induced global warming.

Further, since the elemental data was generated from samples following standard collection and analysis procedures as mentioned in the "Materials and methods" section and compared with baseline data from the remote regions of northern Canada, the average of the low concentrations for each element can probably form a baseline for monitoring quantum of atmospheric heavy metal deposition in future in Svalbard, Arctic.

Acknowledgments We are grateful to Dr. Shailesh Nayak, Secretary, Ministry of Earth Sciences, Government of India for encouragement and research facilities. We are also thankful to The Director, National Research Centre for Grapes, Pune, India for analytical facilities. This is NCAOR publication No. 12/2012.

References

Abollino, O., Aceto, M., Buoso, S., Gasparon, M., Green, W. J., Malandrino, M., & Mentasti, E. (2004). Distribution of major, minor and trace elements in lake environments of Antarctica. *Antarctic Science, 16*, 277–291.

Aslan, A., Budak, G., & Karabulut, A. (2004). The amounts Fe, Ba, Sr, K, Ca and Ti in some lichens growing in Erzurum province (Turkey). *Journal of Quantitative Spectroscopy and Radioactive Transfer, 88*, 423–431.

Benson, C. (1987). Problems of air quality in local arctic and sub-arctic areas and regional problems of arctic haze. In B. Stonehouse (Ed.), *Arctic Air Pollution–Studies in Polar Research* (pp. 69–84). Cambridge: Cambridge Books.

Bergamaschi, L., Rizzio, E., Giaveri, G., Profumo, A., Loppi, S., & Gallorini, M. (2004). Determination of baseline element composition of lichens using samples from high elevations. *Chemosphere, 55*, 933–993.

Blackmith Institute Project (2006). World's worst polluted places—the top ten. A project of the Black Smith Institute.

http://www.blacksmithinstitute.org/top10/10worst2.pdf. Accessed 29 December 2010.

Cabrerizo, A., Dachs, J., Barceló, D., & Jones, K. C. (2012). Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. *Environmental Science & Technology, 46*, 1396–1405.

Chiarenzelli, J., Aspler, L., Dunn, C., Cousens, B., Ozarko, D., & Powis, K. (2001). Multi-element and rare earth element composition of lichens, mosses, and vascular plants from the Central Barrenlands, Nunavut, Canada. *Applied Geochemistry, 16*, 245–270.

Digiovanni, F., & Fellin, P. (2006). Transboundary air pollution. In H. I. Inyang & J. L. Daniels (Eds.), *Environmental Monitoring*. Oxford, UK: Encyclopedia of Life Support Systems (EOLSS) Publishers.

Fountain, A. G., Nylen, T. H., Tranter, M., & Bagshaw, E. (2008). Temporal variations in physical and chemical features of cryoconite holes on Canada Glacier, McMurdo Dry Valleys, Antarctica. *Journal of Geophysical Research, 113*, G01S92. doi:10.1029/2007JG000430.

Hammer, O., Harper, D. A. T., & Ryan, P. D. (2001). PAST: Paleontological Statistics software package for education and data analysis. *Palaeontologia Electronica, 4*, 1–9.

Hong, S., Lluberas, A., Lee, G., & Park, J. K. (2002). Natural and anthropogenic heavy metal deposition to the snow in King George Island, Antarctic Peninsula. *Ocean Polar Research, 24*, 279–287.

Lim, H. S., Han, M. J., Seo, D. C., Kim, J. H., Lee, J., Park, H., Hur, J.-S., Cheong, Y. H., Heo, J. S., Yoon, H., & Cho, J.-S. (2009). Heavy metal concentrations in the fruticose lichen *Usnea aurantiacoatra* from King George Island, South Shetland Islands, West Antarctica. *Journal of the Korean Society for Applied Biological Chemistry, 52*, 503–508.

Loppi, S., Giordani, P., Brunialti, G., Isocrono, D., & Piervittori, R. (2002). Identifying deviations from naturality of lichen diversity for bioindication purposes. In P. L. Nimis, C. Scheidegger, & P. Wolseley (Eds.), *Monitoring with lichens- monitoring lichens* (pp. 281–284). Dordrecht: Kluwer.

Naeth, M. A., & Wilkinson, S. R. (2008). Lichens as biomonitors of air quality around a Diamond Mine, Northwest Territories, Canada. *Journal of Environmental Quality, 37*, 1625–1684.

Nieboer, E., & Richardson, D. H. S. (1981). Lichens as monitors of atmospheric deposition. In S. J. Eisenreich (Ed.), *Atmospheric pollutants in natural waters* (pp. 339–388). Ann Arbor MI: Ann Arbor Science Publishers.

Nieboer, E., Richardson, D. H. S., & Tomassini, F. D. (1978). Mineral uptake and release by lichens: an overview. *The Bryologist, 81*, 226–246.

Nriagu, J. O. (1979). Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere. *Nature, 279*, 409–411.

Olech, M., & Alstrup, V. (1989). Lichens new to Spitsbergen. *Graphis Scripta, 2*, 146–148.

Olech, M., Osyczka, P., & Dutkiewicz, E. M. (2000). Local environmental pollution with heavy metals in the Admiralty Bay region (South Shetland, Antarctica). *Polish Polar Studies, 28*, 99–103.

Osyczka, P., Dutkiewicz, E. M., & Olech, M. (2007). Trace elements concentrations in selected moss and lichen species collected within Antarctic Research Stations. *Polish Journal of Ecology, 55*, 39–48.

Paoli, L., Corsini, A., Bigagli, V., Vannini, J., Bruscoli, C., & Loppi, S. (2012). Long-term biological monitoring of environmental quality around a solid waste landfill assessed with lichens. *Environmental Pollution, 161*, 70–75.

Riget, F., Asmund, G., & Aastrup, P. (2000). The use of lichen (*Cetraria nivalis*) and moss (*Rhacomitrium lanuginosum*) as monitors for atmospheric deposition in Greenland. *Science of the Total Environment, 245*, 137–148.

Scerbo, R., Ristori, T., Possenti, L., Lampugnani, L., Barale, R., & Barghigiani, C. (2002). Lichen (*Xanthoria parietina*) biomonitoring of trace element contamination and air quality assessment in Livorno Province (Tuscany, Italy). *Science of the Total Environment, 241*, 91–106.

Shaw, D. M., Reilly, G. A., Muysson, J. R., Pattenden, G. E., & Campbell, F. E. (1967). An estimate of the chemical composition of the Canadian Precambrian Shield. *Canadian Journal of Earth Sciences, 4*, 829–854.

Shaw, D. M., Dostal, J., & Keays, R. R. (1976). Additional estimates of continental surface Precambrian shield composition in Canada. *Geochimica et Cosmochimica Acta, 40*, 73–84.

Shevchenko, V. P., Pokrovsky, O. S., Zamber, N. S., Konov, K. G., & Starodymova, D. P. (2010). Lichens as biomonitor of atmospheric aerosol composition in the Northwest European Russia. *Geophysical Research Abstracts, 12*, EGU2010–EGU2852.

Søndergaard, J., Johansen, P., Asmund, G., & Rigét, F. (2011). Trends of lead and zinc in resident and transplanted *Flavocetraria nivalis* lichens near a former lead–zinc mine in West Greenland. *Science of the Total Environment, 409*, 4063–4071.

Thomson, J. W. (1984). *American Arctic lichens 1. The macrolichens*. New York: Columbia University Press.

Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta, 59*, 1217–1232.

Xu, Y., Simpson, A. J., Eyles, N., & Simpson, M. J. (2010). Sources and molecular composition of cryoconite organic matter from the Athabasca Glacier, Canadian Rocky Mountains. *Organic Geochemistry, 41*, 177–186.