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Biogeochemical signatures in the lichen *Hypogymnia physodes* in the mid Urals

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Abstract

Multi-element content and uranium (U) isotopes were investigated in the lichen *Hypogymnia physodes* (native and transplants) sampled across a 60-km transect, centred on Karabash smelter town, from Turgoyak Lake (SW) to Kyshtym (NE) to investigate the origin of U. Kyshtym was the site of a major nuclear accident in 1957. ^{234}U/^{238}U activity ratios in native thalli sampled during July 2001 were within the natural isotopic ratio in minerals. Uranium/thorium (U/Th) ratios were higher in native thalli towards the NE (average 0.73) than those in the SW (average 0.57). Element signatures in native thalli and transplants suggest U was derived from fossil fuel combustion from Karabash and sources lying further to the east. Systematic and significant U enrichment indicative of a nuclear fuel cycle source was not detected in any sample. Element signatures in epiphytic lichen transplants and native thalli provide a powerful method to evaluate U deposition.

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Keywords: Lichen; Uranium; Geology; Fossil fuel

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1. Introduction

Point sources, nowadays very rare in many formerly industrialised regions, are natural laboratories to investigate the effects of pollutants and geology on vegetation (Bell and Treshow, 2002; Haugland et al., 2002). *Hypogymnia physodes* (L.) Nyl., an epiphytic foliose (leaf-like) macro-lichen, is widely used to monitor spatial and temporal patterns of radionuclide and metal contamination (Bargagli and Mikhailova, 2002; Seaward, 2002; Rusu et al., 2006). Transplants of lichens such as *Hypogymnia*, involving relocating samples from ‘background’ sites, can be used in polluted regions where lichens are absent to indicate both sources and effects of air pollutants, including particulates.

The South Ural Mountains of Russia are among the most polluted in the world (Tikhomirov, 1990; Biazrov, 1994; Linkov and Wilson, 1997; Nifontova, 1998; Frontasyeva et al., 2001; Cherchintsev et al., 2002; Biazrov, 2005). Mayak, lying 12 km to the west of Kyshtym in the South Urals (Fig. 1) was the site at which Russia’s first plutonium (Pu) production reactor began operating in 1949. Substantial emissions of radioactive substances have occurred from the ‘Mayak Plutonium Production Association’, the 1957 Kyshtym accident leading to the formation of the ‘East-Urals radioactive trace (EURT)’; liquid radioactive waste disposal into the River Techa and Lake Karachay; and in 1967 the drying up of Lake Karachay which led to atmospheric transport of radioactive sediments (Egorov et al., 2002). Because of poor management of low-level radioactive wastes, sands containing monazite group minerals were widely used for building construction, wall and ceiling plastering and road construction (Chukanov and Korobitsin, 1997). Kyshtym is home to the JSC ‘Kyshtymsky medeelectrolitny zavod’ (Kyshtym copper-electrolytic plant). Founded in 1757, the plant was a major producer of Au, Ag, Cu, Ni, H_2SO_4, Pt, Se and Te. At the beginning of the 20th century, a copper refining plant was built, and for the first time ‘Dore alloy’ (Se and Te) was produced (Kyshtym Electrolytic Copper Plant, 2006). To the south lies Karabash town dominated by a copper smelter surrounded by abandoned mine workings, mine tailings and metallurgical waste dumps exceeding 2.5 million m^2 where lichen biomonitoring has previously been undertaken (Udachin et al., 2003; Williamson et al., 2004; Purvis et al., 2004a).

Uranium is naturally present at low concentrations in the global environment, but is generally more abundant than metals such as Sn, Cd, Hg and Pb (Katz and Rabinowitch, 1951; Meinrath et al., 2003). Human activities such as the use of phosphate fertilisers, extracted from rocks with high U contents, and the burning of fossil fuels also contribute to increased levels of natural U in the environment (Warner and Harrison, 1993). Enriched U (containing higher than natural levels of ^{235}U and ^{234}U) has been released into the environment as a result of nuclear weapons testing, nuclear reactor accidents, spent fuel stores, fabrication or reprocessing facilities and waste storage facilities (Warner and Harrison, 1993), with varying degrees of enrichment.

Lichens derive U and other radionuclides from coal-fired plant emissions (Gough and Erdman, 1977), U mines (Jeran et al., 1995; Beckett et al., 1982; Boileau et al., 1982; Fahselt et al., 1995), as a result of accidents (Looney et al., 1985) and from uraniferous substrates (McLean et al., 1998; Purvis et al., 2004a). U uptake by lichens is considered to be metabolism independent ‘biosorption’ (Suzuki and Banfield, 1999; Purvis et al., 2004a). No naturally occurring U-containing compounds or complexes are known in lichens, so that any U they contain must be accumulated from environmental sources such as re-suspended soil particles, dusts and particulate emissions or from solution.

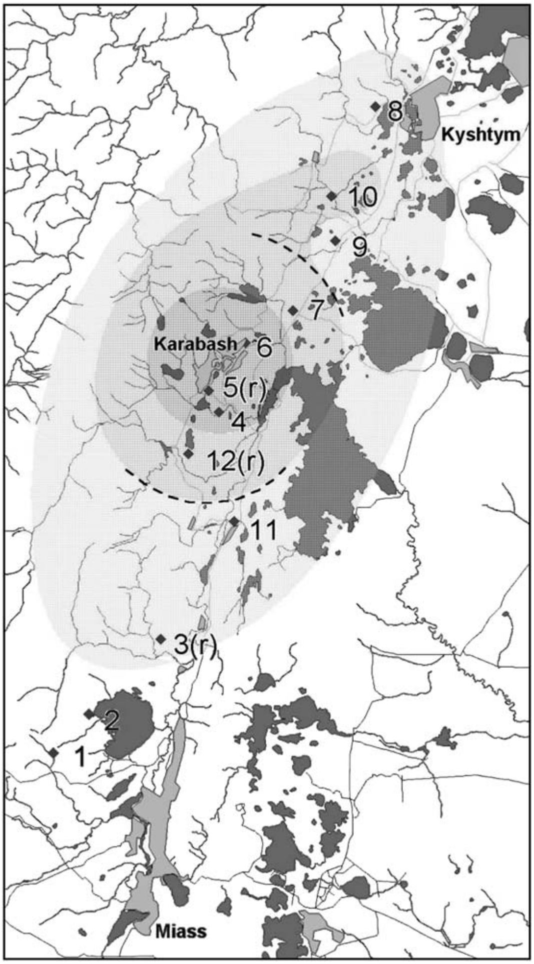

Fig. 1. Sampling sites. Distributional limit of *Hypogymnia physodes* ('native thalli') dotted. Shading corresponds to air quality zones according to lichen diversity (schematic). Dark central region 'impact'; paler middle region 'intermediate' and outer 'background'. September replicate transplant sites are indicated by the suffix 'r'.

Biogeochemical signatures have previously been investigated in *Hypogymnia* samples collected near Karabash in transplants exposed for 2- and 3-month intervals and in native lichens sampled during July, September and October 2001 (Purvis et al., 2004b). Lead isotope abundance (^{206}Pb, ^{207}Pb, ^{208}Pb and ^{204}Pb) was determined in transplants exposed for 3 months (Spiro et al., 2004). Uranium was determined statistically as the main element characterizing native lichens in the NE towards Kyshtym where it reached higher concentrations than elsewhere in the transect, but at low concentrations compared with other studies (Richardson et al., 1985; Jeran et al., 1995; Golubev et al., 2005). Uranium was highly correlated with 23 metals in transplants and six metals in native thalli and samples to the NE contained higher Al levels (Purvis et al., 2004b). Transplants sampled during September 2001 with a high ^{207}Pb/^{206}Pb isotope ratio at Kyshtym suggested a source with a higher ^{235}U/^{238}U ratio (Spiro et al., 2004). The purpose of the present study is to investigate the relationship between U, Al and other element concentrations in the same transplants and native thalli, and the ^{234}U and ^{238}U isotope composition of four native lichen samples sampled from mid Urals in July 2001.

2. Methods

A detailed description of the transplantation method is given elsewhere (Purvis et al., 2004b) and is only summarised here. Over 600 transplants of *H. physodes* were collected between 7 and 8 July 2001 in *Betula* woodland in a sheltered valley about 4 km NW of Turgoyak Lake, about 30 km from the Karabash smelter (site 3, Fig. 1). The bark substrate of 10 samples was carefully glued to the bases of six trees. After a 2- and 3-month period, 50% were collected and bulked for analysis on each occasion, apart from three stations (corresponding to 'intermediate' (site 12), 'impact' (site 5) and 'background' (site 3) in September 2001 when samples were bulked for each tree to provide six replicate analyses (five thalli from each tree). Native thalli were collected (>16.5 km NW and SE of Karabash) from sites 1, 2, 3 and 8 (July 2001) and both transplants and native thalli from sites 3, 8, 9, 10 and 11 (September and October 2001) (Purvis et al., 2004b).

2.1. Chemical analysis

Samples were hand-cleaned under a microscope to remove bark flakes and foreign matter. Digestion was carried out using HNO_3/H_2O_2, the resultant solution filtered and analysed for 35 elements using inductively coupled plasma atomic emission spectrometry (ICP-AES), and ICP mass spectrometry (ICP-MS) (Rusu, 2002). Four replicate native samples collected during July 2001 (sites 1, 2, 3 and 8) were ashed at a high temperature, the U content extracted in a HNO_3 digest and separated by U/TEVA resin extraction chromatography columns (Eichrom Industries). This was followed by electrodeposition and alpha spectrometry (Longden, 2003) for U isotope determination. Two duplicate samples of *H. physodes* collected in July 2003 from Burnham Beeches, Bucks, England (Longden, 2003; Purvis et al., 2005) were investigated as controls.

2.2. Statistical analyses

Multivariate analysis was carried out using principal components analysis (PCA), non-metric multidimensional scaling (MDS) and cluster analysis (CA) from the Package PRIMER 5. As aluminium (Al) is the third most abundant element in the earth's crust, variable Al contents in lichens may contribute towards other metal loadings in lichens through particle fixation. Accordingly, element/Al ratios were also investigated using PRIMER. Statistical tools within MS Excel were used to explore linear and curvilinear relationships in scatter plots. Correlation coefficients and ANOVAs and coefficients of determination (R^2) were calculated together with probabilities. Enrichment factors were calculated for elements in relation to average element concentrations in the earth's upper continental crust (Taylor and McLennan, 1985) according to the formula: $EF_{UCC} = [Element/Ti]_{sample}/[Element/Ti]_{UCC}$. Titanium was selected as the normalising element because Sc, frequently used as an indicator of soil contamination and to calculate enrichment factors, was below detection limits of ICP-MS ($<0.4\ mg\ kg^{-1}$) in all samples suggesting low contamination from soil particulates. Scandium was detected in both terricolous mosses ($0.1–1.45\ mg\ kg^{-1}$) and soils ($1.4–24\ mg\ kg^{-1}$) in the South Ural Mountain moss survey (Frontasyeva et al., 2004) consistent with a lower transfer of elements from soil to epiphytic *Hypogymnia* in the present study.

3. Results and discussion

Statistical analysis of the 35 element dataset identified four major 'groups' (A–D) according to element signatures in native *Hypogymnia* with three subsidiary groups (B1, B2 and B3)

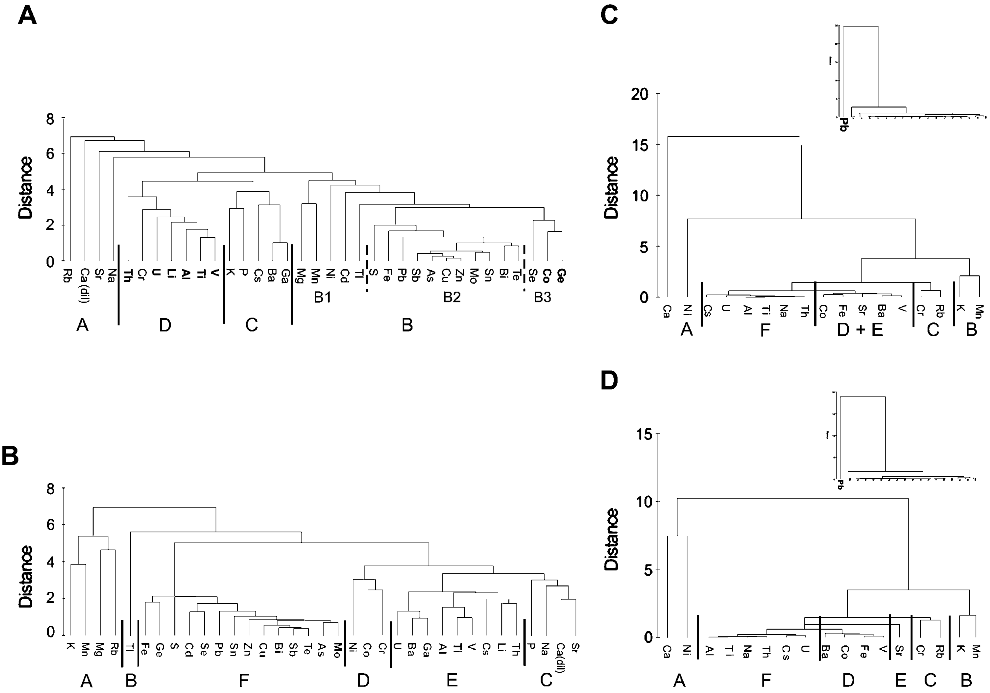

Fig. 2. Dendrograms showing associations between elements in (A) native lichens ($n = 14$); elements reaching highest concentrations at site 10 (19 km NE of Karabash) are indicated in **bold** (B) transplants ($n = 20$); elements reaching highest concentrations at site 5 closest to the smelter for the 3 month period are indicated in **bold**; selected element/aluminium ratios in (C) native thalli and (D) Transplants. Insets in (C) and (D) show Pb omitted for resolution as it swamps the output.

and seven in transplants (A–F) (Fig. 2). Element associations were not identical in native lichens and transplants, partly reflecting variable deposition over the long and short term, and their geographical location. In both cases, group A was least similar and characterised by the labile element Rb, a relatively widespread element present in a range of potassium minerals (lepidolites, biotites, feldspar, carnallite) and readily displaced by protons or cations with a higher binding affinity (Haugland et al., 2002; Purvis et al., 2004b, 2005). The Rb depletion, previously reported in the same samples (Purvis et al., 2004b), reflects loss from minerals. Acidification strongly influences mineral stability in rocks and soils (Blake et al., 1999). Calcium (Ca), an essential element, reached the highest concentration of all elements (60 300 mg kg^{-1}) in *Hypogymnia* at site 11 in calcareous terrain. Higher (2×) Ca contents were recorded in native samples from SW compared with NE. The best resolved groups were characterised by sulphur and 10 metals (group B2 in native lichens) and 13 metals (group F in transplants), spatial patterns of element concentrations and element correlations (Purvis et al., 2004b) consistent with their derivation from sulphurous aerosols from Karabash smelter. Uranium occupied an intermediate position in terms of similarity of element concentrations and correlations in native lichens (Group D) and transplants (Group E). In native lichens, U was closely associated with five elements (Al, V, Ti, Li and Th) which reached highest concentrations at site 10, 19 km NE of Karabash sampled during October 2001. Higher Al concentrations were recorded in native thalli to NE (average, 1023, SD 192, $n = 7$) compared with SW

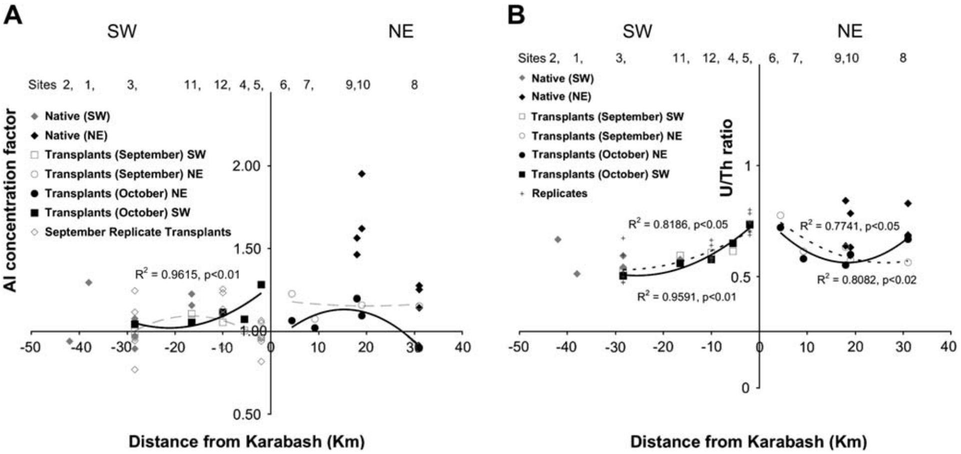

Fig. 3. Diagrams showing relationship between (A) Al and (B) U/Th ratios in native and transplant lichens SW and NE of Karabash. Al concentrations expressed as a ratio to average ‘background’ September transplant values (lowest Al concentration recorded in 25 samples) with distance from Karabash (0 km), (B) U/Th ratios. X-axis marks the average ratio in Upper Continental Crust (Taylor and McLennan, 1985). Coefficients of determination (R^2) and probabilities are indicated where significant.

(average 753, SD 106, $n = 7$) (Fig. 3). Uranium was associated with eight elements in transplants which reached maximum concentrations near the smelter, during October; Al, Ba, Ti, Ga, V, Li and Th (in order of decreasing concentrations) and one element; Cs, in September. The similarity between element signatures in dendrograms ‘C’ and ‘D’ is striking (Fig. 2). Uranium shares the most similar element concentrations and correlations across the transect area with Cs, Al, Ti, Na and Th when element/Al ratios are compared in both native thalli and transplants (see below).

3.1. Enrichment factors (EFs)

Tellurium, Cd, Se, Cu, Pb, Sb and As, elements forming volatile compounds found in the atmosphere and which bioaccumulate in mosses and lichens in areas remote from pollution sources (Bennett, 1995; Berg and Steinnes, 1997; Steinnes, 2001; Chiarenzelli et al., 2001), were most enriched (Fig. 4). Highest EFs were generally recorded in transplants near the smelter confirming Karabash as the primary source. Different enrichment for lichens in the SW and NE was consistent with variable deposition, including from natural geological sources. The lower EF recorded for Al (below 1) than for Ti is consistent with an acidification influence within the short-term (3 month) transplant exposure period. The highest EF recorded for U was 1.34 (site 8 near Kyshtym).

3.2. Origin of uranium

The $^{234}U/^{238}U$ activity ratios, detected activities and summary statistics are shown in Table 1 and Fig. 5. The $^{234}U/^{238}U$ activity ratio expected for natural U in secular equilibrium, i.e. if no isotopic fractionation occurs, is 1. Secular equilibrium in natural matrices, such as soils and minerals, can be disturbed by both natural isotopic fractionation processes and anthropogenic activities associated with the nuclear fuel cycle. The mean $^{234}U/^{238}U$ activity ratios for samples

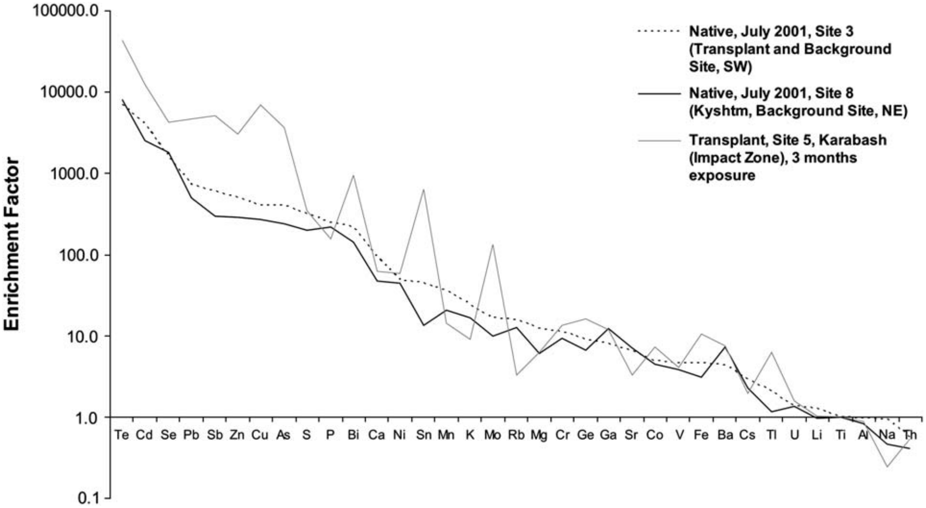

Fig. 4. Enrichment factors for native thalli sampled in SE (‘transplant’ and ‘background’ site) and NE (near Kyshtym) and average element concentrations in all transplants sampled after 3 months normalized to upper continental crust Ti. Arranged in decreasing order of element concentrations recorded in lichens from ‘transplant’ site.

collected from sites 1, 2 and 8 (Kyshtym) and Burnham Beeches all lie within the range expected for natural U in soil (0.5–1.2) (Osmond and Cowart, 1976). The mean detected U activity of native *Hypogymnia* analysed from background site 3 in the SW was lower than those from other samples, resulting in the largest uncertainty in the ^{234}U/^{238}U activity ratio. The upper 95% confidence intervals exceed the range expected for natural U in soil in all samples except K2, some 40 km to the SW of Karabash. Systematic and significant U isotopic enrichment indicative of a nuclear fuel cycle source was not detected in any sample. The ^{234}U/^{238}U activity ratios in U derived from fossil fuel burning would be expected to vary naturally around one due to the isotopic fractionation processes in minerals. On this basis, and considering that

Table 1
The ^{234}U/^{238}U activity ratios, the uranium sources count rate and lichen sample activity, calculated without correction for the efficiency process

Sample	^{234}U/^{238}U	SD	Lichen uranium (234 + 238) detected activity (Bq/kg)	SD (Bq/kg)
K1a	1.26	0.27	1.07×10^{-1}	2.33×10^{-6}
K1b	0.88	0.16	1.23×10^{-1}	3.52×10^{-6}
K2a	0.85	0.12	1.16×10^{-1}	4.36×10^{-6}
K2b	1.03	0.1	2.63×10^{-1}	1.62×10^{-5}
K3a	1.74	0.49	7.63×10^{-2}	8.98×10^{-7}
K3b	1.15	0.32	5.77×10^{-2}	6.12×10^{-7}
K8a	1.18	0.16	3.73×10^{-1}	3.64×10^{-5}
K8b	1.09	0.09	2.34×10^{-1}	2.14×10^{-5}
BB1	0.9	0.15	6.84×10^{-2}	1.93×10^{-4}
BB2	1.09	0.19	8.23×10^{-2}	2.91×10^{-4}

‘Sample’ refers to sampling sites shown in Fig. 1. Prefix K = Karabash, the suffix 1, 2, 3 and 8 indicate the locality number and ‘a’ or ‘b’ replicate analyses. Duplicate control samples from Burnham Beeches are indicated by prefix ‘BB’.

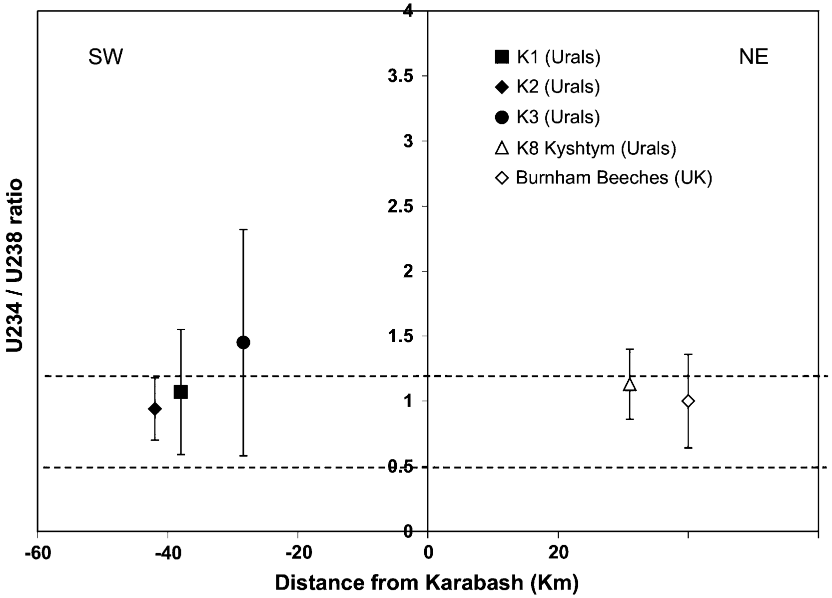

Fig. 5. Mean $^{234}U/^{238}U$ ratios in *Hypogymnia* sampled from Ural Mountains, Russia and Burnham Beeches, UK. Error bars indicate 95% confidence interval. Dotted lines indicate the $^{234}U/^{238}U$ activity ratio range expected for natural U in soil (Osmond and Cowart, 1976).

there was no systematic deviation of the $^{234}U/^{238}U$ ratio above or below one, it is likely that the predominant source of U in the region is a combination of soil/crustal materials and emissions from the smelter.

Trace element mass ratios are sensitive indicators to identify fractionation processes and fluid–rock interactions (Bau, 1996), thus serving as a tool to discriminate groups of different origin and genesis, including in lichens (Dolgopolova et al., 2006). The Th/U ratios in rocks range from 2.55 for oceanic crust (mid-ocean ridge basalt) to 8.4 for lower continental crust (Plant et al., 1999). Lower values led Zhang et al. (2002) to suggest that U in lichen samples was derived from the earth's crust. Coal was considered to be a major factor for U accumulation in *Hypogymnia* from Slovenia as the Th/U ratio of 0.8 was similar to the ratio in Velenje coal (Jeran et al., 1995). The Th/U mass ratios in *H. physodes* in the present study averaged 1.57 (SD 0.24) in native samples and 1.63 (SD 0.18) in transplants, and were therefore similar to signatures in coal. The influence of biological fractionation in lichens has yet to be determined. Uranium was readily leached from *Cladonia* by washing (Trembley et al., 1997). Substances trapped by lichens are not necessarily inert and may be dissolved by rain, by acid delivery in surface run-off or by lichen acid secretion; ions are removed by others with higher binding affinities or of a different isotopic composition (Haas and Purvis, 2006; Spiro et al., 2004).

Cesium is positively correlated with Th, U and Fe in transplants and native thalli (U: Cs, $R^2 = 0.9263$, $p < 0.05$) sampled during July. An association with particulates, U and ^{137}Cs in arctic lichens, was inferred on the basis of highly intercorrelated Fe/Ti and radionuclide associations (Looney et al., 1985), suggesting adsorption of ^{137}Cs either as the ion or very small particulates onto inorganic dust which is available for trapping by lichens. A correlation between ^{137}Cs in soils collected in 1998 from 65 sites in the northern part of Chelyabinsk region and the elements Na Th, U, Al and Ce in mosses from 75 sites suggested an association with accidents at Mayak (Smirnov et al., 2004). Moss biomonitoring studies attributed Na, Mg, Al, Sc, V, Cr, Fe, Ba, Cs, Th and rare earth element associations near polymetallic metallurgical factories at Baia Mare, NW Romania to urban, industrial activities (Culicov et al., 2002). Similar element associations in mosses in sparsely populated, rural northeastern Bavaria were attributed to long-range transport from lignite combustion in the adjacent Saxonian and Czech regions (Faus-Kessler et al., 2001). Lignite coals contain as much as 0.25% U (Plant et al., 1999). These data and $^{234}U/^{238}U$ activity ratios near unity strongly suggest that the elements U, Th, Cs, Na, Ti and Al were partly derived from fossil fuel combustion.

Isotopic results of *H. physodes* do not indicate U isotopic enrichment in spite of highly correlated U and Cs and the proximity to a nuclear reprocessing facility. The study confirms the importance of considering crustal contributions, the influence of acidification and highlights the danger of making assumptions based on total element correlations when identifying sources.

3.3. Future perspectives

The modernisation of Karabash smelter currently underway (Ausmelt, 2005), together with the recently installed gas cleaning equipment and acid plant should dramatically improve sulphur capture and reduce dust emissions. However, a legacy of contaminated land and dusts remains. Information on the mobilisation and transport of metals and radionuclides in the environment is required to estimate exposure to man. This is particularly important in areas such as the Urals where large stockpiles of wastes may result in additional large-scale radioactive contamination as has occurred in the past owing to accidents. Soil contamination with radioactive ^{90}Sr and ^{137}Cs in the area exceed typical background levels for the Northern Hemisphere (Frontasyeva et al., 2001). Further investigations are necessary to determine the combined environmental impact of radionuclides, including Pu and heavy metals in the region. Lichens are useful indicators of ^{239}Pu and ^{240}Pu (Thomas and Ibrahim, 1995; Jia et al., 1997), excellent biomonitors of particulates (Richardson, 1995; Purvis, 1996; Garty, 2001) and have great potential to clarify metal and radionuclide migration pathways in the environment (Bunzl et al., 1999).

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References

Ausmelt, 2005. Annual Report 2005. <http://www.ausmelt.com.au/PDF/Reports/2005%20Annual%20Report.pdf>.

Bargagli, R., Mikhailova, I., 2002. Accumulation of inorganic contaminants. In: Nimis, P.L., Scheidegger, C., Wolseley, P.A. (Eds.), Monitoring with Lichens – Monitoring Lichens. Kluwer Academic, Dordrecht, pp. 65–84.

Bau, M., 1996. Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. Contributions to Mineralogy and Petrology 123, 323–333.

Beckett, P.J., Boileau, L.J.R., Padovan, D., Richardson, D.H.S., Nieboer, E., 1982. Lichens and mosses as monitors of industrial-activity associated with uranium mining in Northern Ontario, Canada. 2. Distance dependent uranium and lead accumulation patterns. Environmental Pollution – Series: B Chemical and Physical 4, 91–107.

Bell, J.N.B., Treshow, M., 2002. Air Pollution and Plant Life. Wiley, Chichester.

Bennett, J.P., 1995. Abnormal chemical element concentrations in lichens of Isle Royale National Park. Environmental and Experimental Botany 35, 259–277.

Berg, T., Steinnes, E., 1997. Recent trends in atmospheric deposition of trace elements in Norway as evident from the 1995 moss survey. Science of the Total Environment 208, 197–206.

Biazrov, L.G., 1994. The radionuclides in lichen thalli in Chernobyl and East Urals areas after nuclear accidents. Phyton 34, 85–94.

Biazrov, L.G., 2005. Lichens as Indicators of Radioactive Contamination. KMK Scientific Press, Moscow.

Blake, L., Goulding, K.W.T., Mott, C.J.B., Johnston, A.E., 1999. Changes in soil chemistry accompanying acidification over more than 100 years under woodland and grass at Rothamsted Experimental Station, UK. European Journal of Soil Science 50, 401–412.

Boileau, L.J.R., Beckett, P.J., Lavoie, P., Richardson, D.H.S., Nieboer, E., 1982. Lichens and mosses as monitors of industrial-activity associated with uranium mining in Northern Ontario, Canada. 1. Field procedures, chemical-analysis and inter-species comparisons. Environmental Pollution – Series B: Chemical and Physical 4, 69–84.

Bunzl, K., Albers, B.P., Shimmack, W., Rissanen, K., Suomela, M., Puhakainen, M., Rahola, T., Steinnes, E., 1999. Soil to plant uptake of fallout Cs-137 by plants from boreal areas polluted by industrial emissions from smelters. Science of the Total Environment 234, 213–221.

Cherchintsev, V.D., Frontasyeva, M.V., Smirnov, L.I., Lyapunov, S.M., Romanov, S.A., Steinnes, E., 2002. Biomonitoring air pollution in Chelyabinsk region (Ural Mountains, Russia) through trace elements and radionuclides. Research contract no 9939/R3 regular budget fund.

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.

Chukanov, V.N., Korobitsin, B.A., 1997. Analysis of the environmental situation in the Urals economic region. In: Linkov, I., Wilson, R. (Eds.), Air Pollution in the Ural Mountains. Environmental Health and Policy Aspects. Proceedings of the NATO Advanced Research Workshop. Magnitogorsk, Russia, 26–30 May, 1997 Nato ASI Series, 2. Environment, vol. 40, pp. 419–422.

Culicov, O.A., Frontasyeva, M.V., Steinnes, E., Okina, O.S., Santa, Z., Todoran, R., 2002. Atmospheric deposition of heavy metals around the lead and copper–zinc smelters in Baia Mare, Romania, studied by the moss biomonitoring technique, neutron activation analysis and flame atomic absorption spectrometry. Journal of Radioanalytical and Nuclear Chemistry 254, 109–115.

Dolgopolova, A., Weiss, D.J., Seltmann, R., Dulski, P., 2006. Dust dispersal and Pb enrichment at the rare-metal Orlovka–Spokoinoe mining and ore processing site: insights from REE patterns and elemental ratios. Journal of Hazardous Materials 132, 90–97.

Egorov, N.N., Novikov, V.M., Parker, F.L., Popov, V.K., 2002. The Radiation Legacy of the Soviet Nuclear Complex, An Analytical Overview. Earthscan Publications, London.

Fahselt, D., Wu, T.W., Mott, B., 1995. Trace-element patterns in lichens following uranium-mine closures. Bryologist 98, 228–234.

Faus-Kessler, T., Dietl, C., Tritschler, J., Peichl, L., 2001. Correlation patterns of metals in the epiphytic moss *Hypnum cupressiforme* in Bavaria. Atmospheric Environment 35, 427–439.

Frontasyeva, M.V., Smirnov, L.I., Romano, S.A., Cherchintsev, V.D., Lyapunov, S.M., Steinnes, E., 2001. In: Frontasyeva, M.V., Vater, P., Peregygin, V.P. (Eds.), Man-made Radionuclides and Heavy Metals in the Environment. Kluwer, pp. 29–36.

Frontasyeva, M.V., Smirnov, L.I., Steinnes, E., Lyapunov, S.M., Cherchintsev, V.D., 2004. Heavy metal atmospheric deposition study in the South Ural Mountains. Journal of Radioanalytical and Nuclear Chemistry 259, 19–26.

Garty, J., 2001. Biomonitoring atmospheric heavy metals with lichens: theory and application. Critical Reviews in Plant Sciences 20, 309–371.

Golubev, A.V., Golubeva, V.N., Krylov, N.G., Kuznetsova, V.F., Mavrin, S.V., Aleinikov, A.Y., Hoppes, W.G., Surano, K.A., 2005. On monitoring anthropogenic airborne uranium concentrations and (235)U/(238)U isotopic ratio by lichen – bio-indicator technique. Journal of Environmental Radioactivity 84, 333–342.

Gough, L.P., Erdman, J.A., 1977. Influence of a coal-fired powerplant on the element content of *Parmelia chlorochroa*. Bryologist 80, 492–501.

Haas, J.R., Purvis, O.W., 2006. Lichen biogeochemistry. In: Gadd, G.M. (Ed.), Fungi in Biogeochemical Cycles. Cambridge University, Cambridge, pp. 344–376 (Chapter 15).

Haugland, T., Steinnes, E., Frontasyeva, M.V., 2002. Trace metals in soil and plants subjected to strong chemical pollution. Water, Air, and Soil Pollution 137, 343–353.

Jeran, Z., Byrne, A.R., Batic, F., 1995. Transplanted epiphytic lichens as biomonitors of air-contamination by natural radionuclides around the Zirovski vrh uranium-mine, Slovenia. Lichenologist 27, 375–385.

Jia, G., Desideri, D., Guerra, F., Meli, M.A., Testa, C., 1997. Concentration and vertical distribution of plutonium and americium in Italian mosses and lichens. Journal of Radioanalytical and Nuclear Chemistry 222, 3–9.

Katz, J.J., Rabinowitch, E., 1951. The Chemistry of Uranium: The Element, its Binary and Related Compounds. Dover Publications, New York.

Kyshtym Electrolytic Copper Plant, 2006. <http://www.kmez.ru>.

Linkov, I., Wilson, R., 1997. Air pollution in the Ural Mountains. In: Environmental Health and Policy Aspects. Proceedings of the NATO Advanced Research Workshop. Magnitogorsk, Russia, 26–30 May, 1997 Nato ASI Series, 2. Environment, vol. 40.

Longden, J., 2003. Determination of an alpha spectrometry method to find the isotopic activity ratio of uranium in soil and lichen samples. M.Sc. thesis, Department of Environmental Science and Technology, Imperial College of Science, Technology and Medicine, London.

Looney, J.H.H., Kershaw, K.A., Nieboer, E., Webber, C., Stetsko, P.I., 1985. The distribution of uranium and companion elements in lichen heaths associated with undisturbed uranium deposits in the Canadian arctic. In: Brown, D.H. (Ed.), Lichen Physiology and Cell Biology. Plenum Press, New York, pp. 193–209.

McLean, J., Purvis, O.W., Williamson, B.J., Bailey, E.H., 1998. Role for lichen melanins in uranium remediation. Nature 391, 649–650.

Meinrath, A., Schneider, P., Meinrath, G., 2003. Uranium ores and depleted uranium in the environment, with a reference to uranium in the biosphere from the Erzgebirge/Sachsen, Germany. Journal of Environmental Radioactivity 64, 175–193.

Nifontova, M.G., 1998. Concentrations of long-lived artificial radionuclides in the moss-lichen cover of terrestrial ecosystems in the Ural–Siberian region. Russian Journal of Ecology 29, 167–171.

Osmond, J.K., Cowart, J.B., 1976. Atomic Energy Review 14, 621–679.

Plant, J.A., Simpson, P.R., Smith, B., Windley, B.F., 1999. Uranium ore deposits; products of the radioactive earth. Reviews in Mineralogy and Geochemistry 38, 255–319.

Purvis, O.W., 1996. Interactions of lichens with metals. Science Progress 79, 283–309.

Purvis, O.W., Bailey, E.H., McLean, J., Kasama, T., Williamson, B.J., 2004a. Uranium biosorption by the lichen *Trapelia involuta* at a uranium mine. Geomicrobiology Journal 21, 159–167.

Purvis, O.W., Chimonides, P.J., Jones, G.C., Mikhailova, I.N., Spiro, B., Weiss, D.J., Williamson, B.J., 2004b. Lichen biomonitoring near Karabash Smelter Town, Ural Mountains, Russia, one of the most polluted areas in the world. Proceedings of the Royal Society of London. Series B: Biological Sciences 271, 221–226.

Purvis, O.W., Chimonides, P.J., Jeffries, T.E., Jones, G.C., Read, H., Spiro, B., 2005. Investigating biogeochemical signatures in the lichen *Parmelia sulcata* at Burnham Beeches, Buckinghamshire, England. Lichenologist 37, 329–344.

Richardson, D.H.S., Kiang, S., Ahmadjian, V., Nieboer, E., 1985. Lead and uranium uptake by lichens. In: Brown, D.H. (Ed.), Lichen Physiology and Cell Biology. Plenum Press, New York, pp. 227–256.

Richardson, D.H.S., 1995. Metal uptake in lichens. Symbiosis 18, 119–127.

Rusu, A.M., 2002. Sample preparation of lichens for elemental analysis. In: Nimis, P.L., Scheidegger, C., Wolseley, P.A. (Eds.), Monitoring with Lichens – Monitoring Lichens. Kluwer Academic, Dordrecht, The Netherlands, pp. 305–309.

Rusu, A.-M., Jones, G.C., Chimonides, P.D.J., Purvis, O.W., 2006. Biomonitoring using the lichen *Hypogymnia physodes* and bark samples near Zlatna, Romania immediately following closure of a copper ore processing plant. Environmental Pollution 143, 81–88.

Seaward, M.R.D., 2002. Lichens as monitors of radioelements. In: Nimis, P.L., Scheidegger, C., Wolseley, P.A. (Eds.), Monitoring with Lichens – Monitoring Lichens. Kluwer Academic, Dordrecht, pp. 85–96.

Smirnov, L.I., Frontasyeva, M.V., Steinnes, E., Lyapunov, S.M., Cherchintsev, V.D., Romanov, S.A., Samosadnyi, V.T., 2004. Multidimensional statistical analysis of the concentration of heavy metals and radionuclides in moss and soil in southern Urals. Atomic Energy 97, 510−515.

Spiro, B., Weiss, D.J., Purvis, O.W., Mikhailova, I., Williamson, B.J., Coles, B.J., Udachin, V., 2004. Lead isotopes in lichen transplants around a Cu smelter in Russia determined by MC−ICP-MS reveal transient records of multiple sources. Environmental Science and Technology 38, 6522−6528.

Steinnes, E., 2001. Metal contamination of the natural environment in Norway from long-range atmospheric transport. Water, Air, and Soil Pollution 1, 449−460.

Suzuki, Y., Banfield, J.F., 1999. Geomicrobiology of uranium. Reviews in Mineralogy and Geochemistry 38, 393−432.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford.

Thomas, R.S., Ibrahim, S.A., 1995. Plutonium concentrations in lichens of Rocky Flats environs. Health Physics 68, 311−319.

Tikhomirov, F.A., 1990. Urals and Chernobyl accidents: Radioecological impact on forest ecosystems. Comparative Assessment of the Environmental Impact of Radionuclides Released During Three Major Nuclear Accidents: Kyshtym, Windscale, Chernobyl. CEC, Luxembourg. EUR 13574.

Trembley, M.L., Fahselt, D., Madzia, S., 1997. Localization of uranium in *Cladina rangiferina* and *Cladina mitis* and removal by aqueous washing. Bryologist 100, 368−376.

Udachin, V., Williamson, B.J., Purvis, O.W., Spiro, B., Dubbin, W., Brooks, S., Coste, B., Herrington, R.J., Mikhailova, I., 2003. Assessment of environmental impacts of active smelter operations and abandoned mines in Karabash, Ural mountains of Russia. Sustainable Development 11, 133−142.

Warner, F., Harrison, R.M., 1993. Radioecology after Chernobyl: Biogeochemical Pathways of Artificial Radionuclides. Wiley, Chichester.

Williamson, B.J., Mikhailova, I., Purvis, O.W., Udachin, V., 2004. SEM−EDX analysis in the source apportionment of particulate matter on *Hypogymnia physodes* lichen transplants around the Cu smelter and former mining town of Karabash, South Urals, Russia. Science of the Total Environment 322, 139−154.

Zhang, Z.H., Chai, Z.F., Mao, X.Y., Chen, J.B., 2002. Biomonitoring trace element atmospheric deposition using lichens in China. Environmental Pollution 120, 157−161.