THE ROYAL SOCIETY FirstCite® e-publishing

Received 13 August 2003
Accepted 3 September 2003
Published online

Lichen biomonitoring near Karabash Smelter Town, Ural Mountains, Russia, one of the most polluted areas in the world

O. William Purvis[1*], P. Jim Chimonides[1], Gary C. Jones[1], Irina N. Mikhailova[2], Baruch Spiro[1], Dominik J. Weiss[3] and Ben J. Williamson[1]

[1]*The Natural History Museum, Cromwell Road, London SW7 5BD, UK*
[2]*Institute of Plant and Animal Ecology, 8 Marta Street, 202, 620144, Ekaterinburg, Russia*
[3]*Imperial College London, Exhibition Road, London SW7 2AZ, UK*

Biogeochemical signatures were investigated in transplanted and native lichens near a major pollution source using sensitive multi-element chemical analysis. Transplants were established across a 60 km transect centred on the smelter town of Karabash, Ural Mountains, Russia. Statistically significant trends in element concentrations were recorded, some below one part per million. Fine metal particles are accumulated from pollution aerosols. Prolonged exposure may lead to cellular damage and enhanced accumulation or element loss. $^{206}Pb : ^{207}Pb$ isotope ratios are similar to those associated with airborne particles in Europe and Russia; an outlier near Kyshtym with a lower ratio indicates a source with a higher $^{235}U : ^{238}U$ ratio. The method is discrete, sensitive, able to detect short-term pollution episodes and useful for understanding element cycling, which is of critical importance for human and environmental health.

Keywords: lichen; biomonitoring; biogeochemical signatures; particles; pollution

1. INTRODUCTION

Hypogymnia physodes is often selected as a biomonitor because it tolerates high metal and SO_2 concentrations. Transplants, involving collecting lichens from 'background' sites and their relocation to new sites, are used where native species are absent (Garty 2001; Nimis *et al.* 2002). Chemical analysis of transplants is usually considered to indicate metal accumulation over the period of relocation, while analysing native thalli will indicate metal accumulation over the lichen's lifespan.

The South Urals Mountains are among the most polluted in the world (Linkov & Wilson 1998). Karabash town (55.47° N, 60.22° E) lies in Chelyabinsk District within a southwest to northeast trending valley (figure 1). The copper smelter, situated towards the town centre, is surrounded by abandoned mine workings and metalliferous waste dumps covering *ca.* 2.1 million m^2 (Williamson *et al.* 2003). Miass and Zlataoust lie towards the south and Kyshtym to the north where, in 1957, the explosion of a radioactive waste storage tank led to formation of the 'East-Urals radioactive trace' (EURT) (Egorov *et al.* 2002), providing a focus for biomonitoring (Biazrov 1994; Frontasyeva *et al.* 2001).

This, to our knowledge, is the first biomonitoring survey of a major point source of gaseous and particulate emissions (Karabash smelter and associated tailings and waste dumps; figure 1) using native lichens and transplants and sensitive multi-element and isotopic analytical procedures, in an area where there is an absence of reliable emissions and biogeochemical data. Lichen diversity was recorded to define 'impact', 'intermediate' and 'background' air quality zones and to establish replicate sites for chemical analysis (figure 1).

2. METHODS

Over 600 lichen transplants were collected on 7–8 July 2001 in a medium-aged mixed birch stand (*Betula pendula*/*Betula pubescens*) in lightly grazed herb-rich grassland *ca.* 4 km northwest of Turgoyak Lake *ca.* 30 km from the Karabash smelter (figure 1*c*) in broadly similar habitats within the same phytogeographical zone. Only young, healthy thalli 3–4 cm in diameter (maximum of 5 cm) were sampled, with a small piece of the underlying bark from birch trunks, and carefully placed in paper capsules to minimize damage and contamination. Ten transplant sites were established (8–13 July 2001) in medium-aged birch stands along an approximately southwest to northeast transect from Turgoyak (*ca.* 42 km south of Karabash) to Kyshtym (*ca.* 31 km northeast of Karabash), including three sites within 5.5 km of the centre of Karabash (figure 1*d*). Six straight trees were selected further than 150 m from roads at each station. Ten thalli were attached to each tree by carefully gluing the bark (to avoid contaminating the lichen) attached to thalli to tree bases within 1 m of the ground in two rows of five thalli facing towards the smelter (figure 1*b*). Transplants were collected after two- and three-month periods and on each occasion five thalli from each tree were sampled at random. Samples were bulked for chemical analysis for each collection period i.e. 30 thalli per site per sampling period with the exception of three stations during September 2001 (corresponding to 'background' (site 3), 'intermediate' (site 12, figure 1*b*) and 'impact' (site 5)) when samples were bulked for each tree to provide replicate analyses for five thalli for each tree. Native thalli were collected, where available, in sufficient quantities for chemical analysis (more than 16.5 km northwest and southeast 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).

*Author for correspondence (w.purvis@nhm.ac.uk).

DOI 10.1098/rspb.2003.2616

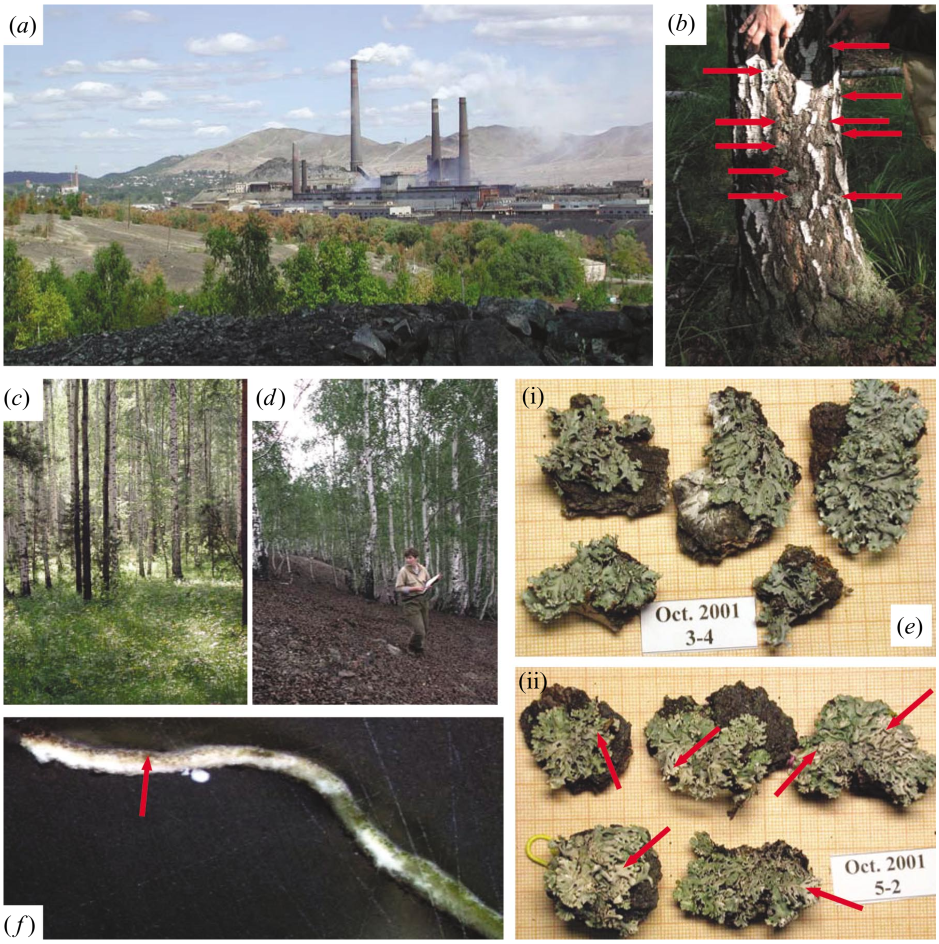


Figure 1. (*a*) View towards de-vegetated Karabash mountain with the smelter in the foreground showing premature autumn colours, 4 July 2001. (*b*) Ten *Hypogymnia* lichen transplants attached to tree base (arrowed) at 'intermediate' site 12. (*c*) Transplant site 30 km from Karabash with well-developed herbaceous layer. (*d*) 'Impact zone' (site 5), 2 km from Karabash where herbaceous vegetation is absent and leaf litter persists. (*e*) *Hypogymnia* transplants collected (i) after three months' exposure from transplant site 3 and (ii) impact zone site 5. Damaged (bleached areas) arrowed. (*f*) Resin-embedded section showing phaeophytinization (arrowed).

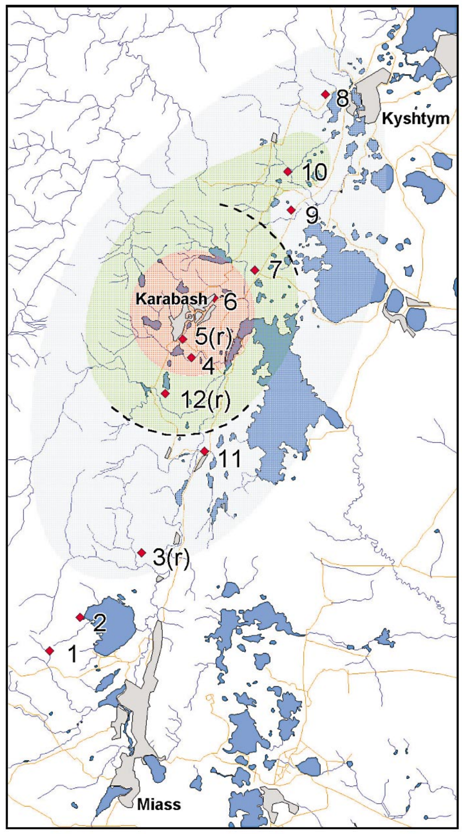
(a) *Chemical analysis*

Samples were hand-cleaned under a microscope to remove bark flakes and foreign matter and digested in HNO_3/H_2O_2 in open vessels under reflux according to method B (Betinelli *et al.* 1996) using standard lichen reference material CRM482, the resultant solution was filtered and analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP mass spectrometry (ICP-MS) (Rusu 2002). For Pb isotope ratios, lichens were digested using a high pressure and high temperature microwave MarsX system with a $H_2O_2/HF/HNO_3$ acid mixture. The Pb was separated from the sample matrix using standard anion exchange column chemistry with an EiChrom Sr-resin and varying HCl acid strengths. Samples were then measured using a Micromass IsoProbe multi-collector ICP-MS. The mass bias was corrected using thallium (Tl) as external dopant. The long-term 2σ reproducibility of the Pb isotope ratio measurements is below 300 p.p.m. for all measured isotopes ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{208}Pb$) and the accuracy after daily adjustment of the Tl ratio was more than 100 p.p.m. for all ratios (Weiss *et al.* 2003).

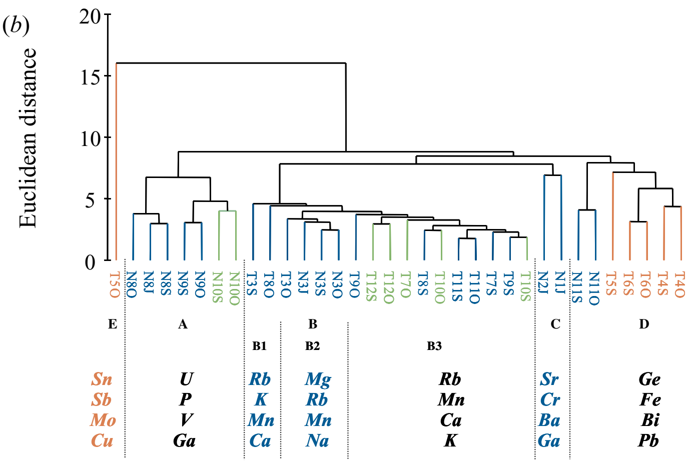
(b) *Statistical analyses*

The package PRIMER 5 and the statistical tools within MS Excel were used. Linear and curvilinear relationships in scatter plots were explored for inter-element concentrations and for element concentrations versus distance from the smelter. Correlation coefficients and ANOVAs were calculated where appropriate, together with coefficients of determination (R^2) and probabilities. Coefficients of variation (CV) were determined to investigate variability within the replicate transplant trees. Multivariate analysis was carried out using principle components analysis (PCA), non-metric multidimensional scaling (MDS) and cluster analysis (CA) (figure 2*b*). Data were transformed (normalized, log, fourth root) to reduce the effects of scale and range in measurements. Correlations were calculated and given a Spearman's rank correlation score and probability. In the CA and MDS, the indices of similarity used were the Bray Curtis and Euclidean distance. For CA, hierarchical agglomerative clustering was carried out using group-average scores. There was very good agreement between PCA and MDS and a further procedure, SimPer (similarity percentage contribution) analysis, was carried out to further check and assess the elemental composition responsible for characterizing and separating groupings (figure 2*c*). The integrity of the groupings A–E was tested with the ANOSim (analysis of similarity) module, a non-parametric alternative to Wilks' lambda test for MANOVA, using randomizing permutation procedures, in which there are no assumptions about, or requirements of, data structure such as equal variance or balanced groupings. The similarities between and within groupings are compared and expressed as a statistic R, where

(*a*)



(*b*)



(*c*)

	A	B1	B2	B3	B	C	D
B	U, Ga, V, Ti						
B1	V, Ti, Al, Cr						
B2	P, U, V, Al	Tl, Na, Mg, Cs					
B3	U, Ga, V, Ti	Tl, Cs, Th, Al	Mg, Na, P, Mn				
C	Ni, Sr, Ca, Th	Sr, Cr, Rb, Li	Sr, Rb, Cr, Th	Sr, Rb, Mg, Cr	Sr, Rb, Cr, Th		
D	K, P, Ca, Rb	Tl, Cr, Co, Fe	Co, Mn, Mg, Cd	Mn, K, Co, Ge	Mn, Co, K, Cd	Sr, Mn, Mg, Th	
E	K, Sn, Mo, Sb	K, Fe, Te, Bi	K, Te, Bi, Sb	K, Sn, Mo, Te	K, S, Te, Sb	K, Te, Sb, Bi	K, Sn, Sb, Te

(*d*)

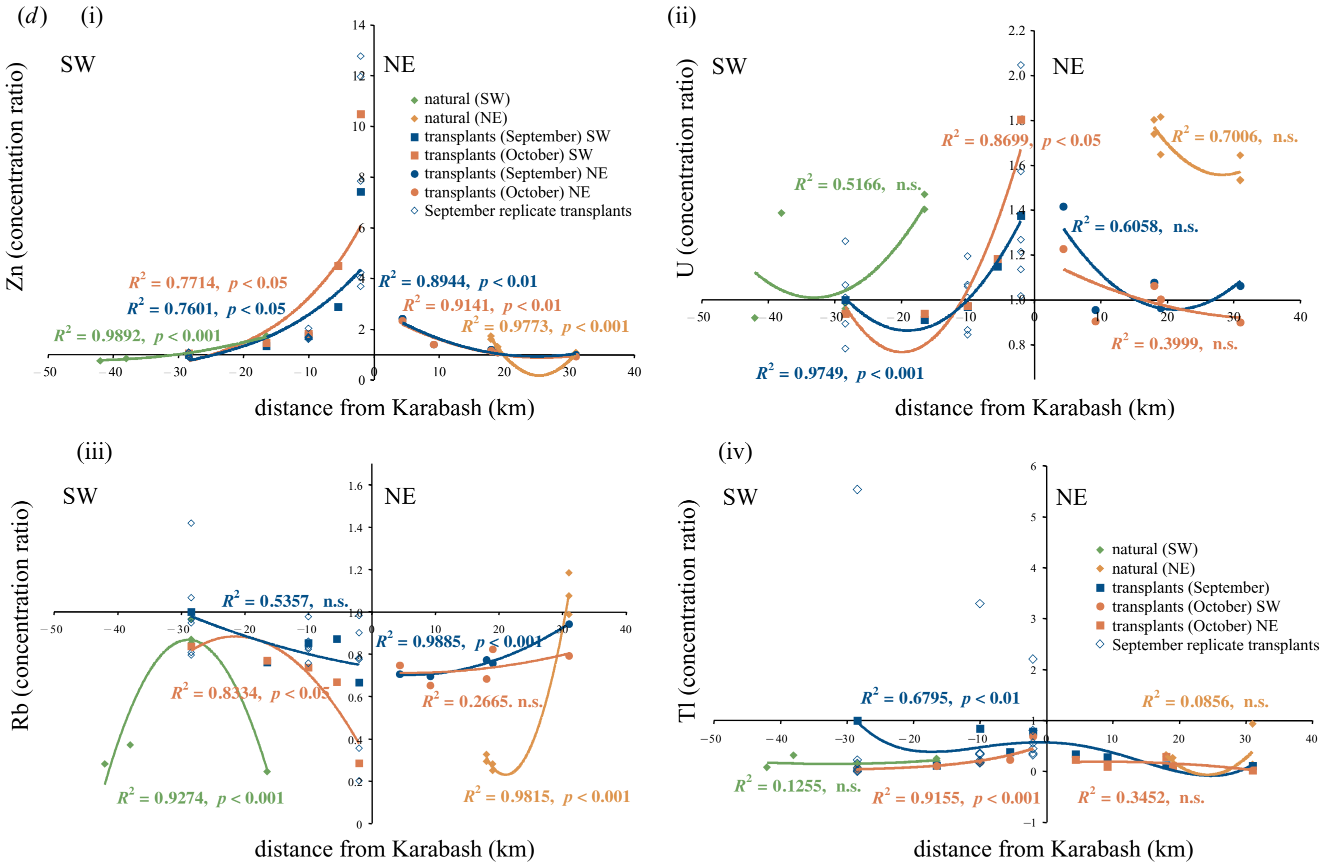


Figure 2. (*Caption overleaf.*)

Figure 2. (*a*) Sampling sites. Distributional limit of *Hypogymnia physodes* ('native thalli') dotted. Shading corresponds to air quality zones according to lichen diversity (schematic). Red, 'impact'; green, 'intermediate'; and blue, 'background'. September replicate transplant sites are indicated by the suffix 'r'. (*b*) Dendrogram from cluster analysis (Euclidean Distance, normalized data) showing site separation. Sites are labelled with three digits, the first according to sample type (T, transplant; N, native), the second to site number (1–12) and the third to sampling period (J, July 2001; S, September 2001; O, October 2001). Elements responsible for defining groups are indicated below. Sites and elements are colour-coded according to 'air quality' zones (see (*a*)) apart from elements (in black) characterizing groups containing sites belonging to more than a single air quality zone. (*c*) Elements serving to distinguish group separations shown in (*b*). (*d*) Relative (i) zinc (Zn); (ii) uranium (U) (key as for zinc); (iii) rubidium (Rb) (key as for zinc); and (iv) thallium (Tl) concentrations in *Hypogymnia* transplants and native thalli across transect with Karabash at the centre. Values are expressed as a ratio to 'background' September transplant concentrations. Values above the horizontal axis indicate enrichment relative to 'background'.

$R = 0$ indicates that there is no difference between any of the constituents and, at the other extreme, $R = 1$ if all within-group similarities are higher than any between-group similarities. The test has two components, a global test of the validity of the overall structure and pairwise testing of the constituent groups.

3. RESULTS

Five groups were resolved by multivariate analysis (figure 2*b*). The global *R*-statistic 0.757 ($p < 0.001$), with no excesses, comfortably supported the groupings present. All pairwise groupings had similarly high *R*-values (0.613–1.000), although the significance values possible in some pairwise tests were elevated because of the small number of sites involved. Groups corresponded (in increasing order of similarity) to:

(i) 'E' (transplant exposed for three months near smelter) is most dissimilar, characterized (in decreasing order of significance) by Sn, Sb, Mo and Cu. Twenty-three elements reached highest concentrations in this sample, with five exceeding 1000 p.p.m.: Fe (0.466%), Zn (> 0.27%), Cu (0.22%), S (0.233%) and Pb (0.12%), followed by Al (894 p.p.m.), As, Ba, Sn, Ti, Cd and Sb (10–100 p.p.m.), V, Se, Ga, Mo, Te, Bi (1–10 p.p.m.) and Co, Ge, Li, Th and U (< 1 p.p.m.). Lowest concentrations were recorded for K, Mn and Rb (figure 2*d*(iii)).

(ii) 'A' (native thalli northeast of Karabash). Characterized by highest U, P, V and Ga concentrations in native thalli.

(iii) 'B' (native lichens at transplant sampling site 3 during July, September and October 2001 and all transplants sampled in 'intermediate' and 'background' zones). Characterized by high Rb, K, Mn, Ca and Mg concentrations. 'B1' (transplant site 3 (September) and site 8 (October)) is separated from 'B2' (site 3, three native thalli and October transplant) (*R*-statistic = 0.714, $p = 0.067$) by higher Tl, lower Na and Mg concentrations and from 'B3' (all other transplants in 'background' and 'intermediate' zones) (*R*-statistic = 0.817, $p = 0.013$) by higher Tl and more variable Cs and Th concentrations.

(iv) 'C' (native lichens at sites 1 and 2 near Turgoyak Lake). Characterized by highest Sr, Cr, Ba, Ga and lowest Bi concentrations.

(v) 'D' (transplants within 'impact zone' (apart from the sample exposed for three months nearest smelter) and native thalli at site 11). Characterized by high Ge, Fe, Bi and Pb concentrations.

The $^{206}Pb : ^{207}Pb$ ratio in all (except site 8) October transplant samples along the transect ranged from 1.141 to 1.154 (average of 1.148, s.d. = 0.0038). Ratio in sample 8 = 1.06.

4. DISCUSSION

Twenty-five elements decreased curvilinearly from Karabash suggesting derivation from smelter emissions or dusts from associated tailings/mine dumps (figure 2). A higher accumulation in transplants towards the southwest is consistent with the local prevailing wind direction (Stepanov *et al.* 1992).

(a) *Trends and biogeochemical signatures*

Many of the particles trapped by lichens are soil and mineral dusts, as shown by Fe : Ti ratios (lithosphere average of 6.5) (Nieboer *et al.* 1978). The accumulation of Fe from minerals is not responsible for high Fe concentrations because ratios are variable and enriched in Fe relative to Ti within the 'impact zone' (ratio of 70–151). Elements Rb, Na, Mg, Ca and Mn, commonly present in minerals, suggest that mineral particle resuspension contributes to metal accumulation in transplants outside the 'impact zone' and native thalli at the 'background site' (figure 2). The element Rb, an alkali element with no known biological function, is sometimes accompanied by Cs; both elements are normally positively correlated with distance from strong chemical sources attributed to displacement by competing protons/cations emitted from smelters (Haugland *et al.* 2002). The elements Cs and Rb are *inversely* correlated in September replicate transplants near the smelter, suggesting an accumulation of particles containing Cs during the period because active, energy-dependent Cs incorporation is impossible in dead lichens (Brown 1976).

Uranium is the main element characterizing native lichens to the northeast (figure 2), highly correlated ($p < 0.001$) with 23 metals in transplants and six metals in native thalli (table 1). Transplant U concentrations increase 1.8-fold after three months near the smelter, reaching 0.06 p.p.m. lower than 'background' concentrations recorded from remote regions (Jeran *et al.* 1995).

$^{206}Pb : ^{207}Pb$ ratios in nine out of 10 October transplant samples correspond to those of airborne particles from northeast Europe including Russia (Bollhoefer & Rossman 2001). Karabash smelter chimney dust has a slightly narrower range (ratio of 1.144–1.149). The lack of a relationship between the isotope ratio pattern and Pb concentrations in October transplants suggests that the Pb budget is dominated by local chimney dust across the transect. A significant natural dust contribution can be

Table 1. Pearson's correlation coefficients between elements: (*a*) twenty-five highest negative correlations and (*b*) twenty-five highest positive correlations.
(n.s., not significant; $^{*}p < 0.05$; $^{**}p < 0.01$; $^{***}p < 0.001$.)

(*a*) transplants ($n = 20$)		native ($n = 14$)	
K : Se	−0.906***	Mg : Se	−0.781***
K : Cd	−0.895***	Mo : Rb	−0.747**
K : Zn	−0.892***	Fe : Rb	−0.717**
K : Cu	−0.891***	Cr : Rb	−0.689**
K : As	−0.887***	P : Sn	−0.688**
K : Bi	−0.886***	Mg : Te	−0.653*
K : Ge	−0.880***	Mg : U	−0.642*
K : U	−0.879***	Ca : Cs	−0.638*
K : Te	−0.871***	Mg : S	−0.627*
K : Sb	−0.867***	Ca : P	−0.593*
K : Ga	−0.860***	Ge : Rb	−0.582*
K : Mo	−0.859***	Li : Rb	−0.580*
K : Pb	−0.842***	Rb : Ti	−0.552*
K : Co	−0.841***	Rb : Sb	−0.545*
K : Sn	−0.833***	Bi : Sb	−0.536*
K : Fe	−0.822***	Cu : Rb	−0.534*
K : Ba	−0.800***	Cs : Mg	−0.532*
Rb : Sn	−0.800***	As : Rb	−0.524 n.s.
Ba : Rb	−0.796***	Rb : Zn	−0.515 n.s.
Bi : Rb	−0.796***	Pb : Rb	−0.487 n.s.
Cu : Rb	−0.792***	Cs : Sn	−0.485 n.s.
Rb : Sb	−0.791***	Co : Rb	−0.471 n.s.
Rb : Te	−0.789***	Cd : Rb	−0.461 n.s.
Pb : Rb	−0.778***	Ga : Mg	−0.458 n.s.
Mo : Rb	−0.774***	Ca : Rb	−0.457 n.s.
total ($p < 0.001$)	40		1
total ($p < 0.01$)	32		4

(*b*) transplants ($n = 20$)		native ($n = 14$)	
Sb : Te	0.999***	Cu : Zn	0.987***
Bi : Sb	0.998***	Sb : Zn	0.985***
Bi : Te	0.998***	Bi : Cu	0.985***
Bi : Cu	0.996***	Bi : Sb	0.983***
Cu : Sb	0.996***	Bi : Zn	0.974***
Cu : Te	0.996***	Cu : Sb	0.971***
Cd : Zn	0.995***	As : Sb	0.971***
As : Mo	0.993***	Ba : Ga	0.965***
Se : Zn	0.993***	Al : V	0.964***
Sn : Sb	0.993***	Al : Ti	0.951***
As : Cu	0.992***	Ti : V	0.950***
Mo : Sb	0.992***	As : Zn	0.941***
Mo : Te	0.992***	As : Bi	0.940***
As : Bi	0.991***	Co : Ge	0.928***
As : Te	0.991***	Fe : Ge	0.926***
Bi : Mo	0.991***	Ge : Ti	0.914***
Cu : Zn	0.991***	Fe : Ti	0.911***
As : Sb	0.990***	Co : Ti	0.907***
As : Zn	0.990***	As : Cu	0.905***
Bi : Zn	0.990***	Al : Li	0.905***
Sn : Te	0.990***	Li : V	0.891***
Te : Zn	0.990***	Ti : U	0.884***
As : Se	0.989***	Cd : Pb	0.883***
Bi : Sn	0.988***	U : V	0.879***
Cd : Se	0.988***	Ge : U	0.870***
total ($p < 0.001$)	222		58
total ($p < 0.01$)	51		52

excluded since the local background $^{206}Pb : ^{207}Pb$ signature is typical for soil and modern average crust (greater than 1.18) (Shotyk *et al.* 1998). The low $^{206}Pb : ^{207}Pb$ ratio from site 8 (Kyshtym) lying within the EURT indicates a source with a higher $^{235}U : ^{238}U$ ratio.

(b) *Toxicity*

The elements S, Cu and Zn, essential biological elements, may reach toxic concentrations in lichens (Nash 1975; Branquinho *et al.* 1999). The absence of *Hypogymnia* within 16.5 km of Karabash and low variation in S, Cu and Zn (figure 2) contents in native thalli suggest critical level excesses. Transplants exposed for three months near the smelter were visibly damaged (figure 1). The highly significant negative correlations observed between concentrations of K with S and toxic metals (Se, Cd, Zn and Cu; table 1) suggest membrane damage and K leakage, an indicator of pollution stress (Garty 2001). The transplants closest to the smelter accumulated 2330 p.p.m. S, 'background' *ca.* 1000 p.p.m. (maximum of 1150–1570 p.p.m.) (Bennett 1995). The levels of Zn (195–447 p.p.m.) and Cu (27–250 p.p.m.) in native thalli are within the upper limits typical for *Hypogymnia* from polluted areas. Tenfold higher (Zn) (figure 2) and 32-fold higher (Cu) levels were recorded in transplants close to the smelter compared with 'background'. Moribund *H. physodes* thalli beneath galvanized wire in North Yorkshire, UK contained fivefold higher Zn than healthy samples (Seaward 1974).

Dead lichens often accumulate more elements than living lichens (Richardson *et al.* 1985). Tissue breakdown and release of organic compounds provide additional sites for cation exchange and metal complexation through metabolism-independent 'biosorption'. The steep decline in metal concentrations (figure 2) contrasts with a much shallower decline for Cu recorded in native moss in the area (Frontasyeva *et al.* 2004). Cu concentrations in lichen transplants 20 km from the smelter were *ca.* 5% of levels in samples near the smelter, compared with moss concentrations of *ca.* 25% of maximum concentrations at the same distance.

(c) *Pollution episodes*

High CVs suggest localized deposition of coarse particles and low CVs in an even suspension or soluble phases (Garty 2001). Tl showed the highest CVs in replicate transplants. Concentrations peaked at site 3 and decreased towards the northeast ($R^2 = 0.6795$, $p < 0.01$; CVs 'background' (2.22), 'intermediate' (1.64) and 'impact' (0.92); figure 2), suggesting a washout of Tl-containing particles. Traces of Tl occur in Cu, Pb and Zn sulphide ores and may be removed from the atmosphere in rain and snow (ToxFAQs 2001). Transplants may therefore record short-term pollution episodes. Very low CVs recorded in replicate transplants and highly significant element intercorrelations for many elements (table 1) suggest an accumulation of fine particles from pollution aerosols, as suggested by Kral *et al.* (1989).

(d) *Implications*

The method is discrete, reliable, sensitive and valuable in the absence of instrumental monitoring, but short-term exposure periods are required near strong chemical sources to avoid membrane damage leading to enhanced element accumulation or loss. Chemical analysis of a few whole thalli normally results in unacceptable variation since older regions normally contain higher concentrations. Several protocols recommend restricting analysis to outer, younger parts of lichens (Nimis *et al.* 2002), but this is not necessary using *Hypogymnia* in this region.

Particulate pollution, especially PM_{10} ($< 10\,\mu m$), is a major concern for human health (QUARG 1996). Large-scale moss monitoring identified higher V, Zn, As, Mo, Cd, Sb, Tl and Bi deposition in southern Norway attributed to long-range atmospheric transport (transboundary pollution; Steinnes 2001). Some elements may be derived from smelters in the east. Our data suggest that *Hypogymnia* biomonitoring is also useful for understanding metal and radionuclide migration pathways, which is essential to estimate potential radiation exposure (Bunzl *et al.* 1999).

O.W.P. and I.M. gratefully acknowledge receiving a Royal Society Joint Project Collaborative grant and everyone's support from MinUrals—Mineral Sources of the Urals: origin, development and environmental impacts supported by a European Commission 5th Framework Programme INCO-Copernicus 2 contract. T. Jeffries is thanked for carrying out ICP–MS. The views expressed in this article reflect those of the authors and not the EU or The Royal Society.

REFERENCES

Bennett, J. P. 1995 Abnormal chemical element concentrations in lichens of Isle Royale National Park. *Environ. Exp. Bot.* **35**, 259–277.

Betinelli, M., Spezia, S. & Bizzari, G. 1996 Trace element determination in lichens by ICP-MS. *Atomic Spectroscopy* **17**, 133–141.

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

Bollhoefer, A. & Rossman, K. J. R. 2001 Isotopic source signatures for atmospheric lead: the northern hemisphere. *Geochim Cosmochim. Acta* **65**, 1727–1740.

Branquinho, C., Catarino, F., Brown, D. H., Pereira, M. J. & Soares, A. 1999 Improving the use of lichens as biomonitors of atmospheric pollution. *Sci. Total Environ.* **232**, 67–77.

Brown, D. H. 1976 Mineral uptake by lichens. In *Lichenology, progress and problems*, Systematics Association Special volume 8 (ed. D. H. Brown & R. H. Bailey), pp. 419–439. London: Academic.

Bunzl, K., Albers, B. P., Schmmack, W., Rissanen, K., Suomela, M., Puhakainen, M., Rahola, T. & Steinnes, E. 1999 Soil to plant uptake of fallout ^{137}Cs by plants from boreal areas polluted by industrial emissions from smelters. *Sci. Total Environ.* **234**, 213–221.

Egorov, N. N., Novikov, V. M., Parker, F. L. & Popov, V. K. (eds) 2002 *The radiation legacy of the Soviet nuclear complex, an analytical overview*. London: Earthscan.

Frontasyeva, M. V., Smirnov, L. I., Romanov, V. D., Cherchintsev, V. D. & Steinnes, E. 2001 ^{90}Sr and ^{137}Cs in surface soil samples from some areas affected by the 'Mayak' plutonium production association. In *Radionucleotides and heavy metals in the environment* (ed. M. V. Frontasyeva, P. Vater & V. P. Perelygin), pp. 29–36. Dordrecht, The Netherlands: Kluwer.

Frontasyeva, M. V., Smirnov, L. I., Steinnes, E., Lyapunov, S. M. & Cherchintsev, V. D. 2004 A heavy metal atmospheric deposition study in the South Ural Mountains. *J. Radioanal. Nucl. Chem.* (In the press.)

Garty, J. 2001 Biomonitoring atmospheric heavy metals with lichens: theory and application. *Crit. Rev. Plant Sci.* **20**, 309–371.

Haugland, T., Steinnes, E. & Frontasyeva, M. V. 2002 Trace metals in soil and plants subjected to strong chemical pollution. *Water Air Soil Pollut.* **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.

Kral, R., Kryzova, L. & Liska, J. 1989 Background concentrations of lead and cadmium in the lichen *Hypogymnia physodes* at different altitudes. *Sci. Total Environ.* **84**, 201–209.

Linkov, I. & Wilson, R. (eds) 1998 Air pollution in the Ural Mountains. Environmental health and policy aspects. In *Proc. NATO Advanced Res. Workshop, Magnitogorsk, Russia, 26–30 May 1997*. NATO ASI series 2. *Environment* **40**, 455.

Nash, T. H. 1975 Influence of effluents from a zinc factory on lichens. *Ecol. Monogr.* **45**, 183–198.

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

Nimis, P. L., Scheidegger, C. & Wolseley, P. A. (eds) 2002 *Monitoring with lichens—monitoring lichens*. Dordrecht, The Netherlands: Kluwer.

QUARG (Quality of Urban Air Review Group) 1996 Airborne particulate matter in the United Kingdom, 3rd report, p. 176. London: Department of the Environment.

Richardson, D. H. S., Kiang, S., Ahmadjian, V. & Nieboer, E. 1985 Lead and uranium uptake. In *Lichen physiology and cell biology* (ed. D. H. Brown), pp. 227–246. New York: Plenum Press.

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

Seaward, M. R. D. 1974 Some observations on heavy metal toxicity and tolerance in lichens. *Lichenologist* **6**, 158–164.

Shotyk, W., Weiss, D. J., Appleby, P. G., Cheburkin, A. K., Frei, R., Gloor, M., Kramers, J. D., Reese, S. & van der Knaap, O. W. 1998 History of atmospheric lead deposition since 12 370 C-14 yr BP from a peat bog, Jura Mountains, Switzerland. *Science* **281**, 1635–1640.

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

Stepanov, A. M., Kabirov, R. R., Chernen'kova, T. V., Sadykov, O. F., Khanislamova, G. M., Nekrasova, L. S., Butusov, O. B. & Baltsevich, L. A. 1992 Kompleksnaya ecologicheskaya ocenka tekhnogennogo vozdeistviya na ekosistemy yuzhnoi taigi (Integrated ecological assessment of technogenic impact on ecosystems of southern taiga). Moscow: CEFP. [In Russian.]

ToxFAQs^{TM} for Thallium 2001 ATSDR (Agency for Toxic Substances and Disease Registry), 11 June. See http://www.atsdr.cdc.gov/tfacts54.html.

Weiss, D. J., Kober, B., Mason, T. F. D., Dolgopolova, A., Coles, B. J., Gallagher, K., LeRoux, G., Spiro, B. & Seltmann, R. 2003 Lead as transient geochemical tracer in the environment: assessing high precision lead isotope ratio measurements in lichen, peat and silicates using multi collector ICP-MS. *Geophys. Res. Abstr.* **5**, 3521.

Williamson, B. J., Udachin, V., Purvis, O. W., Spiro, B., Cressey, G. & Jones, G. C. 2003 Characterisation of airborne particulate pollution in the Cu smelter and former mining town of Karabash, South Ural Mountains of Russia. *Environ. Monit. Assess.* (In the press.)