Environ Monit Assess (2008) 141:227–236
DOI 10.1007/s10661-007-9890-0

The lichen transplant methodology in the source apportionment of metal deposition around a copper smelter in the former mining town of Karabash, Russia

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Received: 3 November 2006 / Accepted: 17 August 2007 /

Abstract The lichen transplant monitoring methodology has been tested for source apportionment of metal deposition around the Cu smelter and former mining town of Karabash. Transplants of the lichen *Hypogymnia physodes (L.) Nyl.*, collected from a 'control' site in July 2001, were set up at 10 stations along a 60 km NE–SW transect centred on Karabash. Samples were collected after 2 and 3 month monitoring periods and analysed using established wet-chemical techniques. The sources of particulate investigated were the smelter blast furnace and converter, floatation tailings, metallurgical slags, local road dusts, top soils and ambient airborne total suspended particulate. From multi-element least-squares modelling the blast furnace was the main source of particulate in transplants close to the smelter (<10 km). Particulate from the converter, with relatively high Pb and Zn, was found to be more widely dispersed, being finer-grained and so having a longer atmospheric residence time. Ambient airborne particulate, sampled in Karabash town using air-pump apparatus, was almost entirely derived from the converter, very different to the lichen transplants from the same area which mainly contained blast furnace particulate. It is proposed that lichens close to the smelter mainly trapped larger blast furnace-derived particulate as they have a low capture efficiency for smaller (converter) particles. The study demonstrates the utility of lichen transplants for monitoring atmospheric deposition and highlights the caution required in their use to assess ambient air quality in human health studies.

Keywords Karabash · Lichen transplants · Monitoring · Smelter · Source apportionment

Introduction

Lichens are widely used in biomonitoring studies as they can provide cost effective tools for mapping spatial and temporal patterns of atmospheric contamination (e.g. Conti and Cecchetti 2001). Lichens

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accumulate metals either from uptake of soluble chemical species from wet or dry deposition or as particles from dry deposition (Williamson et al. 2004a). The presence of metal-rich particles on thallus surfaces and within their interiors has been directly demonstrated using scanning electron microscopy (SEM) (Garty et al. 1979; Olmez et al. 1985; Williamson et al. 2004a). There is general consensus that the trapping of relatively large particles accounts for the bulk of accumulated metals in thalli near industrial sites (e.g. Seaward 1973; Garty et al. 1979). Trapped particles may remain within lichen thalli over long time periods or may be leached out by acid precipitation or lichen organic compounds (Brown 1987).

The epiphytic macrolichen *Hypogymnia physodes (L.) Nyl.* is one of the most widely used lichens in monitoring studies due to its widespread distribution and because it is one of the most tolerant macrolichens to SO_2 and metals (e.g. Garty 2001; Jeran et al. 1996). Where there is an absence of native materials, due to extreme levels of pollution, transplants may be used. This methodology involves the relocation of specimens growing in a relatively unimpacted natural environment to monitoring stations in the polluted area for a fixed exposure period (Mikhailova 2002). Transplanted *H. physodes* have been used to investigate spatial distribution of metals, fluorine, sulphur, nitrogen compounds and radionuclides (e.g. Pilegaard 1979; Gailey et al. 1985; Jeran et al. 1996; Søchting 1995).

The purpose of this study is to assess the effectiveness of the lichen transplant methodology in quantifying the sources of atmospheric deposition in an area of active smelting and abandoned mining operations, specifically where multiple sources exist which yield particles with different size and elemental characteristics.

In order to achieve this the study had three main objectives:

1. To test whether multiple source signatures can be recognised in exposed lichen transplant materials;
2. To quantify the relative proportions of different source signatures and to test the reproducibility of the quantification by comparing the calculated source proportions for multiple sample replicates;
3. To identify variations in the relative proportions of source signatures with distance from a point source (smelter).

This study is an extension of work on the same sample set by Purvis et al. (2004, 2006) and Spiro et al. (2004). However emphasis is placed on identifying and apportioning the main sources of elements in the transplants, indicative of mining-related activities. This has been achieved by carrying out least-squares modelling to fit the compositions of impacted lichen samples from the element profiles of airborne particulate from major local sources.

Study area

The experiment was carried out in a NE–SW transect centred on the copper smelter town of Karabash (55.47°N, 60.22°E), in the Chelyabinsk region in the South Ural Mountains of Russia. In 1995, the Russian Ministry of the Environment and Ecology designated the town as an ecological disaster zone (Polluted Places 2005). The smelter which lies close to the centre of the town mainly produces blister copper, around 41,700 tons in 2001 (Voskresensky 2002). However, from the high levels of Pb and other metals in emissions, it is also thought to be carrying out reprocessing of scrap (Williamson et al. 2004b). There are two main sources of emissions in the smelter, the blast (reverberatory) furnaces where copper concentrates are melted and silicate slag drawn off to produce a molten sulphide matte, and the converter, where remaining elements such as iron and sulfur are removed to produce blister copper (~99% Cu).

Karabash lies within a NE–SW trending flat-bottomed valley with altitudes ranging from 250 to 650 m. The climate is moderately continental with cold winters and warm summers (mean January and July temperatures are −16°C and +18°C, respectively). Precipitation in winter and summer periods is ca. 130 and 300 mm, respectively, with a snow depth in winter of ~40 cm. Prevailing winds are north-westerly (Stepanov et al. 1992), this being the main wind direction during the present study as indicated from a weather station at Chelyabinsk. Phytogeographically, the region lies on the border between taiga and forest-steppe zones, consisting of a mosaic of mesic pine woods (*Pinus sylvestris* mixed with *Betula pendula*, *Betula pubescens* and *Larix sibirica*) and secondary mesic birch woods which have replaced pine following logging or forest fires.

From characterisation studies of airborne total suspended particulate (TSP) collected in the town using air pump apparatus (Williamson et al. 2004b), particulate downwind from the smelter were mainly anglesite ($PbSO_4$), zincite, Zn_2SnO_4 and poorly ordered Zn sulphates, with a mean equivalent spherical diameter of 0.5 μm (s.d.=0.2). Other possible sources of metal-rich airborne particulates in Karabash are waste dumps and tailings which lie to the NE, S and SE of the town. Three tailings dumps cover a total area of around 210 ha (Udachin et al. 1998). In two of the tailings ponds, around 65% of the material has a grain size <0.074 mm. In the third, the “Sak-Elga” tailing, around 11% is <0.074 mm. The mineralogy of the tailings is dominated by pyrite, chalcopyrite, sphalerite, tennantite and magnetite, with quartz, feldspar, sericite, chlorite and barite, and a variety of alteration phases. Metallurgical waste, ground up slag mainly from the smelter blast furnace, covers an area of around 170,000 m^2. This consists of granulated (<0.5 mm) Ca-, Fe-rich silicate glass and minor amounts of sulphides (Udachin et al. 1998). Dumps of pyrite-containing mine waste material cover an area of around 150,000 m^2. Other major sources of dusts include local roads, particularly in summer, and natural wind-blown soil particles from de-vegetated hillsides around the town.

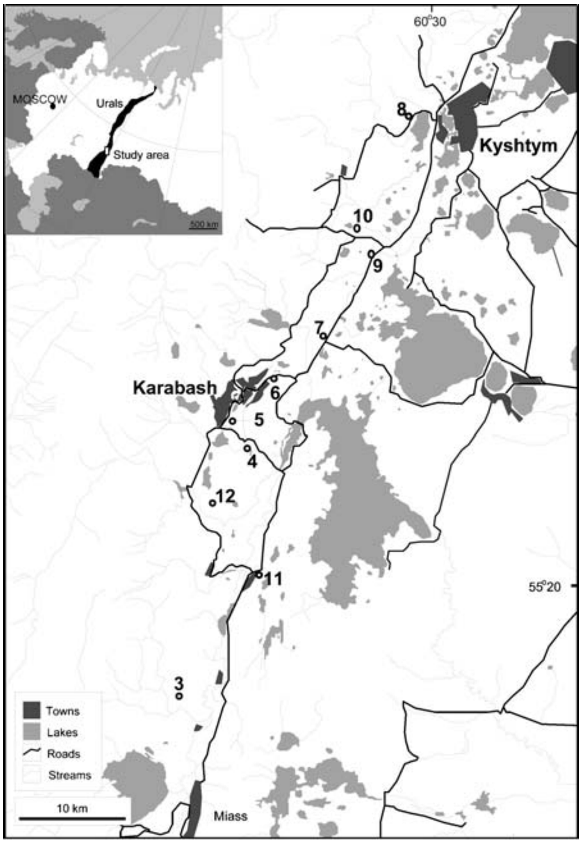

Fig. 1 Locality and drainage map of Karabash and surrounding areas showing the location of lichen transplant sampling points

Materials and methods

Lichen transplants

The lichen transplant methodology used and resulting data has been previously described in Purvis et al. (2004). In brief, lichen transplant materials were collected in July 2001 in a birch (mixed *B. pendula*/*B. pubescens*) stand ca. 30 km from Karabash copper smelter. Healthy *H. physodes* thalli of about 3–4 cm diameter were cut with underlying bark from birch trunks. The material collected was used to set up transplant stations at 10 sites in birch stands along a ca. 60 km transect with Karabash in the centre (Fig. 1). Six birch trees were selected at each transplant site and 10 thalli attached to the bark within 1 m from the tree base in two rows on the north side of trunks. Transplant material was collected after 2 and 3 months (September and October 2001). The material was manually cleaned of bark flakes and other debris, and then attacked using HNO_3/H_2O_2 in open vessels under reflux. Sample solutions were filtered and analysed by inductively coupled plasma–optical emission spectroscopy (ICP-OES) and mass spectrometry (ICP-MS) using standard techniques, and with reference to the lichen standard CRM482. Reproducibility of the lichen transplant methodology was assessed by analysing 6 replicates of samples from three sites collected in September 2001 (see Fig. 2).

Air filter sampling

Methods employed for the collection of air pump-filter and smelter stack samples are given elsewhere (Williamson et al. 2004b), and so are only summarised here. TSP were collected in October 2000 and July 2001 using a J. D. Technical JD8T (UK) airborne particulate sampling pump, from 7 localities within Karabash town. One of the localities (KA6) also corresponded to what we later refer to as the impacted

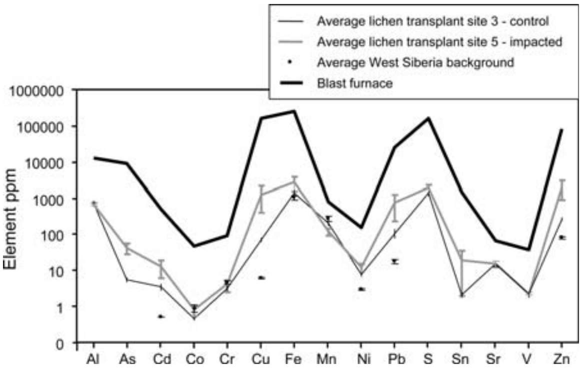

Fig. 2 Average (+/−1 standard deviation) elemental profiles (for six lichen transplant replicates) collected in October 2001 from site 5 (impacted) and site 3 (control). Also shown are values (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn only) for the 'West Siberia background' average (n=42) for *H. physodes* from Valeeva and Moskovchenko (2002)

lichen transplant site (Site 5). The sampling pump was operated at a flow rate of 5 l/min, with the sampling head positioned 110 cm above ground level. Particle collections were made onto 25 mm diameter pre-weighted Millipore polycarbonate filters (pore size 0.4 μm). The TSP filters were divided for wet chemical analysis (ICP-MS and ICP-OES) and SEM.

Road dusts, soils and wastes

Road dust samples were collected by scooping the abundant material off road surfaces directly into a polyethylene bag. Top soils, tailings and metallurgical slags were sampled in a similar way, using a steel shovel. All sample types were air dried, sieved to <2 mm, then ground to a fine powder in a tungsten carbide Tema. Sample powders were attacked using a combination of high purity acids (for wastes and tailings HNO_3/Br_2 to retain S as SO_4, and $HF/HCLO_4$ to attack the silicates). The road dusts were attacked with HNO_3 then $HF/HCLO_4$, and the top soils $HF/NHO_3/HCl$. Sample solutions for the tailings, metallurgical slags and road dusts were analysed by ICP-OES at the Natural History Museum whilst the topsoil samples were analysed by Atomic Absorption (FAAS Perkin Elmer 3110 and GFAAS Analyst 300 with HGA-850) at the Institute of Mineralogy in Miass. The detection limits for soils by FAAS analysis are 10 mg/kg (dry weight) for Zn, Cu, Ni and Mn, 15 for Co, 20 for Cr and Fe, and by GFAAS 0.1 for Pb and 0.04 for Cd. Certified reference material SUR-1 (soil) was regularly analysed, yielding Pb and Cd values within 10% and 5% of the certified values, respectively. Detection limits by ICP-OES (tailings, metallurgical slags and road dusts) vary by element but are less than 100 μg/g (in the solid). The accuracy of analyses was tested by simultaneously preparing and analysing standard rock powders. Analytical precision varies between elements but is generally better than 2%.

Data analysis

Geochemical data for all environmental media is presented in graphical form in 'spidergrams' (Figs. 2, 4 and 6) and ternary (Fig. 3) and scatter plots (Fig. 5) for ease of interpretation by readers from a multitude of disciplines. Spidergrams are widely used in the geochemistry literature for comparing sample multi-element signatures where elements are contained at 'orders of magnitude' different concentrations. The ternary diagrams in Fig. 3 show the relative proportions of Cu, Pb and Zn for different environmental media, where a point lying on the Zn apex contains only Zn, with no Cu or Pb. A point in the centre of the triangle contains all three elements in equal proportions. Because Cu and Zn were found at higher concentrations than Pb in the environmental media, values for Pb have been multiplied by two (Pbx2 apex) in order to achieve a spread of data across the ternary plots. For lichen and TSP samples in Fig. 3a, the size of the symbol for each sample varies with Pb concentration, with the samples containing highest Pb having the largest symbols. Pb was selected, rather than Cu + Zn + Pb, to aid in identifying a signal from the smelter converter, rather than the blast furnace which has an elemental signature dominated by Cu and Zn.

In order to assess the relative signature in the lichen transplants and TSP from different source compositions (smelter converter and blast furnace), a multiple linear least-squares regression mixing model was used (Le Maitre 1979). The compositions of lichen transplants from different distances from the smelter were modelled by mixing the pattern for the control transplant lichen (site 3, average of 5 samples, zero baseline in Fig. 5a and b, omitting spurious value A in Fig. 3a) with varying proportions of the elemental patterns for the blast furnace and converter samples. The suite of elements used in the modelling was limited to Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sn, Ti and Zn. Mn and S were omitted as Mn showed a

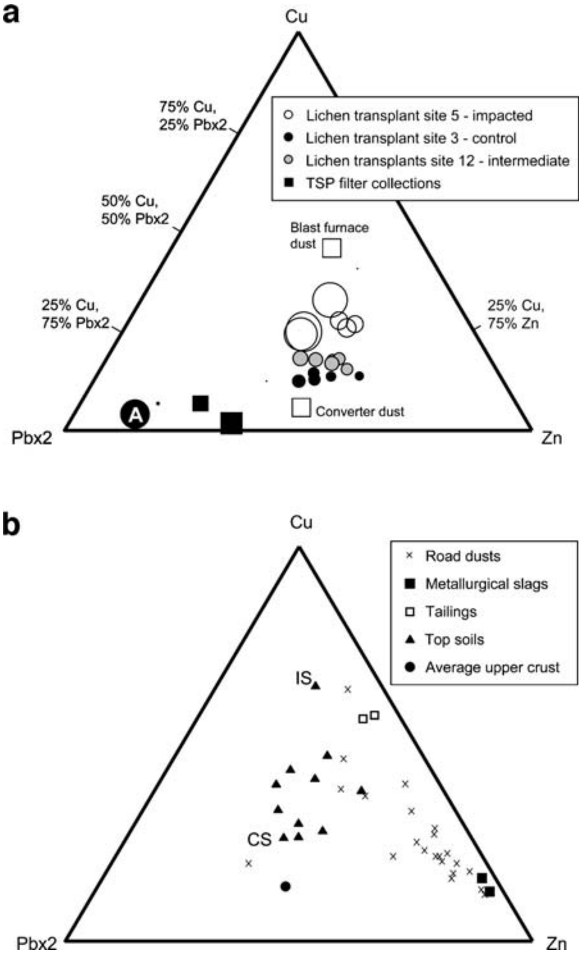

Fig. 3 Ternary diagrams for Cu vs Pbx2 vs Zn for **a** lichen transplants, TSP filter collections and samples from the blast furnace and converter stacks. *Symbol* sizes for lichen transplants and TSP filter collections are proportional to Pb content (relative to other samples from each media type). Point *A* is an anomalous value for lichen transplants from the control site; **b** road dusts, metallurgical slags, tailings and top soils. Also shown is a reference value for the average upper crust from Taylor and McLennan (1985). For top soil samples *IS* = impacted site, *CS* = control site

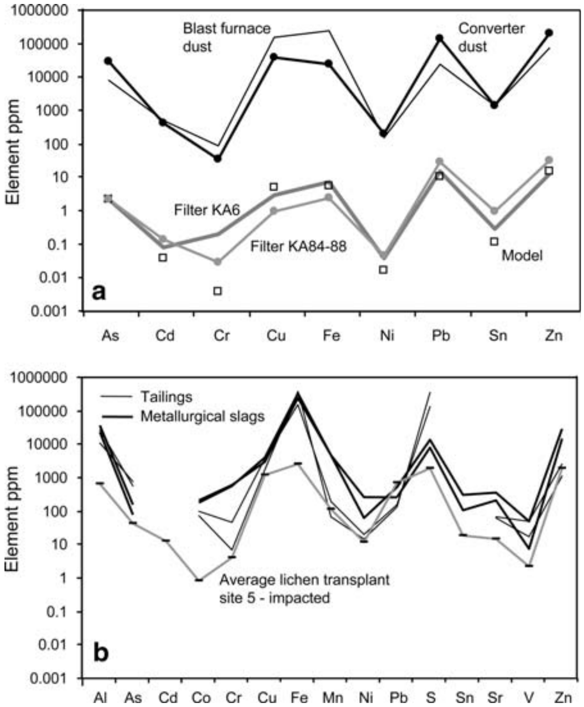

Fig. 4 Elemental profiles for **a** stack samples from the blast furnace and converter compared with air filter samples KA6 (collected Oct 2000) and KA84-88 (collected July 2001, data from Williamson et al. 2004b). Also shown is a least squares fit to the composition of air filter KA6 by mixing the compositions of samples from the blast furnace (18% component) and converter (82%); **b** samples of tailings and metallurgical slags from Karabash, with the pattern for the average for lichen transplant site 5 (impacted) shown for reference (see Materials and Methods). Cd was not detected in either the tailings or metallurgical slags (estimated detection limit 100 μg/g) and Sn was not detected in the tailings (estimated detection limit 50 μg/g)

loss in the impacted compared with the control sample. This is possibly due to electrolyte loss (along with K) as a result of cell leakage from damaged lichen tissue in the polluted environs of the impacted site 5 (Williamson et al. 2004a). Sulphur was not considered suitable for source apportionment as it is already present in high concentrations in the lichen materials but also may be derived from acid precipitation (rain drops) and secondary particles from atmospheric conversion of SO_2. The model yielded the proportions of a) the lichen control composition, b) smelter blast furnace composition and c) smelter converter composition, that best fit the elemental pattern for the lichen transplants along the transect. The results of the modelling are graphically presented in Fig. 5, which shows the modelled percentage of blast furnace and converter signature for lichen transplants collected at different distances from the smelter. To determine the reproducibility of the modelling approach for assessing elemental source apportionment, the modelling was repeated for 6 replicates (September collection) from the impacted, intermediate and control sites (sites 5, 12 and 3, respectively). The average ratios of blast furnace to converter signatures are presented (±1 s.d.) in the table in Fig. 5a, there being a clear distinction between the ratios between sites.

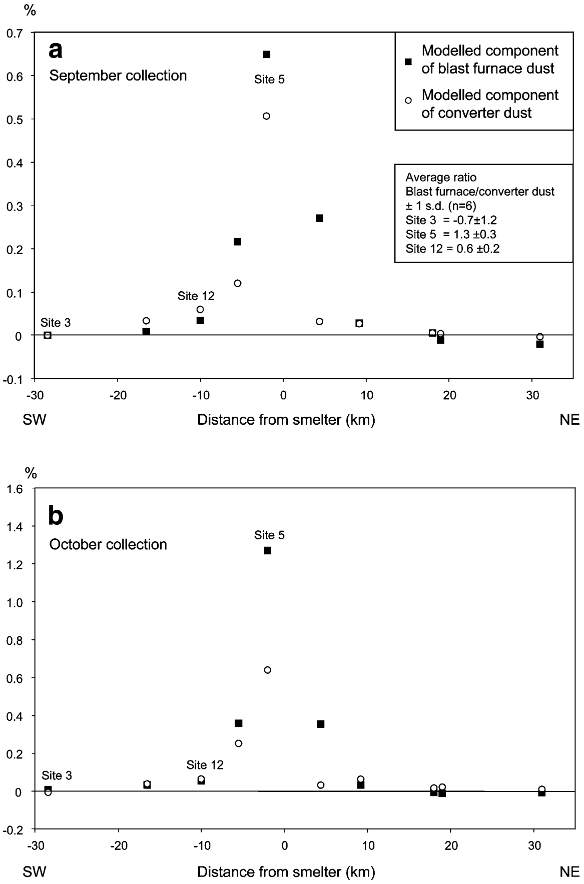

Fig. 5 Results of multi-element (Al, As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sn, Ti and Zn) least-squares modelling for **a** September and **b** October collections (see Materials and Methods)

The accuracy of the fit of the model to the measured elemental patterns of the lichen transplant samples can be visualised on Fig. 6, and has been further assessed by calculating the sum of squares of residuals. The residuals are the differences between the modelled and actual value for each element in the exposed lichen transplants. For the impacted site, the sum of squares of residuals is <3.6, which is low given that the model was carried out by mixing only 3 components. The largest residuals were for As, which was always lower in concentration (by around 4.5×) in the exposed lichen transplants compared with the modelled values. The reason for this is unclear, but it may relate to an analytical problem in the determination of As in the lichen transplants, where no lichen standard for As was available.

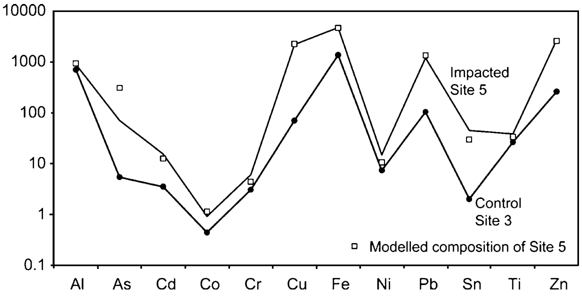

Fig. 6 Elemental profiles (ppm) for the average of replicates from site 3 (control) and site 5 (impacted, September collection), and the modelled composition for site 5 (98.1% site 3 composition; 1.3% blast furnace; 0.6% converter)

Results

Lichen transplants

Figure 2 shows data for the average (+/−1 s.d.) of 6 lichen transplants from the impacted (site 5) and control site (site 3, 30 km south of Karabash) collected in October 2001 after a 3 month exposure period. The profiles are for a wide range of elements, mainly for those considered as diagnostic of mining-related activities in the area, i.e. contained at relatively high levels in local ores and smelter emissions. Compared with the transplants from the control site, the impacted samples show higher levels of As, Cd, Co, Cu, Fe, Ni, Pb, S, Sn and Zn (Fig. 2). There is little difference in the Al, Cr, Sr and V and there is lower Mn. Compared with the average for the 'West Siberia background' (Fig. 2, Valeeva and Moskovchenko 2002), the control site transplants contain higher levels of Cd, Cu, Fe, Ni, Pb and Zn, and similar or lower levels of Co, Cr and Mn (no data available for As or Sn).

On the triangular diagram in Fig. 3a, the replicate transplants from the impacted site lie further towards the Cu apex compared with the control samples, with the intermediate site transplants between. The impacted site samples therefore have a relatively high ratio of Cu to Zn and Pb, compared with the control and intermediate samples. The impacted site samples also have relatively high total Pb (larger circle symbols).

The results of the least squares modelling to determine the relative signatures from the smelter blast furnace and converter in the elemental compositions of the lichen transplants are shown in Fig. 5a for September samples and 5b for October samples. The close fit of the model to the average lichen transplant composition from the most impacted site

(site 5, October) is shown in Fig. 6. The effect of the addition of signatures from other potential sources (road dust, tailings, slags, top soils) to the model was found to be less than the variation in the model using different lichen replicates, and was therefore considered to be negligible. From Fig. 5, it is clear that close to the smelter the signature of the blast furnace is dominant over that of the converter. Further from the smelter the converter signature dominates. Interestingly, to the NE, the modelled component from the blast furnace is negative.

To test the reproducibility of the lichen transplant method in source apportionment, the modelling was applied to 6 replicates from the impacted, intermediate and control sites. From the table in Fig. 5, there is good statistical separation of source signatures between sites, on a scale of >10 km between sample stations.

Air filter and stack samples

In Fig. 4a, the elemental profiles for stack samples from the smelter blast furnace and converter are compared with those of total suspended airborne particulate filter collections from Karabash town (data from Williamson et al. 2004b). The profiles of the downwind air filter samples are more similar in shape to the converter rather than blast furnace samples. This was verified by applying a least squares fit for the pattern of air filter KA6 by mixing the elemental profiles of the blast furnace and converter samples (using the multiple linear least-squares regression mixing model of Le Maitre 1979). The best fit for the model was for an 18 and 82% component of the blast furnace and converter samples, respectively. The closest fit for air filter KA84-88 was 100% converter.

On the triangular diagram in Fig. 3a, the blast furnace sample lies further towards the Cu apex compared with the converter sample. The converter sample lies closer to the composition of the TSP filters although offset towards the Zn apex.

Tailings, metallurgical slags, road dusts and top soils

Elemental patterns for tailings and metallurgical slags, representing other possible sources of particulate around Karabash, are shown in Fig. 4b and compared with the average pattern for transplants from the impacted site for reference. The patterns for the tailings and slags are very different to those of the lichen transplant material, most obviously on Fig. 4b in terms of Co:Cr and Cu:Fe ratios. On the ternary diagram in Fig. 3b, the metallurgical slags fall close to the Zn apex and the tailings near the Cu–Zn tie line.

The data for the road dusts in Fig. 3b fall between the composition of the metallurgical slags and that of the blast furnace sample, and possibly also the tailings. A component of metallurgical slag in the road dusts comes as no surprise as in the field it was noted that this material is being used to surface and possibly grit the roads. It is less likely, although not impossible, that tailings materials have accumulated on road surfaces. However, the tailings dumps are no longer in use and therefore relatively little is likely to have been spread by mechanical means onto nearby road surfaces. The road dusts may also contain a component from the blast furnace which is continuously being deposited across Karabash town.

The data for the top soils mainly falls in an array between the compositions of the blast furnace and converter samples. On Fig. 3, the top soil sample from near the impacted lichen transplant site falls closest to the point for the blast furnace whilst the sample from near the control site (about 5 km west of lichen site 11) falls closer to the composition of the converter sample.

Discussion

From similarities in the shapes of the elemental patterns of impacted lichens to the blast furnace and converter samples it is likely that these are the main sources for the ‘mining-related’ elements shown in Fig. 2. A major source from the metallurgical slags and tailings could not be identified, and if present their signatures appear to be swamped by those from the smelter. Estimation of a contribution from the road dusts is confounded as their signature appears to be dominated by that of the metallurgical slags, which are known to be used in their construction, and possibly deposition from the blast furnace.

A smelter source for ‘mining-related’ metals in the transplants is also evident from the triangular diagram in Fig. 3a. Data for the control, intermediate and impacted transplants lie on a trend, and contain higher Pb contents (larger circles), towards the composition of the blast furnace. This trend is clearly not in the direction of the smelter converter sample, metallurgical slags or road dusts. The blast furnace is therefore considered to be the dominant source. However, that the transplants do contain a more minor component from the converter is indicated by the lateral spread of data for each lichen transplant locality (replicates) towards the Pb apex, with increasing levels of Pb in this direction.

Least squares modelling was carried out to establish the relative proportions of components derived from the blast furnace and converter in the lichen transplants at different distances from the smelter. The signature from the blast furnace was found to be dominant in transplants within 10 km of the smelter. Deposition of blast furnace particles close to the smelter is likely to be due to their relatively large size. This was demonstrated in detailed SEM–energy dispersive X-ray studies of transplants from the impacted site (Williamson et al. 2004a) where Fe–Cu-rich blast furnace-derived particles were found to have a mean equivalent spherical diameter of 2.2 μm (1 s.d. 2.4). From studies of TSP filter collections from Karabash town, particulate from the converter are Pb–Zn-rich and have a smaller mean equivalent spherical diameter of 0.5 μm (1 s.d.=0.2). No Pb–Zn-rich particles were identified on the surfaces of the lichen transplants (Williamson et al. 2004a).

Further from Karabash (>10 km), the converter dominates the elemental signature of the transplants (Fig. 5), probably because many of the blast furnace particles had already deposited out. It may also reflect an increase in particle size of converter emissions during atmospheric transport, due to particle aggregation or hydration, leading to increased deposition.

The dominance of deposition from the blast furnace close to the smelter is also evident from soil samples. On Fig. 3b, soil from the impacted site falls close to the point for the blast furnace and that from the control closer to the converter composition. This is supported by SEM studies, where soils from the impacted site were found to contain numerous large, mainly 40 and 100 μm diameter, spherical Fe–Cu-rich blast furnace-derived particles (see Williamson and Croft 2001). No smaller Pb–Zn-rich particles derived from the converter could be identified.

An important outcome of the present study is that the TSP and lichen samples are not comparable in terms of the compositions (and size) of particles that they sample. Within Karabash town, the TSP filter collections almost entirely contained particulate derived from the converter, whereas the lichen transplants from the same area were dominated by blast furnace particulate. This strengthens the suggestion of Williamson et al. (2004a), from SEM studies of particles on the same set of lichen samples, that a paucity of Pb-rich surface materials on the transplants is due to the low capture efficiency of lichens for smaller, in this case converter-derived, particles. This highlights the caution that must be taken in the use of lichens to assess ambient air quality in human health studies.

An additional interesting observation from Fig. 5 is that to the NE of the smelter, in both the September and October samples, the modelled component from the blast furnace, and for September also from the converter, drops below the zero baseline. It therefore appears that the transplant material contains less from the blast furnace and converter than the control lichen starting material. This is unlikely to relate to uncertainties in the modelling as this pattern is repeated in several samples collected in both September and October. This trend would appear to indicate that the original lichen transplant starting materials at site 3 (Fig. 6) already contained a component from both the blast furnace and converter and that over the 2 or 3 month transplantation experiment there is a net loss of smelter-derived components. This strengthens, and broadens the finding of Spiro et al. (2004), using Pb isotopes for the same lichen material, that over the sampling period the Pb-containing components in the transplants from the control site were replaced. Lichen transplants may therefore provide a transient record reflecting a continuous gain and loss of environmental Pb, as well as other mining-related metals.

Conclusions

The current study has highlighted the dominance of the Karabash smelter as a source of atmospheric deposition of mining- and smelting-signature pollutants as far as 30 km from the smelter. The different smelting processes, those taking place in the blast furnace and converter, produce atmospheric emissions with very different physicochemical properties which are dispersed into the environment in contrasting ways. Deposition from the blast furnace, containing relatively high Cu and Fe, is mostly proximal (mainly

<10 km) compared with more distal deposition of more Pb–Zn-rich particles from the converter.

The use of the lichen transplant methodology in this study has illustrated the following issues relating to its implementation:

(1) Lichen transplant monitoring offers a quantitative methodology for assessing the percent source contribution of entrained components from major sources, at least over relatively short time periods. The method shows good reproducibility, in our example allowing site separation, in terms of source apportionment, over distances >10 km.
(2) The methodology shows size selectivity for entrained components and is therefore not ideally suited for monitoring studies where human respiratory health is being considered. It does however provide a sensitive and cost effective means of assessing environmental atmospheric deposition of pollutants over wide areas (e.g. Conti and Cecchetti 2001).
(3) Lichen transplants display a transient record of atmospheric deposition for the mining–smelting signature elements studied, which is useful in terms of the assessment of short term monitoring studies. However, because of this, lichens, at least *H. physodes* in the environment of the South Urals, may not retain signatures of past pollution events. This feature may however, be useful, if the reduction in atmospheric deposition due to e.g. the closure of a smelter, is being assessed.

We very much hope that this study will encourage future research and monitoring campaigns using lichen transplants, particularly in areas with different elemental source signatures, using other varieties of lichen transplants and new approaches to data analysis which are accessible by the increasingly diverse audience for such research.

It should be noted that in March 2007 a new "hi-tech and environmentally safe" Ausmelt Technology Copper Smelter was installed at Karabash (MEI-Minerals Engineering International 2007).

Acknowledgments BW, OWP, BS and VU were funded as part of the MinUrals project, a 3 year European Union INCO-Copernicus 2 contract (ICA2-CT-2000-10011). IM and OWP were funded by a Royal Society Joint Project Collaborative Grant with Russia (gt/fSU/JP). This article represents the views of the authors alone and not those of the European Community or Royal Society. The European Community and Royal Society accept no responsibility for the use of any data contained in this article.

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