

# Lead Isotopes in Lichen Transplants around a Cu Smelter in Russia Determined by MC-ICP-MS Reveal Transient Records of Multiple Sources

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Transplants of the lichen *Hypogymnia physodes*, which is relatively tolerant to SO<sub>2</sub> and heavy metals, were deployed for 3 months over a 60 km long SW–NE transect centered on a highly polluting Cu smelter and its adjoining town of Karabash, southern Urals, Russia. The abundance of <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb, and <sup>204</sup>Pb were determined by MC-ICP-MS. The measurement of <sup>204</sup>Pb revealed critical features, which would otherwise remain concealed: (i) The precise isotope ratios referenced to <sup>204</sup>Pb allowed several different sources to be resolved even within the small area covered: (a) the obvious pollutant source of the Karabash Cu smelter; (b) two dispersed sources, likely to include soil with lower and different contributions of thorogenic and uranium lead; and (c) one anthropogenic source with higher contribution of <sup>235</sup>U derived Pb. (ii) In part of the transect, the Pb isotope composition changed while the Pb concentrations remained the same. This indicates that the Pb content of the transplantation material from the background site was largely replaced and that the transplants provide a transient record reflecting a continuous accumulation and loss of environmental Pb, probably mainly in the form of extracellular particles. Overall, the method of lichen transplantation coupled with Pb isotope ratio determinations proved effective in assessing the usefulness of lichens in biomonitoring and in resolving different sources of atmospheric deposition.

## Introduction

Lichens such as *Hypogymnia physodes* are widely used to map spatial and temporal patterns of heavy metal fallout. They can tolerate and accumulate high levels (1) because these may be localized in extracellular regions where they do

not interfere with cellular processes. Lichens do not behave as inert recording gauges and like other plants; different species vary in their ability to accumulate specific metals. They may trap metals from soluble phases and insoluble particles in both wet and dry deposition and fix them within or on their thalli by various mechanisms, which in general are still little understood (2). As samples of native *Hypogymnia* may be sparse close to point sources due to high levels of pollution, the method of lichen transplantation is increasingly applied for biomonitoring (3). This technique implies that lichen samples are relocated from a “background” site representative of the region to monitoring stations.

Among the heavy metals emitted into the atmosphere during anthropogenic activities, lead has been recognized as posing a particular health hazard (4, 5). Lead in atmospheric particulates is derived from several primary sources dominated by metalliferous ores and from secondary sources dominated by leaded fuels and waste incineration, making source assessment often very difficult. However, the distinction between local anthropogenic, local natural sources, and background sources is often not trivial but necessary to plan effective abatement strategies. For example, a study of children from Broken Hill, Australia (the site of one of the world’s largest Pb mines), revealed that high blood Pb levels were not the result of the local mining but rather were derived from household paint and gasoline fumes (6).

A powerful method for the identification of the source of lead is based on the variations in the terrestrial relative abundance of its stable isotopes: <sup>206</sup>Pb derived from <sup>238</sup>U, <sup>207</sup>Pb derived from <sup>235</sup>U, <sup>208</sup>Pb derived from <sup>232</sup>Th, and non-radiogenic <sup>204</sup>Pb. Due to the differences in the geochemical behavior of uranium, thorium, and lead, such as mobility under various redox and pH conditions (7) and differences in half-lives of <sup>238</sup>U and <sup>235</sup>U (8), lead from different geological sources has particular relative abundances of the respective isotopes (9). Also, the relation between secondary sources and the original geological source of the Pb can be detected, as the isotope ratios are not significantly modified during low- and high-temperature geological and biogeochemical processes (10, 11). Therefore, the relative abundance of lead isotopes has become a powerful tool for the identification of its sources in environmental geochemistry (12).

However, during source assessment, environmental scientists often neglect to include the <sup>204</sup>Pb isotope due to the more widespread use of quadrupole-based ICP-MS (Q-ICP-MS) instruments in environmental research. Q-ICP-MS has the advantage of high sample throughput but often lacks the required precision to measure the <sup>204</sup>Pb isotope, which in turn can reduce the quality of the source assessment considerably (11, 13).

The potential of using lead isotopes in lichens to identify distinct sources of Pb from atmospheric sources was demonstrated before (11, 14–16). Carignan and Gariépy (11), for example, successfully identified the sources of atmospheric lead deposited in Québec using <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb. The large difference in ratios between the Abitibi ores processed at Noranda and the average Canadian and U.S. Pb emissions enabled the identification of lead derived from Noranda in lichen sampled about 400 km downwind. Another study of epiphytic lichens in western Canada (16) included 42 sampling points over an area 1800 km long. The <sup>208</sup>Pb/<sup>204</sup>Pb and <sup>206</sup>Pb/<sup>204</sup>Pb ratios fell within ranges delineated by the Canadian and U.S. anthropogenic sources, the ores from the Sullivan mine processed at Trail, BC, and a fourth natural end-member. This study demonstrated the value of including <sup>204</sup>Pb during source assessment and illustrated also

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the issue of the scale of sampling for resolving and identifying individual sources using Pb isotopes.

Given the potential of lichens to study atmospheric metal dispersal and of Pb isotopes to trace pollutant sources, we set up the present study to assess the potential of lichen transplants and high-precision Pb isotope measurements with MC-ICP-MS to trace the pollutant sources around a well-confined point source.

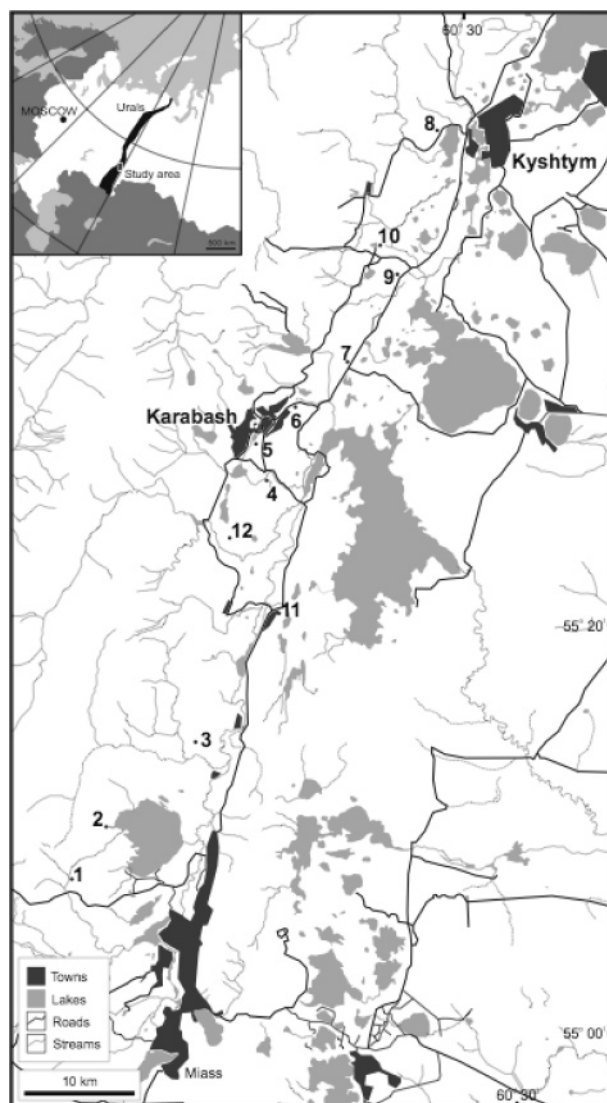
To achieve this, we employed lichen transplants along a short transect of 60 km centered on a Cu smelter in Karabash, Ural Mountains, Russia. The study was a part of a large EU-funded project (MINURALS), which aimed to assess lichen biomonitoring methods and instrumental techniques (15, 17–19). Heavy industrialization of the region in general and copper mining in particular increased at the beginning of the 20th Century. A population of ca. 16 000 lives within a radius of 4 km from the smelter. The town and its surroundings are affected by SO<sub>2</sub> emissions, fallout of metal-rich particulates, effluents from the smelter, leachates from waste dumps, and contaminated stream sediments. The smelter is the dominant visible source of anthropogenic airborne particulates in this area with additional potential contributions from tailings, waste dumps, roads, and domestic burning of coal and wood. The area is regarded as one of the most heavily polluted in the world (4). Previous studies of particulates (19) found the following Pb-bearing phases in the chimney dust and filters: PbSO<sub>4</sub> (anglesite), a Pb+As-rich variant of (Zn,Mn)SO<sub>4</sub>·H<sub>2</sub>O (gunningite), and small amounts of PbS (galena). SEM-EDX studies of lichen transplants near Karabash showed the accumulation of smelter-derived particles and removal of particles typical of the background sites (18).

## Material and Methods

Karabash lies at an altitude of ca. 200 m above mean sea level in a SW–NE trending flat-bottomed valley, surrounded by hills having an altitude up to 610 m. The area is extensively forested apart from small agricultural plots and the conspicuously de-vegetated western slopes of the nearby Karabash Mountain facing the smelter. The prevailing winds are generally parallel to the valley, but no detailed information is available.

A detailed description of the lichen transplantation method used in the present study is given elsewhere (15) and summarized here. Samples of *H. physodes* were collected at a background site (site 3, Figure 1) ca. 30 km SE of Karabash (4 km NE of Turgoyak lake) in early July 2001. The site consists of medium-aged mixed birch stand (*Betula pendula*/*Betula pubescens*). Transplants were placed at 10 sites situated > 150 m from roads spread along a 60 km traverse centered on the town of Karabash for the period of 2 and 3 months. The traverse (Figure 1) runs from Turgoyak Lake NW of the city of Miass along a stretch of ca. 30 km across town of Karabash, which contains the smelter, abandoned mine workings, and metalliferous waste dumps in which no natural thalli of *H. physodes* were detected, to within 3 km SW of the city of Kyshtym.

At each transplant site 10 lichen thalli were glued to the bark of six straight trees, 1 m above ground and facing the direction of the Karabash smelter. Five thalli from each of the six trees at each site were collected after 3 months (in October 2001). Samples were bulked (i.e., 30 thalli per sampling station) so as to provide sufficient material for the various analyses. In several sites aliquots from the individual trees were kept for replicate analysis among the six trees. In addition, native thalli were collected where possible (i.e., mainly beyond a radius of ca. 15 km from Karabash). All lichen samples were removed from the tree bark using a stainless steel knife and plastic gloves. The material was placed in blotting paper, allowed to air-dry, and transported



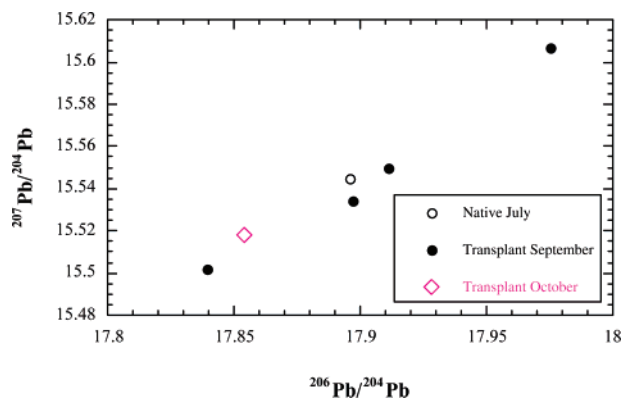
**FIGURE 1.** Map of the Karabash area, South Urals, Russia, showing the location of the Karabash Cu smelter and the adjoining town, the main physiographic features, and the sampling sites extending from the southwest near Miass to the northeast near Kyshtym.

to the laboratory in sealed plastic bags. Samples of chimney dust were obtained from the inner part of three different stacks of the Karabash smelter and were prepared using the same procedure as the lichen samples described below.

Samples were prepared for elemental and isotope analysis by digesting sample aliquots in HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HF in PTFE vessels using a closed vessel microwave MarsX system. Details of the procedures are given elsewhere (20, 21).

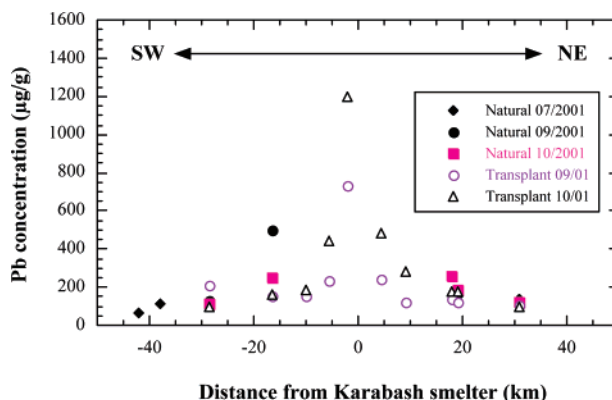
For element concentration determinations, samples were evaporated and then re-dissolved in 5 mL of 1 M HCl to ensure a constant chemically stable acid matrix for the subsequent analysis using a Fisons ARL 3508B ICP-AES (for Pb and Al) and a VG PQ3 Q-ICP-MS (for U and Th), both instruments based at the Natural History Museum. The detection limits for all elements were well below the lowest measured concentration encountered in the samples. Precision and accuracy were determined using certified standard lichen material (CRM 482) and were within 10% for all determinations. Full analytical details of the elemental determinations are given elsewhere (15, 21).

For the Pb isotope determinations, the solution was evaporated to dryness, and the precipitate was taken up in 2 mL of 2.4 M HCl. Lead was then separated from the sample



**FIGURE 2.**  $^{207}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios in samples of *Hypogymnia physodes* from site 3, the background site, including native sample collected in July 2001 (open circles) and transplant samples collected in September (closed circles) and October (open diamonds) 2001. Note: the terms native and natural are interchangeable.

matrix using a single column step with HCl at variable acid strengths (2.4 M for sample loading and 6 M for Pb elution from the columns) using an Eichrom Sr resin. The full details of the ion-exchange column chemistry are given elsewhere (13). Lead isotope analysis was carried out on a GVi IsoProbe MC-ICP-MS at the Natural History Museum/Imperial College London joint analytical facility (NHM/ICL JAF). Details of the procedures for mass spectrometry (regarding mass bias correction, blank contribution, error propagation, etc.) are given elsewhere (13, 22). The errors of the instrumental isotope ratio measurements, estimated by repeated measurements of the synthetic NBS 981 standard over a period of several months, were during the study period as follow (in ppm): 227 for  $^{206}\text{Pb}/^{204}\text{Pb}$ , 326 for  $^{207}\text{Pb}/^{204}\text{Pb}$ , 314 for  $^{208}\text{Pb}/^{204}\text{Pb}$ , 126 for  $^{207}\text{Pb}/^{206}\text{Pb}$ , and 292 for  $^{208}\text{Pb}/^{206}\text{Pb}$ . These errors were similar or slightly higher than the method or within-session instrumental reproducibility, respectively, achieved in our laboratory (for a detailed discussion of the errors, see ref 22). However, the most realistic uncertainty of the transplant method is determined by the variability of several transplants within each sampling site. Consequently, we estimated the variability associated with sampling of *H. physodes* in the study area by measuring four lichen transplant samples from a single site (Figure 2). Each one of these samples was prepared by bulking five individual thalli collected from each one of four trees at the background site (site 3) in September 2001. The overall variability was estimated as (expressed in ppm): 1400 for  $^{206}\text{Pb}/^{204}\text{Pb}$ , 1300 for  $^{207}\text{Pb}/^{204}\text{Pb}$ , 5000 for  $^{208}\text{Pb}/^{204}\text{Pb}$ , 427 for  $^{207}\text{Pb}/^{206}\text{Pb}$ , and 590 for  $^{208}\text{Pb}/^{206}\text{Pb}$ . Moreover, the isotopic ratios measured in one sample of native lichen collected in July 2001, four samples collected from four individual trees in September 2001, and one bulked sample collected in October 2001 fall within this range (Figure 2). The within-site variability in Pb isotope ratios determined during this study is similar to that obtained for Pb isotopes in moss samples analyzed by TIMS (23). It is noteworthy, however, that the variability within the single site follows the general trends of the Pb isotope ratio within the area; hence, these reflect the natural variability inherent to the sampling medium and sampling methodology. While this variability is not an analytical error and is much larger than the precision of the analysis of the standard reported above, this within-site variability has to be considered in the discussion and interpretation of the results and is given with the respective isotope ratios in the figures. The accuracy of the Pb isotope measurements was determined by repeated NBS981 Pb standard measurements during a measurement session and relative to the certified ratios reported by Galer and Abouchami (24). The average accuracy was below 100 ppm for all ratios reported here.



**FIGURE 3.** Concentration of Pb ( $\mu\text{g/g}$ ) in lichen collected from the SW to NE 60 km long transect centered at Karabash. Native lichen were collected in July, September and October in 2001 (natural 07/2001, natural 09/2001, and natural 10/2001, respectively). Transplants were deployed for 2 months (July–September 2001, transplant 09/01) and for 3 months (July–October 2001, transplant 10/01). The transplants deployed for 3 months and the background native samples from site 3 collected in July 2001 were used for Pb isotope analysis.

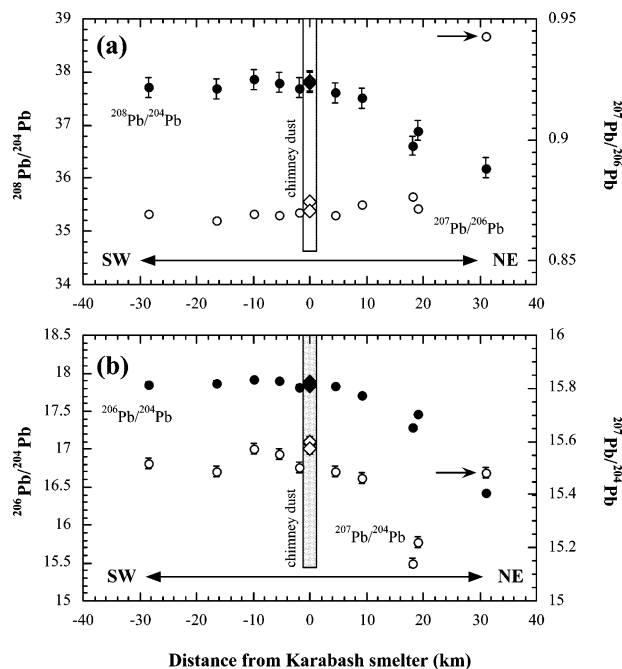
Lead concentrations of the NBS981 Pb standards and samples analyzed were matched to each other, and adjusted for each measurement session depending on the daily sensitivity. In general, the concentrations used were approximately 50 ng/mL, and approximately 0.6 mL of solution was used for 25 readings per block. We aimed to achieve a minimum signal of 100 mV for  $^{204}\text{Pb}$ .

## Results and Discussion

**Pb Distribution in Lichen Transplants.** Lead isotope determinations were carried out on bulked transplant samples deployed for 3 months, July–October 2001, from 10 sites along the 60 km transect and on three samples of chimney dust collected from the three main active chimneys of the Karabash smelter. Lead concentration data presented in Figure 3 include also data for samples of the native lichen along the transect and lichen transplants exposed for 2 months. The profile of Pb concentrations in the transplants exposed for 3 months shows a symmetrical decrease away from a maximum of 1200  $\mu\text{g/g}$  recorded near the smelter to a background level of around 150  $\mu\text{g/g}$ , following a “power-law” behavior indicative of emissions from a point source. This profile has systematically higher Pb concentrations than the transplant samples collected in September—exposed for 2 months. The native samples nearer to the smelter show Pb concentrations higher than the transplants while the transplants furthest away have similar Pb concentrations to the native lichens at the same sites. Natural samples collected in July 2001 at sites 1 and 2 (Figure 1) have Pb contents similar to those of the background site (site 3). Transplants nearest to the smelter showed visible cellular damage after 3 months of exposure. This observation was corroborated by chemical indicators to that effect, such as the loss of potassium (4), and defined the “impact zone” (15).

**Pb Isotope Ratios.** The isotope ratios  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  in all samples fall within relatively narrow ranges of 0.8764–0.8665 (with one high value of 0.9430, see discussion below) and 2.4182–2.4390, respectively, which correspond to those reported for airborne particulates in Russia and central Europe (25–27). This suggests that the Pb in atmospheric deposition within this large area is derived from a geologically common source having small isotopic variability and that gasoline lead, which is the major



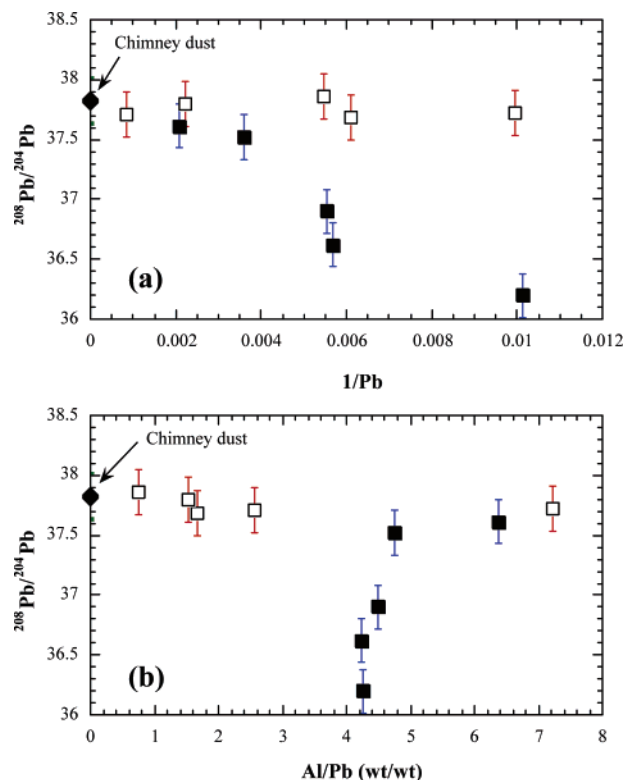


**FIGURE 4.** Profiles of Pb isotope composition of lichen transplants along the 60 km transect centered on Karabash as compared with the chimney dust from the smelter. Each lichen sample is bulked from five individual transplanted thalli from each of six trees. Error bars represent those measured from four samples taken from four trees at the background site 3 (see text for discussion). Shown are (a)  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  and (b)  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ . The isotope ratios are relatively constant in the SW and change NE of the smelter. The sample furthest to the NE (with arrow) has a distinctively high  $^{207}\text{Pb}$  concentration.

component of atmospheric long-range transport might also be derived from this source. However, within this compositional range significant variations exist, which are described below.

**Variations in Pb Isotopes along the Transect.** The profiles of lead isotope ratios in the lichen transplants along the 60 km long SW–NE transect (Figure 4) show a relatively constant value of  $^{207}\text{Pb}/^{206}\text{Pb}$  for the complete transect (0.8665–0.8764) similar to the chimney dust samples (0.870–0.874) except the last samples to the NE (site 8), which has a much higher ratio (0.9430). The  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios in the SW are similar to those of the chimney dust (37.807–37.832) while toward the NE this ratio decreases to 36.199. The ratios  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  follow the same trend except for the sample furthest to the NE (site 8), which has a high  $^{207}\text{Pb}/^{204}\text{Pb}$  value (15.485). These results suggest that Pb derived from the smelter, or a different source Pb having the same isotope signature, is the main component of atmospheric deposition trapped by lichen to the SW of the smelter. The isotopic composition of the chimney dust corresponds to that of massive sulfide ores of Urals deposits (28). However, to the NE there are sources that have different isotopic compositions.

These components are best discernible on the plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  versus  $1/\text{Pb}$  (Figure 5), which present two arrays. One array shows relatively constant  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios independent of  $1/\text{Pb}$ , with values around those of the chimney dust samples. The other array shows co-variation with  $1/\text{Pb}$  whereby at low Pb concentrations the  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio decreases to the value of 36.199, and at high concentrations of Pb, the  $^{208}\text{Pb}/^{204}\text{Pb}$  reaches that of the chimney dust samples (37.821). The near linear character of this array suggests a mixing of two end-members; one end-member being the chimney dust while the other has a low concen-



**FIGURE 5.** Plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $1/\text{Pb}$  in lichen transplants and chimney dust (a) showing that the isotopic composition in lichen transplants are independent of the Pb concentration in samples collected from the SW part of the transect (open quadrangles) but not in samples collected in the NE part (closed quadrangles). This suggests the presence of an additional dispersed Pb source in the NE of the smelter. The plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $\text{Al}/\text{Pb}$  of the lichen transplants and chimney dust samples (b) is showing that the isotopic compositions of lichens from the SW (open quadrangles) do not change with  $\text{Al}/\text{Pb}$  and are similar to the chimney dust. In the NE part (closed quadrangles), the  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio varies, while the  $\text{Al}/\text{Pb}$  remains largely constant with a  $\text{Al}/\text{Pb}$  (wt/wt) of about 4, indicating further the contribution of additional dispersed unknown source.

tration of Pb. The low Pb concentration indicates that it is a dispersed source and therefore not conspicuous in the field. It is noteworthy that the effect of this source seems to increase toward the industrial city of Kyshtym (Figure 1).

The dispersed nature of the source described above might suggest that it is associated with soil. As aluminum is a major element in soil, and its concentration in the chimney dust samples is low; the relation between these two parameters was tested. A plot of  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $\text{Al}/\text{Pb}$  (Figure 5) shows two trends, one in which the  $^{208}\text{Pb}/^{204}\text{Pb}$  is independent of  $\text{Al}/\text{Pb}$  and the other showing a decrease of  $^{208}\text{Pb}/^{204}\text{Pb}$  at  $\text{Al}/\text{Pb}$  (wt/wt) values of around 4. The second source, in the NE, seems therefore to contain Pb with  $^{208}\text{Pb}/^{204}\text{Pb}$  of 36.199 (or lower). In the NE part of the transect, where the  $\text{Al}/\text{Pb}$  ratio remains constant, the  $^{208}\text{Pb}/^{204}\text{Pb}$  changes, while where the  $\text{Al}/\text{Pb}$  increases, the  $^{208}\text{Pb}/^{204}\text{Pb}$  approaches the value of the chimney dust. One sample from the SW has the highest  $\text{Al}/\text{Pb}$  of all samples, but like the other samples from the SW part of the transect, it has a  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio similar to that of the chimney dust.

**Source Resolution.** The three isotope plots in Figure 6 of  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$  (a) and  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$  (b) reveal that the chimney dust has  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  of Ural type volcanogenic massive sulfide deposits as delineated by Tessalina et al. (28). This component has the highest ratios of  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$

and forms one end-member (end-member A). The composition of the chimney dust differs slightly from the lichen samples at Karabash, indicating that even here, there is an influence of other sources. The second and third end-members are identified by the different trends between the SW and the NE samples toward lower  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  on the respective diagrams, indicating a difference between the SW and NE parts of the transect (end-members B and C, respectively, Figure 6). These end-members are resolved better using  $^{208}\text{Pb}/^{204}\text{Pb}$  (see below and Figure 5). The end-members B and C differ also in their chemical nature: while B is simply a dispersed source of Pb, end-member C has a relatively constant Al/Pb ratio. The sample that has the lowest  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  has a higher  $^{207}\text{Pb}/^{204}\text{Pb}$  thus defining the fourth end-member, which is enriched in  $^{207}\text{Pb}$  derived from  $^{235}\text{U}$ . While the overall U/Th ratio decreases toward the NE (Figure 7), the high value of  $^{207}\text{Pb}/^{206}\text{Pb}$  indicates a source having a different U derivation (end-member D, Figure 6). Extension of the mixing lines between C, B, and A leads to values of around 18.8, 15.7, and 38.7 for  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  typical for natural airborne dust (29), and they are in accordance with modern upper continental crust (9). Altogether the three isotope plots of lichen transplants indicate contribution of four sources and possibly the background of natural airborne dust. Grain size analysis of aliquots (18) revealed a paucity of particles  $<2.5 \mu\text{m}$  in the lichen, while this particle size fraction was found to make up a considerable part of the

material collected on filters (19). This difference cannot be attributed to dissolution as Pb-bearing phases in the chimney dust were found to be poorly soluble (19). It is more plausible to relate the difference between particle size distributions on lichen surfaces and on filters to the mode of trapping; passive deposition versus pumping, resulting in a bias against the  $<2.5 \mu\text{m}$  fraction and an over-representation of the coarser fraction of particles trapped by lichens. Consequently, the results of Pb isotope composition studies indicate the presence of Pb derived from four or possibly five sources, but they do not provide a quantitative measure of their

**Lichen as a Transient Record of Atmospheric Particulates.** The present results provide an insight into the properties of the lichen *H. physodes* as a potential record of atmospheric deposition. The isotopic composition of Pb of the native lichen at the background site is similar to that of the chimney dust with a concentration of ca. 110  $\mu\text{g/g}$  (Figure 3). A transplant sample collected at the same site in October had a similar isotope ratio and similar concentration, within the variability of Pb concentration among replicate samples for that site during September 2001 (15). Hence no significant further (net) accumulation took place during this period, nor was there a change in isotope composition (Figure 2).

The results show that the concentration of Pb in the transplants changes as a function of the distance of the transplantation site from the smelter. The concentration profile is quite symmetrical, with a maximum of 1200  $\mu\text{g/g}$  near the smelter and reach concentrations of native lichen in the respective sites and background concentrations at a distance of ca. 30 km, thus providing a measure of the relative rate of deposition. The isotopic ratio  $^{208}\text{Pb}/^{204}\text{Pb}$  in the transplants varies along the transect. In the part of the transect SW of the smelter the values of  $^{208}\text{Pb}/^{204}\text{Pb}$  remain similar to those of the original transplant material and the chimney dust, while to the NE the value drops systematically with distance from the smelter. In the NE the transplants therefore acquire Pb with different isotopic composition. This indicates that the lead content of the lichen transplants was replaced within 3 months. It is not known, however, whether the replacement was total or partial.

That the transplants showed not a net accumulation but an exchange of Pb highlights the sensitivity of lichen transplants for monitoring atmospheric deposition, they do not act as accumulating traps but as dynamic systems perhaps reaching steady state. As the Pb isotope signature changed within a period of months while the concentration did not change, it is unlikely that significant proportions of the Pb content are fixed to organic molecules. Moreover, this study shows that it is not necessary to use transplant material having an initial very low Pb content. Lichen transplants differ from filter-based samplers in that they are not cumulative, they do not collect effectively particles of the size range  $<2.5\ \mu\text{m}$  (18) that can be collected on filters, nor are they calibrated against volume of air. They provide, however, a comparative measure of the rate of deposition. Furthermore, due to the relatively low cost and simple deployment, they allow a simultaneous and intensive monitoring and sampling.

The determination of Pb isotopes in the present study indicates that in addition to the dominant and visible point source of Pb (i.e., the smelter) (source A), the area of investigation is affected by two dispersed sources (sources B and C), which are less conspicuous. A fourth source was identified in a single sampling site (source D). A potential fifth source (E) has Pb isotopic composition corresponding to natural airborne dust or modern upper crust composition. In contrast to previous studies, in which features of airborne particulates trapped in lichen over a large area in the scale of several thousand kilometers were considered (11, 16), the present study investigated lichen transplants in a transect of 60 km dominated by a single visible source thus revealing other features of Pb records in lichens. The study showed that the method of transplantation combined with high-precision Pb isotope ratio determinations by MC-ICP-MS is sensitive to identify the contribution of different (potentially five) sources of Pb.

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## Supporting Information Available

One table showing a summary of concentrations and Pb isotope measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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