Environ. Sci. Technol. **2006**, *40,* 5319−5326

Dispersion of Heavy Metals (Metalloids) in Soils from 800-Year-Old Pollution (Mont-Lozère, France)

S. BARON,* J. CARIGNAN, AND A. PLOQUIN

CNRS−CRPG (Centre de Recherches Pétrographiques et Géochimiques), 15 Rue Notre Dame des Pauvres, BP 20, 54 501 Vandoeuvre-lès-Nancy Cedex, France

Numerous palaeo metallurgical sites ($n = 70$) characterized by slag presenting a homogeneous typology have been reported on the Mont-Lozère Massif (Southern France). These activities took place in the medieval period. The silicated slag matrix comprises mainly Pb (25%), Sb (0.4%), and several thousand parts per million of As, Cu, and Zn. Soil samples were collected in and around two sites, to understand the dispersion mechanism affecting the slag tailings through use of metal concentrations and lead isotopic compositions. The majority of polluted soil samples show high enrichment factors (EF) for Pb and Sb, slightly lower EFs for Cu, and much lower EFs for As and Zn. We show that this "old" metal pollution was physically dispersed, through erosion of workshop soils and slag tailings, in a restricted area (ca. 200 m down slope form the site). There is no evidence for massive leaching of slag metals by soil waters, except for Zn. Thus, the pollution is mainly due to the metal-making process, i.e., smoke-fallout, pieces of ore, the crackling of smelting ore outside the oven during reduction, and charcoal, etc. The lead isotopic compositions of the soils define a binary mixing trend between local granite or background soil and slag (which represent the workshop soil). Simple mass balance equations using either Pb isotopes or Pb concentrations suggest that between 40 and 100% of the total Pb in soils comes from the Medieval workshop pollution, leaving any later pollution negligible. The large number of sites on the Mont-Lozère means this medieval pollution is significant and poses a real environmental risk.

Introduction

Early metallurgists have exploited ore resources since before the Bronze Age, ~ 6000 years BP (*1*). During the Bronze Age and the Roman period, numerous Au, Ag, Sn, Cu and Pb deposits have been exploited such as those at Harz (Germany), Laurion (Greece) and the Rio Tinto mines (Spain). These are among the most important mines for Pb extraction in Europe.

The first important anthropogenic metallurgical impact on the environment occurred during the Roman period (*2*) and is clearly identified in archives such as ice cores (*3*) and peat bogs (*4*). Anthropogenic metallurgical impacts in the Medieval period are much less common and seem to have affected more restricted areas when compared to those of the Roman period (*5*). The Industrial Revolution, ~150 years BP, exhausted a significant amount of heavy metals compared to both Roman and Medieval periods. The Industrial Revolution marks the beginning of an era of worldwide systematic pollution, leading to high contents of anthropogenic heavy metals in natural reservoirs such as the atmosphere, oceans, groundwater, and soils (*6*).

According to their chemical forms in soils, different metals will have different mobility behavior. Recent studies (*7*, *8*) have shown that metals may accumulate in the top 30 cm of soils for a hundred years or more. In such soils, minor fractions of Cd and Zn may migrate through preferential pathways (earthworm's galleries) to a depth of ca. 2 m (*8*). Semlali et al. have suggested that the majority of or the entire Pb pollution in some soils may be inherited from old industrial activities (*9*). In this study, the isotopic composition of Pb was demonstrated to yield crucial information concerning the following: (i) the significance of enrichment factors, (ii) the different Pb sources, (iii) metal fluxes, mixing, and pathways, and (iv) the pollution history. This last point is of key importance in quantifying a given regional mine heritage, which is a problem with regard to the risk of contamination (*10*, *11*) and the responsibility of the polluters (*12*). Indeed, besides documenting the pollution history on a large-scale basis through the study of environmental archives, most studies (*13*, *14*) have focused on actual pollution problems.

Here, we report heavy metal(oid) concentrations (Pb, Sb, As, Zn, Cu) and Pb isotopic compositions of highly contaminated soils from the Mont-Lozère Massif, Southern France. The main intention is to document sources and dispersion processes of the different metals from ca. 800-year-old slag heaps produced by medieval metallurgical activities (*15*, *16*). This aims to demonstrate the importance of characterization and quantification of old (*pre*-Industrial Revolution) pollution in order to document and take into account the mining heritage at a regional scale relative to the impact of contemporary pollution. Furthermore, we would like to highlight the environmental risk of this old pollution, which occurs within a French National Park where activities such as fishing, hunting, pastoral practices, and tourism take place.

Setting

The study area is located on the Mont-Lozère Massif (MLM), in Cévennes Mountains of the Lozère Department, Southern France, and within the Cévennes National Park (PNC). More than 70 metallurgical sites comprising large amounts of slag have been reported within the MLM, suggesting that they formed the locus of Pb−Ag ore smelting in medieval times (Figure 1). The present-day vegetation around these sites reflects the environmental impact of these old metallurgical activities. The details of the historical and economical context of these medieval sites are reported elsewhere (*15*−*18*).

Materials and Methods

Soils Material. Soils from the 70 metallurgical sites mainly comprise arenaceous sands developed on the granitic basement. Two representative sites (3 and 8) were studied. On the downhill side of the sites, the slag heaps are apparent on the surface soil and have dispersed down slope toward a peat bog. Uphill, the slag and charcoal residues have been buried along with the metallurgical workshop soils. Site-3 soil samples were collected during archaeological excavations and site-8 soil samples during bore hole (35 × 40 cm)

---

* Corresponding author phone: +33(0)4-92-34-72-43; fax: +33-(0)3-83-51-17-98; e-mail: sbaron@crpg.cnrs-nancy.fr.

10.1021/es0606430 CCC: $33.50

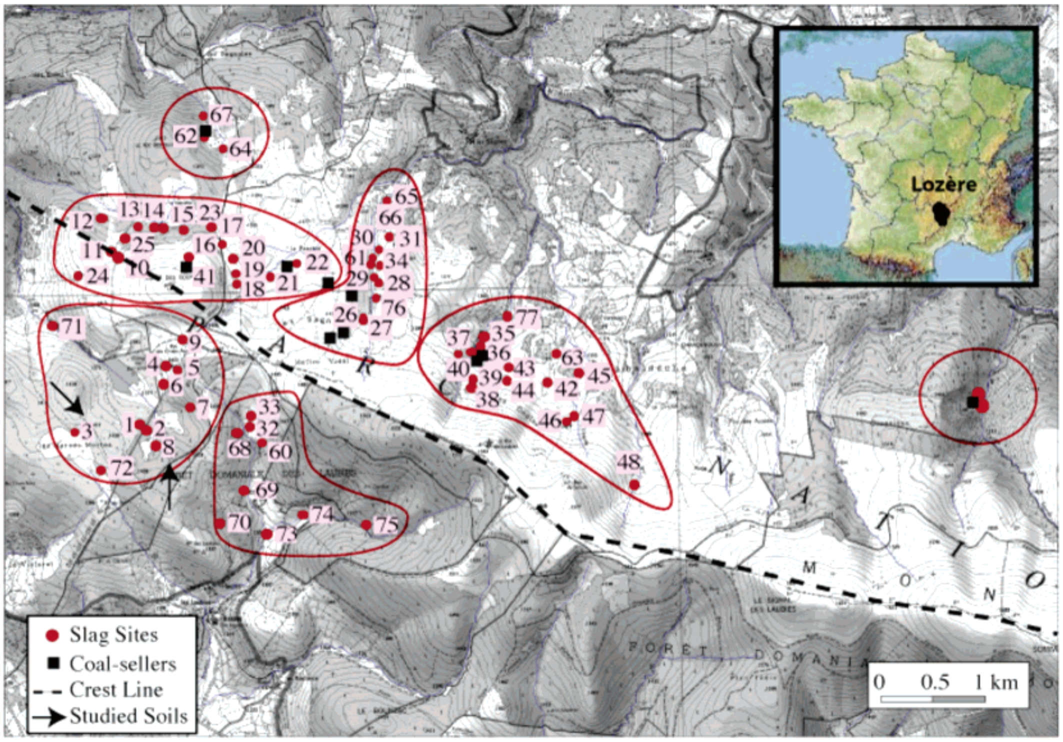

FIGURE 1. Map showing location of the study area within in the Cévennes National Park. The metallurgical sites mainly occur in the northern part of the MLM. Sites 3 and 8 are located in the south western part of the map.

prospecting. At both sites, archaeological black soils (i.e. workshop soils) and adjacent levels (above and under colluviums/in situ soil) were sampled. At site 8, samples were collected along a down-slope profile from within the slag area (but without archaeological level), to the nearby peat land. This profile is 200 m long. Another site-8 sample was collected from a slag-free position, perpendicular to the profile (ca. 20 m). These soils are colluviums from erosion uphill. Soils were transported to the laboratory in plastic bags and were dried at 30 °C during a 1 week period. All the analyses were performed on the <2 mm fraction. Each of the soil fractions were observed under a binocular microscope in order to remove any apparent slag fragments that might cause chemical "nugget effects".

Slag Material. Two main types of slag, black- and white-coated, occur at each site; more details are reported elsewhere (*16*, *17*). Slag samples were collected from within or near to both sites. The slag pieces were cleaned with distilled water and dried at room temperature. Furthermore, concentration profiles of some elements were undertaken across the altered glass surfaces of slag pieces. More details are reported elsewhere (*17*, *18*). As a result, the pieces then showed evidence of surface alteration, but some heavy metals (Pb, Sb) stayed mostly within the altered coating.

Granite Material. Three representative granites were sampled on the MLM in order to estimate the composition of the natural local background. More details are reported elsewhere (*15*).

Elemental Chemical Measurements. *Soils and Granites.* The elemental concentrations of metals were measured by ICP-MS and, for Al, ICP-AES as routine analyses performed by the SARM laboratory at CRPG (*19*). Alkaline fusion was used, and calibration and controls were done by analyzing international geological reference materials. According to the concentration range measured, uncertainties are lower than ±5% for all elements and samples. For the reported elements, the procedural blanks were negligible.

Slag Silicated Matrix. Each sample was crushed and pulverized in an agate mortar prior to analysis. For As analysis, samples were dissolved in a mixture of concentrated HF, HCl, and HNO_3 and the concentration was measured by graphite furnace atomic absorption spectrometry. For Zn, Cu, and Pb analyses, slag samples were dissolved in HF and $HClO_4$ and the concentrations were measured by flame atomic absorption spectrometry. In all cases, procedure blanks were negligible. These measurements were performed as routine analyses by the SARM laboratory at CRPG (http://www.crpg.cnrs-nancy.fr/SARM/index.html). Controls were done by analyzing international geological reference materials, and uncertainties are lower than ±5% for all elements and samples. Antimony was measured by electron microprobe at CRPG following the previously reported procedures (*17*). Slag matrix samples from sites other than 3 and 8 were also collected for analysis in order to estimate chemical heterogeneity.

Pb Isotopic Measurements. *Soil samples* were dissolved according to the protocol reported by Ariès (*20*). Lead was separated from the matrix by ion exchange using the AG1 X8 resin, as reported by Manhès et al. (*21*). Merck Suprapur or distilled reagents were used, and procedure blanks were always negligible. Lead isotopic compositions were measured with a MC-ICP-MS (GV Instruments) equipped with nine Faraday cups allowing simultaneous measurement of all Pb and Tl isotopes, and ^{200}Hg. NIST SRM 981 Pb and NIST SRM 997 Tl were used to correct for instrumental mass bias, according to the empirical technique used by Maréchal et al. (*22*) and reported by White et al. (*23*) for lead application. The correction is based on the relationship measured between Pb and Tl mass bias. Reference values used for both Pb and Tl reference materials were taken from Thirlwall (*24*). A Pb/Tl ratio of 10 was used for both the reference solution and samples. Repeated measurements of NIST SRM 981 Pb yielded recalculated values (using the Pb−Tl relationship) within the uncertainties of the assigned values, with the following standard reproducibility (2 standard deviations): better than 20 ppm for ^{208}Pb/^{206}Pb, 108 ppm for ^{207}Pb/^{206}Pb, 246 ppm for ^{208}Pb/^{204}Pb, 284 ppm for ^{207}Pb/^{204}Pb, and 251 ppm for ^{206}Pb/^{204}Pb. The external analytical uncertainty

TABLE 1. Heavy Metal Concentrations of Soils, Silicated Slag Matrix, and Granite (EF and LOI of Soils Also Reported)

sample ID	depth (cm)	LOI[a] (%)	mineral fraction (%)	colors	As	Cu	Pb	Sb	Zn	Al	EFAs	EFCu	EFPb	EFSb	EFZn
Soils 3															
BAR3.1		8.8	91.3	orange colored brown	22.8	359.9	7 760	91.38	407.8	9992 6	3	48	179	400	8
BAR3.2		25.1	74.9	dark brown	23.3	147.7	4 526	50.76	207	9156 3	3	22	114	242	4
BAR3.3		11.9	88.1	brown	21.9	161 7	15 705	113.6	285.2	9226 0	3	234	392	538	6
BAR3.4[b]		14.8	85.2	brown	324.5	290 7	150 235	2 535	6 561	5961 2	73	650	5 803	18 584	219
BAR3.5		7.9	92.1	orange colored brown	29.2	260.2	9 208	156.1	458.1	9767 4	4	36	217	698	9
BAR3.6		12.1	87.9	brown	47.7	368.4	13 912	241.8	617	9762 1	7	50	328	1 082	13
BAR3.7[b]		25.9	74.1	black-brown	181.4	5 376	72 296	898.4	1 036	7290 7	33	983	2 283	5 385	28
BAR3.8[b]		22.3	77.7	dark gray	310.4	6 460	19 2167	174 9	2 376	5253 6	79	1 639	8 422	14 549	90
Soils 8															
bore A															
BAR8.16	10–30	16.8	83.2	Brown	87.2	652.3	14 473	268.6	1 914	7912 6	15	110	421	1 483	48
BAR8.17[b]	30–40	34.6	65.4	black	471.7	3 280	14 2514	2 043	2 030	3452 4	182	1 267	9 505	25 861	117
BAR8.18[b]	40–45	63.1	36.9	dark brown	39.8	3 485	79 266	345.9	122.2	2294 4	23	2 025	7 954	6 588	11
BAR8.19	>45	10.4	89.6	gray	16.8	622.6	8 832	56.3	159.4	7993 0	3	104	254	308	4
bore B															
BAR8.01	35–65	18.5	81.5	bright brown	21.1	16.93	55	1.404	88.45	9933 6	3	2	1	6	2
BAR8.02	0–35	27.9	72.1	dark brown	15.3	32.98	524	5.312	99.28	7724 9	3	6	16	30	3
bore C															
BAR8.03	15–40	10.3	89.7	bright gray	20.8	350.8	3 384	23.75	283	8078 8	3	58	96	128	7
bore D															
BAR8.05	0–20	8.9	91.1	brown	72.0	541.8	16 953	300.5	3 093	8277 1	12	87	472	1 587	74
BAR8.04	20–45	6.9	93.1	bright brown	26.5	376.8	3 737	34.91	531.5	1026 60	3	49	84	149	10
bore E															
BAR8.06[b]	8–18	27.3	72.7	dark gray	59.1	1 105	26 933	257.7	1 033	6953 0	11	212	892	1 620	30
BAR8.07[b]	18–45	39.2	60.8	dark gray	52.8	1 242	29 658	276.4	727.1	5784 3	12	286	1 181	2 088	25
bore F															
BAR8.10	5–10	20.2	79.8	dark brown	21.7	301	7 536	99.9	632.6	7456 9	4	54	233	585	17
BAR8.09[b]	10–15	27.0	73.0	dark brown	44.3	908.9	15 202	238.5	827.3	7226 4	8	168	484	1 442	23
BAR8.08	15–45	7.6	92.4	yellowish gray	10.7	148.8	1 650	10.3	180	9837 1	1	20	39	46	4
bore G															
BAR8.11	0–30	16.1	83.9	brown	30.8	732.9	72 52	80.47	523.1	8507 6	5	115	196	413	12
BAR8.12	30–45	15.2	84.8	brown	20.4	345.5	3 634	33.77	263.4	8550 5	3	54	98	173	6
bore H															
BAR8.13		24.5	75.5	very dark brown	16.2	95.13	1 382	16.9	149.5	7671 3	3	17	41	96	4
BAR8.14 (duplicate)		25.0	75.0	very dark brown	18.2	87.23	1 436	19.68	152.4	7623 1	3	15	43	113	4
BAR8.15 (triplicate)		24.8	75.2	dark brown	15.9	87.39	1 171	13.97	145.8	7660 6	3	15	35	80	4
bore K															
BAR8.20	6–45	9.6	90.4	yellowish gray	17.1	28.82	176	3.124	181.5	9360 0	2	4	4	15	4
Granites															
C		1.1	98.9		7.8	<ld[c]	31	0.14	45.0	7832 2					
F		0.7	99.3		6.8	6.15	35	0.14	37.8	7944 7					
G		0.7	99.3		6.6	5.65	36	0.26	35.9	7821 4					
mean					7.1	5.90	34	0.18	39.6	7866 1	1	1	1	1	1
Slags															
SO m 7				vitreous black	140	1 205	265 000		1 000						
SO m 60.S 3				vitreous black	260	1 750	231 000	3 900	18 000						
SO m 22				vitreous black	295	1 665	90 000		55 500						
SO m 18				white coated gray	115	2 265	291 000		600						
SO m 5″				white coated gray	375	2 015	296 000		2 800						
SO m 45				vitreous black	230	2 670	110 500		59 200						
SO m 3′				vitreous black	295	1 935	442 000	3 900	12 100						
SO m 3′				white coated gray	820	1 800	382 000		22 600						
SO m 8				vitreous black	290	2 430	183 000		41 400						
median					290	1 930	265 000		18 000						

[a] Loss on ignition. [b] Workshop soils. [c] Limit of determination (ld) is 5 ppm for Cu.

TABLE 2: Lead Isotopic Composition of Soils, Granite, and Slags

sample ID	208Pb/206Pb	207Pb/206Pb	206Pb/207Pb	208Pb/204Pb	207Pb/204Pb	206Pb/204Pb
Granites[a]						
C	1.9622	0.8009	1.2486	38.544	15.733	19.644
F	1.9911	0.8131	1.2298	38.506	15.725	19.339
G	1.9783	0.8085	1.2368	38.483	15.728	19.453
Soils[b]						
site no. 3						
BAR3.1	2.0891	0.8465	1.1813	38.667	15.671	18.511
BAR3.2	2.0891	0.8466	1.1812	38.670	15.676	18.515
BAR3.3	2.0866	0.8466	1.1812	38.625	15.672	18.511
BAR3.4	2.0888	0.8464	1.1814	38.660	15.666	18.508
BAR3.5	2.0897	0.8466	1.1812	38.713	15.683	18.526
BAR3.6	2.0900	0.8467	1.1811	38.681	15.670	18.507
BAR3.7	2.0896	0.8466	1.1812	38.674	15.669	18.508
BAR3.8	2.0896	0.8466	1.1812	38.645	15.663	18.499
site no. 8						
bore A						
BAR8.16	2.0938	0.8482	1.1790	38.665	15.672	18.474
BAR8.17	2.0949	0.8486	1.1785	38.689	15.672	18.468
BAR8.18	2.0949	0.8486	1.1784	38.668	15.671	18.464
BAR8.19	2.0944	0.8485	1.1786	38.665	15.672	18.468
bore B						
BAR8.01	2.0304	0.8218	1.2169	38.747	15.690	19.090
BAR8.02	2.0893	0.8465	1.1814	38.660	15.669	18.509
bore C						
BAR8.03	2.0962	0.8485	1.1786	38.781	15.700	18.503
bore D						
BAR8.04	2.0919	0.8477	1.1796	38.621	15.656	18.467
BAR8.05	2.0941	0.8483	1.1788	38.681	15.672	18.473
bore E						
BAR8.06	2.0940	0.8483	1.1788	38.662	15.671	18.470
BAR8.07	2.0940	0.8483	1.1788	38.662	15.671	18.470
bore F						
BAR8.08	2.0919	0.8474	1.1800	38.679	15.673	18.493
BAR8.09	2.0932	0.8481	1.1792	38.661	15.670	18.475
BAR8.10	2.0934	0.8480	1.1792	38.664	15.671	18.477
bore G						
BAR8.11	2.0934	0.8481	1.1792	38.676	15.676	18.482
BAR8.12	2.0936	0.8481	1.1792	38.673	15.670	18.476
bore H						
BAR8.13	2.0918	0.8473	1.1802	38.674	15.667	18.490
BAR8.14	2.0921	0.8475	1.1800	38.676	15.676	18.494
BAR8.15	2.0915	0.8472	1.1803	38.712	15.688	18.515
bore K						
BAR8.20	2.0774	0.8411	1.1889	38.693	15.667	18.626
Slags[c]						
site 3[d]	2.0922	0.8472	1.1804	38.776	15.701	18.534
site 3′[d]	2.0898	0.8467	1.1810	38.670	15.668	18.504
site 8	2.0938	0.8482	1.1789	38.682	15.670	18.474

[a] Accuracy and uncertainties of granites are reported elsewhere (ref *15*). [b] Accuracy and uncertainties of soils are reported in the manuscript. [c] Accuracy and uncertainties of slags are reported elsewhere (ref *16*). [d] Sites 3 and 3′ are one site, an accumulation of slags having let down the natural slope and giving "another site" (site 3′).

($n = 16$) of a given sample is 136 ppm for ^{208}Pb/^{206}Pb, 114 ppm for ^{207}Pb/^{206} Pb, 451 ppm for ^{208}Pb/^{204}Pb, 431 ppm for ^{207}Pb/^{204}Pb, and 380 ppm for ^{206}Pb/^{204}Pb.

Pb isotopic compositions of slag samples were determined by dissolving lead spherules and analyzing the samples directly without Pb purification. These data, along with those on granites, are reported elsewhere (*15*, *16*, *18*).

Results

Concentrations. The different slag samples present a wide range of elemental composition (Table 1). Thus, the median concentration value for each element was used for mass balance calculations: 290 ppm for As, 1 935 ppm for Cu, 265 000 ppm for Pb, and 18 000 for Zn. Although Sb was measured in only two samples, its content is relatively constant (0.39%) and will be considered as representative.

The soils exhibit very high metal contents over a wide range of values according to their sampling location (Table 1). The highest concentrations of metals analyzed are found in black and dark-brown colored soils. The latter were buried and charcoal-rich and are associated with slag and furnaces (site 3), suggesting that they were the medieval workshop soils, defined as "occupation soils" where medieval smelting took place. These soils were exposed to the load of smelters and integrated materials from smoke-fallout, sorting of ore pieces, smelting ore crackling outside the ovens during reduction, and charcoal, etc. (*18*). There is no relationship between loss on ignition (LOI) values (volatile contents including CO_2, and organic matter) and heavy metal contents, suggesting that the metals are not directly associated to organic matter (charcoal) in these soils. Rather, the metals must mainly occur as mineral species. The BAR8.01 sample of bore B (Table 1), located outside the polluted area, yielded concentrations slightly higher than those found in local granites. For example, the latter have an average Pb content of 34 $mg \cdot g^{-1}$, whereas the BAR8.01 sample yielded 55 $mg \cdot g^{-1}$,

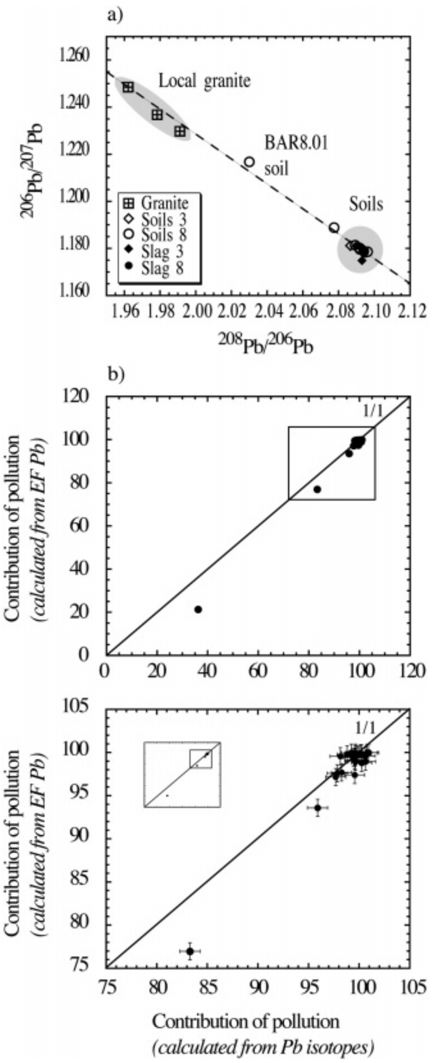

FIGURE 2. (a) ^{206}Pb/^{207}Pb vs ^{208}Pb/^{206}Pb ratio of soils, granites, and slag; (b) percentages of metallurgical Pb in soils calculated from EF Pb and from Pb isotopes. The solid line is the 1:1 correspondence.

suggesting that ca. 40% of Pb measured in BAR8.01 would be in excess relative to local crustal values.

On the whole, the heavy metal contents of soils studied here show some concentrations in the same order of magnitude as soils polluted by modern anthropogenic activities (*25*).

Lead Isotopic Composition of Slag, Soil, and Granite Samples. The lead isotopic compositions of slag, soils, and granites are reported in Table 2.

The average lead isotope ratios of slags 3 and 3′ are 1.1807 ± 0.0004 and 38.723 ± 0.075 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{204}Pb, respectively. Slag 8 yielded lead isotopic values of 1.1789 and 38.682 for the same ratios. Indeed, the two slag samples from site 3 have different isotopic compositions that cover almost the entire range of composition found for samples from 25 other sites (*16*). Workshop soils from sites 3 and 8 have lead isotopic compositions very similar to those measured in slag, with ratios of between 1.1784 and 1.1814 and 38.645−38.689 for ^{206}Pb/^{207}Pb and ^{208}Pb/^{204}Pb, respectively. Thus, the workshop soils are equivalent to slag from the medieval pollution. Three samples of local granite yielded the highest ^{206}Pb/^{207}Pb and ^{208}Pb/^{204}Pb ratios with values ranging from 1.2298 to 1.2486 and 38.483 to 38.544, respectively. In a conventional common Pb space diagram (Figure 2a), all the samples analyzed form a linear array suggesting overall simple mixing between different sources of Pb. These are the local crustal Pb (granites) and the medieval pollution Pb (slag). The BAR8.01 soil, located outside the slag area, has an intermediate position in the Pb−Pb diagram of Figure 2a, suggesting that ca. 40% of its Pb comes from Medieval workshop materials, as supported by its Pb concentration.

Discussion

Enrichment Factors in Soils. To document the anthropogenic contribution in soils for a given metal, we used the enrichment factor (EF) expression (*4*). For a given soil, the heavy metal content is normalized to that of Al, a conservative element relative to silicate crustal materials, to calculate the enrichment factors according to the following equation:

$$\mathrm{EF} = \left(\frac{[\mathrm{X}]_{\mathrm{soil}\lambda}/[\mathrm{Al}]_{\mathrm{soil}\lambda}}{[\mathrm{X}]_{\gamma}/[\mathrm{Al}]_{\gamma}}\right) \qquad (1)$$

where [X] is the concentration of given heavy metal in a given soil (soil λ) or in the granite (γ). The mean concentration of the three granites was used as the reference. Calculated metal EFs in soils present a wide range of values which are reported in Table 1. These are 16−9505 for Pb, 4−182 for As, 4−219 for Zn, 15−25861 for Sb, and 4−2025 for Cu. The decreasing order in EF is Sb, Pb, Cu, Zn, and As. Thus, all the heavy metals found in the studied soils are in excess relative to the local background granite.

Relationships between Heavy Metal Concentrations. *Slags.* There is no systematic difference in metal contents measured in vitreous black slag and white-coated slag. There is also no systematic correlation between metal concentrations except for Zn and Pb, where a somewhat inverse relationship may be evoked. The two slag samples from site 3 fall outside the trend defined by all the other samples. Also, the heterogeneity of the supplied ores might directly explain that of the different slag samples. The slags are heterogeneous in composition, but they define coherent and restricted very high metal content reservoirs compared to natural soils.

Soils. As, Sb, and Cu contents correlate well with Pb, with correlation coefficients (R^2) of 0.82, 0.88, and 0.78, respectively (Figure 3). Zn and Pb contents are less well correlated ($R^2 = 0.46$). Except for Cu, all the data points fall between the field determined for "slag and workshop" compositions and the local soil sample and granite samples. The mixing curves shown in Figure 3 were derived from the median composition of slag and either that of the soil situated outside the polluted area (BAR8.01, "background soil" on the studied area) or the average local granite (three samples). The BAR8.01 soil yielded higher metal concentrations than those measured in the local granites, probably because all the soils were polluted by Medieval fumes prior to the dispersion of the metallurgical workshop materials (see Results section of Concentrations). The most realistic composition for the "low metal" end member certainly falls between the granite and soil fields. The curves model simple physical mixing between soils and slag. Due to the fact that the slag field may be large for some metals, the soil data fit the simple model relatively well, suggesting that physical dispersion of slag is the dominant process. We suggest that the large field for slag is related to the fact that individual slag grains were analyzed. However, it would be surprising if the true average slag composition fell at an extreme measured composition. For this reason, the median concentrations were used to calculate the model mixing curves. Nevertheless, there is still a problem with Cu, the soils being more enriched than both the model curves and the slag field by a factor of 2−10. This means that the composition of slag is not representative of the workshop materials, which contain more Cu (Figure 3). Of all, data from the Sb−Pb relationship best follow the model mixing curves. This confirms the fact that Sb and Pb are both retained

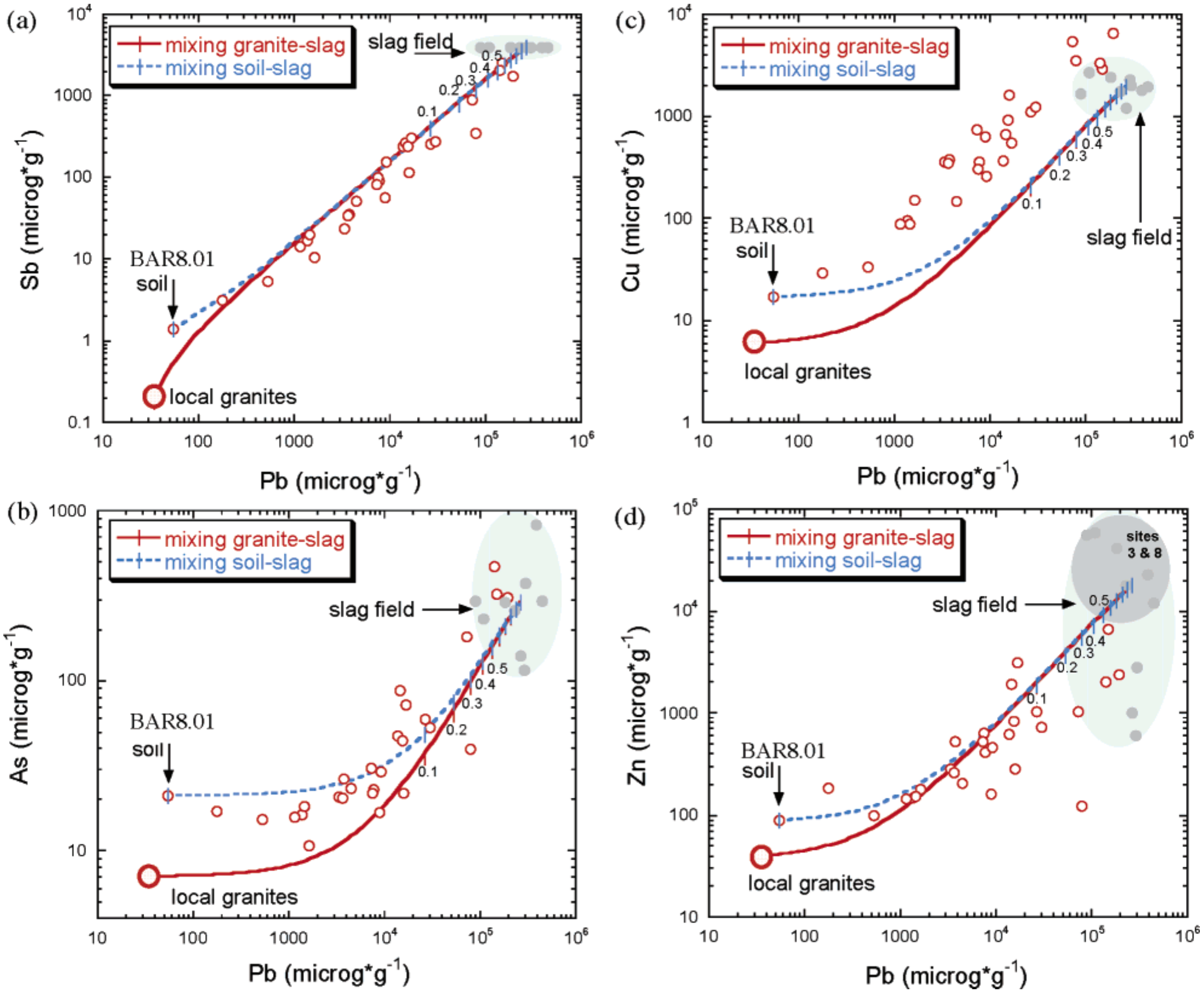

FIGURE 3. Relationship between heavy metals (metalloids) and Pb concentrations in slag and soils: (a) Sb vs Pb, (b) As vs Pb, (c) Cu vs Pb, and (d) Zn vs Pb. The solid and dashed lines define simple mixing models between local granite or the BAR8.01 soil, respectively, and the median values for slag (gray area). The numbers along the mixing curves are the amount of slag materials in mass percent.

in the altered rim of slag pieces so that leaching of these elements by soil water is minimal. On the other hand, many data points plot below the model mixing curves in Zn−Pb space (Figure 3), suggesting that Zn was preferentially removed by soil solutions. Sb is associated with sphalerite, pyrite, and galena type ores such as those that fed the medieval smelters. The boiling points of these elements are quite similar (1587 °C for Sb and 1479 °C for Pb), so it is not surprising to find them in slag. Also, the behavior of Pb and Sb in soils at surface temperature may be similar. Their concentration collinearity in bogs and peat bogs (*26*, *27*) suggests near immobility for periods as long as a few thousand years. As for lead oxide phases found in the altered coating of slag, oxidized Sb in acidic environments, like the Mont Lozère soils, should form stable Sb oxide minerals (*28*). Furthermore, Tighe et al. (*29*) showed that nearly all the Sb^V added to an acidic soil ($pH < 6.5$) was retained by either iron hydroxides or humic acids. This is probably why some authors have found that Sb is not included in the vegetation cycle (*30*) nor involved through the fauna barrier (*31*).

Despite the Zn content heterogeneity measured in slag, some soil samples suggest a Zn deficit relative to Pb. Indeed, many studies have reported a higher mobility for Zn than Pb (mineral forms) in various types of soils (*32*−*34*) and at least a different behavior (*8*). Metal inventories in soils close to important smelting activities in Finland strongly suggest postdepositional Zn migration (*35*, *36*). Zn mobility through soil water might then readily explain the deviation of the data points from the model mixing curve in Figure 3d.

Lead Isotopic Compositions. Slag and soil data form a single trend in the $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$ diagram (Figure 2a), suggesting binary mixing between natural source (granite) and metallurgical Pb, the soil representing the local background having an intermediate composition. Medieval Pb was probably introduced to the soil BAR8.01 by the fumes generated by the smelting activities at the time. The most polluted soils from both sites define a restricted field in the Pb−Pb isotope diagrams (Figure 2a) in which their respective slag is included. As reported by Baron et al. (*16*), the Pb isotopic composition of slag represents the average composition of supplied ore materials, which are more heterogeneous in composition. Metallurgical workshop materials must have been even more heterogeneous in composition because they certainly comprised fumes fallout, pieces of ore sorting, ore materials crackling outside ovens during reduction, and coals, etc. This may explain why these soils are slightly more heterogeneous in Pb isotopic composition than the related slag (Figure 2a).

Contribution of Metallurgical Pb in Soils. There are two available ways to estimate lead source mass balance in soils. If anthropogenic and natural sources contribute equally to the metal content of a given soil, then EF = 2. The contribution of the anthropogenic sources may be expressed by

$$\text{Contribution of pollution Pb} = \left(\frac{\mathrm{EF_{Pb}} - 1}{\mathrm{EF_{Pb}}}\right) \times 100 \qquad (2)$$

where EF is the enrichment factor for a given soil.

The Pb contribution of the anthropogenic sources may be determined independently by using lead isotopes according to

$$\text{Contribution of pollution Pb} = \left(\frac{(\mathrm{R.Pb})_{\mathrm{soil}} - (\mathrm{R.Pb})_{\gamma}}{(\mathrm{R.Pb})_{\mathrm{slag}} - (\mathrm{R.Pb})_{\gamma}}\right) \times 100 \qquad (3)$$

where $(\mathrm{R.Pb})_{\mathrm{soil}}$ is the Pb isotopic ratio of a given soil sample, $(\mathrm{R.Pb})_{\mathrm{slag}}$ is the Pb isotopic ratio of a given related slag sample, and $(\mathrm{R.Pb})_{\gamma}$ is the Pb isotopic ratio of the granitic background. The $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ ratio was used in the calculations.

The percentages calculated with both eqs 2 and 3 are in close agreement such that most values are close to the 1:1 line in Figure 2b. Between 40 and 100% of the Pb measured in soils is from anthropogenic sources, more than 95% for most soils. The least polluted soil (40%) was collected from bore B, distant from the soil workshops (BAR8.01 soil). The most polluted soils (100%) are the workshop soils as described above. Values calculated using Pb isotopes are more scattered and may exceed 100% simply because some soils have lower $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ than the related slag. On the contrary, the Pb concentration in slag is much higher than that in soils, so that no values calculated with EF can exceed 100%. Regardless, the correlation indicates a relationship between element contents and lead isotopic compositions that suggests a simple slag−granite mixing system. It confirms that the metal pollution source came from medieval metallurgical activities.

Contribution of Products from Workshop Soils. A simple mass balance equation may also constrain the mass percentage of workshop materials needed in a given soil to explain its metal contents. According to the results obtained from Pb concentrations and isotopic compositions, one may postulate that the concentration of other metals resulted from a similar simple mixing between metallurgical products (represented by slag compositions) and the local "background" soil or granite, as suggested by the diagrams of Figure 3.

Accordingly, metallurgical products may contribute <0.1‰ to 72% (in mass) to explain the Pb content in soils (Figure 3). Soils with the highest lead content are workshop ones. Pb and Sb yielded very similar values of workshop material contributions to soils, suggesting that these two elements were mainly dispersed through erosion of slag heaps since the Medieval period, though some leaching from soil water, cannot be excluded because Medieval Pb was found in the vegetation of site 8 (*18*). However, more than 25% of the soil samples suggest a "deficit for workshop materials contribution" when Zn concentrations are used for calculations. This may be explained by the higher mobility of Zn compared to Pb, Sb, and probably As, as stated earlier when discussing the concentration relationships. On the contrary, all calculated contributions using Cu for concentrations yielded systematically higher values (including more than 100%) than the ones obtained with Pb. Thus, the old metallurgists probably sorted the ores before smelting operations. Indeed, some pieces of chalcopyrite, separated from Pb ore before smelting, were found in some sites. During the smelting process, iron and copper sulfides may produce "matte" (or "speiss" if As rich) resistant to smelting so that copper sulfides−iron sulfides were previously removed before charging the furnace. The fact that Cu values form a well-defined linear array in Figure 3 suggests that Cu was also dispersed physically in surrounding soils.

This "old" metal pollution is physically dispersed, through soils and slag tailings erosion, in a restricted area, and there is no evidence of massive leaching of metals by soil waters. However, the large number of sites on the MLM means this medieval pollution is significant and likely has a strong impact on the surrounding environment. Further studies are necessary in order to asses if this important medieval pollution has passed over the fauna barrier; thus, some sampling (of trout) has already been carried out on the MLM. Heavy metal speciation studies on these medieval workshops soils will be indispensable in order to understand the modalities of heavy metal integration by the fauna.

Acknowledgments

This work was funded by ADEME (the French Environmental Agency) and by Languedoc-Roussillon Region grants. All the analyses were supported by CRPG (Centre de Recherches Pétrographiques et Géochimiques) and SARM (CNRS), in Nancy. Many thanks to Etienne Dambrine (INRA, Nancy) for help with the soil science. We thank the CERL of Mende and Capucine Crosnier from the National Park of Cévennes (PNC, Florac) for her assistance. Thanks to the "Saint-Etienne du Valdonnez" commune and its mayor, Claude Feybesse, for his technical support during fieldwork and his good reception. Special thanks to Jean Peytavin. We also thank the SRA for supporting the "Programme Collectif de Recherche" entitled "Plomb ancien du Mont-Lozère". This work is included in this PCR, all of the members contributing to a multidisciplinary approach. Thanks to Alice Williams for English corrections. This is CRPG contribution No. 1789.

Literature Cited

(1) Patterson, C. C. Native copper, silver, and gold accessible to early metallurgists. *Am. Antiq.* **1971**, *36* (1), 286−321.

(2) Settle, D. M.; Patterson, C. C. Lead in Albicore: Guide to lead pollution in Americans. *Science* **1980**, *207*, 1167−1176.

(3) Rosman, K. J. R.; Chisholm, W.; Hong, S.; Candelone, J. P.; Boutron, C. F. Lead from Carthaginian and Roman Spanish mines isotopically identified in Greenland ice dated from 600 B.C. to 300 A.D. *Environ. Sci. Technol.* **1997**, *31*, 3413−3416.

(4) Weiss, D.; Shotyk, W.; Appleby, P. G.; Kramers, J. D.; Cheburkin, A. K. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: Enrichment factors, fluxes, isotopic compositions, and sources. *Environ. Sci. Technol.* **1999**, *33*, 1340−1352.

(5) Shotyk, W.; Weiss, Appleby, P. G.; Cheburkin, A. K.; Frei, R.; Gloor, M.; Kramers, J. D.; Reese, S.; Van Der Knapp, W. O. History of atmospheric lead deposition since 12 370 ^{14}C yr BP from a peat bog, Jura Mountains, Switzerland. *Science* **1998**, *281*, 1635−1640.

(6) Nriagu, J. O.; Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **1988**, *333*, 134−139.

(7) Sterckeman, T.; Douay, F.; Proix, N.; Fourier, H. Vertical distribution of Cd, Pb and Zn in soils near smelters in the North of France. *Environ. Pollut.* **2000**, *107*, 377−389.

(8) Sterckeman, T.; Douay, F.; Proix, N.; Fourier, H.; Perdrix, E. Assessment of the contamination of cultivated soils by eighteen trace elements around smelters in the North of France. *Water, Air, Soil Pollut.* **2002**, *135*, 173−194.

(9) Semlali, R. M.; Dessogne, J. B.; Monna, F.; Bolte, J.; Azimi, S.; Navarro, N.; Denaix, L.; Loubet, M.; Château, C.; Van Oort, F. Modeling lead input and output in soils using lead isotopic geochemistry. *Environ. Sci. Technol.* **2004**, *38*, 1513−1521.

(10) Allan, R. Introduction: Mining and metals in the environment. *J. Geochem. Explor.* **1997**, *58*, 95−100.

(11) Pyatt, F. B. Copper and lead bioaccumulation by *Acacia retinoides* and *Eucalyptus torquata* in sites contaminated as a consequence of extensive ancient mining activities in Cyprus. *Ecotoxicol. Environ. Saf.* **2001**, *50*, 60−64.

(12) Pyatt, F. B.; Gilmore, G.; Grattan, J. P.; Hunt, C. O.; McLaren, S. An imperial legacy? An exploration of the environmental impact of ancient metal mining and smelting in southern Jordan. *J. Archaeol. Sci.* **2000**, *27*, 771−778.

(13) Véron, A.; Flament, P.; Bertho, M. L.; Alleman, L.; Flegal, R.; Hamelin, B. Isotopic evidence of pollutant lead sources in northwestern France. *Atmos. Environ.* **1999**, *33*, 3377−3388.

(14) Morin, G.; Ostergren, J. D.; Juillot, F.; Ildefonse, P.; Calas, G.; Brown, G. E., Jr. XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes. *Am. Mineral.* **1999**, *84*, 420−434.

(15) Baron, S.; Lavoie, M.; Ploquin, A.; Carignan, J.; Pulido, M.; de Beaulieu J. L. Record of metal workshops in peat deposits: History and environmental impact on the Mont-Lozère Massif, France. *Environ. Sci. Technol.* **2005**, *39*, 5131−5140.

(16) Baron, S.; Carignan, J.; Laurent, S.; Ploquin, A. Medieval lead making on the Mont-Lozère Massif (Cévennes-France): Tracing ore sources using Pb isotopes. *Appl. Geochem.* **2006**, *21*, 241−252.

(17) Ploquin, A.; Allée, P.; Bailly-Maître, M. C.; Baron, S.; de Beaulieu, J. L.; Carignan, J.; Laurent, S.; Lavoie, M.; Mahé-Le Carlier, C.; Peytavin, J.; Pulido, M. Medieval lead smelting on the Mont-Lozère, southern France. *Archaeometallurgy in Europe*, Milan, Italy, 2003; Vol. 1, pp 635−644.

(18) Baron, S. Traçabilité et Evolution d'une Pollution Métallurgique Médiévale de Plomb Argentifère sur le Mont-Lozère. Ph.D. Thesis, Université de Montpellier II, 2005; 232pp.

(19) Carignan, J.; Hild, P.; Mevelle, G.; Morel, J.; Yeghicheyan, D. Routine analysis of trace elements in geological samples using flow injection and low-pressure on-line liquid chromatography coupled to ICP-MS: A study of geochemical reference materials BR, DR-N, UB-N, AN-G and GH. *Geostand. Newsl.* **2001**, *25*, 187−198.

(20) Ariès, S. Mise en évidence de contaminations métalliques historiques à partir de l'étude d'enregistrements sédimentaires de lacs de haute montagne. Ph.D. Thesis, Université de Toulouse Paul Sabatier, 2001; 248pp.

(21) Manhès G.; Allègre C. J.; Dupré B.; Hamelin B. Lead isotope study of basic-ultrabasic layered complexes: Speculations about the age of the Earth and primitive mantle characteristics. *Earth Planet. Sci. Lett.* **1980**, *47*, 370−382.

(22) Maréchal, C.; Télouk, P.; Albarède, F. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* **1999**, *156*, 251−273.

(23) White, M.; Albarède, F.; Telouk, P. High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chem. Geol.* **2000**, *167*, 257−270.

(24) Thirlwall, M. Multicollector ICP-MS analysis of Pb isotopes using a ^{207}Pb-^{204}Pb double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalisation. *Chem. Geol.* **2002**, *184*, 255−279.

(25) Miller, E. K.; Friedland, A. J. Lead migration in forest soils: Response to changing atmospheric inputs. *Environ. Sci. Technol.* **1994**, *28*, 662−669.

(26) Shotyk, W.; Chen, B.; Krachler, M. Lithogenic, oceanic and anthtropogenic sources of atmospheric Sb to a maritime blanket bog, Myrarnar, Faroe Islands. *J. Environ. Monit.* **2005**, *7* (12), 1148−1154.

(27) Cloy, J. M.; Farmer, J. G.; Graham, M. C. MacKenzie, A. B.; Cook, G. T. A comparison of antimony and lead profiles over the past 2500 years in Flanders Moss ombrotrophic peat bog, Scotland. *J. Environ. Monit.* **2005**, *7* (12), 1137−1147.

(28) Vink, B. W. Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams. *Chem. Geol.* **1996**, *130*, 21−30.

(29) Tighe, M.; Lockwood, P.; Wilson, S. Adsorption of antimony (V) by flood plain soils, amorphous iron (III) hydroxide and humic acid. *J. Environ. Monit.* **2005**, *7* (12), 1177−1185.

(30) Ainsworth, N.; Cooke, J. A.; Johnson, M. S. Distribution of antimony of contaminated grassland: 1. Vegetation and soils. *Environ. Pollut.* **1990a**, *65*, 65−77.

(31) Ainsworth, N.; Cooke, J. A.; Johnson, M. S. Distribution of antimony of contaminated grassland: 2. Small mammals and invertebrates. *Environ. Pollut.* **1990b**, *65*, 79−87.

(32) Scokart, P. O.; Meeus-Verdinne, K.; De Borger, R. Mobility of heavy metals in polluted soils near zinc smelters. *Water, Air, Soil Pollut.* **1983**, *20*, 451−463.

(33) Merrington, G.; Alloway, B. J. The flux of Cd, Cu, Pb and Zn in mining polluted soils. *Water, Air, Soil Pollut.* **1994**, *73*, 333−344.

(34) Camobreco, V. J.; Richards, B. K.; Steenhuis, T. S.; Peverly, J. H.; McBride, M. B. Movement of heavy metals through undisturbed and homogenized soils columns. *Soil Sci.* **1996**, *161*, 740−750.

(35) Derome, J.; Nieminen, T. Metal and macronutrient fluxes in heavy metals polluted Scots pine ecosystems in SW Finland. *Sci. Tot. Environ.* **1998**, *292*, 81−89.

(36) Nieminen, T. M.; Ukonmaanaho, L.; Shotyk, W. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu−Ni smelter in Southwest Finland. *Sci. Tot. Environ.* **2002**, *292*, 81−89.

Received for review March 18, 2006. Revised manuscript received June 11, 2006. Accepted June 15, 2006.

ES0606430