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Isotopic Composition of Zn and Pb Atmospheric Depositions in an Urban/Periurban Area of Northeastern France

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Epiphytic lichens, ambient PM-10, and bus air-filter aerosols collected in a city and the surrounding area were used to monitor urban atmospheric metal deposition in the Metz area, NE France. According to the measured Pb and Zn concentrations, high-enrichment factors (EF) were calculated for lichens collected in 2001 and 2003, suggesting an anthropogenic origin for those metals. Pb and Zn concentrations in lichens and other samples are correlated, probably indicative of the level of pollution recorded. However, different trends and scatters in the relationship suggest decoupling of Zn and Pb sources in this area. The lead isotopic composition of lichens varies largely from downtown, near traffic roads and highways, to suburbs but indicate an overall stability of sources between 2001 and 2003, although some minor variations were noted. Remobilization of Pb from leaded gasoline is still significant. The Zn isotopic composition measured in all lichens yielded fairly homogeneous δ^{66}Zn ranging from -0.2‰ to 0.5‰ relative to Zn$_{JMC}$ solution. Most lichen samples are indistinguishable from urban aerosols (PM-10 and bus air filters, δ^{66}Zn = 0.12 $\pm$ 0.21‰) and from flue gases from the city waste combustor (δ^{66}Zn = 0.13 $\pm$ 0.12‰). No systematic variations of Zn EF and isotopic compositions were observed for and between 2001 and 2003 samples. Some lichens having unradiogenic ^{206}Pb/^{207}Pb ratios displayed high Zn and negative δ^{66}Zn, indicative of a possible traffic source for Zn. A review from the literature on the Zn isotopic composition of terrestrial materials is reported but a few reservoirs seem to have specific compositions. According to the actual precision obtained, Zn isotopes for tracing pollution sources might not be straightforward but might be potentially useful for specific studies.

Introduction

Since the 1970s, Pb concentration and isotopes were used to survey anthropogenic emission, fallout and impact of the heavy metals in the environment. Lead isotopic composition of environmental samples was effective to discriminate different pollution sources and was intensively used in environmental studies to monitor ancient (*1*, *2*) and recent (*3−5*) atmospheric pollution depositions. With the removal of lead additives from gasoline, the flux of atmospheric Pb emission dropped significantly leaving other industrial sources, such as smelters, metal refineries, and power plants, and waste composition of atmospheric depositions often reflects the mean composition of industrial Pb commonly used. Finding new atmospheric pollution tracer is of key importance for environmental studies. Zinc is emitted to the atmosphere in greater quantities than any other trace metals worldwide (*6*). The first Zn isotopic measurements concluded that there was no noticeable Zn isotopic fractionation in terrestrial samples (*7*). However, the advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) permits stable isotope ratio measurements of heavy and transitional elements at a level of precision that is sufficient to resolve isotopic variations of a few tenths of a per mill (*8*). Maréchal et al. (*24*) published the first measurements of Cu and Zn in minerals and biological materials proving the existence of natural isotopic variations for these elements. At the same time, a preliminary study of rainwater reported Zn isotopic variations between samples from urban and rural areas (*9*). Other studies confirmed the significant variation of Zn isotopic composition in terrestrial materials (*10−13*), but our understanding of Zn isotope systematic remains poor. Indeed, the composition of geobiological "reservoirs" is not well constrained and is poorly investigated. However, recent studies (*12*, *14−16*) enlarged our knowledge on Zn isotope systematic and encouraged the use of Zn isotope ratios to assess physical−chemical reactions in the biogeochemical cycling of the trace metals and also as potential pollution source tracers. One of these studies (*14*) reported on Zn isotopic composition of lichens in a Russia mining area and revealed a large range of δ^{66}Zn values, from 0.44‰ to 1.33‰, but these isotopic variations were not clearly explained. Moreover, Zn is not affected by redox reactions, which is well-known to be a major source of fractionation for Cu or Fe. On the contrary, we can reasonably expect large fractionation in anthropogenic derived products because industrial processing including ion-exchange, distillation, and so forth likely induces large fractionation as already observed for Cd (*17*).

On the basis of those previous works, we decided to monitor the atmospheric depositions in an urban and periurban area in 2001 and its evolution 2 years later in 2003. In this aim, we investigated Zn and Pb elemental and isotopic compositions of epiphytic lichens. Previous work realized in this area on Pb was already reported (*18*). To better constrain the possible sources of these metals, we also analyzed urban aerosols sampled on bus air filters, ambient PM-10 from the city center, and urban waste incineration fume treatment residues from the city combustor. These different samples should be representative of urban and industrial compositions.

Sampling and Analytical Techniques

Sampling. Lichen samples used herein were fruticulose and foliose species. Most of them were *Evernia prunastri*, *Ramalina farinacea*, and *Hypogymnia physodes*, collected at the same location in summer 2001 and October 2003, over a radius of 20 km around a 300 000-inhabitant city (Metz, NE France) as described in ref *18*. Lichens were collected from tree branches less than a few millimeters in diameter (likely <5 years old) with precleaned plastic tweezers and were sealed in hermetic plastic containers. In the laboratory, the samples were separated from their substratum, were warm-

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dried, and were powdered before being stored in hermetic vessels. Urban aerosols were collected from bus air filters (provided by Société des transports de Metz) and from ambient PM-10 collectors. Sampling covered different integration times, 9 months from July 2002 to March 2003 for bus air filters and 4−5 days in August and September 2002 for ambient PM-10 particles. Each ambient aerosol sample represented 36 m^3/day pumped through Teflon filters. Urban waste incinerator flue gases (REFIOM) analyzed in this study were sampled in the Metz incinerator during January and July 2003. These materials are considered to likely reflect the mean industrial Pb isotopic composition emitted to the atmosphere (19, 20).

Analytical Methods. Trace element analyses were measured using a Perkin-Elmer ICP-MS SCIEX Elan 5000 and Thermo X7 located at CRPG, Nancy (France), following the method described in ref 21. Lichen sample preparation was done using acid digestion according to ref 22. The accuracy of the method was verified by analyzing lichen standard reference material (CRM BCR 482) and fly ash reference material (CRM BCR 176). Water used for dilution and dissolution was purified using a Millipore deionizing system at 18.2 MΩ. Other reagents used for sample preparation (HCl and HNO_3) were sub-boiled or bought directly as suprapur (HF 48% v/v) and suprapur H_2O_2 for isotope analyses. Separation of lead was achieved using anion exchange chromatography (23). The total procedural blank is ≤100 pg and is considered negligible in all cases. Repeated measurements of the SRM 981 Pb reference material over different analytical sessions yielded uncertainties (2σ) lower than 0.5‰ for $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ and better than 0.2‰ for $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$. Separation of Zn for isotope measurements was done from ref 24 using Biorad column filled with 2 mL of AGMP1 resin, similar to one recently published (25). A second column chemistry was sometimes found necessary (particularly when the Fe/Zn ratio was elevated, as for basalts) to further separate Fe from Zn and to avoid matrix effects (10). The total procedural blank is ≤20 ng and is also considered negligible in comparison to the total amount of Zn from samples processed. Lead isotopic analyses were realized using a MC-ICP-MS (Micromass Isoprobe now GV instruments) located at CRPG, Nancy (France) as already described elsewhere (18, 20, 26). Zinc isotopic measurements were realized with two different MC-ICP-MS. The first one is the Isoprobe at CRPG and the second one is the Plasma 54 (VG elemental), located at the ENS, Lyon (France) and described elsewhere (27−29). Instrumental mass bias was corrected following the empirical method previously published (24, 30, 31) using Tl NIST SRM987 for Pb and Cu NIST 976 for Zn. In addition, the sample−standard−sample technique was applied along Zn isotopic measurements. Results obtained are expressed as a delta per mill (‰) notation relative to a reference solution, the Zn_{JMC} solution.

Results

Isotopic Accuracy Testing for Zn. Various testing on accuracy and precision on the Zn isotopic measurements was done in the course of this study, including the analysis of reference materials (see Supporting Information). Measurements obtained from the two MC-ICP-MS used are fully compatible, and all the results can be considered as a single data set (Figure S1). The IRMM yielded an average value of $\delta^{66}Zn = 0.32 \pm 0.16$‰, and the BCR CRM 482 lichen yielded a $\delta^{66}Zn$ value of 0.07 ± 0.10‰. A $\delta^{66}Zn = 0.32 \pm 0.13$‰ was measured on the BCR1 basalt (Table S1).

Zn and Pb Concentrations. Zn and Pb concentrations contained in lichens sampled during the 2001 campaign were reported elsewhere (18). The concentrations measured in lichens sampled in 2003 are reported in Table 1 as well as

the previous results obtained in 2001 for comparison. Lead concentration in lichens sampled in 2003 range between 3 and 201 μg/g whereas the variation was from 3 to 72 μg/g in 2001 samples. Similarly, lichen Zn concentrations ranged from 34 to 268 μg/g in 2003 against 31 to 141 μg/g in 2001. Despite similar evolution in 2 years, the Zn and Pb concentrations in lichens are only poorly correlated.

Figure 1a reveals a higher dispersion for Zn than for Pb concentrations, especially for lower contents. Indeed, for 10 μg/g Pb measured in lichens, the corresponding Zn concentrations may vary by 1 order of magnitude, from 10 to 100 μg/g. Considering a south−north cross section over the city center, an increasing of both Zn (Figure 1b) and Pb (Figure 1c) concentrations in lichens can be noted in the city center area relative to the more rural areas. This increase is found in both 2001 and 2003 samples, the latter showing an overall larger discrepancy.

The PM-10 and the REFIOM (urban waste incinerator flue gases) have Zn and Pb concentrations close to a 2:1 line, covering more than 2 orders of magnitudes in concentration, with Pb concentrations ranging from 100 and 10 000 μg/g and Zn concentrations ranging from 300 to 30 000 μg/g and the REFIOM having higher metal contents (Figure 1a). The bus air filters show homogeneous high Pb and Zn concentrations, respectively, ranging from 200 to 300 μg/g and from 7500 up to 10 000 μg/g (Table 2). This last material integrated a high Zn input relative to Pb compared to the other samples.

Zn and Pb Isotopic Compositions. The Zn isotopic composition of REFIOM samples was found relatively homogeneous with values ranging from 0.07 to 0.19‰ (Table 2), the mean $\delta^{66}Zn$ value being 0.13 ± 0.12‰ ($n = 3$). Ambient PM-10 aerosols and those collected on bus air filters yielded similar and undistinguishable $\delta^{66}Zn$ within errors, with a grand mean of 0.12 ± 0.21‰ (Table 2). Lichens sampled in 2001 yielded $\delta^{66}Zn$ varying from −0.19 to 0.32‰ whereas lichens from 2003 yielded a ^{66}Zn ranging from −0.15 to 0.50‰ (Table 1).

Data from a south−north cross section, including the city center (Figure 2a), did not reveal any systematic variation of the Zn isotopic composition, neither between city center and more rural areas nor between southern and northern parts of the study area. Extreme compositions were found for lichens collected in the southern rural part of the city. These highly contrasted compositions were found in samples closely located, between 12 and 10 km south of the city center. In each sampling point, Zn isotopic compositions in 2001 lichens were similar to those in 2003 lichens within the uncertainties.

The lichen data reported in Figure 3a do not suggest a simple mixing trend related to Zn concentrations and isotopic compositions. The overall range of $\delta^{66}Zn$ measured in lichens is only slightly larger than the one defined by urban/industrial aerosols and materials.

The Pb isotopic composition of the three REFIOM samples analyzed varies slightly ($^{206}Pb/^{207}Pb$ from 1.1535 and 1.1573) but is within the composition field for such materials from various waste combustors in France (20). Material found on bus air filters have $^{206}Pb/^{207}Pb$ ratios (18) similar but at the low end of the REFIOM field whereas PM-10 aerosols have $^{206}Pb/^{207}Pb$ ratios at the high end of REFIOM's composition (Table 2).

Measured $^{206}Pb/^{207}Pb$ ratios in 2001 and 2003 lichens ranged from 1.1210 up to 1.1613 (Table 1). The distribution of $^{206}Pb/^{207}Pb$ ratios along a south−north cross section, including the city center (Figure 2b), is similar for the 2 years of sampling. A sharp Pb isotopic gradient was observed between city center and more rural areas. However, significant variations of $^{206}Pb/^{207}Pb$ ratios in a given point may be observed. Indeed, in the more rural areas, lichens sampled

TABLE 1. Distance from the City (km) and Direction of Sampling of the Lichens

samples	distance from city center (km)	direction	[Zn]$_{(\mu g/g)}$ 2003	[Zn]$_{(\mu g/g)}$ 2001	EF Zn 2003	EF Zn 2001	[Pb]$_{(\mu g/g)}$ 2003	[Pb]$_{(\mu g/g)}$ 2001[b]	EF Pb 2003	EF-Pb 2001[b]	δ^{66}Zn 2003	δ^{66}Zn 2001	^{208}Pb/^{206}Pb 2003	^{206}Pb/^{207}Pb 2003	^{208}Pb/^{204}Pb 2003	^{207}Pb/^{204}Pb 2003	^{206}Pb/^{204}Pb 2003	^{206}Pb/^{207}Pb 2001[b]
1	15.5	S	59	61	107	90	5	6	34	30	0.07	0.01	2.0956	1.1591	37.930	15.615	18.100	1.1528
2	12	S	57	43	78	66	5	5	27	28	0.22	0.06						1.1552
3	11.75	S	65	51	152	134	4	3	35	31	0.50	0.29	2.1019	1.1548	37.894	15.611	18.029	1.1542
4	10.25	S	56	50	245	77	4	6	60	31	−0.02	−0.19						1.1537
5	7.25	S	52	34	128	90	5	4	48	38	0.00	0.24	2.1041	1.1555	37.949	15.609	18.036	1.1536
6	4.25	S	95	43	82	106	12	5	36	45	0.08	−0.01						1.1523
7	3.5	S	95	43	100	87	15	7	57	48	0.20	0.01	2.1017	1.1540	37.852	15.606	18.010	1.1524
8	15	S	104	53	264	166	5	3	49	38	0.23	0.23	2.0979	1.1570	37.902	15.616	18.067	1.1503
9	12	N	61	61	57	113	11	8	35	60	0.01	0.14	2.0916	1.1613	37.955	15.625	18.146	1.1552
10	9	NE	37	31	39	72	3	6	9	40		0.24	2.1011	1.1574	38.050	15.646	18.110	1.1541
11	8	NE	55	52	73	109	6	7	26	51			2.0963	1.1577	37.958	15.641	18.108	1.1532
12	6	N	138	54	39	85	35	11	35	53	0.34	0.17	2.1100	1.1475	37.759	15.595	17.896	1.1506
14	3.3	N	124	70	57	68	46	34	75	72	0.08	0.28	2.1165	1.1437	37.736	15.589	17.829	1.1455
16	2.5	N	82	75	137	89	20	7	120	52			2.1097	1.1485	37.806	15.601	17.914	1.1523
17	1.5	S	112	135	142	144	35	16	159	124	0.00	0.07	2.1306	1.1290	37.475	15.576	17.583	1.1369
18	1.7	N	182	91	91	99	31	14	55	53	0.02	0.15	2.1094	1.1498	37.826	15.596	17.932	1.1500
20	5.5	NW	149	68	202	84	32	9	156	38		0.19						1.1513
21	1.5	SW	268	141	101	72	201	72	268	99	−0.15	−0.07	2.1395	1.1210	37.324	15.562	17.445	1.1307
22	2.6	SW	85	54	206	170	26	8	181	89	0.13	0.15						1.1454
23	4.25	SW	106	72	97	99	15	25	50	75			2.1116	1.1457	37.739	15.599	17.872	1.1473
24	6.25	SW	50	62	92	108	29	11	97	67	0.17	0.22						1.1485
26	10.75	NW		131		140		6		34		−0.16						1.1465
27	10.75	NW	158	119	73	106	39	29	63	91	0.08	0.16	2.1149	1.1417	37.649	15.593	17.802	1.1415
29	4.75	NW	137	72	69	177	42	17	75	148		0.16						1.1471
30	8.25	SW	131	43	111	70	9	6	27	33		0.11						1.1457
32	5.25	SW	68	54	63	78	17	8	56	41	0.20	0.32	2.1015	1.1550	37.896	15.611	18.027	1.1520
34	8.75	SW	40	43	79	106	6	5	41	26		0.17	2.1048	1.1526	37.863	15.605	17.983	1.1547
35	8.75	SW	34	76	47	63	9	8	46	23	0.21	0.05	2.1016	1.1546	37.866	15.605	18.018	1.1510

[a] Zinc and lead concentrations, enrichment factors, and isotopic compositions are reported for 2001 and 2003 sampling. Different lead ratios in 2003 lichens and ^{206}Pb/^{207}Pb ratio for 2001 lichens are also reported. [b] Cloquet et al. (18).

TABLE 2. Zn and Pb Concentrations and Isotopic Compositions of a Potential Pollution Source (Urban Waste Incineration Flue Gases, REFIOM) as well as Ambient Urban Aerosols PM-10 and Particles Sampled on Bus Air Filters

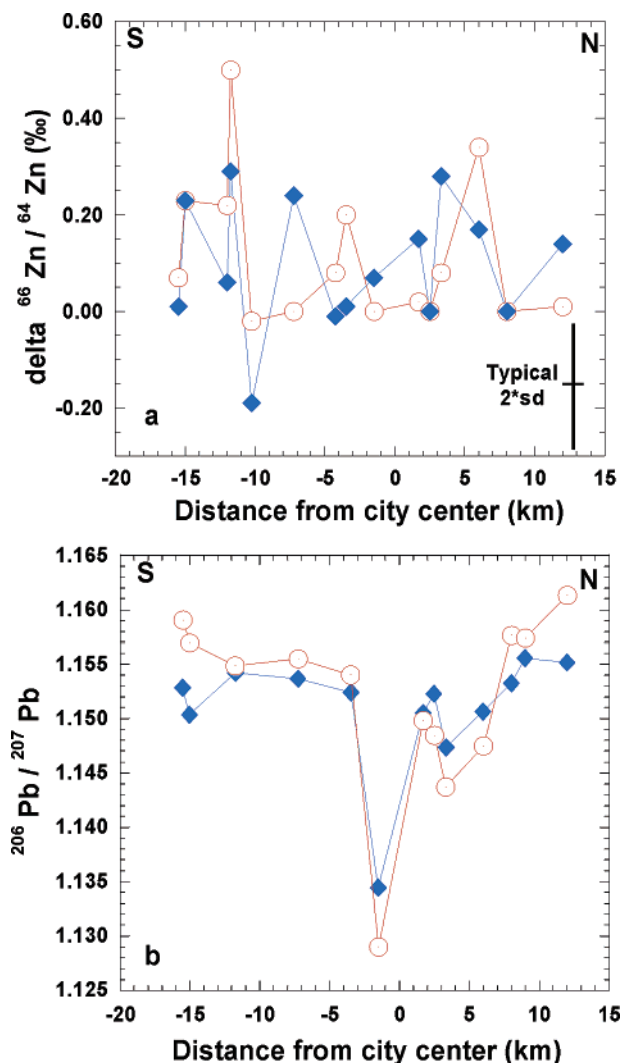| samples	Zn μg/g	Pb μg/g	$^{206}Pb/^{207}Pb$	2*sd	$\delta^{66}Zn$	2*sd	$\delta^{68}Zn$	2*sd
REFIOM 1	18 770	6777	1.1573		0.07		0.15	
REFIOM 2	13 490	7287	1.1553		0.19		0.41	
REFIOM 3	26 510	6040	1.1535		0.12		0.21	
mean industrial signal			**1.1554**	**0.0038**	**0.13**	**0.12**	**0.26**	**0.27**
bus air filter 1	7544	279	1.1536		0.04		−0.04	
bus air filter 2	9207	205	1.1535		0.10		0.18	
ambient PM-10 1	748	283	1.1569		0.12		0.21	
ambient PM-10 2	602	243	1.1560		0.30		0.60	
ambient PM-10 3	276	105	1.1569		0.03		0.11	
mean urban aerosols			**1.1554**	**0.0034**	**0.12**	**0.21**	**0.21**	**0.48**
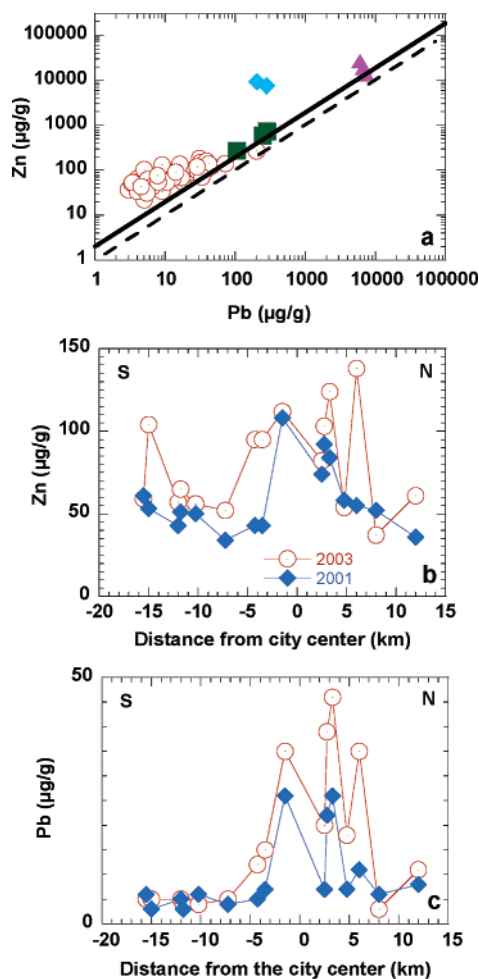
FIGURE 1. (a) Zinc−lead correlation for lichens (open circles), bus air filters (filled diamonds), urban PM-10 (filled squares), and REFIOM (urban waste incinerator flue gases) from Metz (filled triangles). Dashed line represents 1:1 relationship for Zn and Pb whereas plain line represents 2:1 Zn:Pb relationship. (b) Variations of Zn concentrations versus the distance from the city center (km) along a south−north cross section and (c) variations of Pb concentrations along the same cross section. In b and c, filled diamonds are 2001 lichens and open circles are 2003 lichens.

FIGURE 2. (a) Zinc isotopic composition of lichens vs the distance from the city center (km) following a south−north cross section and (b) $^{206}Pb/^{207}Pb$ of lichens along the same cross section. Filled diamonds are 2001 lichens and open circles are 2003 lichens. Typical uncertainty at 2σ (2*sd) level (95% confidence) is presented in a and is included in the points in b.

in 2003 have a slightly, but almost systematic, higher $^{206}Pb/^{207}Pb$ ratio than the one measured in the 2001 samples.

Discussion

To assess the origin of atmospheric metals, enrichment factors (EF) relative to Al contents and the metal/Al of the average upper crust from Taylor & McLennan (*32*) were calculated (Table 1). EF estimate the anthropogenic con-
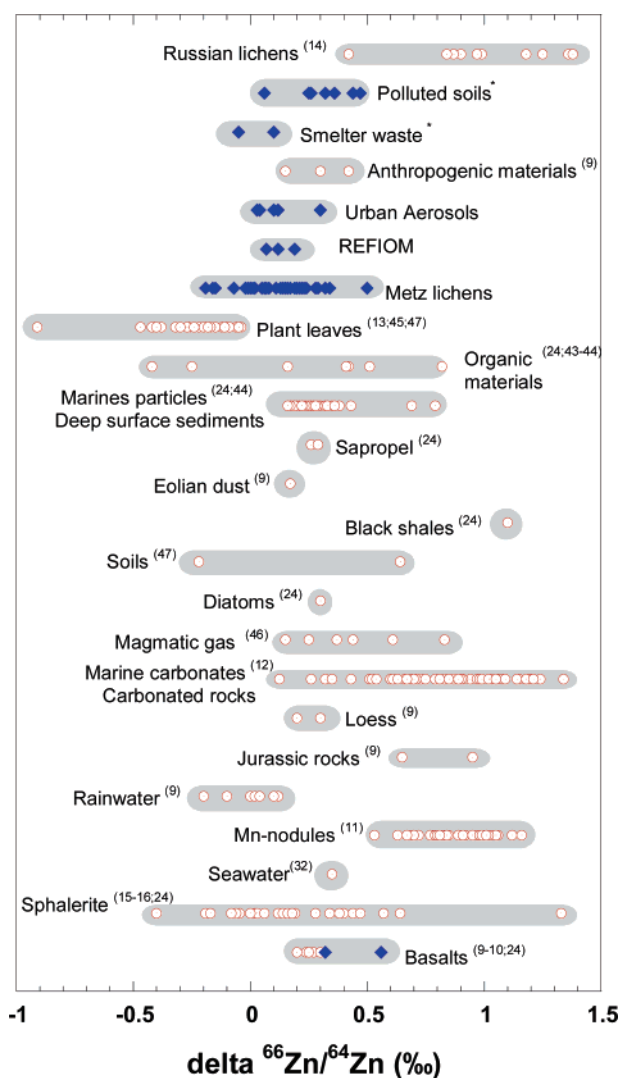
tribution to the total metal concentration in lichens (see ref *18* for details). The Zn EF calculated for the 2003 lichens ranged from 39 to 264, with an average of 108 and a similar but lower median value of 92. Similar values were calculated for the 2001 lichens which provided an average EF Zn value of 101 and a median value of 90. Similar high values are obtained for EF Pb for both years of sampling (from 9 to 268). These results suggest that global anthropogenic contribution
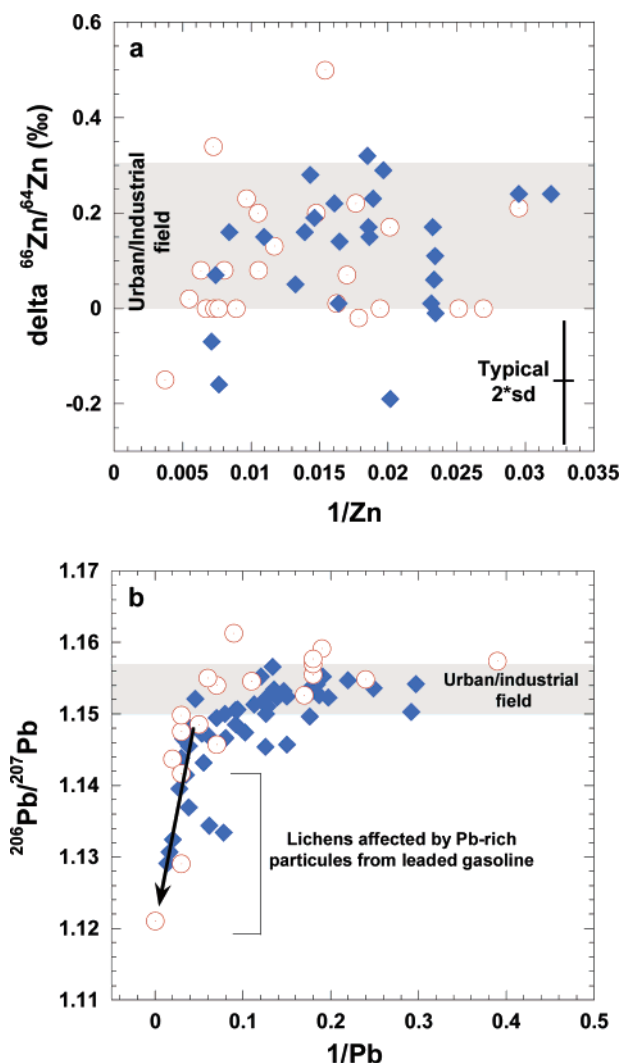
FIGURE 3. (a) Zn isotopic composition versus 1/Zn and (b) ^{206}Pb/^{207}Pb versus 1/Pb. Symbols are as in Figure 2. Gray area represents the urban and industrial field as determined with urban aerosols and REFIOM samples. Typical uncertainty at 2σ (2*sd) level (95% confidence) is also presented in a and is included in the points in b.

[1] Preliminary data

FIGURE 4. Zn isotopic composition of different biogeological materials. Open circles represent data from the literature ([9–13, 15, 16, 24, 40–45]) and filled diamonds are data from this work and from Cloquet ([38]).

largely dominates the metal budget of atmospheric deposition in the area and overall similar deposition fluxes between 2001 and 2003. Zn and Pb isotopic compositions will then be treated as reflecting anthropogenic sources only. Figure 2b revealed slightly higher ^{206}Pb/^{207}Pb isotope ratios in 2003 lichens than in 2001 lichens in the more rural areas suggesting a short-term evolution of the atmospheric fallout mean isotopic composition. On the other hand, one of the city center samples and some other samples close to the city have a ^{206}Pb/^{207}Pb ratio lower in 2003 than in 2001. These locations were influenced by old Pb remobilization ([18]) from leaded gasoline, known to have a low ^{206}Pb/^{207}Pb in France ([19]) and other neighboring European countries ([19, 33–36]). Hence, a higher Pb EF and a lower ^{206}Pb/^{207}Pb ratio in 2003 for these sampling points may be explained by a higher contribution of this remobilized Pb (Figure 3b). This suggests that, whereas Pb addition to gasoline completely stopped in France since about 1999, gasoline combustion Pb is still present in the environment and was remobilized in the atmosphere near roads and highways in 2003. On the other hand, 2003 lichens sampled at other locations have slightly higher ^{206}Pb/^{207}Pb, and sometimes ^{207}Pb/^{204}Pb, than 2001 lichens, suggesting an overall evolution toward the urban/

industrial signal along with the disappearing of the unradiogenic gasoline Pb.

Anthropogenic Zn atmospheric emissions in France were 3 times greater than Pb in 2003 ([37]), and Zn was one of the metals most emitted worldwide in the mid 1990s ([6]). Unfortunately, Zn isotopes in lichens and aerosols from the study area do not vary systematically with geographic position of sampling or concentrations as shown by Figures 2a and 3a. Moreover, there is no correlation between Zn isotopic composition and Zn EF in lichens. Rather, almost all lichens yielded the same Zn isotopic composition within the uncertainties. These results suggest either an effective homogenization of the different Zn emission sources during transport in the atmosphere or a low contrast of the Zn isotopic composition of the various sources or both. The total spread of δ^{66}Zn measured in lichens of the study is 0.7‰ whereas the terrestrial variations for different reservoirs so far reported is close to 2.5‰ (Figure 4).

A compilation of Zn isotope data actually available (Figure 4) depicts the minimal range for each reservoir and the similarity of some natural reservoirs. Most of the materials analyzed yielded a δ^{66}Zn ranging between 0 and 0.5‰. Sphalerites in Zn ores cover a large range of δ^{66}Zn between
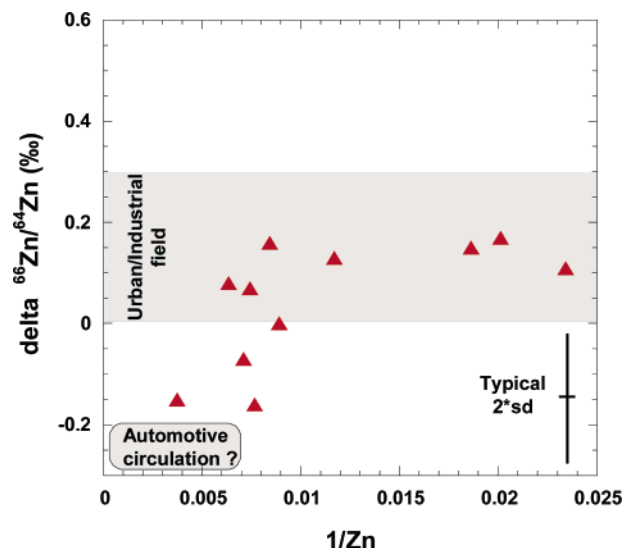
FIGURE 5. Zn isotopic composition vs 1/Zn for selected lichens which yielded a $^{206}Pb/^{207}Pb < 1.15$ suggesting a significant component of old Pb from leaded gasoline. Gray area represents the urban/industrial field (see text for details). Typical uncertainty at 2σ (2*sd) level (95% confidence) is also represented.

−0.4 up to 1.3‰ but mainly yielded results between 0‰ and 0.5‰. The later restricted range for different important Zn ore deposits could explain the restricted range measured in the anthropogenic materials, such as waste combustor flue gases. Nevertheless, industrial processes, such as evaporation and condensation, may induce Zn isotope fractionations (*38*). Commercial Zn solutions, as the one used in this study (Zn Accutrace), may yield highly fractionated Zn suggesting that some refining process indeed fractionated Zn isotopes significantly.

To better constrain Zn sources, a subset of the whole data set may be considered separately. According to lead isotope data, some lichens yielded a significant gasoline Pb component ($^{206}Pb/^{207}Pb < 1.15$). In these samples, Zn and Pb concentrations do not show a better correlation coefficient than that of the whole data set ($r^2 = 0.6$). However, Pb rich lichens also have high Zn contents. In the $\delta^{66}Zn$ versus 1/Zn diagram of Figure 5, lichens having the highest Zn concentrations (and the highest gasoline Pb contribution) have the lowest $\delta^{66}Zn$ values, outside the field defined by PM-10 aerosols, bus air filter materials, and REFIOM. This suggests that an isotopically "light" Zn component may be associated to leaded gasoline or road traffic. Leaded gasoline was not known to be Zn rich material (*35*) contrary to some vehicle components like tire, oil, cooling liquid, safety fence, and so on (*39*). We suggest automotive circulation as a potential important Zn source to the atmosphere and, accordingly, may provide lower $\delta^{66}Zn$ values comprised between −0.2 and −0.3‰ and Zn concentrations >100 $\mu g/g$ in lichens. A significant contribution of such materials could also explain the low $\delta^{66}Zn$ value measured in rainwater (ranging between −0.2 and −0.1‰) collected in Montpellier (Southern France) (*9*) compared to the $\delta^{66}Zn$ value of rainwater (between 0 and 0.15 ‰) collected in a more rural area (*9*) (Figure 4).

Information obtained from Zn isotopes is less straightforward and more limited than expected (particularly from anthropogenic pollution sources). Because global biogeological earth reservoirs do not seem to present typical and characteristic Zn isotopic composition, the use of Zn isotopes as a global environmental source tracer may be restricted.

Acknowledgments

Supporting Information Available

Isotopic accuracy testing for Zn, zinc isotopic compositions, zinc isotopic composition of mixing between Accutrace Zn and JMC Zn, and the same solution of different samples measured on two different MCICP-MS. This material is available free of charge via the Internet at http://pubs.acs.org.

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