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Atmospheric pollutant dispersion around an urban area using trace metal concentrations and Pb isotopic compositions in epiphytic lichens

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Abstract

Epiphytic lichen samples were collected in and around a city of 300 000 inhabitants in NE France to study the dispersion and fallout of Cd, Cu, Zn and Pb. Lichens hanging in small tree branches within a 15 km radius from the city centre, together with bus air filter aerosols and unleaded gasoline samples, were analysed to evaluate the relative contribution of anthropogenic metals. On an average, Pb and Cd concentrations and calculated enrichment factors in lichens showed a radial distribution from downtown, decreasing rapidly within 4 or 5 km and then less so towards more rural areas, whereas it is more diffuse for Cu and Zn despite the more elevated values close to the city centre. Metal concentrations can be interpreted in the light of major wind directions and/or secondary pollution sources to the atmosphere. Lichens sampled in the city and close to high traffic roads had $^{206}Pb/^{207}Pb$ ratios of about 1.13. This ratio was consistently higher (up to 1.157) for lichens sampled at only five kilometres from the city centre. On the other hand, urban aerosols (on bus air filters) have homogeneous $^{206}Pb/^{207}Pb$ ratios of 1.153 ± 0.003. The variation in Pb isotopic composition in lichens can be interpreted as the result of mixing between different industrial sources and old Pb pollution from leaded gasoline combustion re-emitted into the atmosphere. Combining elemental concentrations and isotopic ratios allowed a better understanding of the atmospheric deposition of metals and related sources in urban areas.

Keywords: Isotopic tracing; Biomonitoring; Elementary concentration; Anthropogenic pollution; Lead

1. Introduction

The anthropogenic input of heavy metals (HM) such as cadmium, copper, lead and zinc into the atmosphere has been increasing for the past sixty years (Nriagu and Pacyna, 1988; Patterson and Settle, 1987) due to industrial production (waste incineration, power plants, metal refining, etc.) and vehicular traffic (leaded petrol combustion). Even if

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Zn and Cu are essential for life, these metals can be toxic to humans at a 10–100 mg day^{-1} level. On the other hand, Pb and Cd are toxic at a 1 μg day^{-1} level. These metals are responsible for irreversible hazardous pollution and may have very dangerous impacts on human health (intoxication, poisoning, death). The survey of these heavy metals and the identification of their sources is therefore of key importance for all organisms and their environment. To identify sources of metals and other pollutant elements in the atmosphere, two approaches have been used. The first is based on the multi-elemental composition of atmospheric aerosols (Narita et al., 1999) and precipitation (Fujita et al., 2000; Roy and Négrel, 2001). The second approach, based on differences in lead isotopic composition (Aberg et al., 1999; Chiaradia and Cupelin, 2000; Flament et al., 2002; Getty et al., 1999; Haack et al., 2002; Hopper et al., 1991; Monna et al., 1997; Véron et al., 1999), can distinguish natural emissions from anthropogenic emissions (Boutron et al., 1995; Elbaz-Poulichet et al., 1984; Monna et al., 2000; Weiss et al., 1999). Both approaches are complementary and yield useful information on atmospheric pollution. Previous studies have shown that epiphytic lichens are valuable tools for monitoring trace metal elements in the atmosphere and are representative of the composition of aerosols on both large (Carignan and Gariépy, 1995; Carignan et al., 2002; Getty et al., 1999) and regional scales (Bergamaschi et al., 2002; Carreras and Pignata, 2002; Doucet and Carignan, 2001; Simonetti et al., 2003).

The aim of this study is to monitor the dispersion and fallout of anthropogenic HM at a local scale, around an urban area of 300 000 inhabitants (Metz, NE France), using surrounding epiphytic lichens. Trace metal concentrations were systematically measured and the calculated enrichment factors revealed high metal excess in lichens. The results are correlated with the sampling location and/or the major wind directions. The isotopic compositions of lichens, urban aerosols sampled on bus air filters and unleaded gasoline were used to identify sources of Pb in the urban atmosphere of Metz.

2. Materials and methods

2.1. Settings and sampling

The city of Metz is located in North-eastern France (06°08E, 49°05N) and has about 300 000 inhabitants. The city is located in the Moselle river valley (180–200 m altitude) and is delimited by two hillocks on the east and west side with their highest points at 300 m (sample 16) and 400 m (samples 22–23), respectively (Fig. 1). Winds from south to north are stronger and more frequent than the winds blowing from north to south. Winds blowing along the W–E axis are minor. The major wind directions are shown in Fig. 1. Significant industrial activities such as metallurgy and power plants can be found to the north of the study area (Fig. 1).

Epiphytic lichen samples were collected on small tree branches whenever possible, (typically less than 5 years old), as previously described (Carignan and Gariépy, 1995; Carignan et al., 2002; Doucet and Carignan, 2001). Fifty lichens from 36 sites have been sampled within a 15 km radius of the city centre along different cross-sections (Fig. 1), representing an average of 1 lichen per 16 km^2. The lichens used for analyses represent three different fruticulose species; *Evernia prunastri* and *Ramalina farinacea* dominated the samples, while *Usnea* sp. was a minor constituent. Some foliose specimens of *Hypogymnia physodes* were also analysed. Lichens were sampled with pre-cleaned plastic tweezers and immediately transferred to plastic bags. In the laboratory, lichens were separated from their substratum and other superfluous materials. Different lichen species sampled in the same location were also separated. The samples were dried at 105 °C for 24 h and powdered before being stored in hermetic vessels. The transportation company of Metz (TCRM) provided 6 different bus air filters covering a 9-month period of sampling from July 2002 to March 2003. Each bus covering all of the network, including the city centre, represented the general situation of the urban area and was considered equivalent to aerosol samples. Particles collected on the filters were removed from the filter by shaking. Two unleaded gasoline samples were collected directly from a fuel station.

2.2. Trace metal concentrations

Trace metal concentrations were measured by FI ICP-MS with a Perkin–Elmer ICP–MS SCIEX ELAN 5000 using a one-point "linear through zero" calibration. The calibration solution was a multi-element doped solution of the alkali basalt reference material BR, (Carignan et al., 2001). Approximately 60 mg of each sample was transferred into Teflon® capsules and digested in a

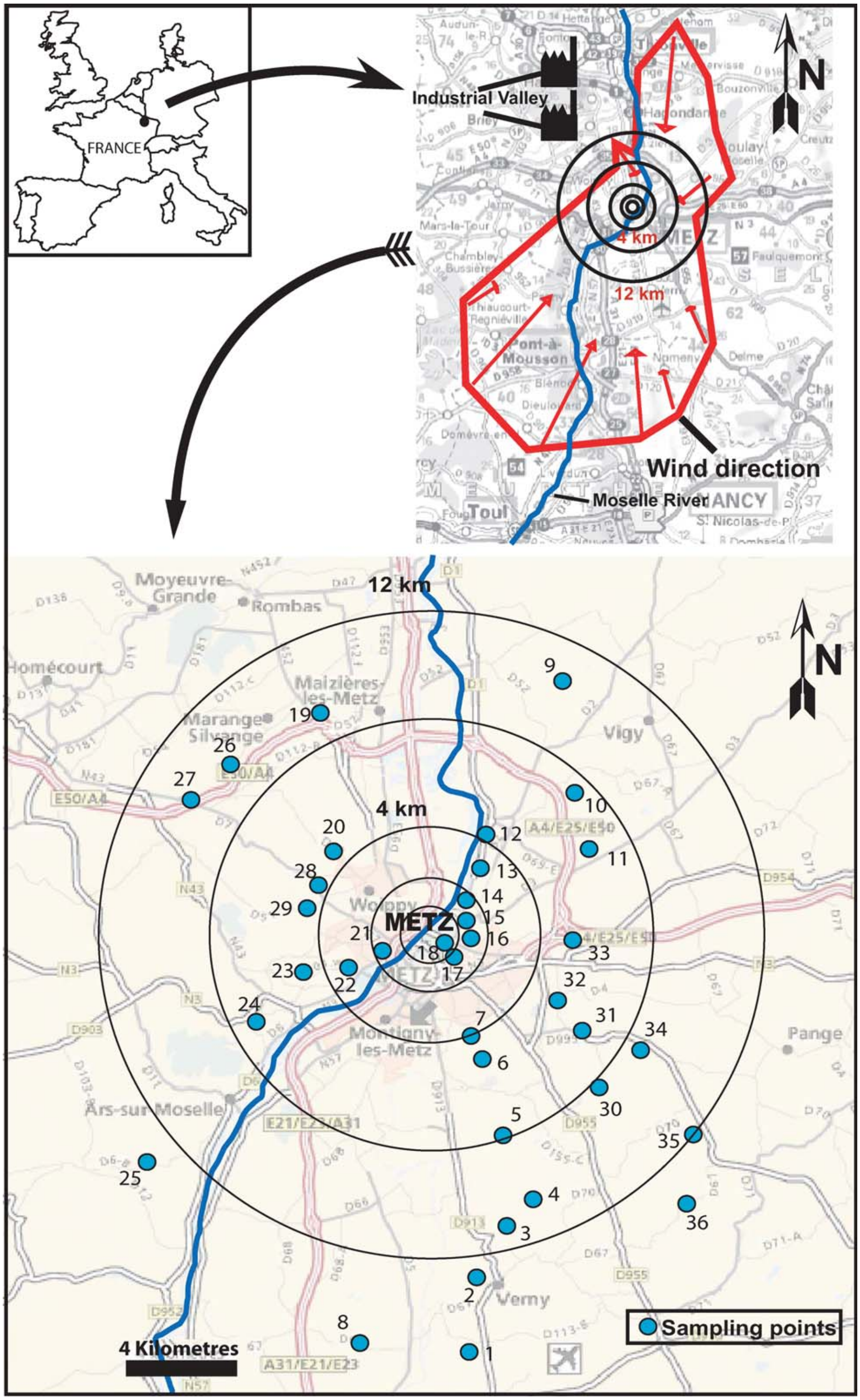


Fig. 1. Location of the studied area, major wind directions, industrial valley (metallurgy and power plants) and sampling sites.

mixture of HNO_3, H_2O_2 and HF. In each preparation batch, the reference material CRM lichen 482 from BCR was prepared along with the samples. For all the elements analysed, our results were in good agreement with those of certified and/or suggested values and were within acceptable levels of uncertainty.

2.3. Isotopic analyses

Lead separation was achieved using anion-exchange chromatography (Manhès et al., 1980). All lead isotope ratios were measured using an MC–ICP–MS (Micromass Isoprobe®, now GV instruments®). This instrument was equipped with 9 Faraday cups allowing all lead isotopes, as well as ^{205}Tl, ^{203}Tl and ^{200}Hg to be measured simultaneously. Thallium NIST SRM 997 was used to correct for instrumental mass bias using a value of 2.3889 for ^{205}Tl/^{203}Tl (Thirlwall, 2002). All parameters were adjusted to obtain the closest values relative to NIST SRM 981 as determined by DS-TIMS (Thirlwall, 2002) following the empirical method published for Cu–Zn analysis (Marechal et al., 1999). Repeated measurements of the SRM 981 Pb standard 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 and were of the same order for long-term reproducibility on CRM BCR 482 and L001 ($\sim$6 months). These results are comparable to those found using similar instruments but different data treatments (Thirlwall, 2002; Weiss et al., 2004). Lichens and aerosol particles prepared for Pb isotopic analyses were digested as described for lichen concentration measurements. Reagent blanks were tested for all procedures and were generally found to be <100 pg.

3. Results

3.1. Trace elements

Table 1 reports the concentration of Pb, Cd, Cu and Zn measured in lichens. A variation in elemental concentration was sometimes observed between two different lichen species sampled at the same location (e.g. samples 9 and 10). This variation was not systematic and was smaller than the observed variation between samples of the same species from the same location (Table 1). Even if some differences persisted in metal–metal ratios, the variation was smaller when the enrichment factors were compared. The results obtained from different lichen species were therefore comparable and were treated as a single data set.

A map of the atmospheric dispersion of HM around Metz was realised using concentrations measured in lichens (Fig. 2). Concentrations were generally lower, by a factor of 2 or 3, within a 4 km radius from the city centre and up to a factor of 10 in more rural areas. The lead concentration (Table 2) increased from about 4 $\mu g\,g^{-1}$ in the more rural areas to up to 40 $\mu g\,g^{-1}$ in the city centre and remained higher than 20 $\mu g\,g^{-1}$ for most lichens sampled in the NW part of the study area. Copper displayed the same range of variation, between 2.5 and 25 $\mu g\,g^{-1}$. Cadmium concentrations ranged between 0.15 and 0.68 $\mu g\,g^{-1}$ in the city centre and remained elevated in the NW section, whereas concentrations were lower than 0.30 $\mu g\,g^{-1}$ in the south. Zinc concentrations ranged from 30 $\mu g\,g^{-1}$ to about 170 $\mu g\,g^{-1}$, with most lichens containing <70 $\mu g\,g^{-1}$ in more rural areas. In the Metz urban area, trace metal concentrations were distributed following a lognormal law. Median concentrations of trace elements in lichens were distributed in the following order (Table 1): $Zn > Pb > Cu > Cr > Ni > As > Cd$ (Cr, Ni and As not shown), a sequence similar to the one already observed in Livorno Province, Italy (Scerbo et al., 2002).

3.2. Lead isotopes

The composition of the lichens showed a large range of isotopic ratios, with ^{206}Pb/^{207}Pb varying from 1.13 to 1.157 (Tables 2 and 3). In addition, the isotopic composition was related to the geographical distribution of lichens. Fig. 3b presents a S–N cross-section showing sharp isotopic gradients over Metz, where lichens display a lower ^{206}Pb/^{207}Pb ratio (1.136) than those from rural areas (1.148–1.157). Lichens sampled close to roads (roundabout and speedways) also had low ^{206}Pb/^{207}Pb ratios. The highest ^{206}Pb/^{207}Pb ratios were measured in lichens sampled in the NE part of the study area. The Pb isotopic composition of particles from bus air filters was also analysed (Table 3). These samples had a relatively homogeneous isotopic composition with ^{206}Pb/^{207}Pb ratios varying between 1.151 and 1.154 (average of 1.153). Finally, different types of gasoline sampled in the study area were also analysed for their isotope

Table 1
Selected trace metal concentrations, median concentration and enrichment factors

Sample site	Dist. (km) from city centre	Species	[Al] ($\mu g\,g^{-1}$)	[Cd] ($\mu g\,g^{-1}$)	[Cu] ($\mu g\,g^{-1}$)	[Pb] ($\mu g\,g^{-1}$)	[Zn] ($\mu g\,g^{-1}$)	EF[a]-Cd	EF[a]-Cu	EF[a]-Pb	EF[a]-Zn
1	15.5	*Evernia prunastri*	764	0.17	7.9	6	61	178	33	30	90
2	12	*Evernia prunastri*	740	0.15	3.9	5	43	165	17	28	66
3	11.75	*Evernia prunastri*	411	0.15	3.2	3	51	279	24	31	134
4	10.25	*Ramalina farinacea*	732	0.20	4.6	6	50	226	20	31	77
5	7.25	*Evernia prunastri*	405	0.17	2.7	4	34	338	20	38	90
6	4.25	*Ramalina farinacea*	433	0.19	7.8	5	43	336	55	45	106
7	3.5	*Evernia prunastri*	563	0.28	4.7	7	43	403	27	48	87
8	15	*Evernia prunastri*	345	0.26	6.0	3	53	599	53	38	166
9 A	12	*Ramalina farinacea*	483	0.20	4.4	7	40	327	28	53	90
9 B	12	*Evernia prunastri*	506	0.27	4.8	8	61	438	30	66	136
10 A	9	*Ramalina farinacea*	514	0.19	3.5	6	31	297	22	43	69
10 B	9	*Ramalina farinacea*	565	0.28	2.5	5	40	386	14	36	76
11	8	*Ramalina farinacea*	537	0.21	4.2	7	52	326	25	51	109
12 A	6	*Hypogymnia physodes*	632	0.18	5.7	9	55	240	29	56	98
12 B	6	*Evernia prunastri*	855	0.15	6.5	11	54	141	24	50	71
13	4.75	*Evernia prunastri*	814	0.17	6.4	7	58	174	25	37	81
14 A	3.3	*Hypogymnia physodes*	1883	0.68	12.2	34	98	298	21	72	59
14 B	3.3	*Evernia prunastri*	980	0.50	8.4	19	70	397	26	73	77
15	2.75	*Ramalina farinacea*	1184	0.36	8.6	22	92	249	23	74	88
16 A	2.5	*Usnea sp.*	1465	0.20	8.4	7	57	112	19	20	44
16 B	2.5	*Hypogymnia physodes*	1021	0.24	7.7	16	84	193	24	64	93
16 C	2.5	*Evernia prunastri*	894	0.24	8.1	9	67	218	29	40	85
17 A	1.5	*Evernia prunastri*	815	0.48	10.1	16	80	485	40	80	111
17 B	1.5	*Hypogymnia physodes*	821	0.64	11.4	36	135	610	43	168	177
18 A	1.7	*Evernia prunastri*	850	1.20	10.2	14	91	1160	38	68	122
18 B	1.7	*Evernia prunastri*	1127	0.57	10.6	11	76	414	30	39	76
19	11	*Evernia prunastri*	1616	0.26	14.7	18	80	134	29	45	56
20	5.5	*Evernia prunastri*	926	0.45	5.6	9	68	396	20	38	84
21 A	1.5	*Hypogymnia physodes*	2703	0.41	34.6	72	168	120	39	103	67
21 B	1.5	*Ramalina farinacea*	1991	0.36	23.3	49	141	142	36	95	76
22	2.6	*Evernia prunastri*	340	0.26	3.9	8	54	588	35	89	170
23 A	4.25	*Hypogymnia physodes*	1082	0.32	6.2	25	99	235	17	89	98
23 B	4.25	*Ramalina farinacea*	821	0.18	5.5	12	72	179	21	61	99
24	6.25	*Evernia prunastri*	624	0.27	5.0	11	62	332	25	67	108
25	12.75	*Evernia prunastri*	678	0.15	4.3	6	48	185	20	34	80
26	10.75	*Hypogymnia physodes*	1055	0.37	7.3	31	131	285	22	120	140
27	10.75	*Evernia prunastri*	1206	0.33	12.3	29	119	216	31	91	106
28 A	5	*Ramalina farinacea*	558	0.23	5.7	10	58	321	31	67	112
28 B	5	*Usnea sp.*	1759	0.57	23.6	38	288	265	43	86	185
29	4.75	*Ramalina farinacea*	438	0.20	5.3	17	72	355	37	148	177
30 A	8.25	*Evernia prunastri*	700	0.28	4.6	5	43	333	21	30	69
30 B	8.25	*Evernia prunastri*	741	0.24	5.2	7	47	262	23	36	71
31	6.5	*Evernia prunastri*	1483	0.19	7.4	13	58	98	15	33	42
32	5.25	*Ramalina farinacea*	750	0.38	6.0	8	54	397	24	41	78
33 A	6	*Ramalina farinacea*	1041	0.48	7.0	8	65	364	21	29	68
33 B	6	*Hypogymnia physodes*	828	0.38	7.1	4	30	377	28	19	41
34 A	8.75	*Ramalina farinacea*	675	0.24	3.3	4	43	296	16	21	72
34 B	8.75	*Ramalina farinacea*	573	0.21	3.1	5	74	289	16	30	139
35	8.75	*Evernia prunastri*	1369	0.21	7.1	8	76	123	17	23	63
36	13.75	*Evernia prunastri*	630	0.21	5.0	7	48	264	24	45	82
	Mean		898	0.31	7.8	14	72	311	27	56	95
	Median		789	0.25	6.1	8	59	292	25	45	86

[a] $\mathrm{EF} = [\mathrm{metal/Al}]_{\mathrm{sample}}/[\mathrm{metal/Al}]_{\mathrm{uppercrust}}$. Uppercrust values are taken from Taylor and McLennnan (1995).

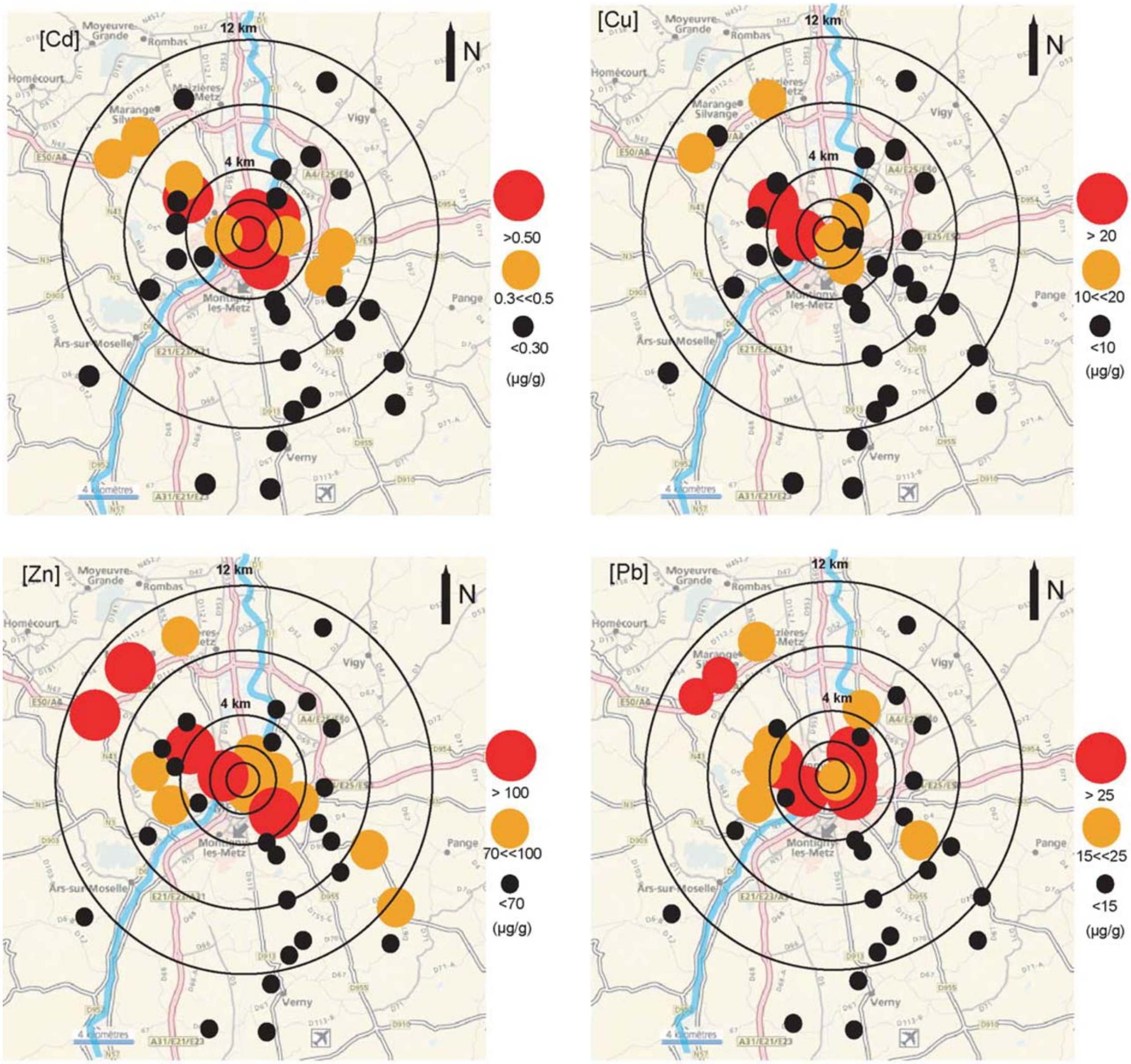


Fig. 2. Maps of Cu, Zn, Cd, and Pb concentration distributions (µg g^{-1}) measured in lichens.

compositions in order to test their homogeneity. These samples yielded a large range of ^{206}Pb/^{207}Pb ratios, from 1.095 to 1.168 (Table 3). This contrasts with the unradiogenic and more homogeneous composition of French leaded gasoline (1.084) reported by Monna et al. (1997). Data from leaded and unleaded gasoline from France cover the whole range of composition measured in lichens.

In Fig. 4a, the isotopic composition of our samples is compared to the Pb industrial line (Haack et al., 2002) and the European Standard Lead Pollution line (ESLP, Haack et al., 2002, 2003). These lines were defined using data from the literature, mainly industrial materials, Pb from car exhaust, and several major ore deposits for the Pb industrial line and materials integrating atmospheric Pb fallout in Europe for the ESLP. Also reported in Fig. 4a is the compositional field for fly ashes and flue gas residues from several municipal solid waste combustors (MSWC) in France (Debout et al., 1999; Monna et al., 1997; Carignan et al., 2005). These represent the average composition of industrial Pb. Whereas MSWC materials and aerosols from bus air filters fall along the ESPL line, lichens

Table 2
Lead isotopic composition and reproducibility on SRM 981 and lichens BCR CRM 482 and LOO1

Sample	Reference	N	^{208}Pb/ ^{206}Pb	^{206}Pb/ ^{207}Pb	^{207}Pb/ ^{206}Pb	^{208}Pb/ ^{204}Pb	^{207}Pb/ ^{204}Pb	^{206}Pb/ ^{204}Pb
NBS 981	Thirlwall DS-TIMS	41	2.16768	1.09310	0.91483	36.722	15.4980	16.9408
	2σ(2*sd)		0.00023	—	0.00007	0.008	0.0025	0.0021
	RSD (ppm)		106		77	218	161	124
NBS 981	Thirlwall DS-MC-ICP-MS	36	2.16770	1.09304	0.91488	36.724	15.4996	16.9417
	2σ(2*sd)		0.00024	—	0.00008	0.009	0.0031	0.0029
	RSD (ppm)		111		87	245	200	171
NBS 981	Typical session	71	2.16782	1.09304	0.91488	36.721	15.4973	16.9391
	2σ(2*sd)		0.00036	0.00011	0.00009	0.011	0.0035	0.0033
	RSD (ppm)		167	102	102	303	228	194
NBS 981	Mean (3 sessions)		2.16781	1.09306	0.91487	36.722	15.4974	16.9395
	2σ(2*sd)		0.00046	0.00013	0.00011	0.016	0.0050	0.0045
	RSD (ppm)		214	117	117	426	323	263
CRM BCR 482	Digestion 1		2.12865	1.13115	0.88406	37.480	15.5661	17.6075
	Digestion 1		2.12874	1.13112	0.88408	37.484	15.5674	17.6085
	Digestion 2		2.12904	1.13103	0.88415	37.501	15.5735	17.6141
	Digestion 3		2.12881	1.13111	0.88408	37.501	15.5739	17.6158
	Digestion 4		2.12870	1.13099	0.88418	37.485	15.5699	17.6094
CRM BCR 482	Mean		2.12879	1.13108	0.88411	37.490	15.5701	17.6111
	2σ(2*sd)		0.00030	0.00013	0.00010	0.020	0.0070	0.0073
	RSD (ppm)		143	115	115	528	450	415
L001	Digestion 1		2.11728	1.14121	0.87626	37.645	15.5801	17.7801
	Digestion 2		2.11716	1.14142	0.87610	37.661	15.5845	17.7885
	Digestion 3		2.11629	1.14166	0.87591	37.630	15.5747	17.7811
L001	Mean		2.11691	1.14143	0.87609	37.646	15.5798	17.7833
	2σ(2*sd)		0.00108	0.00045	0.00035	0.031	0.0098	0.0092
	RSD (ppm)		509	398	398	828	630	517

sd: Standard deviation from the mean; RSD: Relative standard deviation.

are distributed along and between ESLP and Pb industrial lines.

4. Discussion

To discriminate between anthropogenic and natural sources of HM measured in lichens, enrichment factors (EF) were calculated as follows: ($\mathrm{EF} = [\mathrm{metal/Al}]_{\mathrm{sample}}/[\mathrm{metal/Al}]_{\mathrm{uppercrust}}$), using Al as the normalising element because it likely reflects the amount of silicate aerosols. The values of the upper crust were taken from Taylor and McLennnan (1995). The drawbacks identified by Reimann and DeCaritat (2000, 2005) in using such 'global' values for the EF calculation do not apply here because of the small area studied (radius 20 km). Moreover, EF for lichens sampled from the same site are reported in Table 1, providing a measure of the variation. According to the EF, the metal anthropogenic contribution estimated in lichens varies from 93% to 98% for Cu, from 97% to 99% for Zn and from 95% to 99% for Pb where an EF of 9 represents an anthropogenic contribution of 90%. The anthropogenic Cd contribution in each lichen was at least 99%, which corresponds to an EF of 100 (Table 1) and may be up to 99.9%. Copper, Cd, Zn, and Pb revealed large anthropogenic contributions compared to the natural contribution in each location around the city; nevertheless, correlations between the HM EF are not clear. However, along a S–N cross-section, a systematic increase of Pb EF (Fig. 3a) and Cd EF (not shown) from the south toward the city centre was observed. Similar patterns were found along a SW–NE cross-section. The systematic increase towards the city centre is less clear for Cu and Zn EF, although the most enriched samples are found near the city centre. This suggests that HM may have the same anthropogenic sources or the same atmospheric behaviour (transport and fallout). The smooth tailing of Pb EF towards the south may be related to lighter winds, whereas stronger S–N winds may result in more erratic dispersion of atmospheric matter emitted from the urban area. If

Table 3
Lead isotopic composition, lead concentration and enrichment factors in lichens, bus air filters and unleaded gasoline

Species	Sample	Dist. (km) from city centre	^{208}Pb/ ^{206}Pb	^{206}Pb/ ^{207}Pb	^{208}Pb/ ^{204}Pb	^{207}Pb/ ^{204}Pb	^{206}Pb/ ^{204}Pb	EF[a]-Pb	[Pb] (μg g^{-1})
Evernia prunastri	1	15.5	2.1060	1.1528	37.85	15.590	17.973	30	6
Evernia prunastri	2	12	2.0991	1.1552	37.84	15.606	18.028	28	5
Evernia prunastri	3	11.75	2.1016	1.1542	37.84	15.599	18.005	33	3
Ramalina farinacea	4	10.25	2.1009	1.1537	37.81	15.597	17.995	31	6
Evernia prunastri	5	7.25	2.1059	1.1536	37.85	15.580	17.973	40	4
Ramalina farinacea	6	4.25	2.1045	1.1523	37.82	15.597	17.973	47	5
Evernia prunastri	7	3.5	2.1042	1.1524	37.83	15.603	17.980	48	7
Evernia prunastri	8	15	2.1066	1.1503	37.80	15.597	17.942	40	3
Evernia prunastri	9	12	2.1007	1.1552	37.82	15.585	18.003	56	8
Ramalina farinacea	10 A	9	2.1000	1.1555	37.88	15.610	18.037	43	6
Ramalina farinacea	10 B	9	2.1055	1.1526	37.85	15.596	17.976	38	5
	Mean 10	9	2.1028	1.1541	37.86	15.603	18.006	41	5
Ramalina farinacea	11	8	2.1024	1.1532	37.74	15.569	17.953	51	7
Evernia prunastri	12	6	2.1061	1.1506	37.77	15.584	17.931	50	11
Evernia prunastri	13	4.75	2.0992	1.1566	37.89	15.607	18.051	37	7
Hypogymnia physodes	14 A	3.3	2.1156	1.1438	37.74	15.596	17.839	72	34
Evernia prunastri	14 B	3.3	2.1122	1.1473	37.80	15.597	17.894	76	19
	Mean 14	3.3	2.1139	1.1455	37.77	15.597	17.866	74	26
Ramalina farinacea	15	2.75	2.1061	1.1521	37.83	15.592	17.963	74	22
Hypogymnia physodes	16	2.5	2.1057	1.1523	37.84	15.597	17.972	64	7
Evernia prunastri	17 A	1.5	2.1248	1.1344	n.d.	n.d.	n.d.	80	16
Hypogymnia physodes	17 B	1.5	2.1216	1.1395	37.68	15.586	17.760	176	36
	Mean 17	1.5	2.1232	1.1369	37.68	15.586	17.760	128	26
Evernia prunastri	18 A	1.7	2.1093	1.1494	37.81	15.597	17.928	68	14
Evernia prunastri	18 B	1.7	2.1082	1.1505	37.81	15.588	17.934	39	11
	Mean 18	1.7	2.1087	1.1500	37.81	15.592	17.931	53	13
Evernia prunastri	19	11	2.1161	1.1432	37.63	15.555	17.782	45	18
Evernia prunastri	20	5.5	2.1083	1.1513	37.81	15.577	17.934	38	9
Hypogymnia physodes	21 A	1.5	2.1302	1.1291	37.48	15.581	17.592	108	72
Ramalina farinacea	21 B	1.5	2.1267	1.1324	37.53	15.582	17.645	99	49
Ramalina farinacea	21 B	1.5	2.1266	1.1324	37.52	15.581	17.645	99	49
	Mean 21	1.5	2.1285	1.1307	37.50	15.582	17.618	104	61
Evernia prunastri	22	2.6	2.1147	1.1454	37.76	15.589	17.855	94	8
Hypogymnia physodes	23 A	4.25	2.1096	1.1480	37.78	15.600	17.909	93	25
Ramalina farinacea	23 B	4.25	2.1131	1.1466	37.72	15.570	17.853	61	12
	Mean 23	4.25	2.1113	1.1473	37.75	15.585	17.881	77	19
Evernia prunastri	24	6.25	2.1087	1.1485	37.68	15.560	17.870	70	11
Evernia prunastri	25	12.75	2.1072	1.1496	37.79	15.598	17.931	34	6
Hypogymnia physodes	26	10.75	2.1113	1.1465	37.76	15.600	17.886	120	31
Evernia prunastri	27	10.75	2.1157	1.1415	37.66	15.593	17.799	95	29
Ramalina farinacea	28	5	2.1100	1.1474	37.76	15.596	17.896	70	10
Ramalina farinacea	29	4.75	2.1102	1.1471	37.72	15.582	17.874	155	17
Evernia prunastri	30	8.25	2.1108	1.1457	37.64	15.565	17.834	36	7
Evernia prunastri	31	6.5	2.1261	1.1334	37.45	15.540	17.613	35	13
Ramalina farinacea	32	5.25	2.1047	1.1520	37.78	15.583	17.952	43	8
Ramalina farinacea	33	6	2.1073	1.1500	37.73	15.569	17.903	31	8
Ramalina farinacea	34	8.75	2.1001	1.1547	37.73	15.559	17.967	32	5
Evernia prunastri	35	8.75	2.1056	1.1510	37.80	15.599	17.954	23	8
Evernia prunastri	36	13.75	2.1048	1.1534	37.81	15.575	17.964	47	7
	Bus air filter 1		2.1065	1.1544	37.913	15.590	17.998	n.d	n.d
	Bus air filter 2		2.1091	1.1511	37.840	15.586	17.941	n.d	n.d
	Bus air filter 3		2.1090	1.1510	37.859	15.596	17.951	n.d	n.d
	Bus air filter 4		2.1071	1.1536	37.857	15.574	17.967	n.d	n.d
	Bus air filter 5		2.1064	1.1538	37.895	15.593	17.990	n.d	n.d

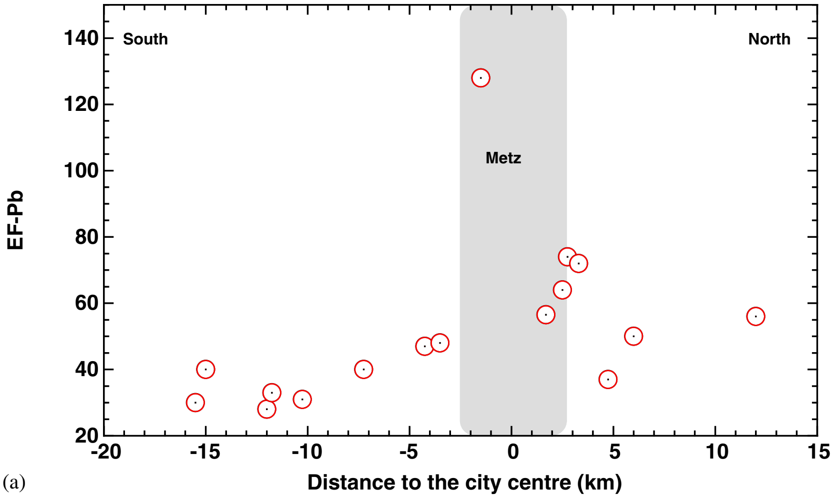
Table 3 (*continued*)

Species	Sample	Dist. (km) from city centre	^{208}Pb/ ^{206}Pb	^{206}Pb/ ^{207}Pb	^{208}Pb/ ^{204}Pb	^{207}Pb/ ^{204}Pb	^{206}Pb/ ^{204}Pb	EF^{a}-Pb	[Pb] ($\mu g\,g^{-1}$)
	Bus air filter 6		2.1084	1.1514	37.868	15.599	17.960	n.d	n.d
	Unleaded gasoline 1		2.16387	1.09453	n.d	n.d	n.d	n.d	0.01^{b}
	Unleaded gasoline 2		2.09297	1.16785	n.d	n.d	n.d	n.d	0.002^{b}

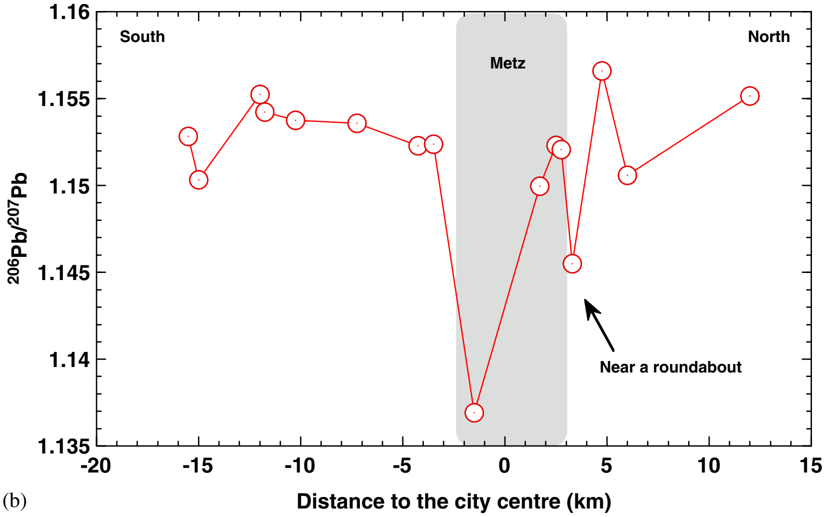
n.d.: not determined.

[a] EF = [metal/Al]sample/[metal/Al]uppercrust. Uppercrust values are taken from Taylor and McLennnan (1995).

[b] Estimation assuming 100% yield from the separative Pb chemistry.



(a)



(b)

Fig. 3. S–N cross-sections showing Pb EF (a) and Pb isotopic composition (b) vs. the distance (km) from the city centre.

Pb and Cd dispersion along the S–N cross-section can be interpreted in the light of the major wind directions, secondary emission sources seem to be dominating for Cu and Zn dispersion as well as for the HM fallout in the NW part of the study area, in the direction of an industrial area (Fig. 1).

The high Pb EF measured in lichens suggests that most Pb was anthropogenic in origin. The Pb

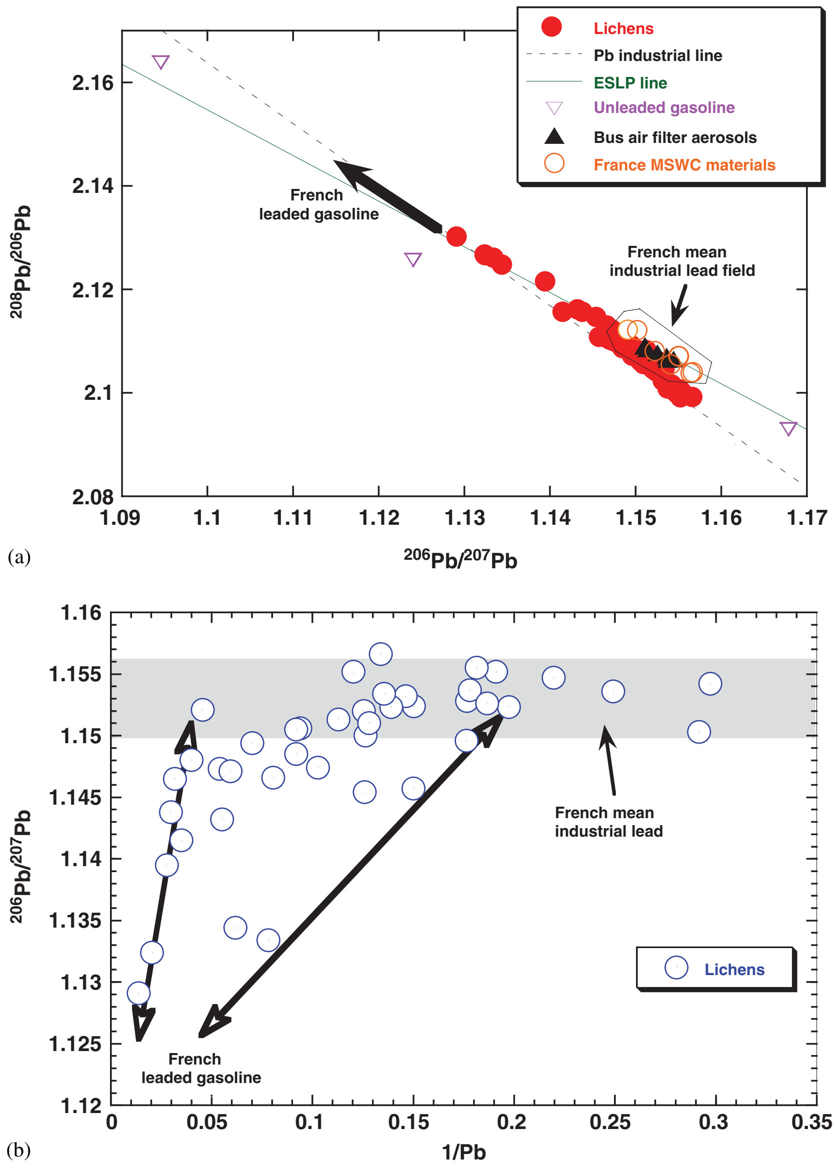


Fig. 4. (a) $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ ratio in lichens. Unleaded gasoline from Roy (1996) and this study and French mean industrial lead field from Monna et al. (1997), Carignan et al. (2005), as defined by municipal solid waste combustor (MSWC) materials. European standard lead pollution (ESLP) line and Pb industrial line are from Haack et al. (2002, 2003). (b) Lichen data in a $^{206}Pb/^{207}Pb$ vs. 1/Pb diagram.

isotopic composition will then be interpreted as a reflection of atmospheric pollution sources. According to Table 3, the heterogeneity of lead isotope ratios suggests that many sources, having distinct isotopic compositions, contributed to Pb content in lichens. In the Pb–Pb space of Fig. 4a, it is surprising that MSWC materials do not plot on the Pb industrial line. This suggests that either the industrial Pb available in France is slightly different from that used by Haack et al. (2003) to define the line, or that available industrial Pb is more heterogeneous than previously reported, and thus does not fit on a single line in a Pb–Pb isotope diagram. However, the fact that lichens plot toward the Pb industrial line suggests that sources similar to those used to define the line are present in the area.

Urban atmospheric particles recently sampled on air filters provided $^{206}Pb/^{207}Pb$ ratios ranging between 1.15 and 1.16 (Debout et al., 1999; Widory et al., 2004). The urban aerosols from bus air filters showed similar homogeneous $^{206}Pb/^{207}Pb$ ratios. Their composition is similar to that of unleaded gasoline measured in this study, and to the composition of MSWC materials. This contrasts with the unradiogenic $^{206}Pb/^{207}Pb$ (less than 1.12) measured in urban aerosols collected in the 1980s (Grousset et al., 1994; Véron et al., 1999), although in cities (e.g. Grenoble, SE France, Bollhöfer and Rosman, 2001), the Pb isotopic composition of aerosols can be highly variable, with $^{206}Pb/^{207}Pb$ ratios ranging from 1.142 to 1.115. Moreover, lead from two different unleaded gasolines had dissimilar isotopic compositions, and were different from previously published values (Roy, 1996). Lead isotopic composition from unleaded gasoline does not have a specific value. In addition, Pb is not suitable to trace gasoline combustion source emissions in France, as Pb has not been added to gasoline since ca. 1999. Note that the measured concentration in unleaded gasoline is very low (2–300 μg L^{-1}, Roy, 1996 and this study). These results suggest that urban atmospheres are no longer dominated by unradiogenic Pb from leaded gasoline, as reported by Widory et al. (2004) for the city of Paris.

Nevertheless, the compositional discrepancy between urban aerosols and lichens collected close to roads within the city of Metz is certainly striking and needs to be addressed. The unradiogenic Pb in lichens certainly originates from traffic itself. Indeed, two lichens sampled 50 and 250 m away from the same motorway showed a shift in isotopic composition, with $^{206}Pb/^{207}Pb$ ratios of 1.1415 (50 m, sample 27) and 1.1465 (250 m, sample 26). Lichens with $^{206}Pb/^{207}Pb$ ratios as low as 1.13 were also observed. In the Pb–Pb diagram of Fig. 4a, these samples plot towards the composition of leaded gasoline. This strongly suggests that lichens sampled near roads may incorporate "old Pb" from the atmosphere. This Pb is probably fixed to small particles on the roadside, which are entrained when cars and trucks pass by. Why these particles are not sampled by the bus air filters is uncertain. It may be because cleaning of city streets significantly reduces the amount of "old Pb" particles or simply because buses travel where traffic is slow, so that atmospheric remobilisation is more difficult. An alternative explanation for the unradiogenic Pb in lichens would be the fact that these organisms can be quite/very old and may have integrated the atmospheric signal over several years, including the period of time in which Pb was still added in gasoline in large quantities. Indeed, the amount of Pb added to gasoline was considerably reduced in the 1990s. This hypothesis is however not compatible with the fact that most lichens were sampled on small tree branches (i.e. <5 years old). Furthermore, Spiro et al. (2004) suggested that Pb concentration and isotopic composition in lichens rapidly equilibrate with the surrounding atmosphere. This was already observed for the Pb concentration in transplanted lichens around Metz (Signoret, 2002). For these reasons, we consider that the unradiogenic character of Pb contained in lichens near roads is better explained by the re-emission of "old Pb" (from leaded gasoline) into the atmosphere.

The Pb isotopic composition measured in lichens is correlated with the measured Pb concentration (Fig. 4b). Indeed, lichens with the highest concentrations yielded unradiogenic Pb whereas samples with lower Pb contents tended toward a more homogeneous radiogenic isotopic composition. This latter composition is in the range of the mean French industrial signal as defined by MSWC materials (Carignan et al., 2005), with a $^{206}Pb/^{207}Pb$ ratio ranging from 1.150 to 1.156. Although the Pb concentration is low in these lichens (3–7 μg g^{-1}, Table 1), the corresponding Pb EF is high enough for these isotopic compositions to be interpreted as reflecting atmospheric pollution. Furthermore, in Fig. 4b, no trend towards a crustal composition field ($^{206}Pb/^{207}Pb$ of 1.19-1.20, Monna et al., 1997; Elbaz-Poulichet et al., 1984) is observed (not represented), confirming the anthropogenic character of Pb. The high Pb content for lichens having unradiogenic Pb supports the hypothesis that "old Pb" pollution from the leaded gasoline combustion is re-emitted into the atmosphere and trapped by lichens, in addition to the actual, more diffuse, atmospheric Pb pollution.

Fig. 5 shows $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ ratios, along with compositional fields of different possible source emission materials. Firstly, and as also observed in Fig. 4a, the lichens do not form a single line but rather 2 "branches", suggesting the involvement of several sources with distinct isotopic compositions. The two "branches" meet at the radiogenic end-member, very close to the mean composition of French industrial Pb. Examples of some radiogenic industrial Pb in Europe are reported in the literature and are mostly comprised of metallurgical plants and coal power plants (Aberg et al., 1999; Chiaradia and Cupelin, 2000;

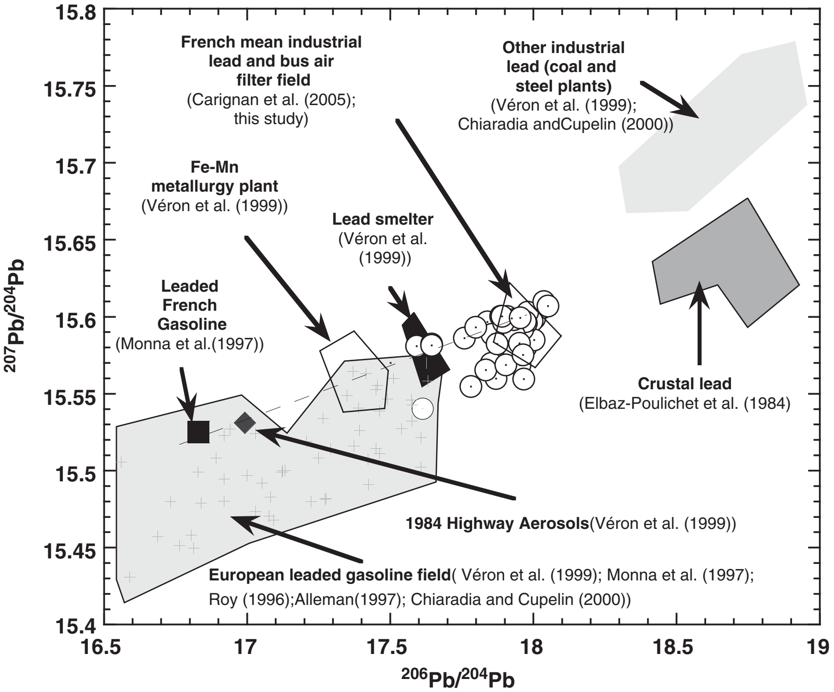


Fig. 5. Lichen ^{207}Pb/ ^{204}Pb vs. ^{206}Pb/ ^{204}Pb ratios with composition fields of different possible source materials : French mean industrial lead and other industrial lead such as coal power plant or steel plant, crustal lead, Pb smelter and Fe–Mn industry and European leaded gasoline (Véron et al., 1999; Monna et al., 1997; Roy, 1996; Alleman, 1997; Chiaradia and Cupelin, 2000). French leaded gasoline and aerosols collected in 1984 near a French highway plot on the high ^{207}Pb/ ^{204}Pb trend defined by lichens.

Haack et al., 2002; Hansmann and Köppel, 2000; Véron et al., 1999; Walraven et al., 1997). A review of all the possible Pb emitters into the atmosphere in the study area is difficult and therefore has not been done. However, such industries are common within and around Metz. The unradiogenic sources are more diffuse. The lichens with higher ^{207}Pb/ ^{204}Pb ratios are certainly well represented by the leaded gasoline "old Pb" pollution, as available leaded gasoline in France at the time had a composition that fits this trend. Furthermore, aerosols sampled near highways in France at that time (Véron et al., 1999) also plot on that trend. Sources having lower ^{207}Pb/ ^{204}Pb ratios are more difficult to identify. Examples of industrial Pb with this composition are scarce in the literature. Spiro et al. (2004) reported a low ^{207}Pb/ ^{204}Pb for transplanted lichens around a major smelter in Russia. Isotopic data on agriculture materials are also scarce, and the Pb isotopic ratios reported are very radiogenic (Roy and Négrel, 2001).

5. Conclusions

Trace metal concentrations and lead isotopic compositions were measured in epiphytic lichens sampled in the urban area of Metz (NE France) within a 15 km radius around the city centre. For the first time, the results permit mapping of the atmospheric dispersion and deposition of HM at a local scale. Trace metal concentrations were higher in the city centre than in the surrounding area. High concentrations were also found in the NW part of the study area. The enrichment factors calculated indicated that HM were derived from anthropogenic activities at all sites. The anthropogenic HM contribution to the lichen samples was at least 93% (for Cu) and reached up to 99.9% (for Cd). The dispersion of HM may be correlated with wind direction and/or secondary pollution sources. Lead and Cd concentrations and EF decreased rapidly within 5 km of the city centre, and more slowly outside this 5 km radius. This trend was less clear for Cu and Zn. Heavy metals may either have similar anthropogenic sources or similar atmospheric behaviour.

Lead isotopic compositions measured in lichens were interpreted as the result of a mixing between different anthropogenic sources. The isotopic composition of aerosols collected on municipal bus air filters indicated that atmospheric lead in urban settings is no longer dominated by unradiogenic Pb from leaded gasoline combustion. Unradiogenic Pb in lichens collected in the city near high traffic roads was interpreted as reflecting "old Pb pollution" re-emitted into the atmosphere. This study shows that urban and more diffuse rural atmospheric Pb pollution are currently quite similar in terms of their isotopic composition. Such a survey of the atmospheric pollution and associated maps may provide a reference framework for future studies. Comparisons through time will permit monitoring of the evolution of the urban atmosphere and estimation of the atmospheric impact of new power plants and their implications on the surrounding environment. Another solution to survey such environmental impacts would be to monitor the isotopic composition of transplanted lichens.

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