Trace elements biomonitoring in a historical mining district (*les Malines*, France)

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- Impacts from historical Zn–Pb mining in southern France are investigated.
- High Pb, Cd and As levels due to historic mining were found in soils.
- Apiary products, especially honey do not show signs of contamination.
- Lichen and moss confirm their potential as bioindicators for Zn, Pb and Cd.
- Pb isotopes allow the identification of pollution sources.

Keywords:
Biomonitoring
Trace elements
Isotopes
Honeybees
Lichen
Moss

The aim of this study is to investigate the trace elements (TE) contents of potential biomonitors in a historical Zn–Pb mining district: apiary products (honey, royal-jelly and beeswax) lichen and moss were sampled and analysed. In spite of high TE concentrations in mining waste and soil, apiary products are free of TE contamination originating from historical mining. Lichen/moss show high TE levels, which suggest atmospheric input of local dust. Pb isotopes analysis proved the origin of TE found in lichen/moss to be mainly mining waste. These results help discuss the choice of relevant organisms for monitoring TE in the environment and bring additional data on the potential impacts of brownfields left after mining, especially on food products from apiaries.

1. Introduction – TE biomonitoring

1.1. Use of apiary products

Honeybees are manageable social insects, which are easily captured to provide material for studies: foragers actively sample their environment in a limited range around the hive (about 7 km^2) and are potentially exposed to soil, air and water contamination (Conti and Botre, 2001). They have been thought of to be potential biomonitors for various contaminants and have been studied as such for trace elements (TE), radionuclides (Tonelli et al., 1990), or pesticides (Lambert et al., 2012). TE contents can be used to certify the geographical origins of honey (Hernandez et al., 2005; Terrab et al., 2005) or to assess honey quality (Devillers et al., 2002; Pisani et al., 2008). Biomonitoring using apiary products has also been extensively investigated (Bogdanov et al., 2007; Tuzen et al., 2007; Pohl et al., 2009) with contradictory outcomes. Tuzen et al. (2007) suggested a possible use of honey, while according to Bogdanov et al. (2007), low concentrations and high natural variations should deter from using honey for TE environmental monitoring. An improved insight could be obtained using honeybees, pollen, propolis and wax according to Conti and Botre (2001). Additional data to clarify these views are required and historical mining may provide information on TE contamination pathways.

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1.2. Use of lichen and moss

The use of lichen, moss or both for monitoring atmospheric contamination has been extensively investigated (Markert et al., 1996; Harmens et al., 2004; Colin et al., 2005) and proved efficient to assess TE contaminations from historical mining (Sondergaard et al., 2010). Some authors use lichen/moss to monitor quick compositional changes related to atmospheric TE contamination (Spiro et al., 2004), while others hypothesise a continuous TE accumulation (Colin et al., 2005). Lichen in particular was shown to be highly resistant to metal stress (Chettri et al., 1998; Sarret et al., 1998) and resident lichen/moss species can be used for direct analysis of their TE content in relation to average atmospheric fallouts over time. This approach has been used at different scales (Doucet and Carignan, 2001) and particularly for historical mining in southern France (Baron, 2005). The approach of Baron (2005) was adapted here for the *les Malines* mining district so as to compare apiary products and lichen/moss as potential biomonitors of TE contamination.

1.3. Tracing contamination sources

The comparison of results obtained using lichen/moss and apiary products should provide additional insights on the fate of TE in historical mining environments. In addition, Pb isotopic ratios have been determined in the different materials, using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), in order to track the different sources of lead. Among the four existing Pb isotopes, ^{208}Pb, ^{206}Pb and ^{207}Pb originate from the radioactive decomposition of ^{238}U, ^{235}U and ^{232}Th respectively, while ^{204}Pb is a non radiogenic isotope, which only represents 1% of the total Pb. As Galena (PbS), the main Pb ore exploited, does not incorporate U and Th, its Pb isotopic composition is frozen from the formation of ore bodies. Subsequently, Pb isotopes are not fractionated in industrial processes, making the identification of sources possible. The technique proved efficient for Pb contaminated lichen/moss in historical mining districts (Baron, 2005; Sondergaard et al., 2010). As a result, ICP-MS measurements were selected for our investigations.

2. Methods and materials

2.1. Study area and sampling sites

The study area, located in southern France (Fig. 1) displays drastic contrasts: it is located in a low population density area (<50 people per km^2), between a national park (*Parc National des Cévennes*, established 1970) and a Special Area of Conservation (SAC) of the *Natura 2000* network (European Union wide network of nature protection established under the 1992 Habitats Directive). Thus, we could expect potential biomonitors from the area to display mere background TE levels. Yet the region also has a mining history: *les Malines*, where an estimated 1Mt ore was extracted from 1885 to 1991 remains the largest Zn–Pb exploitation France ever knew (Leguen et al., 1991). Former mines indicated on Fig. 2 were listed from national surveys (BRGM, 2012).

Previous studies on the mining district reported high TE levels in soil and the occurrence of several metal hyperaccumulator plant species (Grison et al., 2010). High TE levels in fish have also been

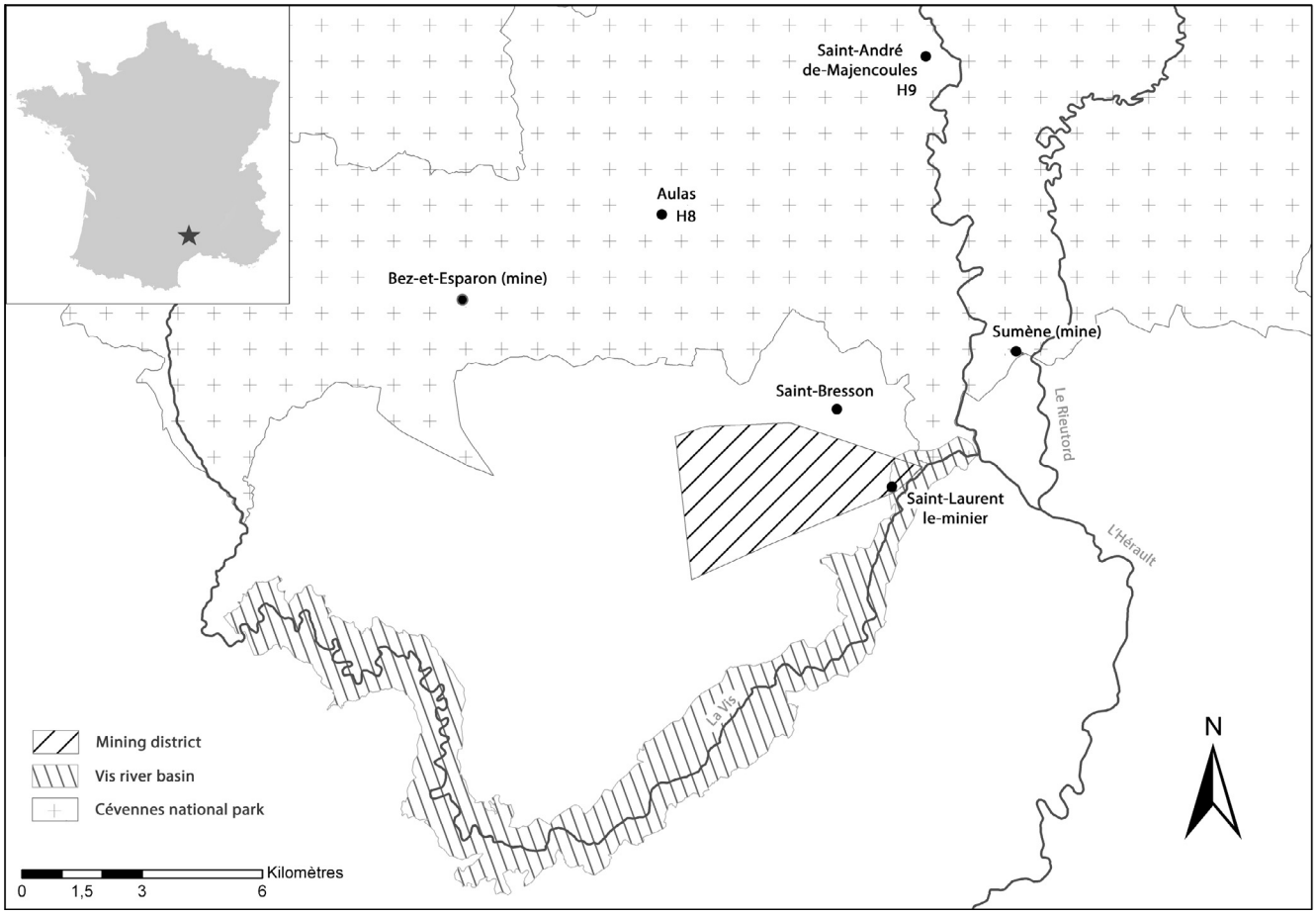


Fig. 1. Context of the 'Les Malines' mining district.

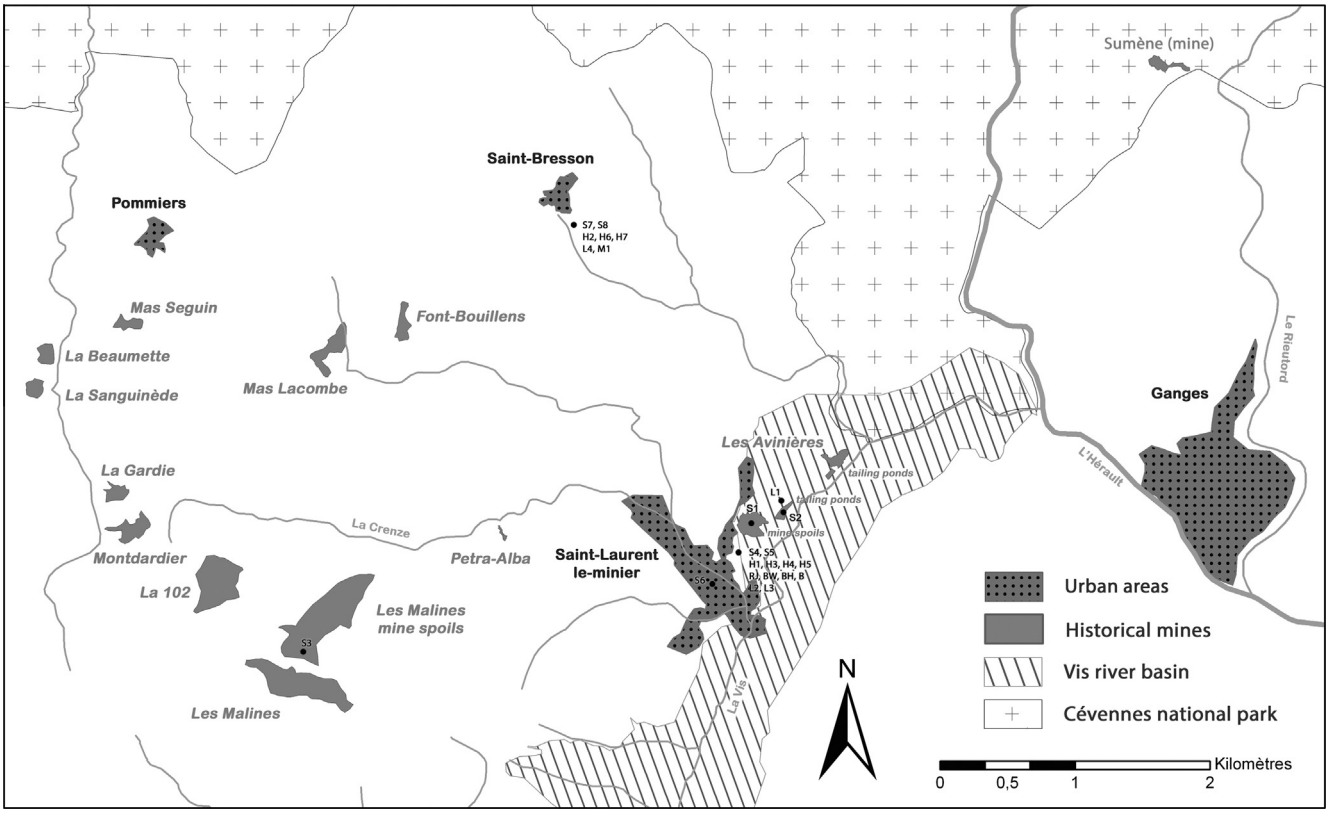


Fig. 2. Detailed map of the sampling area within the *les Malines* mining district.

Table 1
Quality control for apiary products and lichen/moss analysis (values in mg kg^{-1}).

	Mg	P	Ca	Cr	Mn	Co	Ni
Mean (n = 5)	1372	3311	4752	0.477	17.8	0.072	0.557
Standard-deviation	50	131	66	0.06	0.18	0.003	0.071
Certified values (WEPAL IPE 110)	1440	3250	4920	0.493	17.9	0.074	0.554
% Recovery	95	102	97	97	99	97	101
	Cu	Zn	As	Cd	Sb	Ba	Pb
Mean (n = 5)	7.191	32.165	0.083	0.124	0.037	4.910	1.158
Standard-deviation	0.1	0.7	0.002	0.001	0.002	0.03	0.05
Certified values (WEPAL IPE 110)	7.35	32.7	0.0911	0.126	0.0354	5.48	1.15
% Recovery	98	98	91	98	104	90	101

reported elsewhere in the region (Monna et al., 2011), but to date no studies were conducted on apiary products and other biomonitors in the area.

2.2. Sample treatment and analysis

2.2.1. General

All reagents used in this study were of high purity: commercial HNO_3, HCl and H_2O_2 were obtained from Sigma–Aldrich TraceSELECT® range. All solutions were prepared using double deionised water (Milli-Q Millipore 18.2 MΩ cm at 21 °C). For each digestion procedure, blank and standard digestions were carried out the same way and analysed for controls. ICP-MS analyses were performed with a Thermo scientific X Series II ICP-MS (Plateforme AETE – HydroSciences/OSU OREME, Montpellier – France) using In and Bi as internal standards. Lead isotope ratios have been determined on the same ICP-MS platform. ^{206}Pb, ^{207}Pb and ^{208}Pb were measured with respective residence times of 20 ms, 20 ms and 15 ms. 10 runs of 100 sweeps were obtained for each analysis. External mass bias correction using NBS 981 was used (Aries et al., 2001). Dead time was determined for lead isotopes (Monna et al., 1998; Aries et al., 2001) on our X Series II ICP-MS. A value of 35 ns was found and entered in the Plasma Lab software (Thermo Fischer Scientific) to automatically correct the signal intensities. Lead concentrations in NBS 981 standard were adjusted at 20 ppb, while it ranged from 4 to 15 ppb in the samples. Lead concentrations in the samples and standard NBS 981 gave a maximum signal intensity of 10^6 on ^{208}Pb.

Table 2
French guide values for soils TE content ('sensitive use' mg kg^{-1} dry weight).

Element	Zn	As	Cd	Tl	Pb
FIVs	9000	37	20	10	400

2.2.2. Apiary products

Hives locations are indicated on Fig. 2: two apiaries containing 5 and 6 hives respectively were sampled in Saint-Laurent-le-

Table 3
Soil elemental contents (mg kg^{-1} dry weight).

Sample	Type	Location	Distance from mine[a] (m)	Zn	As	Cd	Tl	Pb
S1	Mine spoils	*Les Avinières*	0	86 706[b]	4 247[b]	408[b]	317[b]	66 388[b]
S2	Mine tailings	*Les Avinières*	0	125 456[b]	734[b]	1 605[b]	37.1[b]	88 472[b]
S3	Mine tailings	*Les Malines*	0	56 999[b]	103[b]	386[b]	6.45	3 686[b]
S4	Soil around beehives	*Les Avinières*	250	3 684	147[b]	8.79	16.1[b]	1 234[b]
S5	Soil under beehives	*Les Avinières*	250	2 513	125[b]	7.47	9.5	858[b]
S6	Soil	*St-Laurent*	500	2 879	75[b]	8.26	3.6	1 787[b]
S7	Soil around beehives	*St-Bresson*	1500	50.8	159[b]	<dl	4.8	379
S8	Soil under beehives	*St-Bresson*	1500	202	127[b]	<dl	2.6	369

na = Not available; <dl = value below detection limit.
[a] Distance from the closest mine, which is *les Avinières* for samples collected in *Saint-Laurent-le-Minier* and *Font-Bouillens* for samples collected in *Saint-Bresson*.
[b] Values above FIVs.

Table 4
Honey (H), royal-Jelly (RJ), beeswax (W) (fresh weight) and honeybees (BH, B) (dry weight) elemental content (mg kg^{-1}).

Sample	Location	Distance from mine[a] (m)	Season	Mg	P	Ca	Mn	Zn	As	Cd	Sb	Tl	Pb
H1	Les Avinières	250	04.2011	80.5	40.7	187	5.81	0.806	0.001	0.009	0.002	0.006	0.003
H2	St-Bresson	1500	05.2011	122	78.4	204	9.17	0.556	0.001	0.004	0.001	0.001	0.035
H3	Les Avinières	250	05.2011	125	115	219	6.77	1.4	0.003	0.022	0.003	0.037	0.101
H4	Les Avinières	250	06.2011	44.8	65.6	76.7	3.22	0.905	0.001	0.003	0.001	0.006	0.011
H5	Les Avinières	250	07.2011	163	66.6	277	10.5	0.613	0.001	0.001	0.001	0.012	0.009
H6	St-Bresson	1500	06.2011	101	80.1	200	7.86	0.429	0.008	0.006	0.002	0.013	0.005
H7	St-Bresson	1500	07.2011	66	82.3	168	10.6	0.429	0.002	0.003	0.001	0.019	0.025
H8	Aulas	4000[b]	2011	32.8	59.4	36.4	1.38	<dl	<dl	0.001	<dl	0.012	0.006
H9	Majencoule	7500[c]	2011	145	62.8	206	12.8	<dl	0.001	0.001	0.002	0.003	0.014
RJ	Les Avinières	250	05.2011	33.8	61.7	123	0.304	0.906	0.005	0.007	0.002	<dl	0.168
W	Les Avinières	250	05.2011	167	78.8	305	16.1	1.520	0.012	0.006	0.001	0.013	<dl
BH	Les Avinières	250	05.2011	2 047	13 050	1 857	93.1	167	0.056	2.9	0.026	0.133	1.44
B	Les Avinières	250	05.2011	2 286	14 290	1 783	80.7	172	0.059	2.5	0.025	0.149	0.832

<dl = Value below detection limit.
[a] Distance from the closest mine, which is *les Avinières* for samples collected in *Saint-Laurent-le-Minier* and *Font-Bouillens* for samples collected in *Saint-Bresson*.
[b] Distance from the mine located in *Bez-et-Esparron*.
[c] Distance from the *les Jumeaux* mine in Sumène.

Table 5
Maximum and minimum TE levels previously reported in honeybees (mg kg^{-1} dry weight).

Element	Min	Source	Max	Source
Cr	0.000052	Conti and Botre (2001)	6.1	Kump et al. (1996)
Mn	n.a		59	Kump et al. (1996)
Ni	0.3	Balestra et al. (1992)	2.1	Kump et al. (1996)
Cu	n.a		32.1	Kump et al. (1996)
Zn	200	Kump et al. (1996)	1100	Leita et al. (1996)
Cd	0.00287	Conti and Botre (2001)	7	Leita et al. (1996)
Pb	0.00052	Conti and Botre (2001)	27	Leita et al. (1996)

Minier (*les Avinières*) and Saint-Bresson. Harvest times are indicated in Table 4. Honey was extracted using stainless steel collectors and kept in generic clean glass jars used by beekeepers for honey retail: processing was assessed in order to ensure that no TE contamination resulted from jars or their lids. Royal jelly and beeswax were taken directly from the hives and stored in clean polyethylene jars. As for the bees, dead individuals from a recently collapsed colony were collected both from inside and outside the hive and dried before digestion.

An open vessel wet-digestion, which proved efficient to recover on average 93% of honey TE content was used after Tuzen et al. (2007): samples were warmed to 30 °C and homogenised before 3 g were taken for analysis. 12 mL of an oxi-acidic mixture (2:1 HNO_3:H_2O_2) were added per gram sample and the resulting solution was heated at 100 °C until dry. Dry residues were solubilised in HNO_3 (2.5% v:v) for analysis. WEPAL IPE 110 (yellow clover) obtained from LGC standards, was used as a reference material (Table 1) as no certified reference materials are available for honey. Standard additions also confirmed the result obtained for apiary products. Blank TE levels represented less than 1% of the levels measured in samples of interest.

2.2.3. Lichen and moss

Lichen and moss were collected using Teflon spatulas and clean polyethylene jars, where they were abundant so as to average TE levels over the area around beehives. Different species of lichen (*Cladonia rangiformis* or *Parmelia acetabulum*) or moss (*Scleropodium purum* and *Dicranum scoparium*) were kept separate (Table 6). Samples were treated according to the guidelines by the European Commission, Standards, Measurements and Testing Programme (Quevauviller et al., 1996): samples were air dried and all adhering particles manually removed before crushing in an agate mortar. The powder obtained was then treated according to the procedure described for apiary products. WEPAL IPE 110 was once again used for quality control (Table 1) as well as inter-laboratory certification samples (fodder). For lichen/moss blank TE levels represented less than 0.5% of the levels measured in samples of interest.

2.2.4. Soil digestion

Samples were taken from horizon A using Teflon spatulas and clean polyethylene jars. S1–S3 (Fig. 2 – Table 3) are not actually soil but mining waste and tailings; S4, S6 and S7 are a mixture of mineral soil and humus found around beehives (S4–S7) or pastoral areas in Saint-Laurent-le-Minier (S6); S5 and S8 are a mixture of mineral soil and waste expelled from beehives by bees. Samples were treated according to a house procedure: dried at 60 °C until weight was stable, sieved to 2 mm and homogenised. Approximately 120 mg of sample were digested following the procedure:

Table 6
Lichen and moss elemental content (mg kg^{-1} dry weight).

Sample	Species	Location	Distance from mine[a] (m)	Mg	P	Ca	Cr	Mn	Cu	Zn	As	Cd	Sb	Tl	Pb
L1	*Cladonia rangiformis*	*Les Avinières*	0	1178	698	3855	1.18	22.7	8.01	1041	5	15.1	3.51	0.317	614
L2	*Cladonia rangiformis*	*Les Avinières*	250	3321	548	10032	3.15	97.9	5.34	286	9.28	0.628	1.16	0.902	72.6
L3	*Parmelia acetabulum*	*Les Avinières*	250	2015	1419	25342	2.47	60.9	17.9	107	1.36	0.42	0.308	1.46	33.5
L4	*Parmelia acetabulum*	*St-Bresson*	1500	4238	1910	36349	4.29	382	14.8	70.6	11.4	0.201	1.23	1.08	36.3
M1	*Scleropodium purum + Dicranum scoparium*	*St-Bresson*	1500	3946	2847	12127	1.11	265	11.8	37.2	1.85	0.002	0.557	2.07	13.1

[a] Distance from the closest mine, which is *les Avinières* for samples collected in Saint-Laurent-le-Minier and *Font-Bouillens* for samples collected in *Saint-Bresson*.

Table 7
Pb isotope ratios.

Sample	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
S1	2.0892	1.1723
S2	2.0902	1.1751
S3	2.0921	1.1751
S4	2.1065	1.1548
S5	2.0862	1.1710
S6	2.0872	1.1696
L1	2.0947	1.1696
L2	2.0971	1.1696
L3	2.1011	1.1615
L4	2.1010	1.1588
M1	2.1035	1.1522

(i) 4 mL H_2O_2 (ii) 4 mL HNO_3 (iii) 4 mL HNO_3:HCl (1:3). In each step, the resulting solution was heated at 100 °C until dry. Dry residues obtained after step (iii) were solubilised in HNO_3 (2.5% v:v) for analysis. This procedure was certified by Grison et al. (2010) using BIPEA soil sample 402 (interlaboratory certification) as a reference material. For soil, blank TE levels represented only 0.1% of the levels in samples analysed.

3. Results and discussion

3.1. Soil TE content

In a risk-based approach, French authorities issued guideline values for contaminated land management: Fixed Impact Values (FIVs) based on toxicity studies consider the chronic risks to public health related to the actual land use. 'Sensitive use' values were selected here (Table 2) due to the occurrence of human activities (housing, beekeeping.). These values were defined to be used in a specific scoring framework, but may also provide information on the level of concern for a specific site (Carlon, 2007).

S1 and S2 taken from the *les Avinières* mine spoils and tailing ponds show the highest TE contents (Table 3), with values for Zn, As, Cd, Tl and Pb largely above FIVs. S3 from the *les Malines* tailing ponds is very similar, except for its lower Tl content, and also represents a potential source of contamination. Regarding other samples, they are all below FIVs for Zn and Cd meaning that Zn or Cd contents of samples S4 through S8 should not be considered as potential threats to public health. Values for As on the other hand all exceed FIVs with an average 3.4-fold FIV for As: in this case, potential toxicity and high concentrations should be taken seriously. Tl and Pb are more contrasted with a few values above FIVs. However, there is a clear trend of decreasing Tl and Pb levels as the distance from mines increases: such a phenomenon is very likely to be related to dust transport by winds, an effect previously reported elsewhere (Sondergaard et al., 2010).

Lead exposure was reported in the area, on children known to have used tailing ponds as a playground, and eaten locally grown vegetables. This highlights the crucial need for further investigation in contaminants linkages as water and wind erosion may result in widespread TE contamination: Pb levels above 1000 mg kg^{-1} were measured 4.5 km downstream the Vis river in this case (Escarre et al., 2011). Potential impacts on human health, activities and livelihoods could be serious (Conesa and Schulin, 2010): precautionary measures such as restrictions on the use of local wells for water supply were set up, and restrictions on the trade of locally produced vegetables are currently enforced. To date, the potential impacts of historical mining on beekeeping have not been investigated.

3.2. Elemental contents of potential bioindicators

3.2.1. Honey (Table 4)

Ca, Mg and P with average levels (±standard deviation) at 175 ± 74.1 mg kg^{-1}, 97.7 ± 44.9 mg kg^{-1} and 72.4 ± 20.6 mg kg^{-1} are the main cations present in honey. Mn and Zn are next with average levels at 7.57 ± 3.69 mg kg^{-1}, and 0.571 ± 0.440 mg kg^{-1}. This is in accord with the trends highlighted by Devillers et al. (2002): Ca, Mg, P and Mn are known for their physiological role and their presence in honey is of lesser concern for risk assessment.

Higher Zn contents of statistical significance (Wilcoxon test, $z = -2.460$, $P = 0.0139$) could be measured in honey samples H1 and H3-5 collected in the vicinity of mine dumps (<250 m) compared to H2, H6-9 collected further away (>1500 m). However Zn content in honey from the region appears to be rather low compared to literature data: the highest Zn content previously reported in honey was 113 mg kg^{-1} in a single sample (Pohl et al., 2009) and an average 29.4 mg kg^{-1} related to car exhausts in Italy (Leita et al., 1996). However, usual means for Zn content in honey range from 1.3 mg kg^{-1} (Devillers et al., 2002) to 7.76 mg kg^{-1} (Przybylowski and Wilczynska, 2001). Background levels of Zn in honey from the area (H8, H9) are particularly low: this is probably related to floral composition and beekeepers practices. The influence of floral composition was previously emphasised as a major factor (Bogdanov et al., 2007) and the use of galvanised containers frequently reported as a possible source of Zn (Gonzalez-Paramas et al., 2000). Galvanised containers were not used, and it appears from our measurements that historical Zn mining has no worrying influence on the Zn content of honey.

The presence of other TE could be related to historical mining, namely Pb (26 ± 20 μg kg^{-1}), Tl (13 ± 10 μg kg^{-1}), Cd (7 ± 6 μg kg^{-1}) and As (3 ± 4 μg kg^{-1}). H3 harvested in the vicinity

of *les Avinières* shows the highest Pb (101 μg kg^{-1}), Tl (37 μg kg^{-1}) and Cd (22 μg kg^{-1}) levels, which correlates with soil analyses. As regards Pb, Tl, Cd and As contents, no statistically significant differences could be related to the vicinity of historic mines (Wilcoxon test, $P > 0.05$) and sources of variability other than the presence or absence of mining waste are to be sought. Besides, Pb, Cd and As levels observed here are all within concentration ranges previously described according to the literature (Pohl et al., 2009) and thus, honey consumption should be safe. H8 and H9 (background) actually show the lowest As and Cd levels but an exception occurs for Tl with a high level in H8: an increased attention should be given to this element, which was considered for the first time in this study.

The absence of effect of historical mines was reported in other contexts (Iskander, 1996), and our measurements confirm the views expressed by Conti and Botre (2001): using solely honey cannot provide quantitative information on environmental TE levels. Reciprocally, honey production in a historical mining environment appears to be safe and may support livelihoods.

3.2.2. Royal-jelly and beeswax (Table 4)

Ca, P, Mg, Zn and Mn are the most abundant minerals found in royal jelly and they are those necessary for larvae development. This observation is consistent with previous studies and concentrations of TE in royal jelly are of the same order of magnitude as those previously reported outside mining districts (Stocker et al., 2005). With regards to Zn, Cd and Pb, Leita et al. (1996) reported a higher content in royal jelly compared to the corresponding honey. This is not consistent with homeostasis observations by Stocker et al. (2005) and in our case Zn, Cd and Pb levels were comparable in royal-jelly (RJ) and the corresponding honey (H3). Once again no impacts of mining could be inferred from our measurements. The same trend was observed for beeswax with low Pb, Cd and Tl content. The very low mineral content of beeswax should be noticed and detract from using it for TE monitoring. Our measurements and homeostasis emphasised by Stocker et al. (2005) also show that royal jelly does not provide additional information compared to solely using honey.

3.2.3. Honeybees (Table 4)

Most abundant elements in honeybees are again P, Mg, Ca, Zn and Mn of physiological origin. Table 5 provides a review of previous TE measurements on honeybee tissues: according to these data, Cd levels only are to be considered as high among our samples. Tl for which no comparisons are possible yet, could also endanger bees' health due to its high toxicity. Beekeepers appeared to be worried of the possible impact of TE originating from historical mines on bee colonies: the fact that dead bees collected inside (BH) and outside the hive (B) after a colony collapse show similar TE contents, suggests that climate disturbances affecting food availability could be the major factor. This was previously emphasised, particularly in the Mediterranean regions (Dixon, 2009). It also appears to be difficult to relate qualitative observations on bees to the presence of historical mines and the presence of noxious TE except for Tl and Cd, which could require further investigations. According to such observations, honeybees cannot be used for biomonitoring purposes.

3.2.4. Lichen/moss (Table 6)

Samples showed no visible signs of intoxication due to the presence of metals and levels of major elements such as Mg, P, Ca and Mn are within usual ranges (Szczepaniak and Biziuk, 2003). The decrease in the main nutrients (Mg, Ca and Mn) near the contamination source is nonetheless a sign of depressed health. In the case of *C. rangiformis* potentially toxic elements show different behaviours: Cr, As and Tl concentrations increase with the distance from mine, while Cu, Zn, Cd, Sb and Pb concentrations decrease. Zn, Pb and Cd are particularly remarkable as concentrations decrease by 1 or 2 orders of magnitude from 0 to 250 m. Similar trends were reported for species *C. rangiformis* in Turkey (Cayir et al., 2007) but concentrations remain lower: namely 30.5 ± 9.15 mg kg^{-1} for Zn, 6.95 ± 9.63 mg kg^{-1} for Pb and 0.31 ± 0.14 mg kg^{-1} for Cd. For As and Tl our measurements are the first to be reported and cannot be compared.

As a general rule, samples from *les Avinières*, terricolous lichen (L1, L2) show higher TE contents than corticolous lichen (L3): this is clearly related to soil, an effect previously emphasised by Sondergaard et al. (2010). In the case of L3, where low direct influence of soil is expected, high TE levels are still found, which probably reflects atmospheric dust deposition. For samples originating from *St-Bresson*, TE contents are generally lower, which is consistent with data on soil there. Negative correlations between TE levels and distance from historical mines can be observed, and Zn, Cd, Tl and Pb correlation patterns in lichen/moss are similar to those

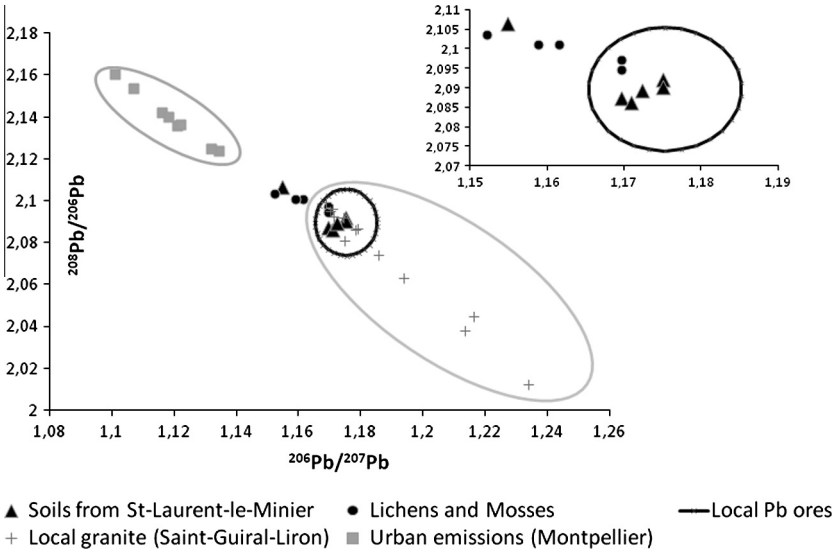


Fig. 3. Lead isotopic data for soil, lichen and moss (this study) and urban emission (Monna et al., 1997).

observed in soil. This shows a very different response compared to apiary products and honey in particular: lichen and moss are contaminated through dust fixation after transport by wind rather than selective bioaccumulation. In addition to elemental content determinations, Pb isotopes determination may improve sources characterisation.

3.3. Pb isotopic data (Table 7)

Ores from *les Malines* show a very homogeneous Pb isotopic composition, which allows precise characterisation (Leguen et al., 1991). Fig. 3 summarises our results on the determination of Pb isotopes in soil and lichen/moss samples taken from *les Malines*. Literature data on the isotopic composition of background Pb from local granite is also included, along with data on Pb originating from general anthropogenic emissions from the area (Monna et al., 1997). The range of Pb isotopic signatures is $^{206}Pb/^{207}Pb$ 1.1008–1.1342 and $^{208}Pb/^{206}Pb$ 2.1236–2.1603 for general urban emissions, $^{206}Pb/^{207}Pb$ 1.1674–1.1857 and $^{208}Pb/^{206}Pb$ 2.0741–2.0978 for ores from *les Malines*. Although such graphs may result from mixing more than 2 sources of Pb (Ellam, 2010), they allow separating definite regions, and identifying potential sources as indicated on Fig. 3.

All soil considered except S6 show the isotopic signature of Pb from *les Malines* ores. This observation associated with data on soil elemental contents strongly suggests, that Pb contamination actually originates from mining and is not the result of a local natural peculiarity. The case of S6 is the result of a combination of a major source, Pb originating from historical mining, and a minor source, probably related to emissions from surrounding larger cities. In the case of lichen/moss, samples L1 and L2 show the signature of Pb ores from *les Malines*, confirming the influence of mining waste on these samples. Other samples (L3, L4 and M1) also show a combination of two sources, historical mining as a major component and urban sources as a minor component. Even 20 years after closure, the influence of mining on the environment is still obvious, with deposition of contaminated dust in the surroundings.

4. Conclusion

As regards apiary products, the results presented here show, that they should not be used for TE environmental monitoring: the *les Malines* mining district presents an obvious problem of TE contamination in soil, but no clear relationship between soil contamination and apiary products TE contents could be emphasised from our data except for Zn. However, honey in particular is not affected by the high environmental TE levels: TE levels are comparable to those observed in uncontaminated areas and beekeeping remains a safe activity, which may support livelihoods.

Lichen/moss on the other hand confirmed their potential to average atmospheric deposits over time: no selective bioaccumulation could be determined from our measurements as lichen/moss elemental content showed similar TE distributions as soil. Pb isotopes determination proved efficient to discriminate sources of Pb in lichen/moss: historical mining is a major source of Pb in atmospheric deposits over the area, and dust transport by wind appeared as a major factor. Other minor anthropogenic sources could also be identified, but their intensity was lower than historical mining. Thus, we would recommend further investigations on dusts transport in the area as it appears to have a critical role in TE diffusion. Lichen/moss could be used as an efficient tool for such purposes.

In addition to data on TE levels in potential biomonitors, isotopic distribution for Pb may provide increased information: it could prove particularly useful in cases where the *polluter pays* principle should apply.

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