

# Heavy metal distribution in some French forest soils: evidence for atmospheric contamination

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## Abstract

This study is one of very few dealing with the distribution and the origin of heavy metals in French soils from *a priori* non-polluted forest areas. The abundance of heavy metals measured in these soils decreases as follows: Cr > Zn > Pb > Ni > Cu > Co ≫ Cd. Total concentrations of Pb, Cr and Ni in some soils exceed the European thresholds for non-polluted soils and even the French association of normalization critical values for sludge spreading. The lowest heavy metal contents are observed in acid soils while the highest concentrations are in the calcaric cambisol and in the mollic andosol, which is rather scarce as compared with the other French forest soils. With the exception of the podzol, Cr and Ni concentrations increase with depth in all soil profiles. The distribution pattern of Co, Cu, Zn depends on the soil characteristics. In some acid soils, however, Cu and Zn decrease with depth. Pb and Cd are accumulated in the upper soil horizons. Heavy metals accumulate in deep soil horizons in relation to important clay content in the dystric planosol and stagnic luvisol. The concentration of each heavy metal is always controlled by different parameters (soil pH, iron and aluminum oxide content, clay content, organic matter and cation exchange capacity), which are heavy metal specific. This study highlights the metal-trapping character of andosol and calcaric soil, the weak heavy metal retention in acid soils, the leaching and trapping character in leached clayed soils, and the migration of heavy metals in the podzol. Pb and Cr concentrations indicate a significant enrichment in surface horizons from various soils in areas which receive significant acid atmospheric pollution. Particularly, the highest Pb content is observed in a soil located in the N-NE part of France. Lead isotope ratios measured in the cambic podzol and the calcaric cambisol, exhibit the importance of the anthropogenic sources and particularly the influence of global atmospheric inputs from leaded gasoline compared to regional and local industrial emissions. The anthropogenic Pb contribution is estimated to 83, 30 and 11%, respectively, for surface, intermediate and deep horizons of the cambic podzol located in the northern part of France, and to 68% in surface horizon of the calcaric cambisol located in the Alps.

**Keywords:** Heavy metals; Forest soils; Acidity; Organic matter; Iron oxides; Clay; Enrichment factor; Pb isotopes; Anthropogenic impact

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## 1. Introduction

The impact of heavy metal pollution on ecosystems due to anthropogenic activities like smelting or mining activities has been frequently investigated (Adriano, 1986; Chuan et al., 1996; Cambier, 1997; Dijkstra, 1998; Sheppard et al., 2000). In industrial countries, atmospheric pollutants have affected forests and soils during the last century. Particularly, long range atmospheric transport of heavy metals can lead to pollutant deposition even in supposedly pristine areas (De Vries et al., 2002). However, according to the EEA (1998), the large-scale impact of heavy metals in forest ecosystems is not so evident. In Sweden for example, with the increasing industrial activity, Pb, Cd and Hg con-

tents have increased by 50% in the upper soil organic layers (EEA, 1998).

Bergkvist et al. (1989) draw attention over the lack of data on the distribution of heavy metals in pristine or non heavily polluted areas. Some investigations aimed to understand the behaviour of heavy metals, such as Cr, Co, Ni, Cu, Zn, Cd and Pb, in soils (Kabata-Pendias and Pendias, 1992). Particularly, Hertz et al. (1990) have shown that the distribution of heavy metals in solid phases depends on their amounts, their type and their origin. The binding involving mechanisms of heavy metals vary with soil depth, depending on the physical and chemical properties of the soil like pH, redox potential and water content, which all play an important role for the rate of chemical

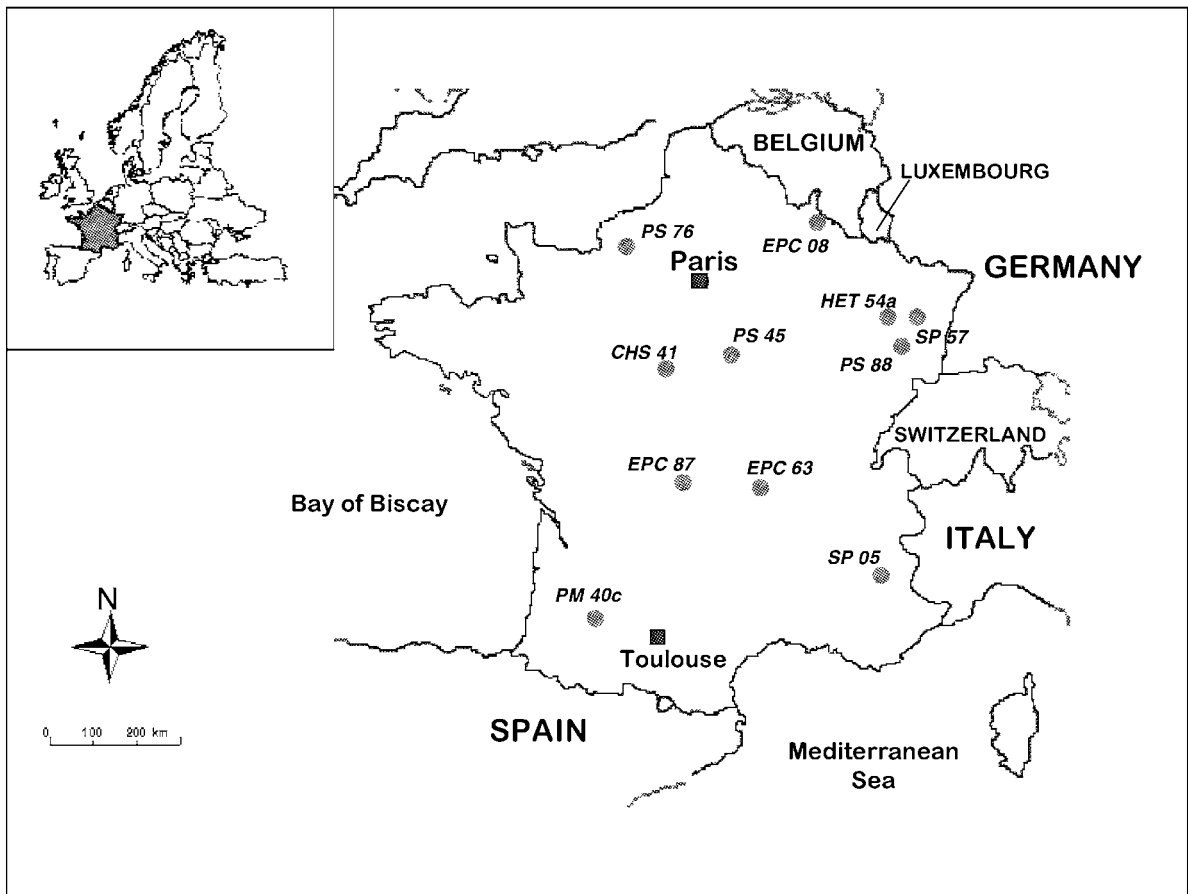


Fig. 1. Location of the 11 selected sites.

transformation of an element in a solid phase (Sposito, 1989).

Heavy metals have been found to accumulate in surface organic layers and consequently affect the biological activity in forest soils because of their strong affinity with organic matter. Consequently, the rates of soil organic matter decomposition are delayed (McBride et al., 1997; Dijkstra, 1998). Also, acidity inputs can lead to mineral dissolution and leaching of some heavy metals (Tyler et al., 1984), such that, it is often difficult to establish whether an impact is due to acidification processes or to anthropogenic deposition of heavy metals.

It is obviously to know the natural contents of heavy metals in soil (pedogeochemical background) before to detect the pollution intensity in forest soils and to compare the results with any norm or regulation (Baize, 1997; Huisman et al., 1997). Anthropogenic atmospheric inputs are often inferred to be significant because of important Pb and/or other heavy metal contents in surface soils horizons. For example, the upper horizons of forest soils often show an accumulation of heavy metals as a result of the air-filtering effect of the vegetation. It was proposed that this enrichment in surface could be taken as an indicator of the degree of atmospheric deposition (Berthelsen et al., 1994).

The total amount of heavy metals does not prove anthropogenic pollution since high heavy metal accumulations might also result from natural processes. Sr and Pb isotopes have been demonstrated to be powerful tools to determine the respective contribution of lithogenic and anthropogenic sources in soils (Steinmann and Stille, 1997; Probst et al., 2000; Aubert et al., 2001; Semlali et al., 2001; Teutsch et al., 2001).

Up to date there are very few studies in France, dealing with heavy metal behaviour in pristine forest sites, affected only by atmospheric deposition. The objective of this paper is (i) to determine the range and the distribution of heavy metal concentration in the forest soils, (ii) to assess the principle physical and chemical controlling factors of their distribution according to the different soil types, (iii) and, to evaluate the anthropogenic vs. lithogenic contribution in some of the selected soils.

For that purpose, the selected soils were chosen from the French RENECOFOR network (Réseau National de suivi à long terme des Ecosystèmes Forestiers, National Network for the long term Monitoring of Forest Ecosystem, Ulrich, 1995), managed by the ONF (Office National de Forêts, i.e. National Forest Board).

## 2. Materials and methods

### 2.1. Sampling sites

The soil samples concern 11 selected forested sites in France, reflecting various chemical and physical soil characteristics, as well as different types of atmospheric deposition (Fig. 1). The characteristics of the selected sites located across the country are described in Table 1. The studied soils have been classified according to their main characteristics in agreement with FAO (1990) and Brêthes and Ulrich (1997). Most of the French forest soil types are represented, however, acid soils (PM 40c, EPC 08, EPC 87, PS 76, PS 88, SP 57) are dominant because the RENECOFOR network aims to survey the forests mainly located in areas sensitive to acid atmospheric inputs.

### 2.2. Sampling procedure

The soil sampling procedure has been established according to the RENECOFOR network criteria (Brêthes and Ulrich, 1997). After some previous investigations, a soil profile was selected to be the most representative of the station. Particular caution was taken to avoid metal contamination when sampling. A large pit has been dug. Then, each soil horizon was refreshed by removing the soil which was in contact with the tools. A maximum of three representative horizons were sampled down the profile. The soils were sampled in 1994, dried at room temperature and stored in polypropylene bottles in a soil archive. For the present study, we used the available samples i.e. generally three samples per soil profile. The nature of the bedrock is well-known but unfortunately no bedrock sample was available.

Table 1  
Description of sampling sites

Site (code)	Location	Altitude	Latitude	Longitude	Vegetation	Soil type (FAO reference)	Bedrock
CHS 41	Loir et Cher	127 m	47°34'09"N	1°15'36"E	Quercenion robori-petraeae	STAGNIC LUVISOL	Silt over clay
EPC 08	Ardennes	480 m	49°56'51"N	4°48'35"E	Quercenion robori-petraeae	CAMBIC PODZOL	Schist
EPC 63	Puy de Dôme	950 m	45°45'20"N	2°57'58"E	Luzulo sp. pl. –Fagion sylvaticae	MOLLIC ANDOSOL	Basalt
EPC 87	Haute Vienne	650 m	45°48'00"N	1°48'55"E	Luzulo sp. pl. –Fagion sylvaticae	HUMIC CAMBISOL	Granite
HET 54a	Meurthe et Moselle	325 m	48°30'35"N	6°42'23"E	Lonicero periclymeni-Carpinenion betuli	DYSTRIC PLANOSOL	Marl
PM 40c	Landes	150 m	44°02'46"N	0°00'02"W	Ericenion ciliaro-tetralicis	FERRIC PODZOL	Sand
PS 45	Loiret	145 m	47°49'12"N	2°26'04"E	Quercenion robori-petraeae	DYSTRIC PLANOSOL	Silty sands over heavy clays
PS 76	Seine Maritime	70 m	49°27'14"N	0°44'53"E	Quercenion robori-petraeae	HAPLICE PODZOL	Flint
PS 88	Vosges	500 m	48°13'17"N	6°41'45"E	Quercenion robori-petraeae	CAMBIC PODZOL	Weathered sand/conglomerat
SP 05	Hautes Alpes	1360 m	44°29'25"N	6°27'33"E	Geranio nodosi-Fagenion sylvaticae	CALCARIC CAMBISOL	Marl
SP 57	Moselle	400 m	48°36'36"N	7°08'02"E	Luzulo luzuloidis-Fagenion sylvaticae	DYSTRIC CAMBISOL	Sandstone

Ponette et al. (1997).

### 2.3. Analytical methods

Only the fine fraction (<2 mm) of representative samples from the dried soils was chosen to be analysed. Careful handling was carried out to avoid input or loss of trace elements during preparation and analysis of the samples. Nylon sieves were used for the granulometric separation; all materials used for analysis were in Teflon or heavy metal free. To ensure the representativeness of the sample fraction to be analysed, each soil sample was carefully separated into four equivalent subsamples. Then, two opposite subsamples were mixed and separated again into four subsamples. This procedure was repeated three times. Finally, the final representative subsample was carefully crushed in an agate mortar.

#### 2.3.1. Physico-chemical soil parameters

The main soil parameters (granulometry, pH, organic carbon content, cation exchange capacity (CEC), nitrogen content, carbonate, phosphorus extracted and free iron and aluminium) have been analysed at the INRA Laboratory of Soil Science—Arras (France) following classical methods (Ponette et al., 1997).

#### 2.3.2. Major elements

A complete dissolution by alkaline fusion of the soil samples was performed. The method consists in melting 0.1 g of a representative sample in the presence of lithium tetraborate at 1000 °C. Major elements were then determined by inductively coupled plasma atomic emission spectrometry at the Centre de Géochimie de la Surface from Strasbourg (France). The analytical error is less than 2% depending on the element.

#### 2.3.3. Trace elements

Complete dissolution of soil samples was done by acid digestion using a mixture of HF/HNO<sub>3</sub>/HClO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> on hot plates at atmospheric pressure. According to the well-tested chemical attack in the laboratory, a 0.1 g subsample of the fine fraction (<2 mm) of each soil sample was weighed into a PTFE beaker and then 1 ml of concentrated HF was added. The samples were placed into the ultrasonic bath for 15 min, then 1

ml of concentrated HNO<sub>3</sub> was added, the beaker closed and kept at 100 °C for 12 h. Then 1 ml of concentrated HClO<sub>4</sub> was added and the beaker was closed and heated again for 12 h; finally, 0.5 ml of H<sub>2</sub>O<sub>2</sub> was added; after the effervescence has disappeared, the beaker was closed and heated. H<sub>2</sub>O<sub>2</sub> was added until the complete dissolution of the sample. Every step was followed by a partial evaporation of the sample. Trace element concentrations were then determined using a Perkin-Elmer ELAN 6000 ICP-MS (inductively coupled plasma mass spectrometry) at the Laboratoire des Mécanismes et Transferts en Géologie, Toulouse. The reference soil sample 'Light sandy soil 142R' was used following the same method to ensure the quality of the analytical procedure. The detection limit is 10 ng g<sup>-1</sup> for Cr, Sc, Co, Cd, Ni, Zn, Cu and 1 ng g<sup>-1</sup> for Pb; the analytical error is less than 5%.

#### 2.3.4. Pb isotopes: principle and measurement

The Pb isotopic composition allows the identification of lead sources and the determination of their respective contributions (Erel et al., 1997; Steinmann and Stille, 1997; Hansmann and Köppl, 2000; Teutsch et al., 2001; Semlali et al., 2001). Lead has four stable isotopes: <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb. The radiogenic <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb are produced by radioactive decay of long-lived radioactive parents <sup>238</sup>U, <sup>235</sup>U, and <sup>232</sup>Th, respectively. Lead ores display isotopic signatures that depend mainly on the original composition and on the age of the ore bodies, thus Pb emissions from anthropogenic sources reflect the isotopic composition of these ores.

The isotope ratios were measured with the Perkin-Elmer ELAN 6000 Q-ICP-MS (quadrupole inductively coupled plasma mass spectrometer) at the Laboratoire des Mécanismes et Transferts en Géologie, Toulouse. The lead isotope ratios are often measured by thermal ionization mass spectrometry due to its higher precision than ICP-MS but it is extremely time consuming. Measurement by ICP-MS is more rapid and generally offers an adequate precision (Halicz et al., 1996; Aries et al., 2001). The model used to correct mass bias effects is an external mass bias correction ('standard-sample bracketing technique') using NIST

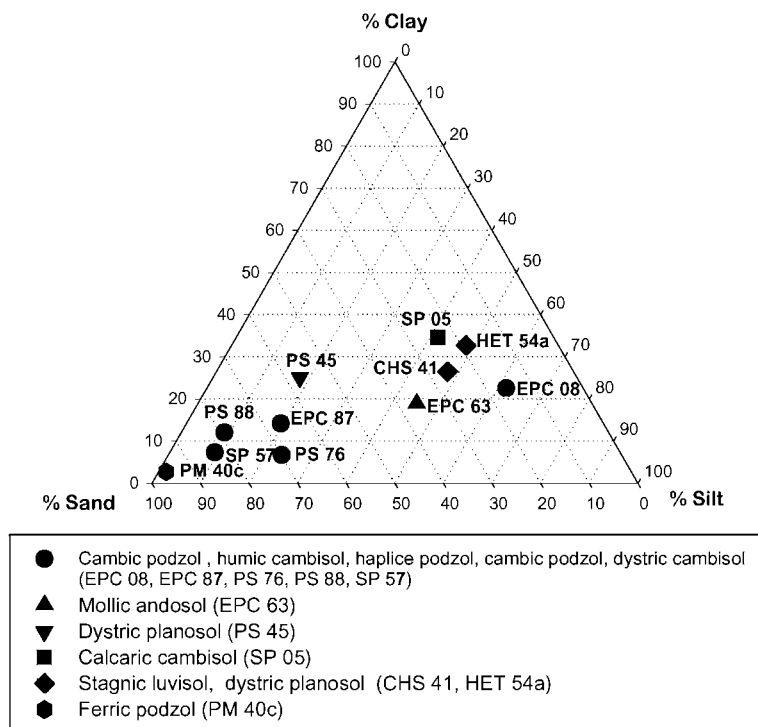


Fig. 2. Ternary diagram of soil texture: each point represents the average value of the three horizons for each soil sample (fine fraction <2 mm).

SRM 981 as the reference standard. The correction used is a linear correction. The average long term precision were approximately 0.3% for the  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios.

### 3. Results

#### 3.1. Physico-chemical characteristics of the soils

The texture of the soils is presented in Fig. 2. The cluster of points shows that the soil texture regularly spread out from a sandy end-member to a silt-clay end-member in which the average ratio silt over clay is approximately 2. All the acid soils are sandy (>60% sand) while the other soils are rather silty-clayey. Clay proportion increases with depth in CHS 41, SP 57, PS 45 and HET 54a, whereas it decreases in SP 05, EPC 63 and EPC 08 and the surface layers of these soils have a significant proportion of clay.

The organic matter content is highest in surface horizons and varies greatly between 10–300 and 1–30  $\text{g kg}^{-1}$ , respectively, for surface and deep horizons according to the different soils. It decreases with depth in all the profiles, as an indication of litter accumulation and degradation in the soil surface. The lowest value in surface horizon is for the stagnic luvisol and the dystric planosol (CHS 41 and HET 54a), whereas the mollic andosol (EPC 63) is the most enriched in organic matter.

The pH ( $\text{pH}_{\text{H}_2\text{O}}$ ) varies between 3.6 and 6.9; 80% of the sites are acid ( $\text{pH} < 5.6$ ), only the calcaric cambisol (SP 05) and the deep layer of the mollic andosol (EPC 63) present pH values > 5.6. Generally, pH increases with depth.

The CEC is within a range of 0.2–29  $\text{cmol kg}^{-1}$ , decreasing with depth. This is partly explained by the decrease of organic carbon content. The highest CEC value is found for calcaric cambisol (SP 05) whatever the horizon, whereas

Table 2

Content and distribution of heavy metals and major elements in the selected samples (fraction &lt;2 mm)

Station	Depth (cm)	Trace elements ( $\mu\text{g g}^{-1}$ )								Major elements (%)						
		Cr	Co	Ni	Cu	Zn	Cd	Pb	Sc	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
EPC 08	0–4	83.08	1.56	4.65	23.77	45.01	0.28	134.45	5.34	58.6	10.6	0.22	0.1	2.6	0.6	1.42
	30–45	102.66	4.59	7.59	19.9	42.91	0.23	29.46	14.35	69.3	15.3	0.38	0.11	4.7	0.52	1.64
	70–90	107.57	3.02	11.00	32.15	40.23	0.22	18.4	14.06	70.2	16.0	0.42	0.12	4.8	0.52	1.73
EPC 87	10–30	14.35	1.36	4.12	3.05	67.04	0.17	23.83	3.17	63.6	14.0	0.27	0.15	2.4	0.27	0.63
	30–50	21.72	2.8	7.04	3.78	79.19	0.19	23.00	4.21	70.4	13.5	0.27	0.13	2.2	0.29	0.69
	100–120	27.46	4.97	12.14	5.04	81.79	0.19	20.96	4.68	68.3	16.4	0.58	0.22	3.0	0.35	0.8
PS 76	0–4	20.69	0.58	2.3	3.29	8.77	0.13	9.03	1.58	92.00	1.6	0.03	0.08	0.6	0.11	1.4
	6–15	25.8	0.87	2.24	3.94	12.19	0.14	11.41	4.96	92.5	2.00	0.05	0.08	0.9	0.16	1.49
	20–70	32.13	2.02	4.27	1.67	15.12	0.13	8.23	4.98	92.00	3.00	0.09	0.11	1.2	0.13	2.95
PS 88	0–0.5	11.08	0.56	3.6	7.31	33.59	0.15	39.2	1.25	70.2	3.1	0.11	0.08	0.8	0.63	2.97
	12–17	14.82	1.13	4.49	2.5	24.67	0.11	12.04	1.89	87.4	4.6	0.14	0.03	1.3	0.64	2.86
	50–65	15.02	0.84	4.61	2.27	16.31	0.11	11.96	2.14	87.9	5.2	0.17	0.03	1.5	0.37	2.04
SP 57	0–7	9.14	0.75	2.17	2.07	9.07	0.11	26.29	1.52	90.8	2.5	0.06	0.01	0.5	0.64	2.57
	40–60	13.68	2.19	6.61	3.94	18.54	0.1	10.15	3.8	92.4	3.7	0.15	0.02	0.9	0.72	2.78
	120–140	19.2	2.44	8.95	2.74	13.19	0.12	12.11	5.53	88.1	6.4	0.35	0.01	1.5	0.69	3.43
EPC 63	3–10	48.52	12.66	15.73	23.00	116.00	0.63	51.82	39.72	29.00	13.5	0.96	1.55	7.0	1.84	4.15
	10–25	42.08	11.96	14.74	20.06	125.2	0.53	43.14	36.95	34.8	16.1	1.2	1.82	8.2	1.76	4.35
	30–40	57.11	22.8	28.14	26.53	119.87	0.53	10.13	14.49	42.3	19.9	3.61	5.03	11.8	2.15	4.18
PS 45	0–7	13.92	1.21	3.31	2.01	18.46	0.18	29.77	2.7	83.8	5.6	0.06	0.1	0.5	1.72	1.11
	25–40	17.1	1.25	3.34	1.75	24.35	0.1	28.5	2.61	87.7	6.1	0.09	0.1	0.8	2.14	1.42
	60–75	58.36	16.06	14.66	9.48	84.73	0.16	34.99	10.41	70.3	15.0	0.78	0.45	4.7	2.55	1.35
SP 05	0–15	102.77	15.92	52.75	29.45	116.6	0.26	27.67	15.63	52.3	15.5	1.56	0.99	6.4	0.12	1.17
	25–35	117.75	20.52	63.45	36.32	132.1	0.14	26.37	17.02	59.3	17.8	1.58	0.39	7.6	0.14	1.42
	70–100	144.87	18.91	72.64	37.85	134.57	0.18	25.15	17.71	57.5	20.0	1.77	0.53	7.8	0.13	1.73
CHS 41	15–30	37.77	6.27	8.05	10.41	61.87	0.17	17.96	9.62	86.3	5.7	0.27	0.12	2.1	0.52	1.24
	45–60	61.59	9.72	16.89	10.31	80.93	0.21	21.6	15.44	79.2	9.3	0.57	0.1	4.2	0.54	1.31
	70–95	73.83	12.17	23.38	9.39	95.95	0.22	24.24	12.06	76.2	11.3	0.75	0.13	5.4	0.14	2.49
HET 54a	15	48.2	8.62	11.39	4.45	35.37	0.24	31.61	7.26	84.5	6.4	0.33	0.15	2.1	0.5	2.07
	25	53.17	8.11	12.27	4.36	36.88	0.23	19.8	8.56	82.8	7.0	0.37	0.15	2.4	0.68	2.83
	90	95.63	6.72	28.81	19.16	55.34	0.16	20.61	15.86	63.9	17.2	1.5	0.18	7.6	0.79	3.02
PM 40c	0–10	8.21	0.23	0.03	1.12	3.95	0.09	3.34	0.64	91.7	0.3	0.02	0.05	0.00	0.05	0.11
	10–20	3.01	0.16	0.55	1.31	4.91	0.21	3.2	0.5	89.7	0.3	0.01	0.04	0.00	0.04	0.08
	30–40	3.52	0.16	0.66	0.87	2.49	0.12	1.34	3.75	97.5	0.3	0.04	0.00	0.00	0.02	0.08
	55–100	4.01	0.09	0.32	0.52	1.56	0.14	4.85	2.38	95.5	0.9	0.03	0.00	0.00	0.07	0.35

the lowest values are found in acid soils (EPC 08, EPC 87, PS 76, PS 88, SP 57, PM 40c) where aluminum dominates. Two soils present a high CEC value in the deep horizons (PS 45 and HET 54a). This has to be related to the relative abundance of clay in the deep horizons. In these two soils as well as in SP 05, calcium is the most important exchangeable base cation.

As seen in Table 2, all samples present very low base cation content ( $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} < 6\%$ ), except the mollic andosol EPC 63 ( $\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$ : 8–15%). The soil samples spread out from the silica end-member (corresponding to the sandy soils) towards the aluminium and iron oxides end-member (corresponding to the silty-clayey soils).

### 3.2. Heavy metal content and distribution in soil profiles

Fig. 3 and Table 2 show the soil content and the distribution of the different heavy metals vs. depth. The lowest concentrations are for Cd, Co, Cu, Ni and Pb and the highest for Cr and Zn. The average abundance order of heavy metal contents in soil samples is:  $Cr > Zn > Pb > Ni > Cu > Co \gg Cd$ . This abundance is the same as for the main soils of the world (Kabata-Pendias and Pendias, 1992), except Pb which presents in our soils relatively higher levels of concentration. For almost all the sites, the heavy metal content is less than the standard values proposed for non-polluted soils and for European norms (Kabata-Pendias and Pendias, 1992; Rademacher, 2001) (Table 3), except Pb (EPC 08), Cr (EPC 08, SP 05) and Ni (SP 05) for some soil samples. It is also important to notice that some concentrations are close to, as for Cr, or even higher (as for Ni, Pb) than the critical values given by the French association of normalization (AFNOR, 1996) for sludge spreading in France (Table 3).

Acidic sandy soils (PM 40c, SP 57 and PS 88) present the lowest heavy metal content, whereas the highest concentrations are found in EPC 08, EPC 63 and SP 05. The calcaric cambisol (SP 05) is the most enriched for all heavy metals, except Cd. The distribution of heavy metal with depth varies according to the element and to the soil type (Fig. 3). Given that no bedrock heavy metal could be measured, the pattern of concentration between the different soils is referred to the content of the bedrocks described in the literature (Kabata-Pendias and Pendias, 1992). Sandy acid rocks are supposed to present very low metal content, except Pb. On the opposite basalts and calcareous contain important amount of heavy metals like Ni and Cr. This pattern is as a whole in agreement with the pattern observed for the studied soils. However, some discrepancies occur which could indicate in the soils a source of elements other than lithogenic.

The concentration of Cr and Co increases in most soils with depth, except the ferric podzol (PM 40c) and the dystric planosol (HET 54a) for which Co decreases. The lowest Co concentrations are in acidic soils. Ni concentration increases with

depth in almost all soils samples, except for the ferric podzol (PM 40c) in which the intermediate horizons are enriched. Cu concentration does not show a systematic pattern. Like Zn and Ni, it slightly accumulates in the Eh-horizon of the ferric podzol (PM 40c). Zn is the most abundant heavy metal in acid soils and its concentration increases with depth in calcaric cambisol (SP 05), dystric planosol (HET 54a, PS 45) and stagnic luvisol (CHS 41). For other soils, Zn concentration decreases or it remains rather stable within the profile.

The Cd content in soil samples is low within the typical range of non-polluted soils (Kabata-Pendias and Pendias, 1992). In general, Cd content decreases with depth or it remains stable, with the exception of the stagnic luvisol (CHS 41) where it increases and the ferric podzol (PM 40c) where it accumulates in the Eh horizon like Cu and Zn.

The highest Pb concentrations are found in surface horizons and Pb content decreases generally with depth. Like Zn, Cr and Ni, Pb is enriched in the deep layers of the dystric planosol and the stagnic luvisol (PS 45, CHS 41). This could be related to the clay content which increases significantly with depth. However for Pb, the enrichment found in the deep rich clay horizon of the dystric planosol (HET 54a) is very low. We can also note that the soils with the highest Pb content in surface layers are located in the north-eastern part of France (EPC 08, PS 88, SP 57, HET 54a).

### 3.3. Relationships between trace and major elements

Cr, Co, Ni, Zn and Cu are significantly correlated according to Pearson's coefficient since data normality has been checked (Table 4). Cd and Pb are less significantly related to the previous group of elements because Cd and Pb are generally enriched in the upper soil horizons compared to the other elements. Nevertheless, the most significant relationships between Cd, Pb and the other elements can be observed for Cu and Co (only for Cd).

The heavy metal contents are strongly related to the total Al and Fe contents ( $0.47 \leq r^2 \leq 0.77$ ,  $n = 34$ ), except for Cd and Pb. Such a relationship is



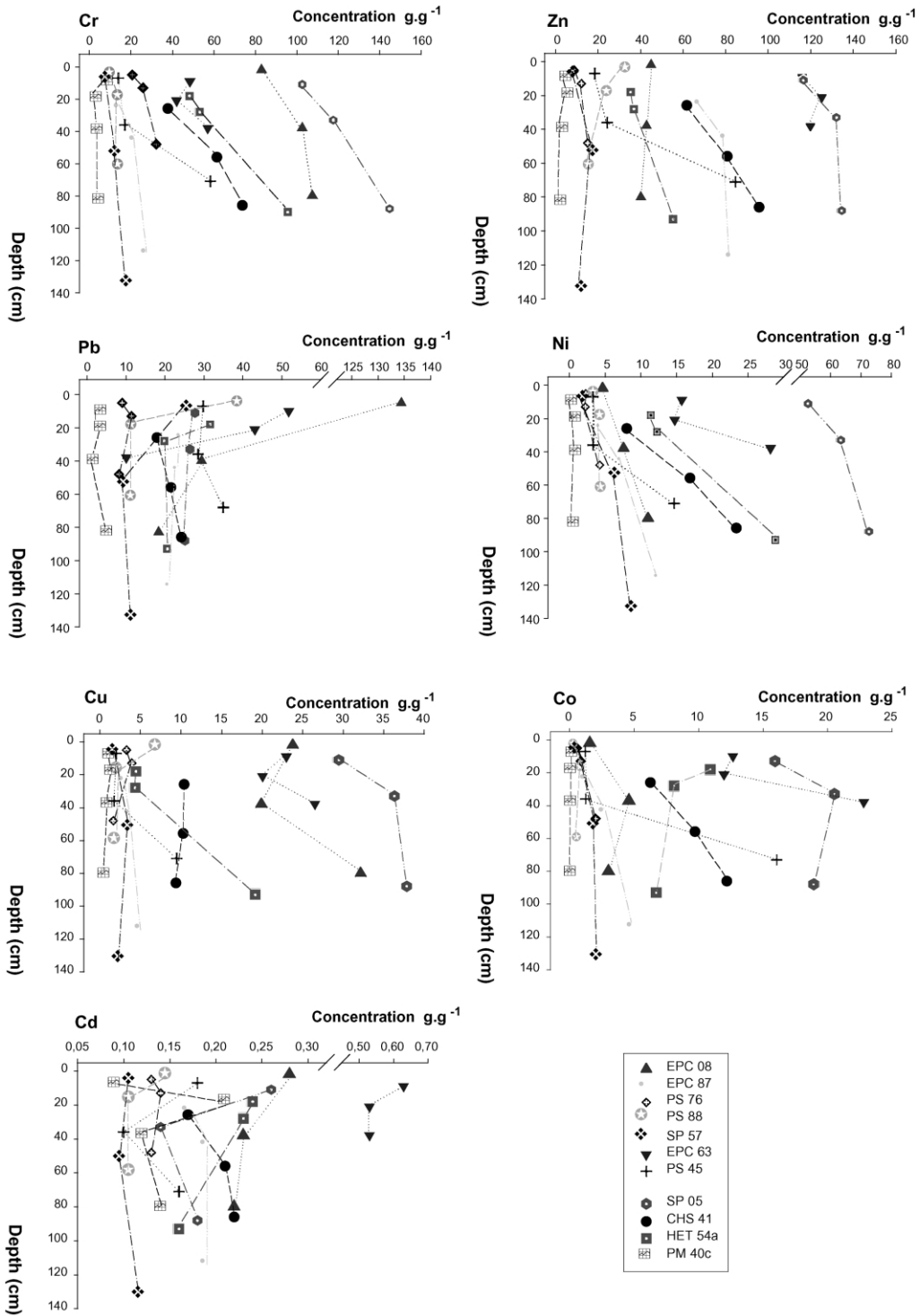


Fig. 3. Evolution of heavy metals concentrations in soil profiles (<2 mm).

Table 3

Standard values of heavy metals for sludge spreading, soils and atmospheric fallout

Element	Standard value <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	World range in non-polluted soils <sup>b</sup> ( $\mu\text{g g}^{-1}$ )	Atmospheric fallout <sup>c</sup> ( $\mu\text{g g}^{-1}$ )	AFNOR value X44-041 <sup>d</sup> ( $\mu\text{g g}^{-1}$ )
Cr	50–100	5–120	1.4	150
Co	20–50	0.1–20	1.6	–
Ni	30–60	1–200	7.3	50
Cu	30–60	6–60	8.8	100
Zn	100–200	17–125	29	300
Cd	0.8–1.5	0.07–1.10	0.25	2
Pb	50–100	10–70	11	100

<sup>a</sup> From European norms (Rademacher, UN/ECE; 2001).<sup>b</sup> Kabata-Pendias and Pendias (1992).<sup>c</sup> In topsoil to 20 cm depth, estimated 100 year accumulation (Allen et al., 1995).<sup>d</sup> Sludge spread regulation (Baize, 1997).

particularly significant for Zn (Fig. 4a and b) and Cu ( $r^2=0.77$  and  $r^2=0.69$ , respectively,  $n=34$ ,  $P<0.0001$ ), which indicates the strong affinity of these two elements for Al and Fe oxides. Especially in the surface horizons, the correlation between Zn and total Fe is the most significant ( $r^2=0.93$ ,  $n=11$ ,  $P<0.0001$ ). Huisman et al. (1997) have already shown that in soils from Netherlands, Al and Fe contents can help in determining the heavy metal background values.

Cu is also well related with iron oxides in surface and intermediate horizons ( $r^2=0.73$ ,  $n=11$ ,  $r^2=0.82$ ,  $n=12$ , respectively,  $P=0.0008$ ) whereas deeper in the soil profiles, the clay content becomes an important parameter explaining the Cu distribution pattern. The relationship between Cu and aluminium is, however, less significant ( $r^2=0.62$  and  $r^2=0.69$ , respectively,  $n=34$ ,  $P<0.0001$ ).

Ni, Cr, Zn and Cu present a negative relationship with silica, except for the calcareous cambisol (SP

05) and the mollic andosol (EPC 63) where the relationship is positive. The relationships between heavy metals (except Pb) and Mg are positive and significant, which can probably be related to the weathering of biotite, a mineral relatively heavy metals enriched. This relationship becomes very significant (as example, Ni–MgO,  $r^2=0.90$ ,  $n=28$ ,  $P<0.0001$  Fig. 5a) when excluding SP 05 and EPC 63, i.e. considering acid and lixiviated soils only. A similar pattern can be observed also for Ca particularly when avoiding mollic andosol (EPC 63) (as example, Ni–CaO Fig. 5b,  $r^2=0.61$ ,  $n=31$ ,  $P<0.0001$ ). It is interesting to note that the less Si and the more Al are in the soils, the higher are the heavy metal contents as observed for EPC 08, SP 05 and EPC 63.

#### 3.4. Relationships between heavy metal content and the physico-chemical soil parameters

The relationships between the main soil parameters and heavy metal contents have been

Table 4

Correlation matrix for heavy metals in selected samples ( $n=34$ ; bold  $P\leq 0.0001$ ; underlined  $P<0.03$ , italic: non significant)

	Cr	Co	Ni	Cu	Zn	Cd	Pb
Cr	1	<b>0.4646</b>	<b>0.6416</b>	<b>0.7979</b>	<b>0.4295</b>	<i>0.0638</i>	<i>0.1046</i>
Co		1	<b>0.6705</b>	<b>0.5152</b>	<b>0.7641</b>	<i>0.2885</i>	<i>0.0129</i>
Ni			1	<b>0.6312</b>	<b>0.5958</b>	<i>0.0383</i>	<i>0.0046</i>
Cu				1	<b>0.5605</b>	<i>0.2336</i>	<i>0.1369</i>
Zn					1	<b>0.3697</b>	<i>0.0744</i>
Cd						1	<i>0.1279</i>
Pb							1

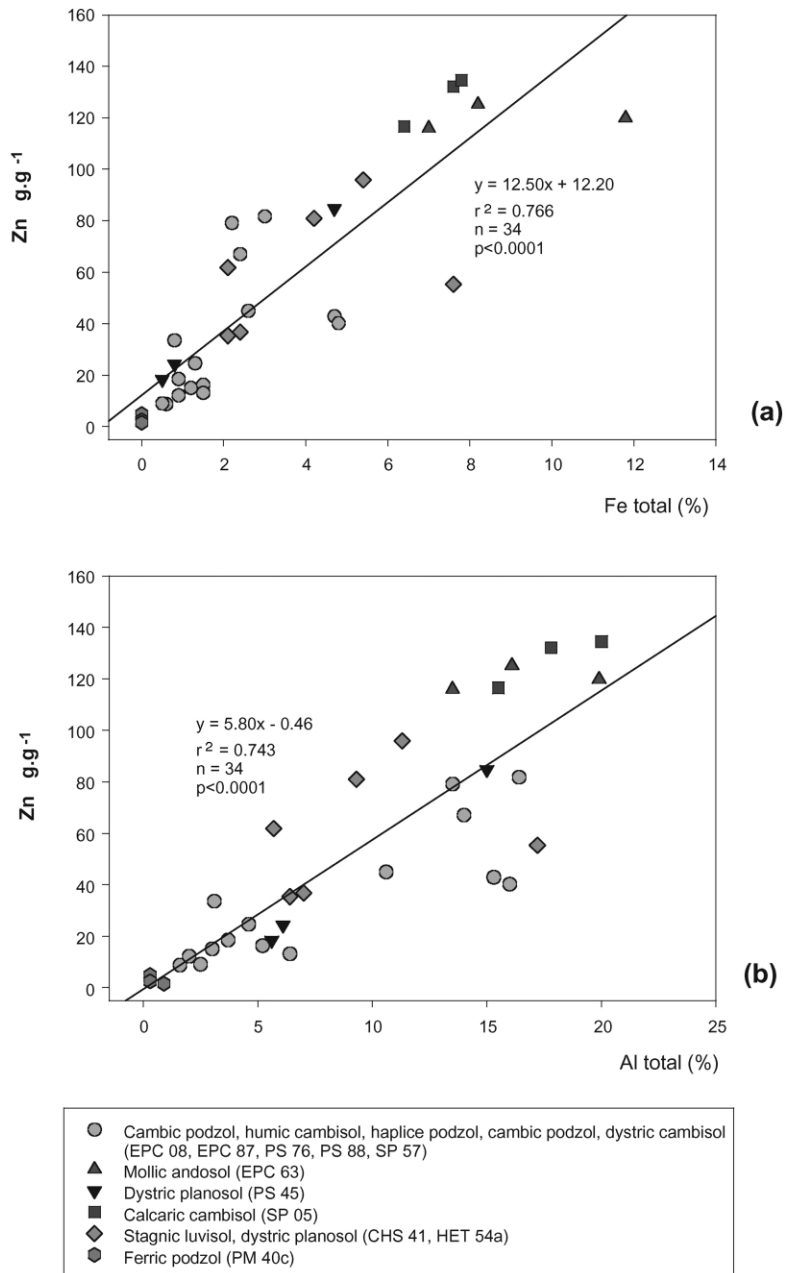
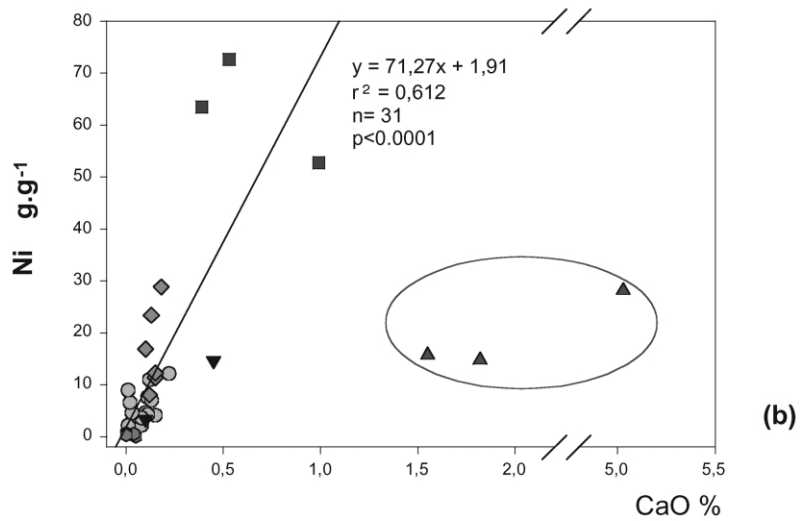
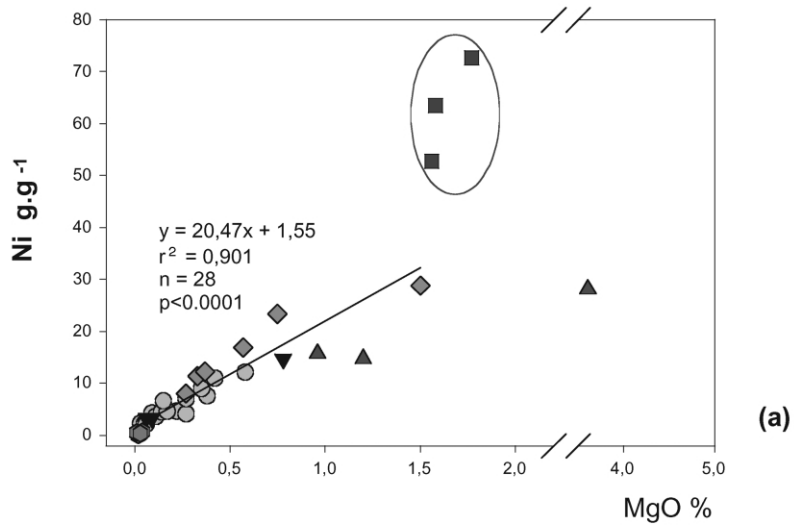


Fig. 4. Relationship between zinc content and total iron (a), and total aluminium (b) in soil samples.

assessed using single (Figs. 6 and 7) and multiple regression analysis (Table 5).

As can be seen in Fig. 6a and b, Ni and Cr contents are significantly correlated to  $pH_{H_2O}$  for

all the soils samples. For the other heavy metals, this relationship is less significant, except for Co ( $r^2=0.66$ ,  $n=34$ ,  $P<0.0001$ ) and Zn ( $r^2=0.43$ ,  $n=34$ ,  $P<0.0001$ ).



- Cambic podzol, humic cambisol, haplice podzol, cambic podzol, dystric cambisol (EPC 08, EPC 87, PS 76, PS 88, SP 57)
- ▲ Mollic andosol (EPC 63)
- ▼ Dystric planosol (PS 45)
- ◆ Stagnic luvisol, dystric planosol (CHS 41, HET 54a)
- Calcaric cambisol (SP 05)
- ⬡ Ferric podzol (PM 40c)

Fig. 5. Relationships between nickel content and the percentage of total MgO (a), and total CaO (b) in soil samples. On (a), SP 05 and EPC 63 (encircled) are not considered in the relationship. On (b), EPC 63 (encircled) is not considered in the relationship.

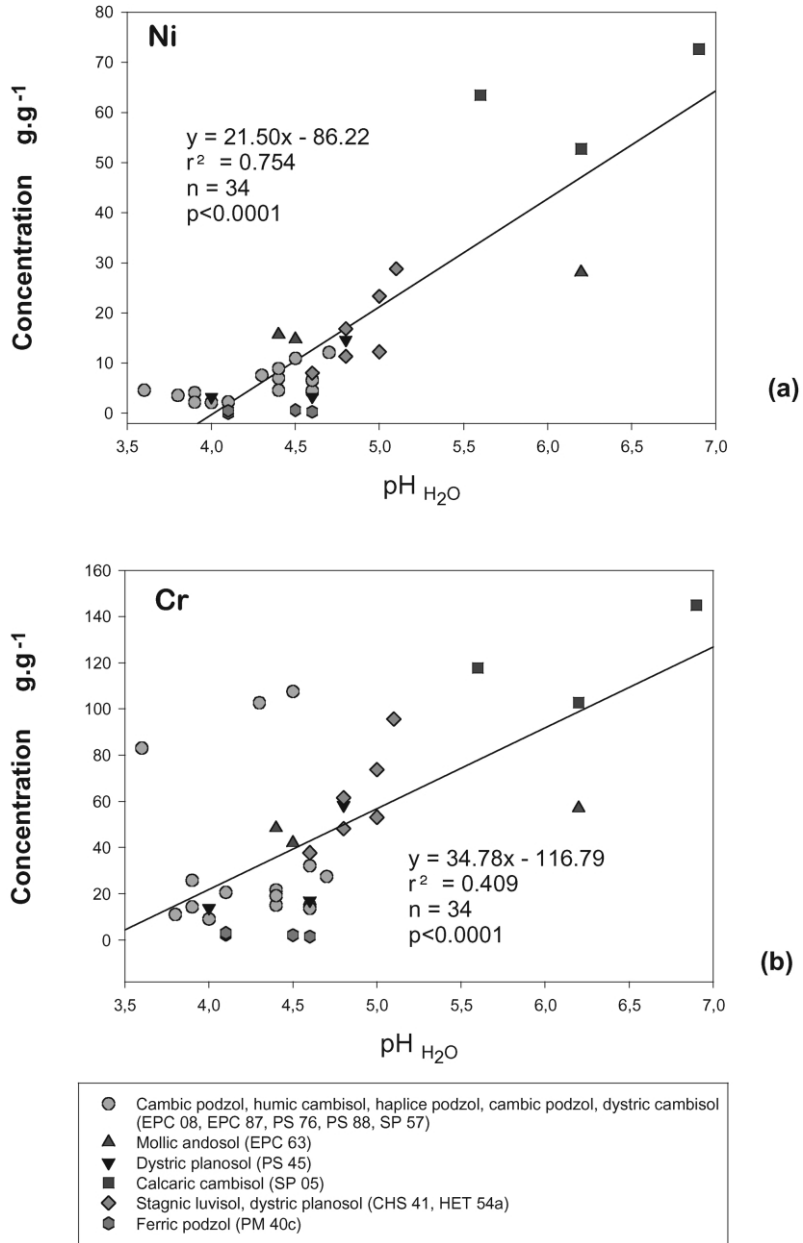


Fig. 6. Relationships between Ni content and  $\text{pH}_{\text{H}_2\text{O}}$  (a), and Cr content and  $\text{pH}_{\text{H}_2\text{O}}$  (b) in soil samples.

A significant and positive correlation can be observed between the CEC and the clay proportion for the different soil horizons ( $r^2=0.67$ ,  $n=34$ ,  $P<0.0001$ ). However, significance of this relationship becomes weaker with soil depth. Cr, Co and Ni are the only heavy metals related to CEC: Cr

( $r^2=0.32$ ,  $n=34$ ,  $P<0.0005$ ), Co ( $r^2=0.37$ ,  $n=34$ ,  $P<0.0001$ ) and Ni ( $r^2=0.38$ ,  $n=34$ ,  $P<0.0001$ ).

Clay proportion and heavy metal contents are positively correlated particularly for Cr ( $r^2=0.44$ ,  $n=34$ ,  $P<0.0001$ ), Co and Ni ( $r^2=0.37$ ,  $n=34$ ,

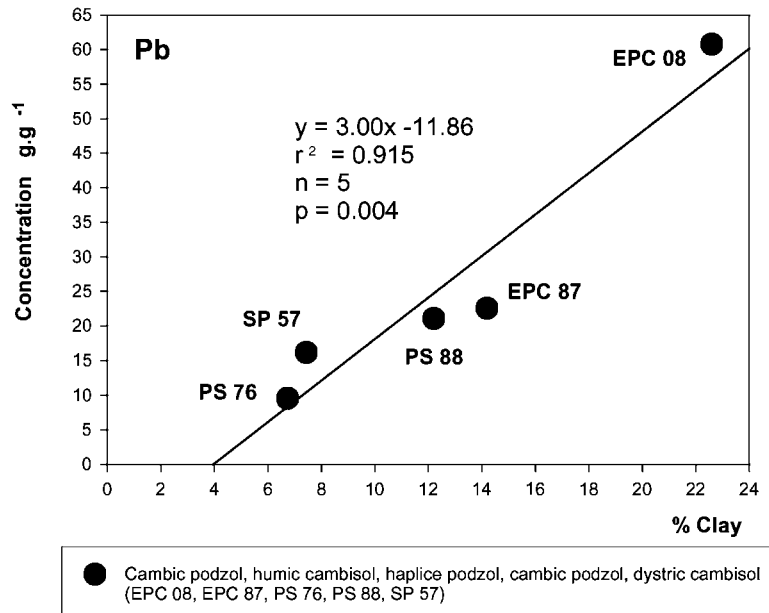


Fig. 7. Relationship between Pb content and clay proportion in acid soil samples (average of three horizons for each soil profile).

$P < 0.0001$ ). The correlation is stronger for Ni ( $r^2 = 0.43$ ,  $n = 31$ ,  $P < 0.0001$ ) if the calcareous cambisol (SP 05) and the mollic andosol (EPC 63)—for which the relationship is negative—are not considered in the relationship. In these two latter soils as well as in the humic cambisol (EPC 87), the clay content decreases with depth, implying that Cr and Ni are clearly associated with primary minerals. A significant relationship is found between Zn content and clay content in surface horizons ( $r^2 = 0.78$ ,  $n = 11$ ) and in middle soil

horizons ( $r^2 = 0.69$ ,  $n = 12$ ) for all soil samples. For the deep horizons, this relationship is less significant.

Considering all soil samples, Pb content is not significantly related to clay content. However, considering the average Pb content for each soil profile, the relationship calculated only for acid soils (Fig. 7, EPC 08, EPC 87, PS 76, PS 88, SP 57) becomes significant ( $r^2 = 0.92$ ,  $n = 5$ ,  $P = 0.004$ ). The cambic podzol (EPC 08) has on an average the highest Pb content corresponding to

Table 5  
Most significant multi-parameter relationships for heavy metals in soil samples

	pH <sub>H<sub>2</sub>O</sub>	Clay (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	CEC (cmol kg <sup>-1</sup> )	O.M. (g kg <sup>-1</sup> )	Al <sub>Tamm</sub> (%)	Fe <sub>Tamm</sub> (%)	SiO <sub>2</sub> (%)	r <sup>2</sup>	F	P
Cr	—	—	15.5	—	—	0.11	—6.48	48.04	—	0.955	159.23	****
Co	3.29	—	1.26	—0.37	0.19	—0.013	—	—0.136	0.930	61.95	****	
Ni	16.10	—0.23	4.09	—1.08	—	—	—1.74	—0.702	0.960	112.28	****	
Cu	—	—0.41	6.62	—	—	0.07	—1.42	—	0.940	117.94	****	
Zn	22.86	—	—	2.15	—	—	—	—0.980	0.943	169.92	****	
Cd	23.8 × 10 <sup>-3</sup>	2.4 × 10 <sup>-3</sup>	—	—	—4.4 × 10 <sup>-3</sup>	5 × 10 <sup>-4</sup>	10.7 × 10 <sup>-3</sup>	—	—	0.967	172.15	****
Pb <sup>a</sup>	1.25	0.265	—2.38	1.41	—	0.109	—	—	—	0.925	68.91	****

F, Fisher F-test; significance threshold (P), \*\*\*\* < 0.0001.

<sup>a</sup> Calculated without the high Pb concentration in EPC 08 surface horizon which is out of the cluster of points due to heavy contamination.

the highest clay content. A good relationship can also be observed for Zn considering all samples ( $r^2=0.33$ ,  $n=34$ ,  $P=0.0004$ ); for acid soils only without considering the humic cambisol (EPC 87), the relationship with clay content is much stronger for Zn and Cd ( $r^2=0.81$ ,  $n=12$ ,  $P=0.0001$ ).

Surprisingly, there is no significant relationship between organic matter content and heavy metal concentration, except for lead ( $r^2=0.32$ ,  $n=34$ ,  $P=0.0005$ ) and cadmium ( $r^2=0.38$ ,  $n=34$ ,  $P=0.001$ ), particularly in the middle soil horizons ( $r^2=0.82$ ,  $n=12$ ,  $P<0.0001$ ).

Because no single parameter can be detected as clearly related to each heavy metal content, multiple regression analysis were investigated. A backward stepwise procedure in the linear regression technique was used to determine the multivariate parameters (Systat® 10.0 Statistics software, SPSS Inc., 2000).

The most significant multiple regressions that have been calculated between heavy metals and soil parameters are summarised in Table 5. For most of the heavy metals, soil pH, Fe and Al oxides and organic matter content enter significantly in the multiple regressions and to a lesser extend, clay content, CEC and free Al and Fe. However, each heavy metal is closely related to one, two or three main parameters: Cr to Fe-oxides and free Fe, Co to pH, CEC and Fe-oxides, Ni to pH and Fe-oxides, Cu to Fe-oxides, Zn to pH and Al-oxides, Cd to pH and free Al and Pb to pH, Al-oxides and clay content. SiO<sub>2</sub> appears to be a significant negative parameter only for Co, Ni and Zn.

### 3.5. Anthropogenic vs. lithogenic sources of heavy metals

#### 3.5.1. Enrichment factor and anthropogenic/lithogenic contribution

In order to evaluate if the present-day heavy metal content in soil derives from natural or anthropogenic sources, an enrichment factor was calculated for all studied soils using Scandium as a reference element which is generally considered as mainly originated from natural lithogenic sources (rock weathering). The enrichment factor is the relative abundance of a chemical element in

a soil compared to the bedrock. Sc can be a substitute for Al<sup>3+</sup>, Fe<sup>3+</sup>, Y<sup>3+</sup> and Ti<sup>3+</sup> and it has been already used for calculating anthropogenic metal enrichments (Shotyk et al., 2000). The reference values were taken on one hand, for some metals from the earth's crust (Eq. (1), Sc=16 μg g<sup>-1</sup>, Cr=100 μg g<sup>-1</sup>, Co=20 μg g<sup>-1</sup>, Ni=80 μg g<sup>-1</sup>, Cu=50 μg g<sup>-1</sup>, Zn=75 μg g<sup>-1</sup>, Cd=0.11 μg g<sup>-1</sup>, Pb=14.8 μg g<sup>-1</sup>, Wedepohl, 1995) and on the other hand, for all the considered metals from the concentrations in each deepest soil horizon (Eq. (2)); this is to determine a relative range of enrichment factors.

$$EF_1 = ([M]/[Sc])_{\text{soil}} / ([M]/[Sc])_{\text{Earth's crust}} \quad (1)$$

$$EF_2 = ([M]/[Sc])_{\text{soil}} / ([M]/[Sc])_{\text{deeper soil horizon}} \quad (2)$$

where [M]=total heavy metal concentration measured in soil sample (μg g<sup>-1</sup>) and [Sc]=total concentration of Sc (μg g<sup>-1</sup>). EF values ranging between 0.5 and 2 can be considered in the range of natural variability, whereas ratios greater than 2 indicate some enrichment corresponding mainly to anthropogenic inputs.

The concentration of lithogenic heavy metal can be calculated as follows:

$$[M]_{\text{lithogenic}} = [Sc]_{\text{sample}} \times ([M]/[Sc])_{\text{lithogenic}} \quad (3)$$

where  $([M]/[Sc])_{\text{lithogenic}}$  corresponds to the average ratio of the earth's crust. Then, the anthropogenic heavy metal can be estimated as:

$$[M]_{\text{anthropogenic}} = [M]_{\text{total}} - [M]_{\text{lithogenic}} \quad (4)$$

The results of these calculations are summarised in Table 6 for all heavy metals and illustrated on Figs. 8 and 9, respectively, for Pb and Cr taken as example because Pb is known as partly coming from anthropogenic atmospheric input and on the opposite Cr is often supposed to be of lithogenic origin.

Fig. 8 shows that almost all the soil samples are enriched in Pb when compared to average crustal abundances, except the stagnic luvisol (CHS 41),

Table 6

Enrichment factors EF<sub>1</sub> (against the earth's crust value) and EF<sub>2</sub> (against the deep horizon value) and anthropogenic contributions (%) for Pb, Cd, Co, Zn, Cu, Ni and Cr in the studied forested soils (bold: EF>2)

Station	Depth (cm)	Cr			Co			Ni			Cu			Zn			Cd			Pb									
		EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.	EF <sub>1</sub>	EF <sub>2</sub>	% Anthrop.							
		Crust		DSH	Crust		DSH	Crust		DSH	Crust		DSH	Crust		DSH	Crust		DSH	Crust		DSH							
EPC 08	0–4	<b>2.1</b>	1.7	52.6	42.0	0.2	1.2	–	13.3	0.1	0.9	–	–	1.2	1.7	17.2	39.4	1.5	<b>2.5</b>	34.4	60.0	<b>6.5</b>	<b>2.8</b>	84.5	64.8	<b>23.1</b>	<b>16.3</b>	95.7	93.9
EPC 87	10–30	0.7	0.8	–	–	0.3	0.4	–	–	0.3	0.5	–	–	<b>4.5</b>	1.2	77.8	17.4	<b>7.8</b>	1.3	87.2	24.3	<b>8.1</b>	1.7	87.7	40.4	<b>8.1</b>	1.7	87.7	40.4
PS 76	0–4	1.2	1.2	16.6	13.9	0.2	0.5	–	–	0.2	1.0	–	–	0.4	<b>3.6</b>	–	71.9	0.7	1.0	–	4.4	<b>6.9</b>	1.8	85.4	44.6	<b>3.5</b>	2.0	71.7	49.5
PS 88	0–0.5	1.0	0.9	0.2	–	0.3	0.8	–	–	0.4	0.9	–	–	1.3	<b>3.9</b>	24.3	74.3	<b>4.0</b>	<b>2.5</b>	75.3	59.8	<b>12.3</b>	1.6	91.9	39.3	<b>23.9</b>	<b>4.0</b>	95.8	74.8
SP 57	0–7	0.8	1.5	–	33.1	0.3	1.0	–	–	0.2	0.8	–	–	0.4	<b>2.4</b>	–	57.9	1.1	<b>2.2</b>	9.0	53.7	<b>9.1</b>	<b>2.9</b>	89.0	65.3	<b>16.1</b>	<b>6.8</b>	93.8	85.3
EPC 63	3–10	1.0	1.5	–	34.3	1.3	1.0	<b>20.1</b>	–	0.4	1.0	–	0.1	0.9	1.6	–	35.6	<b>3.1</b>	1.7	67.3	42.3	<b>11.3</b>	2.1	91.2	53.0	<b>6.9</b>	<b>9.2</b>	85.6	89.1
PS 45	0–7	0.9	1.0	–	–	0.4	0.3	–	–	0.3	0.9	–	–	0.3	0.9	–	–	1.5	0.9	35.0	–	<b>10.2</b>	<b>4.6</b>	90.2	78.1	<b>12.6</b>	<b>3.5</b>	92.0	71.1
SP 05	0–15	1.1	0.8	7.1	–	0.8	1.0	–	–	0.7	0.8	–	–	0.6	0.9	–	–	1.6	1.0	38.6	0.4	<b>2.5</b>	1.7	59.6	40.3	<b>2.0</b>	1.3	48.9	21.6
CHS 41	15–30	0.6	0.6	–	–	0.5	0.6	–	–	0.2	0.4	–	–	0.3	1.4	–	28.0	1.4	0.8	27.1	–	<b>2.6</b>	1.0	61.1	–	<b>2.0</b>	0.9	50.5	–
HET 54a	15	1.2	1.2	16.0	18.9	1.1	<b>3.1</b>	6.0	68.1	0.4	1.0	–	–	0.2	0.6	–	–	1.2	1.6	14.1	36.1	<b>5.4</b>	<b>3.7</b>	81.4	72.8	<b>5.3</b>	<b>3.8</b>	81.0	73.4
PM 40c	0–10	<b>2.1</b>	<b>7.6</b>	51.3	86.9	0.3	<b>9.5</b>	–	89.5	0.0	0.3	–	–	0.6	<b>8.0</b>	–	87.5	1.3	<b>9.4</b>	24.1	89.4	<b>20.5</b>	<b>2.4</b>	95.1	58.2	<b>5.6</b>	<b>2.6</b>	82.3	61.0

EF<sub>1</sub> is calculated against the earth's crust value; EF<sub>2</sub> is calculated against the deep soil horizon value; % Anthropogenic is calculated against the earth's crust value (Crust) and against the deep soil horizon value (DSH).



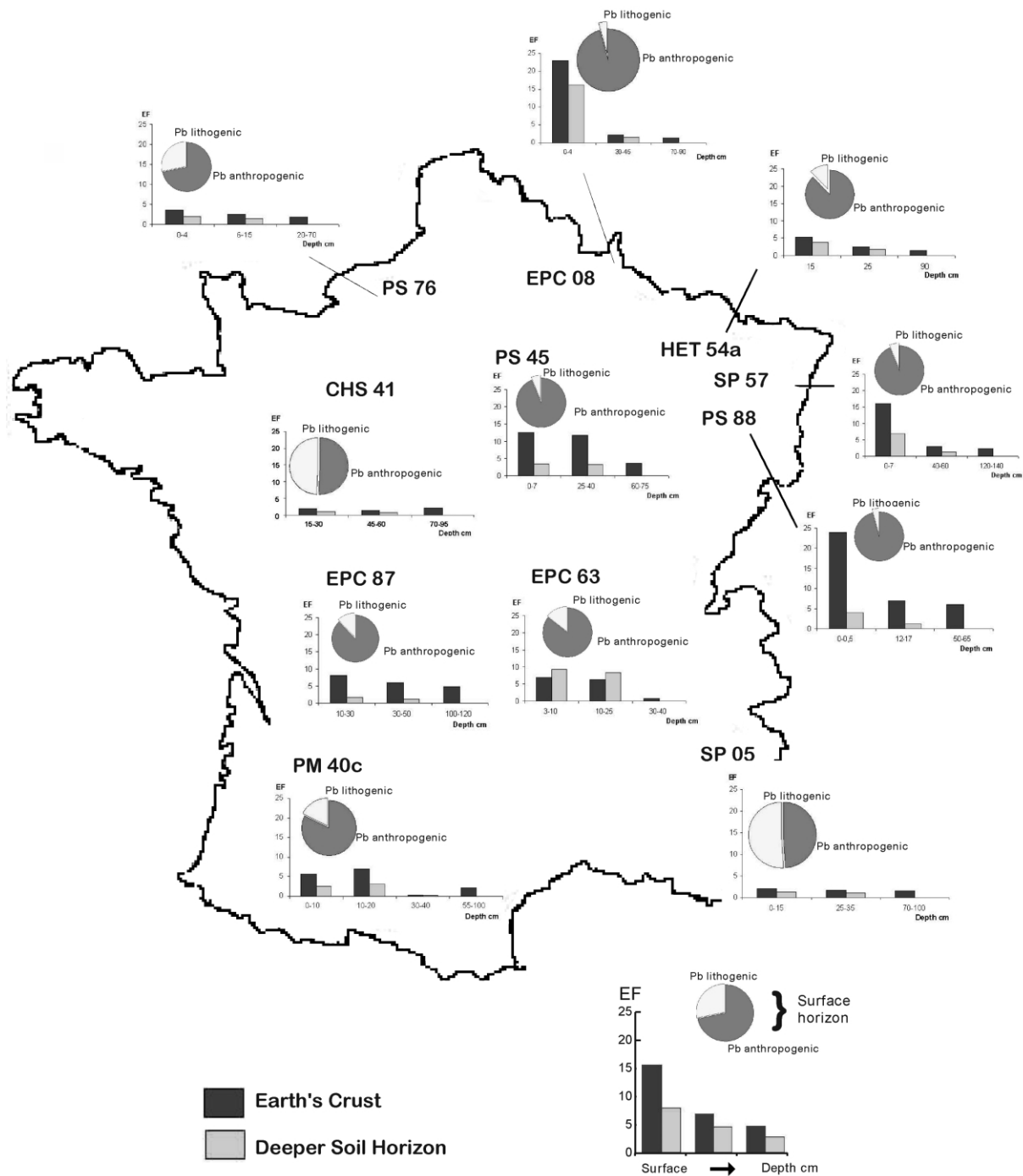


Fig. 8. Lead enrichment (EF) in the different soil samples and lead anthropogenic proportion with reference to the earth's crust content in surface horizons.

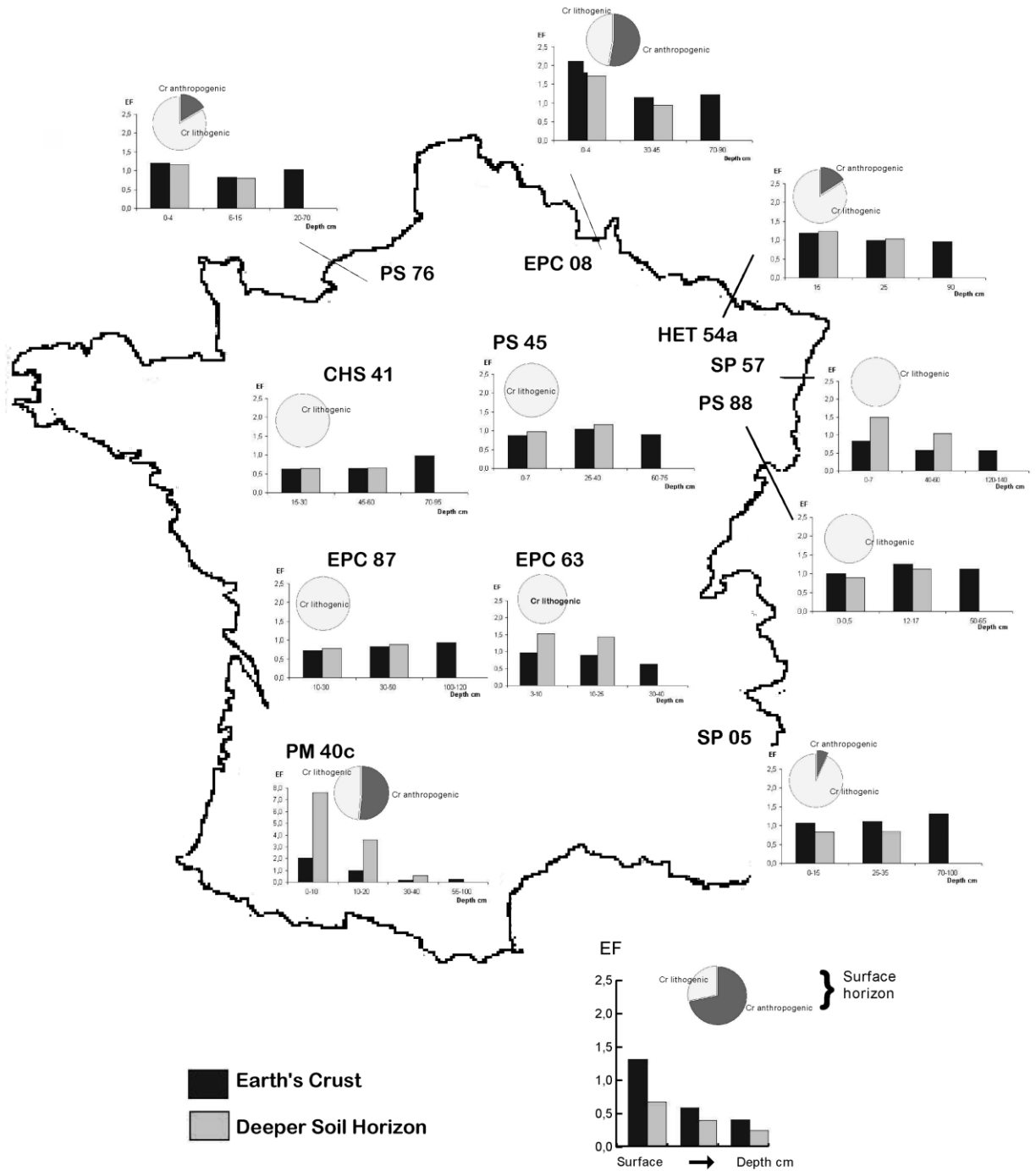


Fig. 9. Chromium enrichment (EF) in the different soil samples and chromium anthropogenic proportion with reference to the earth's crust content in surface horizons.

the calcaric cambisol (SP 05) and the haplic podzol (PS 76). Most of the enriched samples are in the surface horizons from the soils located in the north-eastern part of France (EPC 08, PS 88, SP 57). If the enrichment is calculated with regard to the deepest horizon, enrichment is still obvious, albeit less so. For the mollic andosol (EPC 63) only, the enrichment factor calculated with the deep soil layer contents as a reference is higher than that calculated with the earth's crust values. This can be attributed to lower Pb content in the deeper soil layer as compared to the earth's crust.

The least Pb enriched soils are the calcaric cambisol (SP 05) and the stagnic luvisol (CHS 41) which are located in the French Alps and in the central part of France. Despite their low Pb concentrations, the soils PM 40c and PS 76 show a rather significant Pb anthropogenic contribution. For the soils EPC 08, PS 88, SP 57, PS45, 90% of Pb content is related to anthropogenic sources. For the calcaric cambisol (SP 05), the anthropogenic contribution is approximately 50%. This should be considered as a minimum value for anthropogenic contribution.

The Cr enrichment, calculated like for Pb with respect to the earth's crust value and to the deep horizon content, is weak (Fig. 9). It is worth noting that the discrepancy between calculated lithogenic contributions using earth's crust and deep horizon reference values is less important than for Pb. That means that on one hand the reference lithogenic value is quite uniform and that deep soil profiles are not disturbed by Cr sources other than lithogenic origin. However, the enrichment factor is more important using the deep soil horizon as a reference for the mollic andosol (EPC 63), the dystric planosol (PS 45), the dystric cambisol (SP 57) and mainly the ferric podzol (PM 40c) in relation to significantly lower Cr/Sc ratios in the deep soil profile than in the earth's crust. Nevertheless the high enrichments calculated for the ferric podzol (PM 40c) must be considered cautiously because the heavy metal concentrations are very low.

In contrast with Pb, Cr in the surface horizons appears to be mainly of lithogenic origin in almost all soils except PM 40c (13–49%) and EPC 08 (48–58%). Nevertheless, for PS 76 and HET 54a,

Cr is also not totally from lithogenic origin (81–86%).

For other heavy metals (Cd, Co, Cu, Ni and Zn) almost all soil samples are not heavy metal enriched with reference to the deep soil horizon ( $EF_2 < 2.0$ ) (Table 6). However, some surface soil horizons present enrichment factors ranging between 2.0 and 4.0, and even greater than 4.0: Cd (4.6) for PS 45, Co, Cu, Zn, Cr (9.5, 8.0, 9.4 and 7.6, respectively) for PM 40c despite its lowest heavy metal concentration. The enrichment factors calculated taking into account the deep soil horizon or the earth's crust data are in the same range of values for Co, Cr and Ni. As for Pb,  $EF_1$  (crust reference) is much higher for Cd in most of the soils whereas  $EF_2$  is higher for Cu and Zn. Thus the corresponding calculated anthropogenic contribution is more important. All these differences can be attributed to the disparity between the earth's crust and the deep soil horizon concentrations, particularly for Sc concentration which is generally lower in the deeper soil horizons than in the earth's crust except for SP 05. Consequently, without bedrock data reference for the studied soils, the accurate value for enrichment factor and anthropogenic contribution is in between the values given in Table 6.

### 3.5.2. Pb isotope constraint

To check if the Pb enrichment is really related to anthropogenic deposition according to the previous calculations using Sc, Pb isotopes were analysed. For this purpose, one has selected two soils: one cambic podzol (EPC 08) located in the northern part of France with a high Pb content and an important enrichment in surface horizon, and one calcaric cambisol (SP 05) located in the French Alps with relatively high Pb content but weak enrichment in surface horizon. For the latter, the Pb isotopes could only be measured in the surface horizon.

Fig. 10a presents the relationship between  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  and Fig. 10b  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $1/[\text{Pb}]$ . For both soils, the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio vary from 17.03 to 18.51; for the cambic podzol (EPC 08), the lowest isotopic value and the highest Pb content are found in the surface horizon and decrease with depth (Fig. 10a). The

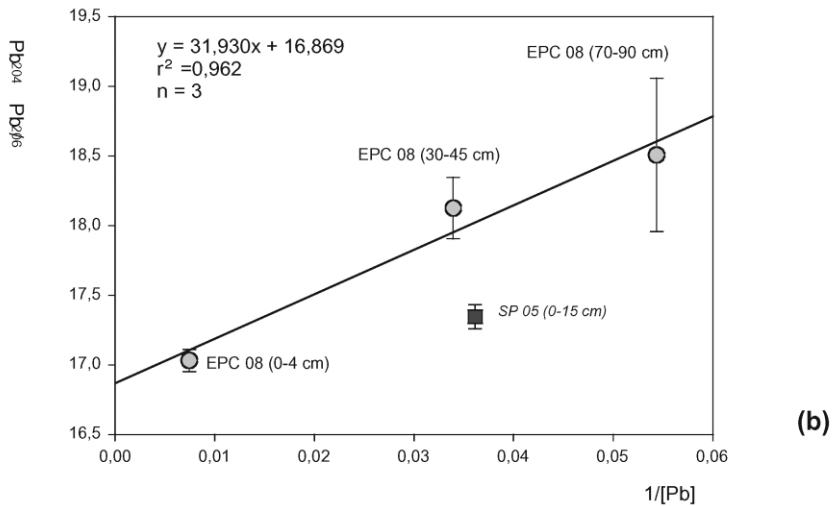
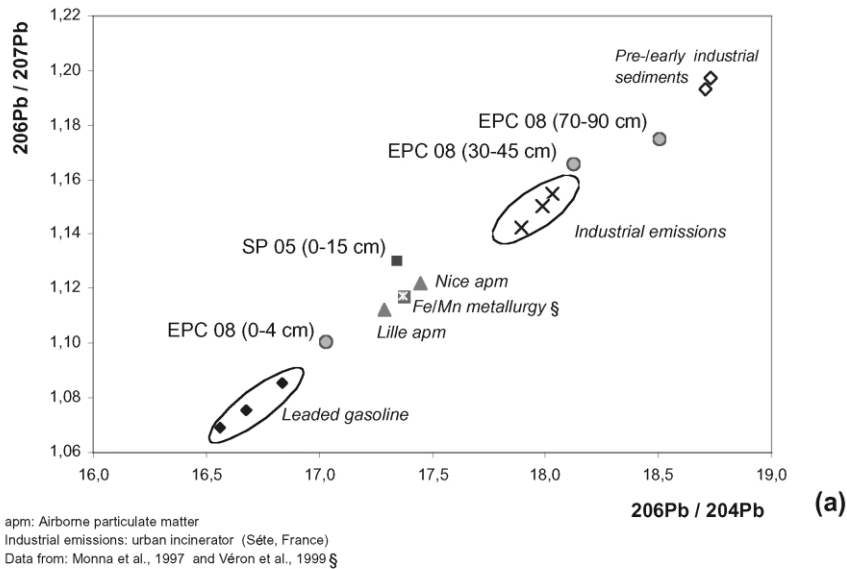


Fig. 10. Lead isotopic composition diagram ( $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) (a), and  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $1/[\text{Pb}]$  diagram (b) for EPC 08 profile and SP 05 surface horizon.

relationship between  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $1/[\text{Pb}]$  is almost linear. The surface horizon of SP 05 is found to be in an intermediate position close to the mixing line. The linear relationship between  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  (Fig. 10a) indicates that each sample correspond to a mixing between

two main end-members. One can observe that the Pb isotopic ratio in surface horizon (0–4 cm) of the cambic podzol (EPC 08) is close to the values of the leaded gasoline originating from various European countries (Monna et al., 1997) whereas the deep horizon value of the same soil is near the

pre-early industrial sediment values (Monna et al., 1997). The intermediate soil horizon of EPC 08 is in an intermediate position on the mixing line showing that an anthropogenic contribution of lead has progressively been incorporated in the soils from surface to depth. Given that the Pb isotopic behaviour has been measured only in the surface horizon of the calcaric cambisol, the intermediate isotopic value indicates a non negligible anthropogenic contribution (with reference to the same end-members), however less important than that for the EPC 08 surface horizon.

Isotopic ratios of airborne particulate matter from Nice (south of France and close to the site SP 05) and Lille (north of France close to the site EPC 08) as well as industrial emission data (from Sète Waste incinerator, South of France) have been indicated (Fig. 10a). Their isotopic values are located in between leaded gasoline and pre-industrial sediment data. The influence of leaded gasoline thus seems to contribute more to anthropogenic lead in soils than industrial emissions or modern airborne particles. The anthropogenic contribution for the different soil horizons has been estimated, for these data, as follows: 83, 30 and 11%, respectively, for surface, intermediate and deep soil horizons of EPC 08, and 68% for surface horizon of SP 05. These values for surface horizons are in agreement with those calculated previously using the earth's crust lithogenic data as references.

The anthropogenic contribution for chromium detected in EPC 08 has probably to be related to metallurgic industrial activities located in the region, particularly the steel industries located in the South of Luxembourg.

#### **4. Discussion and conclusion**

This study highlights the distribution, behaviour and controlling factors of heavy metals in some selected French forest soils (ferric podzol, cambic podzol, haplice podzol, dystric cambisol, humic cambisol, dystric planosol, stagnic luvisol, calcaric cambisol and mollic andosol).

These forest soils generally have low heavy metal contents, within the range of concentration for non-polluted soils and for the main world soil

types (Kabata-Pendias and Pendias, 1992). However, it is important to notice that in some soil samples located far away from local pollution sources, the heavy metal concentrations may be greater than the standard values of French AFNOR regulation and European norms.

The pattern of soil sample distribution from Al-Fe oxides end-member to silica end-member reflects the well-known soil evolution between clayey-silty soils to sandy acid soils, indicating that the selected soils represent a wide range of pedogenetic conditions.

Zn and Cr are the most abundant heavy metals in soil samples. The high Cr content in deep horizons of PS 45, CHS 41 and HET 54a, could be explained by the fact that Cr like Zn, Ni and Cu are strongly bound to clay minerals (Baize, 1997).

Cr, Co and Ni concentration in surface horizons for almost all soil samples seems to be of lithogenic origin. The lithogenic origin of Cr which is present in some primary minerals (Baize, 1997) is reflected in concentration of Cr in some deep soil horizons.

The increasing concentration of Cr and Ni with depth may indicate both the weathering origin of these two metals and/or a leaching within the soil profile. According to Baize (1997), Cr can be mobilized within the profile due to clay leaching processes associated with Fe oxides.

Co is generally most concentrated in deep horizons as it was also observed in several French cultivated soils by Baize (1997). The higher Co concentrations in deep horizons of EPC 63, PS 45 and CHS 41 could be associated to the clay contents in these soils, as shown by Krasnodębska-Ostęga et al. (2001) for forest soils.

Cu shows relatively little variation in the soil profiles, and it is mainly related to Fe and Al-oxides and soil pH (Kabata-Pendias and Pendias, 1992; Oliver, 1997). The copper concentration increases with depth in some of the acid soils. According to Baize (1997), Cu can be mobilized under extreme acid conditions (podzols, for example) or during gleying processes. The surface layers of the studied soils do not have high Cu content which might reflect recent anthropogenic inputs of this metal as shown by Kabata-Pendias

and Pendas (1992) and Baize and Sterckeman (2001).

The behaviour of Zn in the calcaric cambisol (SP 05) and the mollic andosol (EPC 63) is controlled by organic matter, clay, Al and Fe-oxides, all of which lead to a stronger adsorption capacity for zinc than sandy soils or soils with low organic matter content (Kabata-Pendas and Pendas, 1992; Alloway, 1994; Oliver, 1997).

The low Cd content in soil samples indicates that the sites are not exposed to high deposition of atmospheric Cd pollutant (Table 5). Kabata-Pendas and Pendas (1992) consider that the main factor determining Cd content in soils is the chemical composition of the parent rock and its high mobility in acid environments. One can suggest that the Cd content in the studied soils is mainly of lithologic origin, except in upper soil layers. Rautengarten et al. (1995) suggest that the Cd distribution is controlled by small mineral particles and organic matter, its mobility being determined mainly by clay content.

As already shown by Kabata-Pendas and Pendas (1992), Berthelsen et al. (1994) and Rademacher (2001), this study confirms that the organic soil layer acts as a sink for Pb.

No clear relationship can be assessed in these French forest soils between the level of heavy metal concentration and the soil sample properties even if the sorption of heavy metals is known to be influenced by physical and chemical properties in soils as shown by Chlopecka et al. (1996) for polluted soils in Poland.

Soil pH which has a strong influence on heavy metal adsorption, retention and movement in soil profiles, shows highly significant correlations in single and multiple regression analysis as shown also by McBride et al. (1997), Römken and Salomons (1998) and Kotaś and Stasicka (2000). Significant relationships exist between CEC and clay content because the clay-size fraction has the highest CEC due to greater surface area per unit of clay mineral mass (see for example, Caravaca et al., 1999). Consequently, the clay proportion has a great importance for metal behaviour in the different soils and plays a major role in the physico-chemical processes and to metal retention

in soils. This is particularly true for Pb content in acid soil.

The relationships between organic matter content and heavy metals found in our soil samples are weak, except for Pb and Cd and more generally for upper soil organic horizons. Harter (1983) and McBride et al. (1997) suggest that the absence of correlation between total soil organic matter content and heavy metal adsorption can be attributed to the fact that the reactive fraction of the organic matter could not be assessed in the relationship.

Almost all heavy metals are strongly correlated to Fe and Al oxides, particularly Cu and Zn in accordance with Ramos et al. (1994) and Chlopecka et al. (1996).

The results of regression analysis have shown a large variety and complexity in relationships between the different parameters and heavy metals in soil samples. Heavy metal concentrations cannot be related to only one parameter; nevertheless, pH, iron and aluminium oxides, and to a less extent, clay content and organic matter play an important role in heavy metal retention and migration in these soils. The multiple regression models let us identify more clearly the control parameters for each heavy metal in selected forest soil samples. However, it is important to keep in mind that the amount of heavy metal in soils is mainly distributed between the non-residual fractions (adsorbed onto the solid phases) and the residual fraction (i.e. heavy metal contain in the mineral structures) which is not controlled by any physico-chemical soil parameter, except the mineralogical composition (Hernandez, 2003 (in press) and Hernandez et al., in preparation).

The calcaric cambisol (SP 05) presents the highest heavy metal contents and a different metal behaviour with respect to the other soil profiles. The range of heavy metal content is in agreement with the origin of the soils regarding the parent rock (Kabata-Pendas and Pendas, 1992). The relatively high heavy metal contents in the mollic andosol (EPC 63), could be mainly related to the presence of allophanes, in accordance with Denaix et al. (1999) and Semlali et al. (2001), the allophanic soils being known to show a strong retention of heavy metals (Cd, Pb and Zn particularly).

For the calcaric cambisol (SP 05) and the mollic andosol (EPC 63), the importance of the annual precipitation amount and of the anthropogenic inputs might explain the heavy metal behaviour, since EPC 63 is located in the Massif Central and SP 05 in the French Alps (Table 1). Pb is the most abundant heavy metal found in rainwater (Teutsch et al., 1999) but, no significant relationship was found between annual precipitation amount and heavy metal contents as already shown by Roy and Négrel (2001) for the Massif Central area.

Consequently, the incorporation of anthropogenic Pb in the mollic andosol (EPC 63) and in the ferric podzol (PM 40c) is weak as already indicated by Semlali et al. (2001) using Pb isotopes in two soils close to EPC 63 and PM 40c. Indeed, the recent atmospheric deposition of anthropogenic Pb had only a weak effect on these soils.

The ferric podzol (PM 40c) has a dominant sandy texture, high permeability and porosity, and low heavy metal concentrations. The Landes area was not influenced by significant industrial activities; nevertheless some sulphuric acid inputs were measured in this area (Croisé et al., 2002). According to Saur and Juste (1994) heavy metal inputs in soils, in the region of PM 40c, may be mainly the result of long-range atmospheric transportation due to the influence of Western winds.

One of the key observations of this study is the metal-trapping character of the andosol and of the calcaric soil, the weak heavy metal retention in acid soils, the leaching and trapping character in leached clayey soils, and the migration of heavy metals in the podzol.

It is important to notice that the soil sample profiles with higher Pb content are located in the north-north-eastern part of France where significant acid atmospheric pollution occurs (Probst et al., 1995; Landmann and Bonneau, 1995; Party et al., 1995). More recently Probst et al. (2000) and Aubert et al. (2001) have clearly detected using Nd and Sr as tracers, the influence of atmospheric pollutant inputs on forest soils from this region.

The anthropogenic contributions of Cr may be related to industrial activities near the affected sites (PS 76, Rouen industrial area, EPC 08 and

HET 54a, Rhür basin, RFA and northern France industrial areas).

Pb and Cd show an important enrichment in surface horizons from all the forested soils which can be derived from long range transportation of anthropogenic atmospheric pollutants. Consequently, Pb and Cd anthropogenic contribution is the most important compared to the other heavy metals. The Pb isotopic study has indicated that the enrichment in the surface horizons of EPC 08 and SP 05 is from an anthropogenic origin. For the calcaric cambisol (SP 05), the origin of Pb in the surface horizon is similar to that of the airborne particulate matter from Nice city (i.e. indicating an anthropogenic contribution of 65%). In the cambic podzol (EPC 08) profile, Pb pollution is mainly due to the leaded gasoline contamination in the surface horizon. The incorporation of anthropogenic Pb has been progressive, as shown by the linear relationships between Pb concentration and Pb isotope ratios. Soil Pb contamination is thus rather the result of many years of deposition enriched in transboundary leaded gasoline particles than of a local or regional industrial sources. In the northern part of France, Pb from airborne particles have been recently attributed to local industrial activities rather than to gasoline (Véron et al., 1999). However, Pb from airborne particles represents the present-day atmospheric conditions, whereas the soil surface reflects several years of atmospheric deposition.

This study highlights that atmospheric pollution inputs have impacted the soils in northern hemisphere forest areas, and that soil surface accumulates heavy metals in areas where acid pollutant inputs are significant but also in more remote areas.

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