Chapter 4
Potentially Harmful Elements in Forest Soils

A Pedological Viewpoint

Denis Baize and Folkert van Oort

Abstract Forest ecosystems differ from agroecosystems, in the first place by the established vegetation cover of deciduous or needle trees, associated with a specific biochemical cycling of forest organic matter. The presence of a forest floor (litter O and humus-rich A horizons) introduces additional pathways of biogeochemical cycling of potential harmful major and trace elements (PHTE), with respect to soils under agricultural land use. Moreover, unlike agroecosystems, forest soils are predominantly affected by only one way of PHTEs inputs, deriving from atmospheric deposition. Aged and established forests are generally in a state of equilibrium with respect to elemental cycling. In such forest soils, especially in their deep horizons which are most often little affected by any contamination, PHTE contents are fairly close to the initial natural pedo-geochemical background concentrations. Consequently, they can be used as a reference for other soils developed in the same parent material, but under agricultural land use and affected by anthropogenic contaminations. Exceptions are forest soils located in the proximity of industrial or mining areas, which are more exposed to short-range industrial atmospheric fallout.

Forest soils often have a lower buffering capacity against acidification than agricultural soils due to the adding of acid-neutralizing amendments (fertilization, liming, and compost) to the latter. In strongly acid forest soils, the risks of mobility of PHTEs are well-established and migration may occur in soluble, pseudo-soluble or particulate forms. Soil acidity may lead to high levels of Al and Mn, representing additional risks of aluminium or manganese toxicity. The forest floor represents a particular metal trapping medium in soils. When a mor-type humus layer is present

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at the surface of forest soils, exogenous pollutants accumulate, as a first step, in a fully organic surface horizon. But the fate of contaminants in terms of permanent retention, or subsequent partial or even full release, and times of retention are items that are still under debate. In the particular case of podzols with strongly acidified soil conditions, PHTEs are susceptible to migrate to depth and to a part intercepted (long-term, permanently?) in the B horizons whereas another part may leach out of the soils and possibly transferred to the groundwater.

For a good understanding and a relevant interpretation of PTHE concentrations through the soil profile, in terms of accumulation or impoverishment, the limits of the morphological horizons must be respected during sampling. Such horizons may be of small thickness (for instance Bh horizons in podzols), but they can demonstrate substantially contrasted concentrations, for instance in the case of strongly differentiated soils (cf Table 4.3). Taking into consideration the characteristic processes involved in the formation of soil horizons, is essential for a better insight into mechanisms and pathways of cycling of PTHEs. Hence, for a valid assessment of the presence, distribution and fate of PTHEs in forest soils, and in order to allow an appropriate comparison with anthropogenic contaminated agricultural soils, it is crucial to take account of different soil parameters, such as the nature of the parent material, pedological characteristics and specific physico-chemical conditions. Moreover, and surely, it is essential to adopt a soil sampling strategy that is adapted to the aims and/or different parts of multidisciplinary study programs.

Keywords Forest soils • PTHEs • Geochemical background • Soil forming processes • Biogeochemical cycles

1 Introduction

Almost any chemical element, trace as well as major elements may become harmful in soils at high concentrations, with respect to ecological components and human health, regardless from its origin, geogenic or anthropogenic (Adriano 2001). But more than its total concentration, harmful effects of elements depend on its chemical form (speciation) that governs its bioavailability. Chemical speciation of elements in soils is complex, it varies according to different environmental conditions. The soil pH, as well as the soil's nature, and mineral, organic and biological composition, and land use are important parameters to consider for environmental risk assessment. In this chapter we will evoke different elements: a major (Al) and several trace metals (Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn).

1.1 Specific Characteristics of Forest Soils

Forest soils have physicochemical properties that may considerably differ from those in soils under agricultural land use. To a part, these differences are due to the fact that the occurrence of large forest areas is nowadays often restricted to situations which are considered as little or non-suitable for agronomic purposes, because too poorly drained, too steep, too stony, too shallow, or too poor. But forest soils also differ by some unique properties: the deep rooting of trees, the role of microorganisms associated with the forest vegetation, and a specific cycling of organic carbon. Often, at high latitudes and altitudes, there is formation of a forest floor, the O horizon composed of more or less decomposed organic debris (leaves, needles, bark, fruits and lignified materials). Then, decaying of litter produces organic acids that promote eluviation and lixiviation processes (Binkley and Fisher 2012). The occurrence of a litter layer exerts a great influence on the soil's physical, chemical and biological properties. Such specific characteristics of forest soils are associated with a distinct soil profile development and macro- and micromorphological features. Forest soils will become more acidified if the acid neutralising capacity of the parent material is small (van Breemen and Finzi 1998). When developed on comparable parent material, forest soils often, but not always, demonstrate a lower soil pH (Ugolini and Edmonds 1983; Hesterberg 1998; Bacon and Hewitt 2005) than those observed in agricultural soils. Such a difference is often related to the application of chemical and/or organic fertilization, or soil amendments with acid-neutralizing treatments in agricultural soils (Blum et al. 1997; Goulding and Blake 1998; Andersen et al. 2002). Soil acidification enhances the liberation of major metal elements, such as Al, Fe and Mn, which at low pH become more mobile and potentially toxic. An additional major difference between forest and agricultural soils is the annual ploughing and other tillage operations in the latter ones.

1.2 Origin of Trace Metal Contamination

In comparison with open agricultural land, forest soils are quasi-exclusively affected by atmospheric deposition. Forest soils have been frequently mentioned to accumulate more trace metals in the surface horizons than is observed for soils under agricultural land use (Blum et al. 1997; Adriano 2001). Abundant literature is available for the accumulation of airborne lead (e.g. Jensen and Svensmark 1989; Hanschmann and Opp 1993; Keller and Védy 1994; Johnson and Petras 1998; Hernandez et al. 2003; Bacon and Hewitt 2005; Steinnes and Friedland 2006). Forest ecosystems represent an efficient filter for toxic substances (Schlesinger and Reiners 1974; Binkley and Fischer 2012), due to the height and density of the tree canopies that intercept atmospheric dust by dry and wet deposition (Bergkvist et al. 1989). Consequently, although many large forest areas are often considered as natural ecosystems and only little impacted by anthropogenic contamination, forest soils may demonstrate surprisingly high surface concentrations of trace elements. The origin of such accumulations is to a large extent ascribed to long-range atmospheric deposition (Jensen and Svensmark 1989; Wang et al. 1995; Adriano 2001; Steinnes and Friedland 2006) deriving from human activity such as coal combustion, metal smelting, waste disposal etc. (Nriagu and Pacyna 1988; Ragsdale and Berish 1988). But besides interception of long-range pollution, forest soils may also be the receptor of short-range pollution, i.e. industrial atmospheric deposition, for instance for situations close to industrial metallurgical complexes (Ruan et al. 2008). Both in cases of long-range and short range atmospheric deposition, the amounts of anthropogenic (exogenous) trace elements may widely dominate the natural (endogenous) trace element concentrations (Semlali et al. 2001a, b; Fernandez et al. 2008; van Oort et al. 2009).

1.3 Fate of Trace Metals

Particularly under prevailing acid conditions in many forest soils, the pH to a large extent determines whether one will observe a net accumulation or loss of a given metal element in the humus-bearing upper horizons, and hence, the time of its residence at the soil's surface (Steinnes and Friedland 2006). Metals predominantly present in a free, or exchangeable form (Zn, Cd) are susceptible to pH fluctuations (McBride 1989; McBride et al. 1997; Sauvé et al. 2000). With a decrease of the soil pH, they will easily migrate in the soil solution toward depth. Downward moving trace metals may be either partly intercepted and sorbed on negatively charged soil constituents such as clays and iron and manganese oxides (van Oort et al. 2006, 2008) or leach out of the soil toward the water table. Other trace elements, with a less mobile character and a great affinity for organic matter, such as Pb and Cu are less susceptible to soil pH or become mobile at lower pH values than Zn and Cd. Yet they may migrate in colloidal form (Erel et al. 1997; Citeau et al. 2003; Semlali et al. 2004), associated with organic matter (or oxides) and either precipitate in the upper B horizon or may leach even to greater depths (van Oort et al. 2006).

1.4 Forest Stands Sometimes Mask Ancient Cultivation or Industrial Activity

Several authors have noted that large areas nowadays under forest have been cultivated several centuries ago, sometimes as early as the Roman Empire period, as was shown by work of Dupouey et al. (2002) and Dambrine et al. (2007) for large areas in north-eastern France. Such more or less ancient cultivation probably had only small impacts as far as the trace metals are concerned. By contrast, extended forest areas may include, and mask, numerous sites affected by historical mining activities, as it was demonstrated for instance in the Harz region (Germany) and Morvan area (France) (Monna et al. 2000, 2004). Therefore, the widely spread idea that forest soils represent long-lasting natural ecosystems only little affected by human activity, always needs careful checking.

1.5 Objectives

In this chapter, we do not intend making an exhaustive overview of the fate and behaviour for the different trace elements in soils, since excellent references exist on that topic (e.g. Alloway 1995; Adriano 2001). The aim of this chapter is to present from a pedological point of view the key factors for a valid understanding of the distribution and fate of some major and trace elements in forest soils in comparison to soils under agricultural land use. It is clear that many soils occurring under forest are still calcium-saturated, or even calcareous, but these soils were not much studied because considered as presenting fewer risks towards human health or our environment. Therefore, our contribution will focus on the occurrence and dynamics of trace metals in more or less acidified forest soils of temperate climate in Western Europe. Note that the case of poplar stands or short-term rotation woodlands will not be discussed, because they can be considered as lignified monocultures and so are little different from usual agricultural soils (Binkley and Fischer 2012).

In this chapter, we emphasize items about (1) the key factors for interpreting concentrations of different trace metals in soils, (2) how to distinguish natural from anthropogenic trace elements, (3) specific behaviour of some trace metals in forest soils in comparison with soils under agricultural land use. In Sect. 5 we illustrate these items with examples from case studies on trace metal (Zn, Pb, Cd) accumulations, distributions and movements in forest systems located in France.

2 Concentrations of Trace Elements in Soils: The Three Keys

2.1 The Initial Inheritance: The Geochemical Background

Under any climate, the **number one key** which from the outset determines the concentrations in potentially harmful trace elements (PHTEs) found in soils today is the chemical composition **inherited** from the parent material, usually called “geochemical background”. This corresponds to the mineralogical composition of the rock whether originally-formed (in the case of extrusive and igneous rocks) or

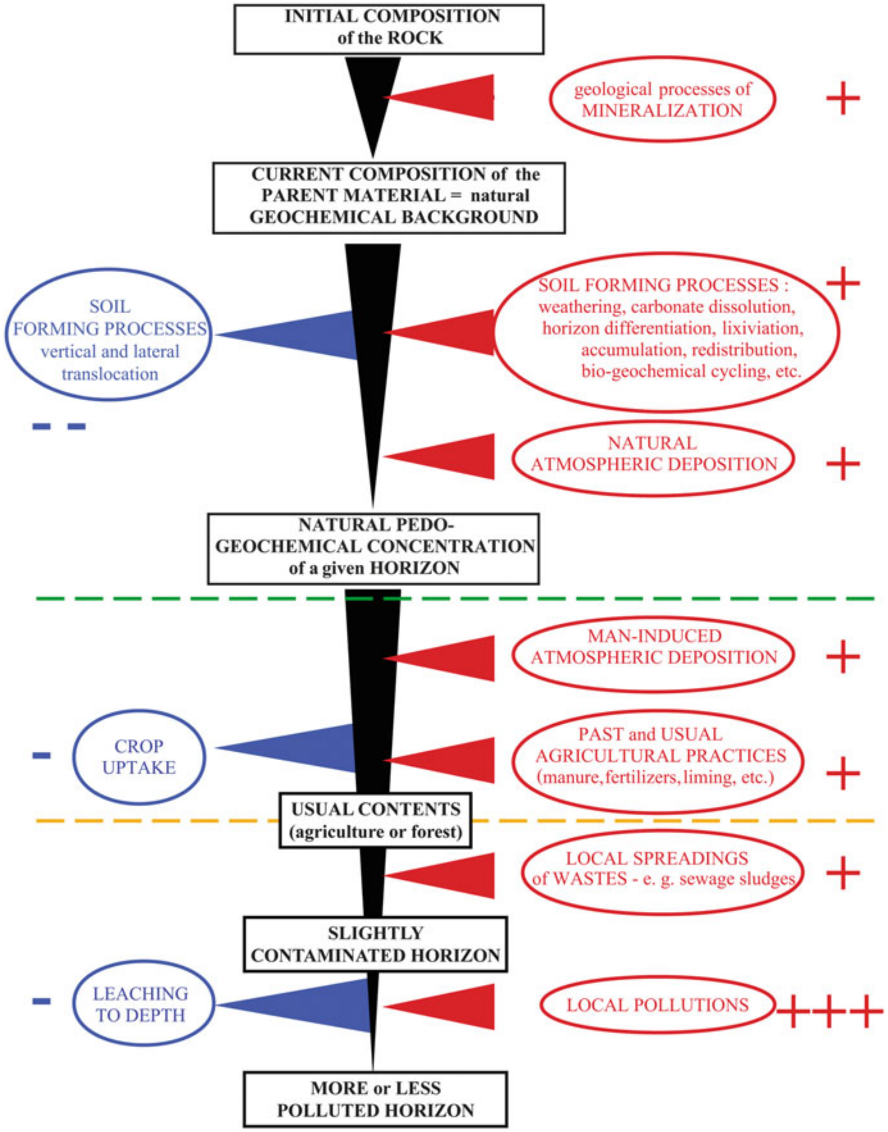

Fig. 4.1 Progressive acquisition of trace element composition of a soil horizon: from the initially-formed rock to the ploughed surface horizon (Ap horizon). On the *right*, in *red*: factors increasing the trace element contents. On the *left*, in *blue*: factors decreasing them

initially deposited (in the case of marine sediments, moraines, loess and alluvium), which have sometimes been modified by subsequent mineralization (Fig. 4.1).

A first example is given by still weakly differentiated soils, which are abnormally rich in nickel and chromium, because they developed from rocks containing

Table 4.1 Strong anomalies of nickel and chromium due to ferromagnesian primary minerals (olivine, pyroxenes, and amphiboles)

				Cr	Ni	Fe	Mg
Horizon	Depth (cm)	pH in water	Total C (g kg^{-1})	(mg kg^{-1})		(g kg^{-1})	
Davos – # 1							
A	4–6	5.1	102	2,600	411	68	40
Bw1	8–15	6.0	30	2,800	587	91	52
Bw2	20–30	6.4	12	1,650	1,115	64	166
BC	50–60	6.6	4	2,300	1,702	62	207
C	80–90	6.8	2	1,750	1,996	59	215
Mauriac							
A1	4–7	5.2		293	168	75.6	8.4
A2	8–24	5.2		376	213	94.5	10.9
R	24–55			371	214	78.4	53.7
Bassin plat							
	0–20	5.4	22	930	1,040	209	
	20–60	5.2	17	780	980	194	
	60–85	6.2	7	880	896	207	
	85–130	6.6	5	1,110	989	219	

Davos: Soil developed in serpentinic rock slide material. Swiss Alps, under subalpine climatic conditions, near **Davos** (Gasser et al. 1995); **Mauriac**: Mountain grassland; altitude 700 m; mean annual rainfall 1,300 mm; the parent material is a slightly weathered basaltic flagstone of the Tertiary era. Trace metals are determined by alkali fusion (Soubrand-Colin et al. 2007); **Bassin plat**: Réunion Island. Andic cambisol developed in volcanic ash (Doelsch et al. 2006)

large amounts of olivine, pyroxenes, chromite, spinels, etc., which are all minerals bearing Ni and Cr. This is the case, for example, of the basalts and basanites of the French Massif Central (Soubrand et al. 2007) or of the Réunion Island (Doelsch et al. 2006) and the serpentinites in the Swiss Alps (Gasser et al. 1995). See Table 4.1.

Another example comes from soils developed in alluvium showing abnormally high contents of some PHTEs. As a general rule, alluvium display extremely variable particle-size (from heavy clays to large boulders), but above all, their composition is totally dependent on the lithology of materials abraded upstream. So, some alluvial soils of little streams flowing down the Vosges or the Cévennes (France), exhibit high concentrations of Pb, Zn, and Cu, simply because these alluvium are located downstream of strongly mineralized rocks.

The case of moraines is different, being deposited by Alpine glaciers (Switzerland – the canton of Geneva and France – the Savoy region). The glacial tills deposited by the ancient Rhone glacier contain numerous little fragments of "green stones". That is the reason why the still weakly differentiated soils developed in them are heavily loaded in nickel (40–220 mg kg^{-1}) and chromium (78–226 mg kg^{-1}), whereas they are poor in iron and of medium texture (see Table 4.2, Fig. 4.2). No similar findings are observed in the case of the Jura glaciers.

Table 4.2 Soil composition mirrors that of their parent material (Buatier and Wiart 1997)

			Cr	Ni	Co	Cu
Depth (cm)	Clay (g kg^{-1})	pH in water	(mg kg^{-1})			
0–30	245	6.1	164	117	16.9	26.3
30–60	216	6.7	175	126	18.4	25.9
60–90	327	7.7	226	188	23.3	34.1

Calcium-saturated soil developed in a calcareous moraine (Pays de Gex, France). Natural anomalies in Cr and Ni are due to little fragments of "green stones" in the parent material. This table also illustrates the interest of the vertical comparison

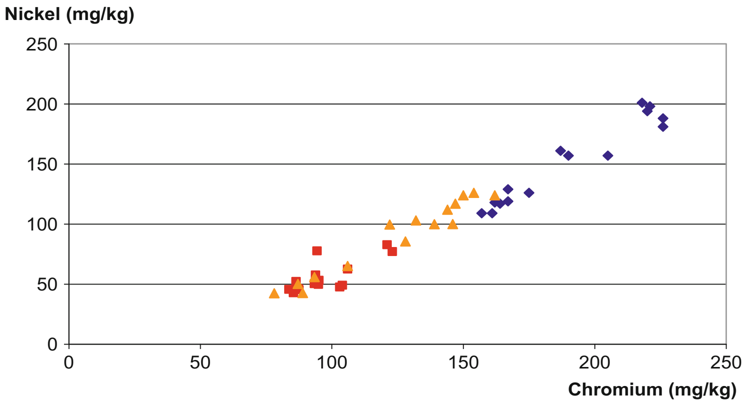

Fig. 4.2 Soils developed in alpine morraines (*Pays de Gex*, France). Relationship between nickel and chromium; N = 45 (3 different plots × 5 replicates × 3 sampling depths), r = 0.98 (Buatier and Wiart 1997)

These examples show the importance of considering the initial geochemical composition of the parent material for understanding and a correct interpreting of observed PHTE concentration (Blaser et al. 2000; Baize and Sterckeman 2001).

2.2 The Second Key: Soil Processes Leading to Natural PedoGeochemical Concentration (NPGC)

In regions with temperate climates and in those with cold climates, the **soil forming processes which can markedly change this inheritance** in upper soil horizons are few. These are:

(a) Partial or total dissolution of carbonates, resulting in a relative accumulation of non-lixiviated PHTEs; the total dissolution of limestone causes huge changes since the calcite may represent between 90 and 99 % of the dissolved rock. Thus, the constituents that have not been evacuated out of the soil (clay

Table 4.3 Total PHTE concentrations in a forested planosol developed in glauconitic "green sands" (Albian – Champagne humide, France) (Baize 1997a)

Horiz.	Depth (cm)	Clay	Org. Carbon	Total Cu	Total Cr	Total Cd	Total Pb	Total Zn	Total Ni	Total Fe
		(g kg^{-1})		(mg kg^{-1})						(g kg^{-1})
A	0–5	169	81.1	5.3	26.6	0.19	22.5	37	6.4	14.1
E	10–20	107	15.2	4.7	31.5	0.03	12.8	14	3.9	12.8
Eg	25–40	115	7.3	3.8	35.9	0.03	14.7	10	4.3	17.0
Bg	43–48	490	6.1	6.4	130.0	0.03	18.7	53	25.8	78.6
B	60–75	523	3.3	7.3	127.0	0.02	18.0	56	31.2	74.0
B/C	90–110	375	2.4	6.6	115.0	0.01	17.8	46	30.1	62.5
C	140–155	400	1.5	6.8	121.0	0.03	16.1	51	37.9	67.4

A marked contrast can be observed between upper horizons with a low Fe, Cr, Ni, Zn content and the deeper ones with a much higher content. Lead is more abundant in the surface humus-bearing horizon and remains unrelated with iron and clay contents, because of the global long-range atmospheric deposition

minerals, iron oxides, cadmium, and zinc) may reach very high concentrations in residual soils (Baize 1997b; Dubois et al. 2002; Prudente et al. 2002).

(b) Translocation of clay particles (vertical or lateral illuviation – *e.g.* case of Luvisols and Planosols) leading, over the long-term, to the formation of upper soil horizons with markedly lower PHTE content than deeper soil horizons (McKeague and Wolynetz 1980) (see Table 4.3). Large losses of TEs associated with clay particles or iron oxides can also occur in very old residual clayey soil mantles, leached down into the karst network (Baize 2012);

(c) Direct and total weathering of clay minerals by acidolysis, ferrolysis, etc. leading to the development of upper soil horizons very poor in major (Al, Fe) and trace elements (e.g. Petersen 1976; Brinkman 1979; Semlali 2000);

(d) Podzolization, where iron, aluminium and most trace metals form organo-metallic complexes, that are able to move down from the upper A and E layers and accumulate at depth in "spodic" B horizons. This translocation can affect natural substances as well as anthropogenic ones (Tables 4.4 and 4.8) (Delas 1966; Saur and Juste 1994; Filipe 1999; Semlali et al. 2000, 2001b; Brännvall et al. 2001; Kaste et al. 2003; Steinnes and Friedland 2005). Such an extreme soil forming process remains rather uncommon under temperate climates but represents a more common soil type in Scandinavia as well as in the vast territory of boreal forests covering large parts of North America and Russia. Podzols preferentially develop in very acid and permeable parent materials with little amounts of reactive soil components, able to develop strong chemical bonds with metals such as clay minerals and hydrous oxides.

(e) Dilution by very abundant organic matter (in the case of Umbrisols with humose topsoils);

(f) In soils with redoximorphic features, trace metals tend to accumulate associated with Fe and Mn oxyhydroxides acting as adsorbers (Latrille et al. 2001). These natural accumulations may display a wide variety of sizes and shapes but

Table 4.4 Evidence of vertical translocation of natural or anthropogenic metals through podzols

Horizon	Depth (cm)	pH in water	Org. matter[a] (g kg^{-1})	Total Pb (mg kg^{-1})	Total Cu (mg kg^{-1})
Sore					
O	0–4	4.0	262	17.5	
A	4–37	3.8	32.7	10.1	
E	37–67	4.3	3.7	5.8	
Bh	67–97	4.8	28.7	13.2	
Bs	97–127	4.5	6.7	8.9	
C	127–160	5.0	5.0	7.5	
Cestas			**Total carbon (g kg^{-1})**		
	0–20		29.5		1,880
	20–37		23.2		3,131
	37–55		4.9		350
	55–70		3.7		137

These two soils have in common to be thick podzols developed in quartzose aeolian sands *("sables des Landes de Gascogne",* France). **Sore**: Dry moor. An iron pan is visible at 67 cm (Saur and Juste 1994). **Cestas**: Pollution by copper salts in a site of pine timber treatment (Delas 1966); See also Table 4.8

[a] Organic matter determined by ashing 6 h at 800 °C

Table 4.5 Mineralization of a rock transmitted to the soil

Depth	Clay (g kg^{-1})	Carb. (g kg^{-1})	pH in water	Cd (mg kg^{-1})	Pb	Zn	Ni	Fe (g kg^{-1})	Mn (mg kg^{-1})
0–26	247	12.3	5.9	1.20	134	436	64.5	41.7	5,833
26–40	531	6.4	7.0	2.50	192	783	78.6	60.4	7,385
40–58	524	5.7	7.2	3.40	218	968	97.1	65.1	9,200
58–90	592	5.4	7.4	4.30	245	1,138	101.0	69.4	9,045
90–95	603	4.2	7.7	n.d.	n.d.	1,999	n.d.	85.5	24,975

This soil is developed in the total carbonate dissolution residue of a strongly mineralized marly limestone (Sinemurian platform, Burgundy; Baize and Chrétien 1994; Mench et al. 1997; Baize 1997b). The black deeper horizon (90–95 cm) exhibits particularly high iron, manganese and zinc concentrations. This table also demonstrates the interest of the vertical comparison when the surface horizon shows abnormally high PHTE contents which do not result from anthropogenic pollution but are a natural anomaly

generally remain in the soil horizon with heterogeneous distributions in relation with the mottled colour pattern. More often in deeper horizons, a strong absolute accumulation of iron, manganese and a suite of associated trace metals can occur, leading to singular soil horizons with a blackish hue (see Table 4.5**,** the deepest layer).

A good example of the above-mentioned process in ***a*** is provided by soils formed in the clayey residue resulting from the total carbonate dissolution of Jurassic limestone with an unusually high cadmium content (i.e. with 0.40–8 mg kg^{-1} rock – France, Swiss Jura). A large part of the freed cadmium is immobilized *in* *situ*, sorbed onto iron and manganese oxy-hydroxides, giving rise to soil horizons with natural concentrations that may exceed 2 mg kg^{-1}, sometimes reaching values as high as 22 mg kg^{-1} (Baize and Sterckeman 2001; Dubois et al. 2002; Prudente et al. 2002; Rambeau et al. 2010). See also Box 4.1.

Box 4.1: Cadmium in Soils of Haut Jura (Prudente 1999; Prudente et al. 2002)

The site thoroughly studied is a large fir forest (common forest of Les Fourgs – France), very close to the Swiss border, located at an altitude of about 1,150 m above sea level. 93 soil samples taken in 31 soil pits were analysed after dissolution by HNO_3 (according to Swiss regulation). These samples come from surface A horizons as well as from deeper ones, in contact with the underlying, limestone which was also analysed at 23 sites. After crushing, the rock samples were dissolved by acetic acid in a solution buffered at pH 5. As a result, Cd determined in this way corresponds solely to that linked with the carbonate phase.

In soils, Cd concentrations range from 0.10 to 22.3 mg kg^{-1} with a median of 1.0 mg kg^{-1}. Fifty six samples exceed the "indicative value" of the Swiss regulation fixed at 0.80 and only 6 show Cd contents higher than 7.0 mg kg^{-1}. In addition, there is a strong variability in space, vertically (from one horizon to another) as well as laterally (from place to place). As a general rule, it can be observed rather low values in the upper layers and much higher values at depth, in the horizons in contact with the limestone.

Cadmium concentrations in the underlying rocks range from 0.05 to 3.59 mg kg^{-1} regardless of their lithofacies. During the soil formation by calcite dissolution, the freed cadmium may be lixiviated or, conversely, be fixed onto iron and manganese oxy-hydroxides.

Another illustrative case is that of "chestnut-coloured" soils of the Sinemurian "back slope" in Burgundy (Table 4.5, Fig. 4.3). The locally mineralized marine limestone included a wide variety of trace elements (As, Cd, Cu, Co, Ni, Pb, Zn, Tl). These PHTEs originate from hydrothermal venting along a network of faults delimiting an old Hercynian horst. Soils have developed in the residual clay resulting from the limestone dissolution, which provoked a further PHTE concentration process in soils. These soils consequently have much higher contents than the underlying rock (Baize and Chrétien 1994).

In very old strongly and deeply weathered soils of the inter-tropical areas with a perhumid climate, many elements are lixiviated (e.g. Mg, Ca, Si), but others accumulate *in situ* (*e.g*. Cr, Ni, Cu, Mn, Ti, V, Zn, Pb) and combine with the diverse iron oxide forms (e.g. Nalovic and Quantin 1972; Anand and Gilkes 1987; Becquer et al. 1995; Trolard et al. 1995; Lang Burak et al. 2013).

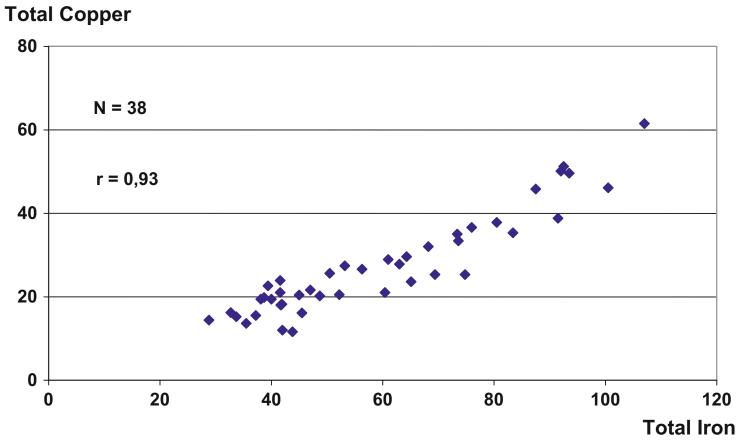

Fig. 4.3 "Chestnut-coloured soils" over Sinemurian marly limestone (Burgundy, France – Baize and Chrétien 1994) showing a broad range of unusual large values; 38 samples taken at different depths at 14 sites; Cu concentrations are expressed as mg kg^{-1}; Fe as g kg^{-1}

2.3 The Third Key: Contamination Induced by Human Activities

Diverse anthropogenic contributions have much more recently been added to the pre-existing natural stocks: (i) atmospheric fallout from long-range of short-range origins; (ii) trace elements added unwittingly by fertilizer, sewage sludge or waste spreading. The level of the latter type of contamination and its chemical nature primarily are of great concern for agricultural soils.

3 Distinguishing the Natural from the Anthropogenic

3.1 Relevance

An excellent summary of this question was given by Mol et al. (2009): "*For environmental risk assessment the question of reactivity is of even greater relevance than the question of total concentration because it determines the mobility, human exposure and ecotoxicological importance of the elements. For proper environmental soil management it is of vital importance to be able to distinguish between natural pedogeochemical concentrations and anthropogenically elevated levels of trace elements*". By making this distinction, it is possible to obtain an initial assessment of possible dangers to human health, especially through phytoavailability of metals to cultivated plants. Trace metals of anthropogenic origin are generally much more reactive species than those of natural origin, even when in abnormal abundance. In fact, the latter have been strongly adsorbed for millennia onto various solid phases or are co-precipitated with Fe or/and Mn oxy-hydroxides. The determination of local natural pedogeochemical concentrations (NPGC) and subsequently of the local level of contamination allows us not to declare as being "polluted" (with the serious socio-economic or financial consequences which may ensue) a plot of ground in a context of strong natural anomalies. If necessary, it allows us to fix realistic and relevant target values for pollution cleanup, suited to the geological and pedological context.

3.2 Sampling Strategy

The distinction between trace metals originating from atmospheric and non-atmospheric (recycling by root uptake in the soil) origin in the upper part of soils is complicated. Different approached can be used. Some of them are rather easy to implement, but others are fairly laborious and imply expansive analyses.

Three simple approaches have been proposed for assessing the overall level of trace element contamination of soil horizons (Baize 1997b): the vertical comparison, the lateral comparison and the typological approach. For a correct application, it is essential to use chemical dissolution methods such as hydrofluoric acid or alkaline fusion, that extract the "total" amounts of elements, including those present in the crystal structure of silicate minerals.

3.2.1 Vertical Comparison

Principle: the trace element contents of the surface plough layer (coded as Ap horizon in the FAO classification – IUSS Working Group WRB 2006) are compared with those of the underlying soil horizons. Basically, there is no reason that these concentrations should be much higher in the surface horizons. On the contrary, under climates of Western Europe, soils show often lower contents of clay, iron and associated PHTEs in upper horizons than at depth (case of Luvisols and Planosols).

Examples are given in Tables 4.2 and 4.5: when examining the PHTEs only in the Ap horizons, one might consider that these two soils are markedly contaminated. Yet, their concentrations continuously increase toward depth, the hypothesis of a strong natural geochemical anomaly is imperative. This approach is very simple: only three or four samples have to be collected at different depths at each site and it does not require much knowledge in soil science or pedology. For interpreting values, one must consider possible carbon, clay or iron gradients in the soil under study. This approach can be used only for estimating the level of contamination of surface Ap horizons. Its use is more problematical for Pb and Cd that frequently show values higher in the surface layer than in deeper soil horizons. This approach is based on the assumption that the pollutants have remained

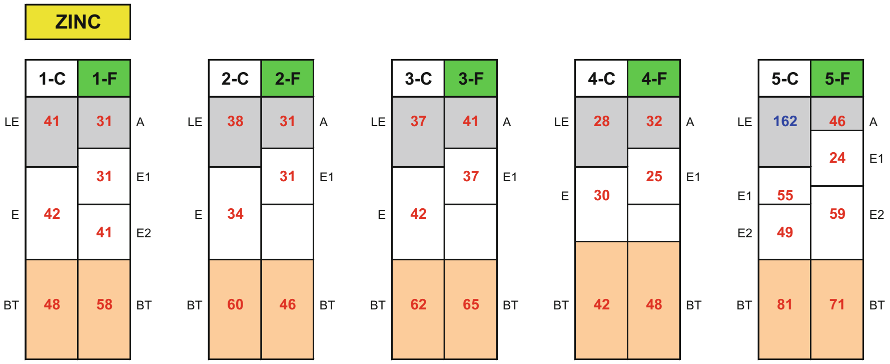

Fig. 4.4 Lateral comparison. Five couples of forested (*F*) versus cultivated (*C*) Albeluvisols (south-east of the Paris basin – Baize 1997b). Zinc concentrations are expressed as mg kg^{-1}. The site 5-C received heavy sewage sludge spreading during the 1970s and, as a consequence, has been markedly contaminated

predominantly in the surface layer. In the case of downward migrations, an accurate interpretation becomes impossible.

3.2.2 Lateral Comparison with a Forest Soil

Principle: the PHTEs concentrations in soil horizon samples from cultivated soils are compared with those measured in the equivalent horizon of the same soil series, located closely **under forest**. An analogical reasoning is used, very similar to that used in agricultural experiments.

This second approach implies simple superposed samplings both at the studied site and the forest soil used as a “reference”, and offers the possibility to deal with any horizon of the profile, not only the Ap horizon (see Fig. 4.4).

Forest soils do not always occur at short distance and/or do not have the same pedological characteristics. Besides, the forest soil may sometimes have been contaminated (recently or in ancient times) without clear evidence. Finally this approach requires pedological knowledge for recognizing the similarity between the paired soil profiles and the lateral equivalence of horizons.

3.2.3 Typological Approach

Principle: the analytical results of a given soil horizon are compared with data previously collected on similar horizons from the same soil series. This approach is more reliable and more sensitive, and represents the best among the three cited sampling strategy approaches. Moreover, it considers any type of soil horizon.

Basically, for a particular soil series, strong natural geochemical relationships exist which are used as a base for assessing accumulations or losses of trace

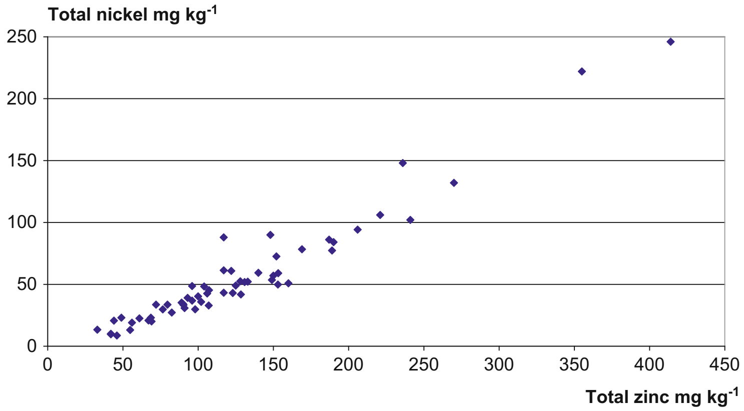

Fig. 4.5 Strongly differentiated soils developed in "clay with cherts" (Burgundy, France). The Ni – Zn relationship (total concentrations) is practically perfect (r = 0.96). The very broad range of values can be noticed; 59 samples were taken (most of them from forested soils) at different depths

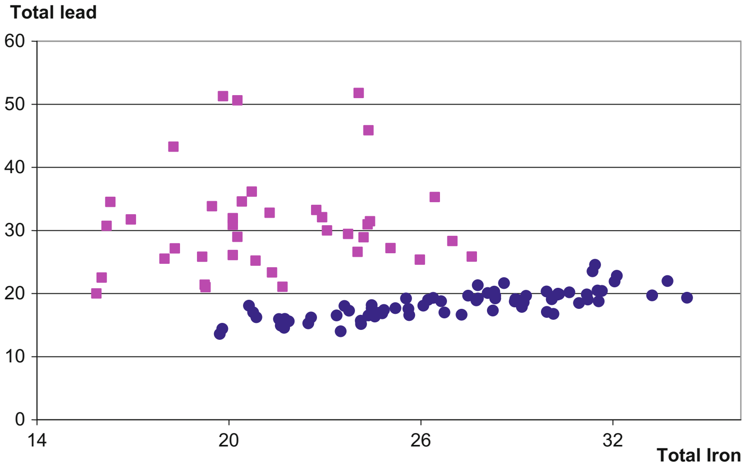

Fig. 4.6 Cultivated soils developed from loess in the Northern France: relationship between total lead and total iron (Sterckeman et al. 2006); *pink squares* for Ap horizons, *blue circles* for all other deep horizons. The natural geochemical relationship between Pb and Fe is strong for all deep horizons indicating the absence of anthropogenic additions. In the surface horizons, no Pb –Zn correlation is observed and that underlines a more or less strong lead contamination. Pb concentrations are expressed as mg kg^{-1}; Fe as g kg^{-1}

elements. For instance, such relationships may link iron contents to trace metal contents (see Fig. 4.3) or one trace metal with another (see Figs. 4.2 and 4.5). Consequently, in case of soil contamination, even minor, it is easy to detect it (Figs. 4.6 and 4.7 Bézu). The deviation of values with respect to the correlation base

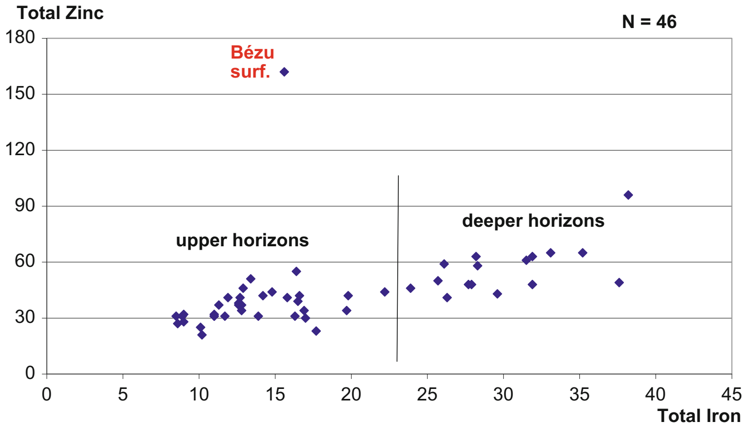

Fig. 4.7 Albeluvisols developed in a loamy aeolian deposit (South-east of the Paris basin). Fourty-six samples were taken at different depths from forest and cultivated soils. Strong correlation between total concentrations of Zn and Fe is observed. One sample, outside this correlation comes from an experimental plot amended with sewage sludge at high rates (Ap horizon – site Bézu). See also Fig. 4.4; Zn concentrations are expressed as mg kg^{-1}, Fe as g kg^{-1}

line, representing the pedogeochemical background level of the soil series, gives an estimation of the amount of contamination for each trace metal (Lamy et al. 2006; Fernandez et al. 2007).

The determination of the natural pedogeochemical concentrations of PHTEs for a given soil series demands field experience and insight in the historic and ways of dissemination of contaminants. Between 25 and 50 soil samples, as little contaminated as possible, must be analysed for each soil series. Therefore, the sampling strategy must be organized by giving priority to (i) soils for a long time **under forest** which may have received some atmospheric deposition but are free of agriculture derived contamination; (ii) deep horizons of cultivated soils, assumed to be uncontaminated. This approach requires consistent previous geological and pedological knowledge relative to the soil series under consideration: good morphological and analytical definition of the series and the determination of PHTE concentrations for several dozens of soil samples. Consequently, this approach is rather time and finance demanding, needing intervention of scientists skilled with soil science. In this approach also, the forest soils are used as reference systems. Some restriction in its application may arise: (1) in case of acid physicochemical conditions in forest soils favouring a partial lixiviation of some metal elements toward depth or even out of the soil, (2) for soils in the proximity of mining or industrial metallurgical sites, where surrounding areas have diversely been contaminated over several kilometres distance (Sterckeman et al. 2000), including forest land. Examples of such situations are discussed and illustrated hereafter (Sect. 5.1).

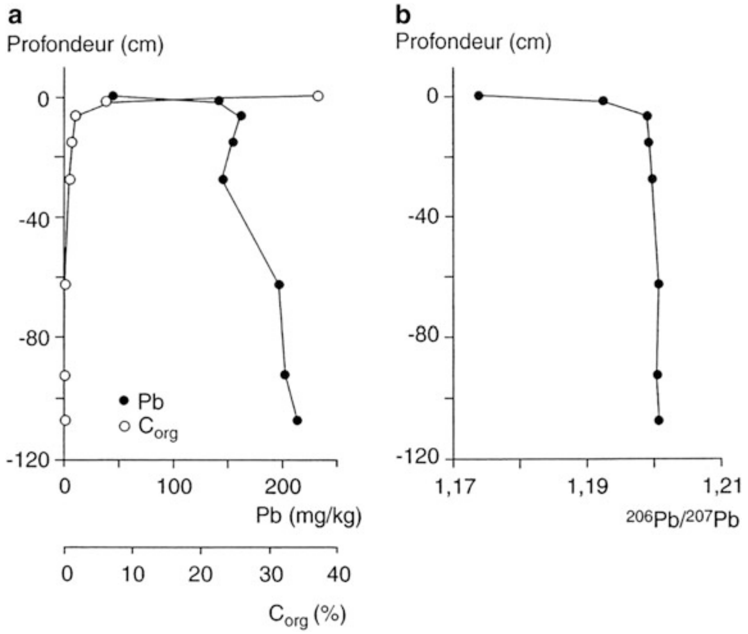

Fig. 4.8 Soil profile "*Bois de Belle Verne*" (Northern Morvan, France) (Lévêque et al. 2002); (**a**) distribution profile of organic carbon and Pb concentrations, (**b**) vertical distribution of lead isotopic ratio $^{206}Pb/^{207}Pb$

3.2.4 Use of Stable or Radioactive Isotopic Ratios

For some decennia, the isotopic ratio approach was widely used for lead to trace Pb sources in the environment. The use of stable lead isotope ratios is a very powerful tool that in most cases allows a definite distinction between the natural, geogenic lead in soils and the amount added by air pollution (Bacon et al. 1992; Erel et al. 1997; Monna et al. 2000; Lévèque et al. 2002; Semlali et al. 2000, 2001a, 2004; Bacon and Hewitt 2005; Steinnes and Friedland 2005; Fernandez et al. 2008) (see Figs. 4.8, 4.13 and 4.15).

"*Pb naturally present in a soil generally shows a different isotopic composition to that of Pb from anthropogenic sources* (excepted in the case of mining activities). *So, the isotopic signature of Pb constitutes a useful additional recorder of contamination*". In addition, "*stable isotopic signature of the Pb can be studied associated with the different fractions giving valuable information about soil processes when applied to partitioning studies*" (Emmanuel and Erel 2002).

More recently, such isotopic ratio approaches have been applied also to distinguish different pools of cadmium and zinc (Cloquet et al. 2006; Weiss et al. 2008; Juillot et al. 2011).

3.2.5 Enrichment Factors (EF) Assessment

This approach considers the abundance of the metal of interest, relative to the abundance of a conservative lithologic element (such as Zr, Sc, Ti or Al) with no significant anthropogenic source (Blaser et al. 2000; Semlali et al. 2001a; Shotyk et al. 2001). This ratio can then be normalized to the corresponding ratio in the upper continental crust (e.g. Sterckeman et al. 2006) and such an EF is known as "crustal enrichment". Therefore, it seems more reasonable that the assessment of enrichment factors for topsoils would be made by comparison with the deeper horizons or parent material of each individual soil profile (Blaser et al. 2000; Bourenanne et al. 2010).

Note that the very principle of this method is contested by Sucharovà et al. (2012). These authors argued by comparing O horizons with the correspondent B horizons in forest soils of the Czech Republic but, in our opinion, B horizons were sampled at too shallow depth and, therefore, cannot represent the unweathered parent material.

The two latter approaches (isotopic ratios and EF) are quite elaborate methods and need precautions, funds and time (for sampling, pre-treatments, and analyses).

4 Special Features of Forest Soils in Regard to Soils Under Agricultural Land Use

4.1 A Lower Impact of Anthropogenic Contaminations

Forest soils generally are exempt of anthropogenic inputs related to agronomical practices (fertilisers, organic amendments, liming, sewage sludge, waste water, etc.), all of them possibly containing unwilled substances, including PHTEs. In forest soils, the only inputs of anthropogenic origin are nearby or remote air-borne deposition.

For a long time it has been well-recognized that long-range transport of pollutants in the atmosphere affects both remote rural as well as industrial or urban areas and that forest ecosystems and regions with high precipitation are most strongly influenced by atmospheric deposition (e.g. Heinrichs and Mayer 1980). These authors concluded that there is probably no land surface in central Europe where the local balance for most heavy metals on the ecosystem level is not strongly influenced, or dominated, by atmospheric deposition pollution. The bulk of the atmospheric input measured nowadays would be of anthropogenic origin as far as heavy metals are concerned.

Bergkvist et al. (1989) gave us a good insight of what is atmospheric deposition. "*Metals are deposited to the tree canopy as wet and dry deposition. Wet deposition includes precipitation in the form of rain and snow as well as fog and cloud droplets. Dry deposition comprises particle deposition and gas sorption. Bulk* *deposition is commonly defined as the total wet and dry fallout collected in a continuously open vessel placed in an open field*". The dry deposition to a forest is much greater than to a grass-cover or otherwise open area (see Sect. 5.1). Due to aerodynamic properties and the greater leaf area, conifers are much more efficient in trapping aerosols than are deciduous trees. The dry deposition to deciduous trees is greater when they are foliated than during the winter. However, the higher pollution load of metals commonly occurring during the winter may well increase the deposition.

Another specificity of forests with high trees is that there are interactions of rainwater with foliage or needles (not forgetting the stemflow). As a result, the solution which reaches the « forest floor » has not exactly the same composition than the deposition at the top of the canopy (Gandois et al. 2010).

4.2 Fluxes of Atmospheric Deposition (Present or Past)

These fluxes considerably vary from a place to another and, at least, three main types of air-borne deposition can be distinguished:

- **local point-sourced deposition** close to a well-identified source, located at a distance less than 4–6 km. A typical case is that of industrial activities (e.g. Godin et al. 1985; van Oort et al. 2001, 2009), where a rapid and generally exponential decrease of the total concentrations measured in the surface horizon can be observed with increasing distance from the emitting source, until reaching the local background UAC or UFC (see Box 4.2.).
- **long-range diffuse air-borne deposition**: numerous sources merge, including mobile ones, the impacts spread as far as about 30–300 km (e.g. Saur and Juste 1994; Blaser et al. 2000; Steinnes et al. 1989, 1997, 2005; Kaste et al. 2003; Berg et al. 2006);
- **global diffuse deposition** which affects the entire surface of the Earth, even if the fluxes remain very small (e.g. Hong et al. 1994; Boutron 1995; Shotyk et al. 1998).

As far as lead is concerned, figures found in the literature broadly vary from 1 to 85 g ha^{-1} $year^{-1}$ for remote rural areas far from any big city and from 100 to 400 g ha^{-1} $year^{-1}$ in rural areas of Poland, Germany, Wallonia and Great Britain (Galloway et al. 1982; Navarre et al. 1980; Alloway et al. 1999). Some studies on the evolution of lead contents in soils in France gave the following values for the Paris suburban region: 930 g ha^{-1} $year^{-1}$ at Versailles between 1929 and 1984 (Juste and Tauzin 1986); 650 g ha^{-1} $year^{-1}$ between 1938 and 1999 at Grignon (Baize and Bourgeois 2005); 50–300 g ha^{-1} $year^{-1}$ at Versailles between 1990 and 2000 (Semlali et al. 2004).

Box 4.2: NPGC and UAC

The natural pedo-geochemical concentration (NPGC) is the concentration of any substance resulting from natural geological and soil forming processes, without any man-induced addition (Adriano et al. 1997; Baize 1997b). From one place to another, this natural content is greatly variable, according to the parent material composition and the soil type (Fig. 4.1).

It is always essential to specify for what territory the NPGC is defined: for instance a country, a watershed, a county, a land plot, the area where spreads a particular typological soil unit.

The most interesting, the local NPGC, can be defined for a precise soil horizon, one soil profile or a specific soil-series. These values can be determined by using peculiar approaches, methods of analysis, and analogical thought processes (see text).

The usual agricultural contents (UAC) are the most frequent range of concentrations measured in the ploughed horizons under "normal" agriculture (i.e. without waste application or local industrial pollution). Commonly, the range of values contained between 10th and 90th percentiles is used, known as "frequent values range". Once again, the territory under consideration must be defined. These usual agricultural contents can be determined for any soil series. They result from the addition of:

- the effects of past agricultural practices,
- plus the atmospheric deposition,
- less the losses due to an open biogeochemical cycle (export in crops) or to lixiviation and lessivage. . . . . .to the natural NPGC (Fig. 4.1).

Usual forest contents (UFC) can also be defined in the same way, taking into account the different nature of organic and organo-mineral layers.

Establishing a nationwide budget of atmospheric Hg in Norway, Berg et al. (2006) reported that "*the current mercury levels in sediments. . .are substantially affected by long-range atmospheric transport. Compared to the pre-industrial lake sediments the surface sediments had significantly elevated Hg concentrations, usually by a factor of 2–4 in the country as a whole.*" For the period 1990–2002, the mean annual Hg deposition has varied between 21 and 9 μg m^{-2} $year^{-1}$.

Current rates of atmospheric trace metal deposition were in southern Norway (in 1992) about 9 mg m^{-2} Zn, 4 mg m^{-2} Pb and 0.1 mg m^{-2} Cd. Total deposition of these metals in this region from 1976 to 1992 averaged roughly 310 mg m^{-2} Zn, 170 mg m^{-2}, and 5 mg m^{-2} Cd (Berthelsen and Steinnes 1995).

Besides their great variability in space, these fluxes have broadly varied in the course of time. From the antiquity, several periods of mining and industrial activities were followed by periods of interruption. Such variations were recorded in sediments, peat-bogs, or glaciers (Sugden et al. 1991; Jensen 1997; Steinnes

1997; Monna et al. 2004). In modern times, a strong increase of lead atmospheric deposition was observed corresponding first with the development of the industrial revolution in Europe, and then with the introduction of lead in petrol as anti-knock additive. Currently a marked decreasing input of Pb can be observed due to the withdrawal of the leaded fuel (e.g. Miller and Friedland 1994; Candelone and Hong 1995; Azimi et al. 2003; Steinnes and Friedland 2005).

The works of Shotyk and colleagues achieved on peat-bogs in Switzerland have shown that antique mining and metallurgical works have been recorded and could be still recognized today some thousand years later. These activities were located far from Switzerland and fluxes recorded highly varied with time (Shotyk and Blaser 1999; Shotyk et al. 1998, 2000).

The PHTEs mainly involved in medium- and long-range air-borne contaminations are Pb, Cd, Hg, Zn, and Cu. In soils, Ni, Cr and Co most often have a geogenic origin (with the exception of areas located close to smelters such as these in the Kola peninsula – Reimann et al. 2001).

4.3 Strong Acidity

Very often, forest soils show a strong acidity but that is not a general rule: numerous soils under forest are calcium-saturated or even calcareous.

Many studies on impacts of trace metal deposition on natural forest ecosystems have been conducted in Scandinavia, Northern Russia or North America because the soils are to a large extent chemically very poor and acid. Hence, great concern has risen for the ecosystems, in particular related to forest decline and acid rains. Yet, most of studied soils are podzols[1] with a particular type of pedogenesis characterised by eluviation/illuviation of humus-metal complexes (see Sect. 4.3.4). There are three main consequences of strong soil acidity (the particular case of podzols will be dealt with apart, see Sect. 5).

4.3.1 Possible Vertical Mobility of Zn and Cd

For all soils, a main pattern of leachability is associated with soil acidity (Bergkvist et al. 1989). In the literature, field studies under forests are quite rare and most often limited to the "purely organic mor horizons" (e.g. Tyler 1978) or "A horizons" (e.g. Tyler 1981). Most of the research is dedicated to polluted agricultural soils (e.g. Degryse et al. 2001) and often carried out in the laboratory conditions on soil samples in columns.

A good means of studying the matter translocating through the soil profile is the use of lysimeters. These are not easy to implement (Keller and Védy 1994) but the

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[1] *Spodosols according to the USDA Soil Taxonomy.*

composition of the waters collected in this way gives useful information. Fluxes of trace metals as well as major elements are usually measured in the soil solution after filtration through a 0.45 μm membrane and mass balance calculation are then based on soluble compounds (Ugolini and Dahlgren 1987; Bourg and Védy 1986). This size limit is arbitrary but conventional. In some cases (especially that of podzols or heavily polluted sites), it is necessary to take into account the whole content of the gravitational water because transported matter can be in particulate or colloidal forms also (Guillet et al. 1981; Keller and Domergue 1996; Citeau et al. 2003, 2006, 2009).

Römkens and Salomons (1998) gathered *in situ* soil solution samples at 6 depths in 30 Dutch forest and arable sandy soils. Their conclusions were as follows. "*The solubility of trace metals under field conditions is linked strongly to soil parameters such as pH, soil organic matter and dissolved organic carbon. In very acid soils (pH $<$ 4.5) 80 % of all Zn and Cd concentrations exceeded current ground water quality standards as a result of the high metal solubility at this low pH. Taking into account the low acid buffering capacities in these sandy soils, continuous acidification may cause further increase of metal concentrations in soil solution*". In case of conversion of these poorly productive soils to forest or wetlands, remobilization of Cd and Zn, therefore, is likely to occur in the topsoil after afforestation.

4.3.2 Risk of Aluminium and Manganese Toxicity

In soils with pH in water $>$ 5.0, aluminium is chiefly in the form of insoluble oxyhydroxides. When soils are obviously acid (i.e. pH $<$ 5.0), the exchangeable aluminium becomes abundant on the adsorbing complex and may become phytotoxic, in particular for seedlings. At lower pH the oxyhydroxides forms evolve to ionic forms $Al(OH)_2^+$ or $Al(OH)^{2+}$, and finally to Al^{3+}, if the soil pH decreases under 4.5. These ionic forms can provoke an inhibition of root growth (Bonneau 1995). This kind of toxicity has been revealed since a long time for *Pinus maritimus* (Juste 1966). Toxicity features appear at about 50 mg Al L^{-1} in the soil solution and is clearly marked for concentrations of 200 mg L^{-1}. Sugar maple (*Acer saccharum*) would be particularly sensible to Al-toxicity (from a concentration of 4 mg Al L^{-1}). Even in acid soils, concentrations of ionic Al rarely exceed 5 mg Al L^{-1} in the soil solution. So, a real toxicity would not be reached under temperate climates for the common species with a moderate resistance (such as *Picea abies, Abies alba, Fagus sylvatica*). Rather than toxicity, the competition of Al with Ca and Mg may lead to problems to forest stand health even if the root growth (criterion often chosen for assessing the toxicity) is not hindered (Bonneau 1995).

Contrarily to the case of Al^{3+} which chemical form primarily depends on the soil pH, the phytoavailability of manganese is mainly function of the present oxidation-reduction and moisture conditions. Only the most reduced forms of Mn (Mn^{2+} and Mn^{3+}) are easily available to plant roots. Therefore, manganese toxicity can occur both in the case of strongly acid soils and of poor drainage conditions.

Accumulation of these reduced forms in uppermost humose horizons can affect adversely seedlings of conifers.

4.3.3 A Much Higher Phyto-Availability of Trace Elements to Plants Through Roots Absorption

In forest ecosystems, PHTEs incorporated in trunks, branches, and leaves will represent virtually no risk with respect to human health. By contrast, a strong pollution of the surface horizons can contaminate the edible parts of mushrooms and forest berries (blueberries, raspberries, strawberries, or brambles) giving rise to potential hazards for consumers (e.g. Michelot et al. 1998; Kalac and Svoboda 2000; Benbrahim et al. 2006).

One approach is widely adopted to characterize metal behaviour in soil and sediments with the aim of estimating their potential bioavailability. It consists in partitioning the metals in the solid phase into various operationally-defined fractions by using chemical extractants of increasing strengths (Tessier et al. 1979). Very usual for polluted agricultural soils, this method is less often used for forested ones (e.g. Chlopecka and Hutchinson 1997).

In literature, we did not find references presenting toxicities to plants in a forested environment due to natural trace elements. The main processes reported are involving aluminium and manganese (see above Sect. 4.3.2).

4.3.4 The Special Case of Podzols

Podzols are very acid, highly permeable soils, with low clay contents, where the occurrence of high amounts of reactive organic compounds favours the downward movement of trace elements in the form of humus-metal complexes. In podzols, migration of pseudo-soluble forms (i.e. cheluviation) is responsible for the formation of podzolic B illuvial horizons after migration through the E horizon (e.g. Duchaufour 1982; Driessen and Dudal 1991; Keller and Domergue 1996). Such conditions lead to increased risks of translocation of pollutants introduced at the surface toward depth and *in fine* to the water table (Delas 1966; Saur and Juste 1994). Some selected literature quotations illustrate the special lixiviation character of acid podzols for trace metals, even for the low-mobile lead.

Steinnes et al. (2005) in a quantification work of pollutant lead in podzols in Norway note: "*It is apparent from the present data that the vertical transport of Pb differs considerably between the sites. Whereas some sites show little or no pollution-derived Pb in the B horizon, around 70 % of the Pb in the upper B horizon at the three southernmost sites comes from atmospheric deposition. This means that, in the south of Norway, a major part of the pollutant Pb is no longer in the O horizon but has moved down to the E and B horizons. Similar conclusions were reached in the corresponding Swedish study (*Brännvall et al. 2001*). Possible reasons for the more extensive transfer in the south include higher total input of Pb* *and possibly a greater turnover of humic matter at higher mean annual temperatures. The most important factor, however, is likely to be the significantly higher atmospheric deposition of acidifying substances in the south, which may, to a great extent, release Pb from exchange sites in the humus layer and promote downward leaching"*.

Berthelsen and Steinnes (1995) carried out an investigation of the vertical distribution of Zn, Pb, Cd and Cu in podzol profiles, comparing 12 forested sites and 9 clear-cut areas. According to these authors, "*Clear-cutting of forests leads to drastic changes in the underlying soil, both concerning direct effects on the humus layer and soil solution chemistry. The lack of trees reduces the evapotranspiration, thus giving higher water content in the soil and increased water percolation through the soil in clear-cut areas.*" With respect to the movement of low-mobile elements such as Pb in acid soil conditions of podzols, these authors note: *"The total content of Pb in the L + F + H horizons was significantly lower in clear-cut than in forested areas attributable to distinctly lower Pb contents in the H horizons of clear-cut areas soils. This fact combined with significantly thinner humus layers in clear-cut areas compared to forested areas presents evidence for increased losses of Pb from the humus layer after clear-cutting. Higher Pb contents in the Ae and B horizons of the clear-cut area soils than in forest area soils, show that at least parts of the Pb lost from the H horizon in clear-cut areas were re-adsorbed or re-precipitated in the Ae and B horizons."*

4.4 Impact of Waterlogging

Some forest soils show temporary or quasi-permanent waterlogging, and they are most often not reclaimed by drainage as it is frequently the case for agricultural areas. What are the consequences on the dynamic of PHTEs of these temporary but frequent phases of reduction followed by phases of re-oxidation? Their association with Fe and Mn hydrous oxides leads to their reversible adsorption, a subsequent desorption is possible according to the physico-chemical conditions (e.g. Alloway 1995; Strawn et al. 2012). As Mn oxides are more easily reducible than Fe oxides, they often control trace elements availability and so their mobility in the environment. The chemical and bacterial dissolution of Mn oxides favour the release of associated trace metals under reductive conditions (Quantin et al. 2002).

Charlatchka and Cambier (2000) implemented artificial waterlogging experiments on undisturbed soil blocks. They concluded: "*pH variations definitively influence trace metal solubility, whatever they are induced by reductive dissolution, organic acid formation or other processes and that strong acidification can be obtained with well buffered soil when about 1 % of the available carbon is anaerobically transformed into organic acids. … Given a steady pH, reducing conditions enhance the mobility of trace metals, at first by dissolution of Mn and Fe oxides; Pb appeared more sensitive to these processes than Zn, and finally Cd. As a general rule, hydromorphy in a well buffered contaminated soil at a first step should increase the mobility of divalent trace metals, by decreasing pH and* *reducing Mn and Fe oxides, but prolonged flooding can lead to fix trace metals again, rather by re-adsorption or precipitation phenomena than by formation of insoluble sulphides".*

4.5 The Bio-geochemical Cycling of Elements

Elements (nutrients as well as PHTEs) are more or less absorbed by roots in surface A and deeper soil horizons, and then partially transferred up to the surface organic layers by means of the fallout of dead aerial organs (leaves, needles, stems and twigs). If this cycle remains closed, the fluxes are small but as it is a long-lasting process (several thousands of years) the amounts of elements involved in that cycle may be sizeable. If there is removal of wood by yielding of timbers and branches or harvesting of the litter, then the cycle is broken. The soil, particularly its uppermost layers, becomes increasingly impoverished in nutrients as well as in PHTEs.

For quite some time, a warm controversy about the biological cycling of lead is under discussion. For some authors, the processes of "plant-pumping" and then that of "organic binding" must be preferred for explaining the accumulation of lead in the forest floor of Scandinavian and Northern Russia forest soils (Rasmussen 1998; Reimann et al. 2001). The possible return from the depth to the soil surface, due to the absorption by roots and the natural cycle, have also been envisaged by Denaeyer-De Smet 1974; Bruckert et al. 1979; Guillet et al. 1980. Conversely, most authors (such as Heinrichs and Mayer 1980; Blaser et al. 2000; Kaste et al. 2003; Steinnes et al. 2005; and many others) explain this uppermost accumulation of PHTEs solely by long-range deposition from urban and industrial areas.

Another way of presenting the debate is to ask the question: is lead abiotic? For some authors, the answer is positive (Heinrichs and Mayer 1980; Craig et al. 1991). Bergkvist et al. (1989) state: "*The first sink for Cu and Pb is the litter and mor layers*". And these authors add: "*The organic topsoil is often regarded as an almost permanent sink for Pb*" (in contradiction with findings in Sect. 4.3.4: this is not true in the case of podzols).

4.6 Accumulation of Air-Borne Pollutants

Air-borne pollutants as well as recycled geogenic trace metals can accumulate in the organic litter (coded O) and organo-mineral horizons (coded A). The metals incorporated in the ligneous tissues are withdrawn from the geochemical cycle for the lifetime of the forest, and will be partially exported from the ecosystem when the forest is harvested.

A thorough field study carried out in Central Germany (Heinrichs and Mayer 1977, 1980) has clearly shown that the metals bound in the cycling fraction reach the soil together with litterfall within a short time i.e. after <1year in a beech forest, after <7 years in a spruce forest. Very often, there is a strong binding in organic matter and the metals are accumulated in the organic topsoil or humus fraction again being withheld from further cycling. According to the same study, lead is strongly accumulated in the organic surface layer which retains 80–100 times the amount of Pb found in annual litterfall. The Pb concentrations are clearly decreasing from the top to the deeper soil horizons.

Bourg and Védy (1986) studied the dissolved trace metals in gravitational water of two acid sandy soils of the Vosges Mountains (France), both developed in weathered sandstones and located under forests. One was a Dystric Cambisol with a mull type humus form and the second an Orthic Podzol with a mor type humus layer. In conclusion, they established that: "*the fate of the trace metals associated with the dissolved organic matter should follow the dynamics and evolution of their organic vectors. The free metal fraction whose size depends on the organic complexation constants, is available for either biological uptake (including upward recycling, a significant phenomenon in acid brown soils) or for further downward migration.*" Besides, this study illustrates a major difference of trace metal cycling in "acid brown" soils and podzols.

4.7 Organic Matter Gradients

As a consequence of the previous point, **organic matter (OM) gradients** with depth can be observed under forests, different from OM gradients characteristic for agricultural cultivated or grassland soils. Very often, under forest vegetation, there is a thick accumulation of humified organic matter and most of the PHTEs are tightly linked with organic matter whatever its forms! Considering the differences in bulk density of organic, organo-mineral or mineral horizons, we must be careful in using concentrations of PHTEs. A better approach is to reason with metal stocks and consequently, different pedogenetic layers must be sampled separately (cf. Sect. 5.1).

4.8 Impacts of High Concentrations of PHTEs on Ecosystems

If these PHTEs are of natural (geogenic) origin, no impact will be seen on the forest ecosystem because:

1. the local microbial and arthropod populations are adapted for a long time to such conditions;
2. the easy-labile chemical forms are less abundant than the little or non-labile forms because more mobile species have leached in the course of time.

On the contrary, if these **high concentrations** are the result of **pollution**, a chronic exposure to the solid and liquid phase can give rise to toxicity to indigenous soil microbial communities, resulting in a weakening or a strong reduction of biologic activity, a decreasing rate of degradation of the soil OM, a decrease of incorporation of OM to deeper soil horizons by bioturbation and an abnormal accumulation of PHTE-rich organic matter at the surface, as was demonstrated for metallophyte grassland under sparse poplar/birch vegetation in northern France (Balabane et al. 1999; Dahmani-Muller et al. 2000; van Oort et al. 2002a, 2009).

Moreover, a study by Bringmark and Bringmark (2001) has shown an inverse correlation between microbial respiration and Pb and Hg concentrations in the mor layers of soils in southern Sweden. This observation was readily explained by toxic metal effects. An alternative explanation, that metals and microbial respiration both co-vary with degree of decomposition in the humus layer, has been convincingly shown for a few sites but cannot explain why the respiration/metal correlations were strongest for all sites with high loads of Pb or Hg.

5 Importance of Soil Forming Processes and Land Use on the Distribution and Fate of Trace Elements – Two Case Studies

One major difference between forest and agricultural soils lies in the nature and dynamics of organic matter. Extended forest covers occupy land areas for long periods and large amount of organic materials are returned to soils as fallen litter and decaying roots (Binkley and Fisher 2012). The role of soil organic matter (SOM) as a metal sorbing agent has been frequently stressed (McBride 1989; Krosshavn et al. 1993), and the stability of SOM-metal interactions is recognized to be a crucial factor governing the fate of metals in soils (McBride et al. 1997; Sauvé et al. 2000; Labanowski et al. 2007). Therefore, the distribution and biochemical cycling of organic matter in soils under different land use is essential to consider when assessing trace element concentrations in forest soils, in comparison to agricultural land (Blum et al. 1997; van Oort et al. 2002b, 2009).

Hereafter, a first case study highlights the importance of land use on the fate (deposition, incorporation, redistributions) of air-borne trace metals, derived from past industrial activity in northern France in soils under different land use. The example illustrates some difficulties which may arise when assessing ‘soil contamination’ of fairly comparable metal pollutant inputs in soils that evolve differently due to influences of human activity (soil tillage, fertilization and amendments in arable land soils), biological perturbation (earthworm activity in grassland soils) and soil acidification (promoting eluviation/lixiviation processes of trace metals in forest soils).

The second case study gives evidence for the migration of lead, widely considered as a low or non-mobile metal in soils, in two forest ecosystems in France. The first is an andosol developed on volcanic basaltic scoria in the Massif Central, the second is a podzol developed in sandy textured sediments in the “Landes de Gascogne”. These two sites are affected by medium- and long-range atmospheric deposition, respectively. The migration dynamics of Pb are discussed in relation to specific features of pedogenesis in these two different forest systems.

5.1 Relevance of an Adapted Sampling Strategy for Survey of Spatial Airborne Metal Contamination

Inputs, incorporation dynamics and biochemical cycling of organic matter in soils widely diverge under different land use and lead to clear different macromorphological soil characteristics (Fig. 4.9). Moreover, forest topsoils frequently contain higher trace metal contents than arable land and grassland soils, ascribed by many authors to diffuse atmospheric deposition favoured by a greater filter action of forest canopies (e.g. Schlesinger and Reiners 1974; Heinrichs and Mayer 1980; Jensen and Svensmark 1989; Hanschmann and Opp 1993; Hernandez et al. 2003; Steinnes and Friedland 2005). Under different land use, the concentration profiles of trace metals were mentioned to be related, to a large extent, to the distribution of organic matter concentrations (Blum et al. 1997). With time, the distribution of trace elements added to soils by atmospheric deposition will change according to soil nature, soil behaviour and human practices. Consequently, for assessing soil contamination in soils under different land use, an adapted sampling strategy must be used that considers both soil morphology and the incorporation dynamics of trace elements, as well as the type of contamination. Taking into account of these aspects is a *sine qua non* for “comparing the comparable” (Thiry and van Oort 1999; van Oort et al. 2007).

The comprehension of metal dynamics in soils in relation to land use requires knowledge on related soil development characteristics and behaviour. Consequently, the use of a sampling strategy that considers metal concentrations in genetic soil horizons is essential (Cf. Sect. 3.2.3). Differences in profile development under different land use, but on similar parent material (Fig. 4.9a), mainly result from of a combination of factors: specific biochemical cycling of organic matter, vegetation, faunal activity, and agronomic practices.

The examples presented in Fig. 4.9 correspond to (i) a soil under pine-beech forest, (ii) a soil used for cereal crop production and (iii) a soil under permanent grassland, un-ploughed for one century. The arable and permanent grassland soils are developed in aeolian cover sands, under the same topographic, climatic and pedological conditions and differ mainly by their agronomical land use, remaining unchanged during the twentieth century (Fernandez et al. 2007). The forest stands occur on the same parent material, but at an altitude of about 5 m higher. These varying land use and environmental conditions have led to widely diverging physicochemical soil properties. Fairly similar airborne metal loads arriving at the surface of the three soils are incorporated differently according to processes

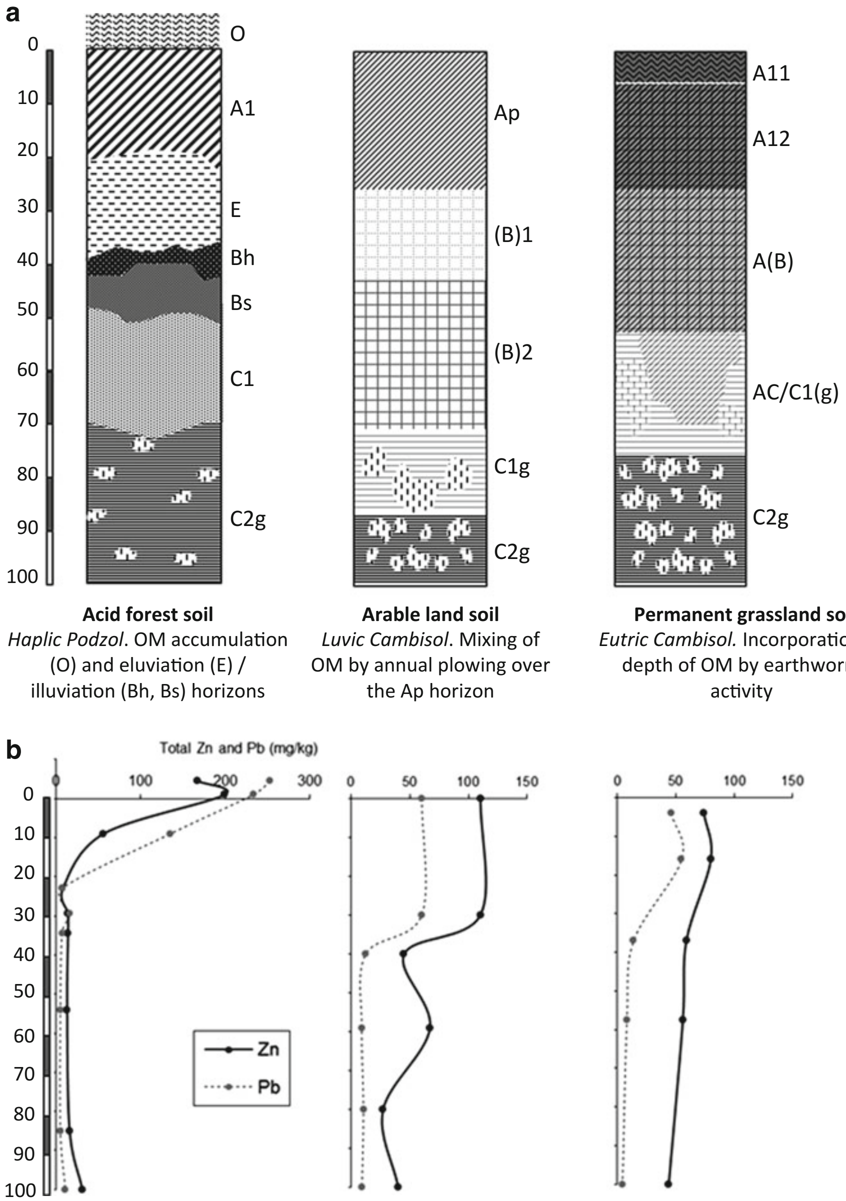


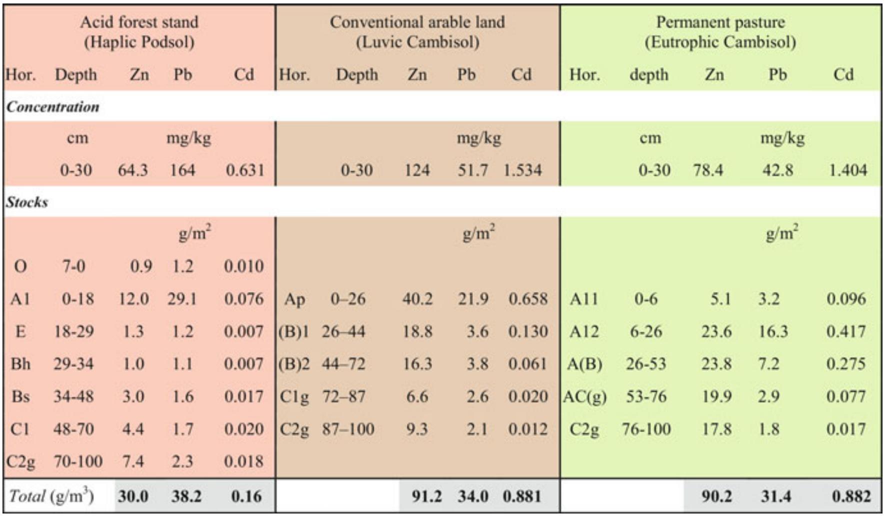
Fig. 4.9 Soil profiles and metal distribution to depth in soils under different land use. (**a**) Macromorphology of soils under forest, arable and grassland developed in aeolian cover sands in northern France, affected by industrial atmospheric metal deposition from a zinc smelter plant active between 1901 and 1962. All three sites are located windward with regard to the former industrial complex, at distances of 3,500, 3,250 and 3,100 m, respectively; (**b**) corresponding depth profiles of Zn and Pb concentrations (Adapted from van Oort et al. 2009). Soil classification according to IUSS Working Group WRB (2006)

specific of each type of land use. In Fig. 4.9b, metal concentrations in the genetic horizons of the three soils are presented. The metal contamination derives from short-range atmospheric fallout deposition emitted during the first half of the twentieth century by a zinc smelter complex in northern France (Thiry et al. 2002), disseminating large amounts of Zn, Pb, and Cd in the environment (van Oort et al. 2009). When focussing on the distribution of concentrations with depth for a mobile (such as zinc and cadmium) and a little or no-mobile trace metal (such as lead), 50 years after cessation of metallurgical activity, great differences of Zn and Pb concentration distributions are observed, both between the soils, but also between the two metals. In the O horizon of the forest soil, large Pb concentrations are observed, more than five times higher than in adjacent agricultural soils (Fig. 4.9b). Moreover, in the upper 20 cm of the forest soil, in the O and A1 horizons, the Pb concentrations are much larger than for Zn, and remain about equal in the E and Bh horizons until about 40 cm depth. This is contrarily to what is observed in the arable land and grassland soils where concentrations of Zn are larger than of Pb.

This example clearly illustrates the importance of considering land use and soil morphology when performing sampling for geochemical survey in an area to assess soil pollution. The analysis of metal concentrations on samples collected at arbitrary depths (but frequently referred to as representing ‘the soil’s surface layer’) may lead to substantial over- or underestimation of metal concentrations, because soil horizon thickness, physicochemical and physical soil conditions usually greatly vary from one soil to another:

- *under acid forest stands*, where organic matter frequently is the predominant metal sorbing soil constituent, largest concentrations are found in the litter layer (Keller and Védy 1994) containing large amounts of decaying organic fragments, also designates as ‘particulate organic matter (POM)’, very efficient metal binding compounds in soils (Wang et al. 1995; Balabane and van Oort 2002; Labanowski et al. 2007). Yet, being composed of solely organic matter, the O horizon has a very low bulk density, and despite its often large metal concentrations, the contribution of this horizon to the total metal stock in the soil is only minor. Moreover, in forest soils with often more acid soil conditions, metals are generally more mobile (McBride 1989) and more or less transferred downward, partly in dissolved form (Zn) or associated with colloids (Pb) (Citeau et al. 2003).
- *under arable land*, atmospheric deposition is incorporated by annual ploughing, the metal concentrations are homogenized over a depth of about 30 cm and fertilization and liming practices favour metal retention in the plough layer (Adriano 2001; Fernandez et al. 2007),
- *under permanent grassland*, soil homogenization is to large extent due to roots and faunal activity, notably earthworms (Nahmani et al. 2003). Consequently, a part of the metal contaminants, both mobile Zn as well as the immobile Pb, is mechanically incorporated and transferred to depth by worm activity (Fernandez et al. 2010).

Table 4.6 Surface concentrations (0–30 cm) and calculated amounts (stocks) of Zn and Pb stored in each soil horizon (in g m^{-2}) for soils under forest, arable and permanent grassland and cumulated stocks for 1 m^3



Acid forest stand (Haplic Podsol)					Conventional arable land (Luvic Cambisol)					Permanent pasture (Eutrophic Cambisol)				
Hor.	Depth	Zn	Pb	Cd	Hor.	Depth	Zn	Pb	Cd	Hor.	depth	Zn	Pb	Cd
Concentration														
	cm		mg/kg					mg/kg			cm		mg/kg	
	0-30	64.3	164	0.631		0-30	124	51.7	1.534		0-30	78.4	42.8	1.404
Stocks														
			g/m²					g/m²					g/m²	
O	7-0	0.9	1.2	0.010										
A1	0-18	12.0	29.1	0.076	Ap	0–26	40.2	21.9	0.658	A11	0-6	5.1	3.2	0.096
E	18-29	1.3	1.2	0.007	(B)1	26–44	18.8	3.6	0.130	A12	6-26	23.6	16.3	0.417
Bh	29-34	1.0	1.1	0.007	(B)2	44–72	16.3	3.8	0.061	A(B)	26-53	23.8	7.2	0.275
Bs	34-48	3.0	1.6	0.017	C1g	72–87	6.6	2.6	0.020	AC(g)	53-76	19.9	2.9	0.077
C1	48-70	4.4	1.7	0.020	C2g	87–100	9.3	2.1	0.012	C2g	76-100	17.8	1.8	0.017
C2g	70-100	7.4	2.3	0.018										
Total (g/m³)		**30.0**	**38.2**	**0.16**			**91.2**	**34.0**	**0.881**			**90.2**	**31.4**	**0.882**

Data compiled from Fernandez et al. (2007); van Oort et al. (2009)

For more valid assessment of the importance of metal contamination in an area including forest and agricultural soils, for instance with the aim of producing spatial distribution maps of total metal contents in soils, a better sampling strategy consists in comparing metal concentrations in the soil's surface layer with comparable thickness of the plough layer where the atmospheric deposited metal loads are annually homogenized, i.e. 30 cm (Table 4.6). Collecting such samples also in soils under grassland and forest signifies that the atmospherically added metal loads are artificially homogenized over a depth of 25–30 cm in order to obtain comparable soil volume with respect to the samples collected in the ploughed layer of the arable soil. Such approach is illustrated in Fig. 4.10, presenting the mean concentrations of Zn, Cd and Pb from samples of 0–30 cm depth, collected in different soil transects across agricultural and forest land.

Such an approach gives quite another view of metal accumulations in the surface layer: Pb concentrations are still largest in the forest soil (Fig. 4.10b), but largest Zn and Cd values are found in surface horizons under arable land, whilst smallest in the soils under forest (Fig. 4.10a, c). Moreover, the variability of total metal concentration is large, as shown by the error bars, particularly for Zn and Cd in agricultural land soils. This is mainly ascribed to variable pH values in the latter (pH: 5.5–7.5) in comparison to the acidified forest soils (pH: 3.5–4.5) but also to phenomena of temporary waterlogging in soils close around the forest edge occurring in lower topographic positions, inducing increased mobility of Pb (cf. Sect. 4.4) The forest soils (Haplic Podzols) located at 850 m from the forest edge, have developed in well-drained conditions.

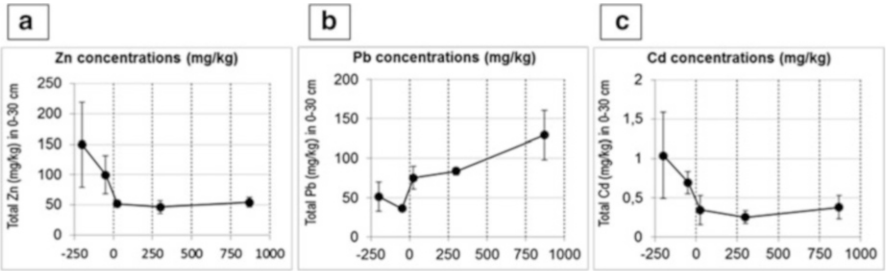


Fig. 4.10 Total concentrations of (**a**) Zn, (**b**) Pb, and (**c**) Cd in the 0–30 cm layer (average plough depth of Ap horizons of arable soils) of soils under cultivation, permanent grassland and forest stand in an area located approximately 3–4 km from a former zinc smelter in northern France. Average values calculated for three transects with five sampling sites located in agricultural land 200, 50 m before the forest edge (0 m), and 25, 300 and 850 m inside the forest (Modified and completed after van Oort et al. 2001)

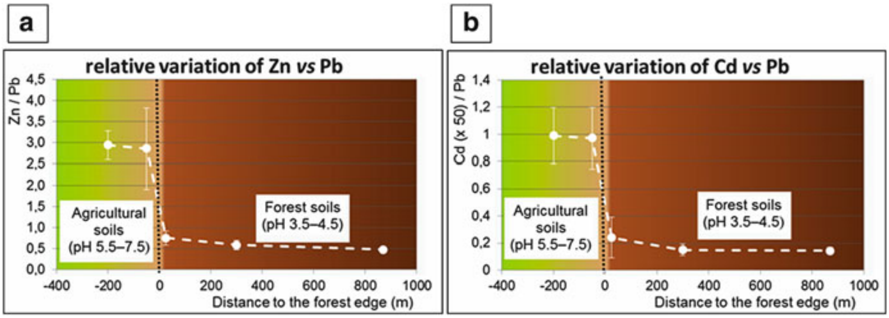


Fig. 4.11 Total metal concentration ratios between more mobile (Zn, Cd) and a little or non-mobile trace element (Pb) in agricultural and adjacent forest soils, affected by past industrial metal fallout. (**a**) Zn/Pb ratios, (**b**) Cd/Pb ratios (Cd concentrations × 50). Average metal concentrations measured on bulk samples from the 0–30 cm layer of soils under arable land, permanent grassland and forest land, located between 3 and 4 km from the former zinc smelter complex (Modified and completed after van Oort et al. 2001, 2009; Fernandez et al. 2007)

When presenting these same data as the concentration ratio of mobile (Zn, Cd) and little or non-mobile (Pb) metals, better insight is obtained in the dynamics of these elements in soils under different land use (Fig. 4.11). Such expression of total trace metal concentrations in surface horizons by using metal concentration ratios clearly reveals the behaviour of mobile metals (Zn, Cd) in acid conditions of the forest soils, where the major part of Zn and Cd contaminants has been leached to depth during the twentieth century.

In the view of such an important migration of mobile trace metals in soils, particularly in forest soils with low pH, a well-adapted approach for studying the fate of metal contamination under different land use consist in comparing the metal stocks over the depth of the profiles. Reasoning in metal stocks, instead of metal concentrations gives better insight in the incorporation and redistributions of metal elements as well as in possible outputs of trace metals to the water table. This approach is illustrated in Table 4.6 for the three soils presented in Fig. 4.9, under forest, arable land and permanent grassland.

These data were calculated by multiplying the average trace metal concentrations in the horizon ([M], expressed as g kg^{-1}), the mean thickness of each horizon (E, m), and the bulk density (Da, $kg.m^{-3}$) of each horizon. When cumulating the amounts of metals for 1 m soil depth, total metal stocks in the soil profiles are obtained, presented as g m^{-3} in Table 4.6. These data illustrates very well that in the two agricultural soils, total stocks cumulated over 1-m depth are very similar, both for mobile and non-mobile elements, indicating that, although differently incorporated in the soils under arable land use or permanent grassland, little or no metal have leached out of these soils, as confirmed by validating and prospective modelling work (Mallmann et al. 2012; Rheinheimer et al. 2013).

In the forest soil, the total stock of Pb is in the same order with respect to those observed in the agricultural soils, even larger, illustrating the capacity of tree canopies to intercept more atmospheric metal-bearing dust than cultivated plants. By contrast, the Zn and Cd stocks in forest soils are much smaller than under agriculture, and that demonstrates the important leaching of mobile trace elements in the podzolic conditions. In the permanent grassland soil, Pb stocks at 50–60-cm depth are larger than at comparable depth in the arable land soil, and due to biomechanical incorporation by earthworms (Fernandez et al. 2010). When considering the fairly constant average Zn/Pb ratio of about 3.5–4 found in surface horizon under cultivation, and after subtracting the estimated local pedogeochemical concentrations for Zn, Pb, and Cd (Fernandez et al. 2007; van Oort et al. 2009), the total nowadays observed Zn stock (30 g m^{-3}) only represents 1/5th of what would have been the global Zn deposition stock ($\approx$ 130–150 g m^{-3}). Consequently, about 80 % of airborne Zn has leached out of the first metre of the forest soil profile. For Cd, the findings are similar.

These findings have great implications for some general ideas about the metal mobility and bio availability often considered to increase in acid soil conditions. But in the case of past atmospheric metal contaminations of acid forest systems, where with time a large proportion of more mobile elements such as Zn and Cd have been leached out of the soil profile, their remaining pools may be nowadays more strongly retained by reactive soil constituents. This fact is illustrated in Table 4.7 by data from EDTA extractions of Zn, Pb and Cd in acid forest soils and adjacent agricultural soils. The proportions of non-extractable Zn and Cd in the 0–30 layer acid forest soils are noticeably larger (1.5–2 times) than the non-extractable pools in agricultural soils, whereas for Pb these pools are similar. Such a hypothesis of very large non-EDTA extractable pools of Zn and Cd in acid soil conditions was recently put forward in work of Camizulli et al. (2013) in the case of large forested areas in the Morvan (France), where soils have been contaminated by historical mining activities.

Table 4.7 Proportions of Zn, Pb, and Cd, **non-extractable** by EDTA in forest soils and in soils under agricultural land use in northern France, affected by past metallurgical atmospheric fallout

		Zn	Pb	Cd
Soil reference	pH (water)	mg/kg		
Forest soils				
MN-F 19	4.5	75	34	82
MN-F 21	4.2	86	56	68
MN-F 26	4.3	84	21	75
MN-F 29	4.2	71	28	63
	Mean	79	35	72
Agricultural soils				
MN-CA 1	6	40	10	15
MN-CA 10	6	58	30	48
MN-PP 2	5.5	54	50	31
	Mean	51	30	31

Determinations carried out on bulk samples collected in the 0–30-cm surface layers

5.2 Evidence for Migration of Metal Trace Elements in Forest Soils: The Case of Pb

Trace metals occurring in the soil solution predominantly in a free or exchangeable form and pH susceptible, such as Zn and Cd, will easily migrate in acid soil conditions (e.g. McBride 1989; Adriano 2001, cf. Table 4.6). For less mobile elements, such as Cu and Pb, with strong affinity for organic complexes, findings diverge. For instance, Wang et al. (1995) conclude for a full retention of atmospheric lead in podzols of the northern Hardwood forested ecosystems (New Hampshire, USA). Andersen et al. (2002) showed that after afforestation, no increase of higher solubility of Pb was observed despite soil acidification. In a review paper, Steinnes and Friedland (2006), mention a general consensus for "*a slow movement of Pb out of the mineral soil, but that the loss of any significant lead from the mineral soil will take a century or more*". They underlined the need for field monitoring studies. Moreover, Steinnes et al. (2005) note that vertical movement of pollution-derived Pb in forest soil from Norway greatly differed between the study-sites and that in the south of Norway, about 70 % of Pb in the Bh horizon derived from atmospheric deposition. Such a vertical distribution of low-mobile metals is often ascribed to colloidal transport (Kretzschmar et al. 1999; Citeau et al. 2003, 2006), notably by organic complexes or iron oxi-hydroxide compounds. Citeau and collaborators performed field monitoring between 2000 and 2002 on metal fluxes in gravitational water collected at the base of genetic horizons of soils under different land use. They demonstrated that for the acid forest soil, Zn occurred mainly in a free, dissolved form, whereas Pb was predominantly associated with organic substances, either as labile or stable complexes (Fig. 4.12).

For some trace elements, in particular for Pb, the use of isotopic ratios offers the possibility to distinguish the lead pools of anthropogenic (or exogenous) and natural (or endogenous) origin in soils (e.g. Bacon et al. 1992; Erel et al. 1997; Bacon and

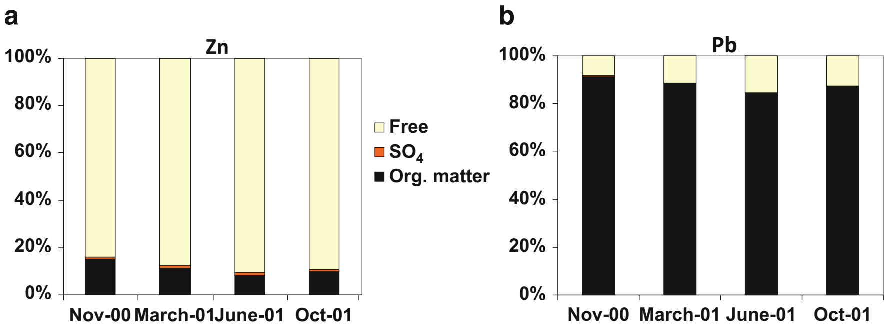


Fig. 4.12 Theoretical speciation of Zn (**a**) and Pb (**b**), calculated by Soilchem (Sposito and Coves 1988) on gravitational soil water collected at the base of the O horizon of the Haplic Podzol of Fig. 4.9 (From Citeau et al. 2009), during different seasons between November 2000 and October 2001. Metals in the soil solution occur either as free, dissolved elements (frequently the case for Zn), in a complexed form with inorganic ligands (sulfate) or associated with organic compounds (frequently the case for Pb)

Hewitt 2005); and to demonstrate the incorporation and distribution of anthropogenic lead at depth in soils (Semlali et al. 2001a, 2004). To illustrate the usefulness of this isotopic tool for unraveling the incorporation dynamics of a low mobile element such as Pb in soils, we compare the distributions of exogenous and endogenous Pb in two forest soils: an andosol developed on volcanic basaltic scoria, with neoformation of short-range order aluminosilicates (allophane), highly reactive toward heavy metals, and therefore acting as an trace metal-accumulating medium, and a podzol developed in a quartzose sandy sediment which is a highly lixiviating medium. For the first site, lead accumulation in the surface horizon was ascribed to former mining activities, located several tens of kilometres away, but large Pb concentrations in rains with heavy storms occurring annually, have been reported nowadays (Négrel and Roy 1998). In sandy podzols of the "Landes de Gascogne" and receiving dominantly western winds from the Atlantic Ocean, noticeable lead concentrations in the surface horizons have been mentioned by Saur and Juste (1994) and ascribed to long-range aerosol transport. Some selected characteristic pedo- and geochemical data of the andosol and podzol are presented in Table 4.8.

Both soils show substantial Pb concentrations in the organic litter horizons, reaching up to 62.7 mg kg^{-1} in the Oa horizon of the Andosol and 25.5 mg kg^{-1} in the O layer of the podzol. In the andosol, the Pb concentrations decrease progressively from the A1 horizon to the C horizon, whereas in the podzol a noticeable Pb increase occurs in the illuvial Bh and Bs horizons, almost twofold the Pb concentrations of the overlying A1 and E horizons.

When analyzing lead isotopic ratios for the soil horizons of the andosol forest site (Fig. 4.13), the variation of $^{206}Pb/^{207}Pb$ *vs* $^{206}Pb/^{204}Pb$ is linear and progressive from the surface to depth, with highest ratios in the C and R horizons, and lowest in the uppermost Oi horizon (Fig. 4.13a). In the podzol (Fig. 4.13d), the lowest signal

Table 4.8 Selected pedogeochemical data of a young andosol in the Massif Central and a podzol in the "Landes de Gascogne", France

Haplic andosol under *Pinus sylvestris*, Puy de la Vache (St Gènes – Champanelle, France); altitude: 1,000 m, ann. Precip. 700–1,000 mm					Haplic podzol under *Pinus pinaster*, Les Landes (Marquèze, France); altitude: 75 m, ann. Precip. 1,100 mm				
Hor	Depth	pH	Org. C	Pb	Hor	Depth	pH	Org. C	Pb
	cm		g/kg	mg/kg		cm		g/kg	mg/kg
Oi	7.5–2.5	–	521	19.1					
Oa	2.5–0	–	278	62.7	O	7.5–0	–	394	25.5
A1	0–14	5.5	68	19.6	A1	0–45	3.8	33	4.7
A2	14–40	5.9	59	12.5	E	45–100	4.2	2.7	4.0
Bw	40–55	6.3	32	6.6	Bh	100–155	4.1	28	9.2
C	55–60	6.7	7.5	4.1	Bs	155–210	4.3	8	8.5
R	> 60	8.5	0.8	4.3	C	> 210	4.5	1.2	5.7

Data from Semlali et al. (2001a)

is also found in the O horizon, but within organo-mineral soil horizons, the ^{206}Pb/^{207}Pb ratio is highest in the A horizon, followed by the E, C, Bs, and Bh horizon. Such a sequence suggests that in the podzol, exogenous Pb migrated to depth and is preferentially accumulated in illuvial horizons.

Relations between metal distributions and specific pedogenetic processes can be interpreted from their distribution patterns among specific particle-size fractions. Physical fractionation in water represents an original approach for isolating soil fractions in size classes that may express differences in mineralogical composition, nature of organic matter (Christensen 1992) and reactivity toward heavy metals (Ducaroir and Lamy 1995; Labanowski et al. 2007; Lang Burak et al. 2013). When applying the isotopic ratio chemistry on such soil fractions of the andosol, the ^{206}Pb/^{207}Pb ratio increases in the A horizon from the finest <2 μm fraction to the coarse >2 mm fractions (Fig. 4.13b), similar to the organic carbon distributions (Semlali et al. 2001a). In the Bw horizon, the lowest ^{206}Pb/^{207}Pb ratio is for the 200–2000-μm fraction (Fig. 4.13c), ascribed to preferential retention of Pb on thin neoformed mineral coatings of smectite and amorphous allophanic compounds, a first stage of mineral weathering at depth in the andosol (Jongmans et al. 1998).

In the Bh horizon of the podzol, the lowest ^{206}Pb/^{207}Pb ratio among the size fractions is obtained for the 100–200-μm fraction (Fig. 4.13e). This fraction is quasi-exclusively composed of quartz grains with amorphous humus-illuviation coatings (Fig. 4.14a). These results indicate that Pb in such humus coatings is mainly of an exogenous origin (Semlali et al. 2001a) and suggest either the interception of dissolved Pb^{2+} by the organic compounds of the humus coating or the illuviation and precipitation of colloidal 'Pb-organic substances' in the Bh horizon.

Additional evidence for the migration of Pb in podzols and its significant accumulation in the humus-illuviation coatings on quartz grains can be visualized by using synchrotron-facilitated micro X-ray fluorescence (μ-SXRF). In Fig. 4.14, a small 50 × 325 μm surface of a soil thin section, including thin humus coatings

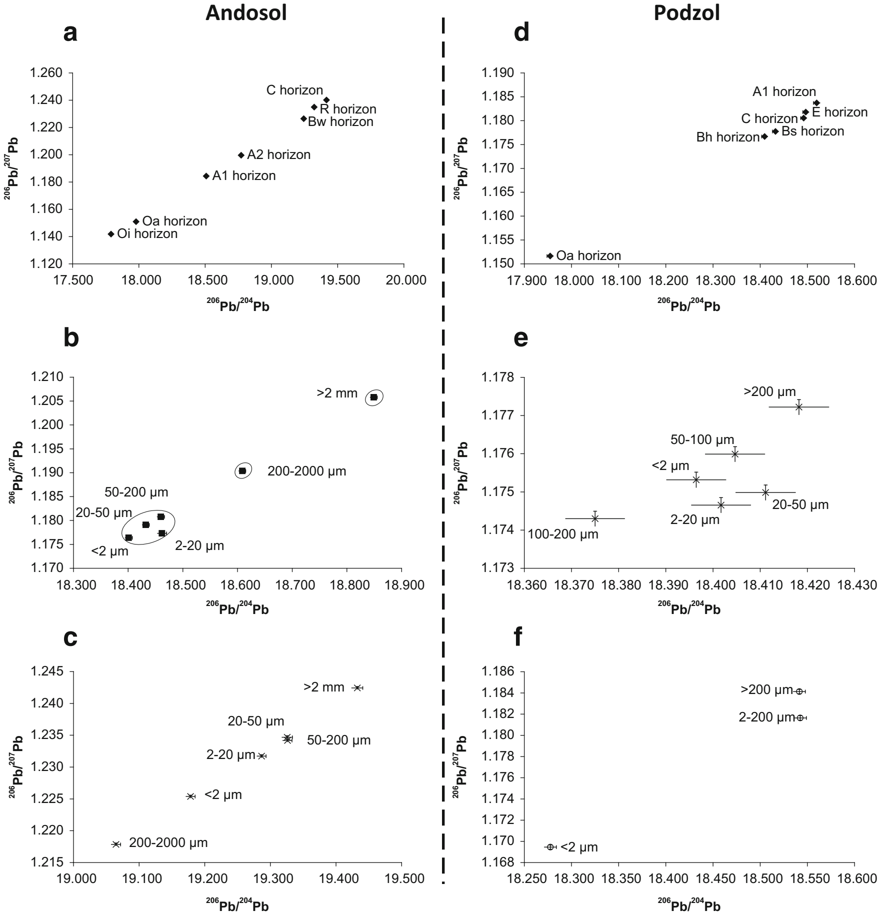


Fig. 4.13 Isotopic lead composition in soil horizons and in particle-size fractions in selected soil horizons, (**a**) in all andosol horizons, (**b**) in size fractions of the andosol A horizon, (**c**) in size fractions of the andosol Bw horizon, (**d**) in all podzol horizons, (**e**) in size fractions of the podzol Bh horizon, (**f**) in size fractions of the podzol C horizon (From Semlali 2000)

covering quartz grains (Fig. 4.14a) was analyzed by µ-SXRF using a beam spot of 25 × 25 µm and a dwell time of 1,000 s (modified after Semlali 2000). Chemical distribution maps of Si, Mn, Fe and Pb are thus obtained (Fig. 4.14b). These maps clearly demonstrate a simultaneous occurrence of lead, iron and manganese in the humus coatings, corroborated by strong correlation coefficients (Fig. 4.14c) and their absence in the quartz grains (negative correlation of trace metal with Si).

The 100–200 µm fraction in this illuvial Bh horizon contains only 6.8 g kg^{-1} of organic carbon and has a Pb concentration of 12.9 mg kg^{-1} (Semlali et al. 2001a), whereas in the bulk Bh horizon, the total Pb concentration reached 9.2 mg kg^{-1} (Table 4.8). When attributing the Pb concentration in this 100–200-µm fraction to

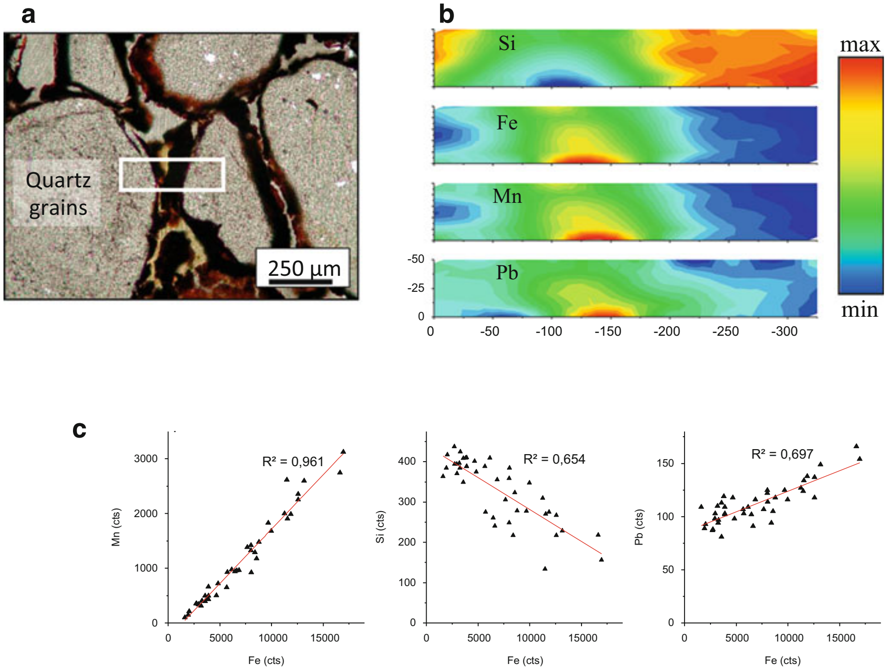


Fig. 4.14 Elemental distribution maps obtained by synchrotron facilitated micro X-ray fluorescence on a soil thin section of the podzol Bh horizon. (**a**) Optical microscopy photograph of the studied area showing *dark brown* humus coatings of about 50–100-µm thickness; (**b**) elemental distribution maps of Si, Fe, Mn and Pb of a 50 × 325 µm area (beam spot of 25 × 25 µm; number of analyzed points: 42; dwell time 1,000 s). The maps show that Fe, Mn, Pb are located in the humus coatings; (**c**) selected elemental correlations for Mn/Fe with $R^2 = 0.961$, for Si/Fe with $R^2 = 0.65$ and for Pb/Fe with $R^2 = 0.697$ ($n = 42$, $p < 0.001$) (Modified and completed after Semlali 2000)

its organic matter content, by considering the OM as the exclusive metal-intercepting soil phase, the Pb concentration of the organic carbon of the humus coatings would reach almost 200 mg Pb kg^{-1} Org C, much higher than when attributing the global horizon Pb concentration to its global organic carbon content, only 30 mg Pb kg^{-1} Org C. Moreover, in the C horizon, at more than 2-m depth, the $^{206}Pb/^{207}Pb$ ratio in the <2-µm fraction is much lower than in coarser fractions (Fig. 4.13f), indicating that exogenous lead has been transferred to great depth.

From these isotopic ratio data, a distinction can be made, at the scale of the total soil profile as well as at the scale of soil fractions, between natural and anthropogenic lead, by using scandium (Sc) as a conservative endogenous element to estimate the endogenous lead pools in the soil horizons (Semlali et al. 2001a). Scandium is known to have no significant anthropogenic source (Shotyk et al. 2001) and is low or non-mobile in soils. In Fig. 4.15, the distribution of endo- and exogenous lead is presented for the two forest soils. In the andosol (Fig. 4.15a), exogenous lead widely dominates in the surface horizons and decreases with depth

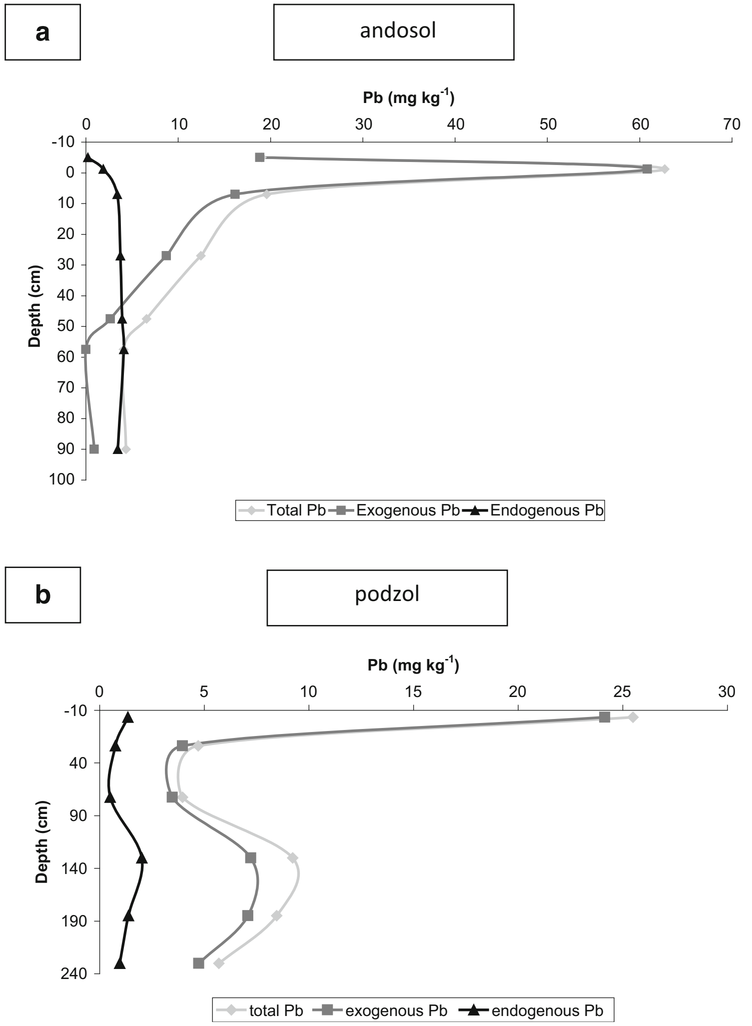


Fig. 4.15 Distributions at the scale of the soil profile of total, endogenous and exogenous lead concentrations (**a**) in an andosol of the Massif Central, (**b**) in a podzol of the Landes de Gascogne (From Semlali 2000)

suggesting that exogenous lead is strongly associated with organic matter and amorphous secondary soil constituent such as allophane. Considering that little exogenous Pb is currently present in gravitational water and in throughfall, in comparison to other elements such as Zn and Cu (Semlali et al. 2001b), the incorporation of exogenous lead as deep as in the Bw horizon probably illustrates its migration in the past, during intensive mining activities. Endogenous Pb is still predominantly located in unweathered primary minerals, such as feldspar. The distribution of exogenous lead preferentially occurring in the finest fractions, its general decrease with depth, as well as an endogenous Pb pool fully representing the total Pb content in C and R horizons (Fig. 4.15a) illustrate the highly metal-sorbing properties of the soil constituents, and are in full agreement with specific character of andosol pedogenesis.

In the podzol, the distributions of endo- and exogenous lead are strongly different (Fig. 4.15b). Exogenous lead is the dominant metal pool in the O, A, and E horizons. In the A horizon, the coarse sand fraction is *virtually* free of exogenous lead, indicating that the organic matter, sole lead bearing soil phase, and mineral compounds occur as juxtaposed constituents. In deeper Bh and Bs horizons, the exogenous Pb pool still represents an important proportion of the total lead content and is dominantly present in humus and iron coatings, respectively. In the C horizon, the total Pb concentration of 5.7 mg kg^{-1} (Table 4.8), mainly located in the $<$ 2-μm fraction, is composed predominantly of exogenous Pb (more than 80 %). Considering the quasi exclusive coarse sand texture (99 %, less than 1 % of clay) in the C horizon, these findings strongly suggest that in this well drained, acid forest soil, exogenous lead has leached out of the soil profile. As seen for the andosol, the Pb distribution patterns at a micro and macro-scale in the podzol are concordant with its typical soil-forming processes.

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