Pb – Lead

Introduction

Lead belongs to group 14 of the periodic table, which also includes C, Si, Ge and Sn. Lead has the most metallic characteristics of this group. The element has an atomic number of 82, an atomic mass of 207, two oxidation states (+2 and +4) and four naturally occurring isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb), of which ^{208}Pb is the most abundant at 52% of the total mass. Lead is the most abundant of the transition metal elements (Greenwood and Earnshaw 1984).

Lead is a chalcophile metallic element forming several important minerals including galena PbS, anglesite $PbSO_4$, cerussite $PbCO_3$ and minium Pb_3O_4. It is also widely dispersed at trace levels in a range of other minerals, including K–feldspar, plagioclase, mica, zircon and magnetite. Lead is one of the seven metals known in antiquity, because of its relative ease of extraction as a metal. The Roman civilisation, in particular, used large quantities of lead for plumbing purposes.

The Pb^{2+} ion (119 pm) is intermediate in size between K^+ (138 pm) and Ca^{2+} (100 pm) and so it replaces these ions in K-feldspar, mica and, to a lesser extent, plagioclase and apatite. As a consequence, it is enriched in felsic igneous rocks relative to mafic rocks, and Pb is mobile in late-stage magmatic processes (MacDonald *et al.* 1973). The enrichment in felsic igneous rocks is confirmed by the values quoted by Mielke (1979): ultramafic 1 mg kg^{-1}; basaltic 6 mg kg^{-1}; granitic 15–19 mg kg^{-1}; syenite 12 mg kg^{-1}; and a crustal abundance of 13 mg kg^{-1}.

In sedimentary rocks, the distribution of Pb is controlled by the presence of primary detrital minerals, such as feldspar, mica and sulphides, clay minerals (Heinrichs 1974, Heinrichs *et al.* 1980) and organic matter. Pure limestone (*ca.* 5 mg kg^{-1}) and quartzitic sandstone (*ca.*10 mg kg^{-1}) are typically depleted relative to shale and greywacke (*ca.* 23 mg kg^{-1}). The sedimentary rocks with the highest concentrations are black shale, reflecting the affinity of Pb for organic matter. Loess has an average Pb content of 13 mg kg^{-1} (McLennan and Murray 1999). Around 35% of Pb in stream sediment occurs in the sand fraction, but the majority is found in the silt and clay fractions, associated with kaolinite and mica, and secondary iron oxide precipitates (Song *et al.* 1999). The average concentration of Pb in river particulates is 150 mg kg^{-1}, a value that is definitely affected by anthropogenic factors (McLennan and Murray 1999).

Lead is used as a pathfinder for Sedex and VHMS deposits, and also for gold under some conditions, though not in lateritic terrains.

The natural Pb content in soil is, of course, related to the composition of the parent rock. Although the species of Pb vary considerably with soil type, it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations (Kabata-Pendias 2001). A baseline Pb value for surface soil on the global scale has been estimated to be 25 mg kg^{-1}; levels above this suggest an anthropogenic influence (Kabata-Pendias 2001).

In areas of sulphide mineralisation, Pb is mobilised by acidity derived from the weathering of galena and other sulphide minerals. The oxidation of Pb sulphides results in high concentrations of Pb in stream water, particularly around sites of base-metal mining. Lead is generally present in the aqueous environment as Pb^{2+}(aq) below pH 6, but it also forms complexes with organic anions, chloride and hydroxide, and insoluble or poorly soluble compounds with sulphide, sulphate, hydroxy carbonate and phosphate anions. Lead mobility is restricted by sorption on clay, organic matter, secondary iron and manganese oxides, and the formation of secondary minerals with low solubilities such as anglesite $PbSO_4$, cerussite $PbCO_3$ and pyromorphite $Pb_{10}(PO_4)_6Cl_2$. Biofilms also strongly adsorb Pb and can significantly influence the distribution of lead in solution (Nelson *et al.* 1995). Although Pb is more soluble in non-calcareous soil below pH 5.2, it is adsorbed on iron oxides in preference to Cu and Zn (O'Day *et al.* 1998) and, therefore, does not migrate readily to groundwater (Martínez and Motto 2000). Lead concentrations in unpolluted rainwater and snow are about 1 µg l^{-1}, which is also typical for most unpolluted surface and ground waters (Hem 1992). In lower alkalinity and pH water, however, the dissolved Pb concentration can be significantly higher (Hem 1992).

Lead from vehicle exhausts, in the form of tetraethyl Pb, was, until recently, a significant source of contamination. In urban environments, road dusts can contain very high levels of Pb (Archer and Barret 1976), although the introduction of unleaded petrol has reduced this potentially toxic hazard in developed industrialised countries. In addition, metalliferous mining (especially sulphide ores), metallic detritus, Pb-bearing glass and pottery glazes, batteries, old lead-based paints, the corrosion of lead pipes in areas of soft water and sewage sludge are all potential sources of Pb. Anthropogenic sources of pollution may cause local enhancement of Pb levels in surface water by an order of magnitude compared to background values (Patterson 1965).

Lead has no known biological role in plants or animals and is highly toxic to mammals and aquatic life. It can cause mental impairment in young children, causing neuropathy and hypertension in adults and may be lethal at high levels, *e.g.,* over 25 µg kg^{-1} of body weight (WHO 1996). Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains. Thus, lead pollution is a worldwide issue.

Table 52 compares the median concentrations of Pb in the FOREGS samples and in some reference datasets.

Table 52. Median concentrations of Pb in the FOREGS samples and in some reference data sets.

Lead (Pb)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median mg kg^{-1}***
Crust1)	Upper continental	n.a.	n.a.	Total	17
Subsoil	**FOREGS**	**790**	**<2.0**	**Total (ICP-MS)**	**17.2**
Subsoil	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**10.0**
Topsoil	**FOREGS**	**843**	**<2.0**	**Total (ICP-MS)**	**22.6**
Topsoil	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**15.0**
Soil2)	World	n.a.	n.a.	Total	17
Soil, C-horizon3)	Barents region	1357	<2	*Aqua regia* (GFAAS)	2.09
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**40.7**
Humus3)	Barents region	1357	<2	Total (HNO$_3$, ICP-MS)	19.6
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.093 (µg l^{-1})**
Water4)	World	n.a.	n.a.		0.03 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**20.5**
Stream sediment	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**14.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**22.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**16.0**
Stream sediment5)	Canada	82 461	<0.18	*Aqua regia* (ICP-AES)	8

1)Rudnick & Gao 2004, 2)Koljonen 1992, 3)Salminen *et al.* 2004, 4)Ivanov 1996, 5)Garret 2006.

Pb in soil

The median total Pb content (ICP-MS analysis) in subsoil is 17.2 mg kg^{-1} and in topsoil 22.6 mg kg^{-1}; the range of Pb values varies from <3 to 938 mg kg^{-1} in subsoil and from 5.3 to 970 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 1.364.

In subsoil, low Pb values (<12.5 mg kg^{-1}) are prevalent over northern Fennoscandia, most of central Finland and central Norway, over the Quaternary sediments of northern mainland

Europe, in the Baltic countries, western Ireland, south-central Spain, central Hungary and on the island of Crete. The southern limit of the ice-age glaciation is well marked on the maps, through Germany and Poland, where the northern part has much lower values.

Areas that have high Pb content in subsoil (>24.9 mg kg^{-1}) include northern Portugal and Galicia (crystalline basement of the Iberian Massif), southern Portugal and the Spanish Sierra Morena (granitic lithology), an area in France centred on the Massif Central, the Alps, the Black Forest in south-west Germany, the border area of Germany with the Czech Republic, the Tyrrhenian fringe of Italy, the karstic coastal areas of Croatia and of Slovenia, Slovakia, the Attica region in Greece (including Lavrion), and an area in northern Finland. Isolated anomalies occur near the former mining district of Newcastle in England and in north-eastern Castilla in Spain. Lithology and mineralisation seem to be the main factors influencing the dispersion of lead in subsoil, with particular enrichment in some known mineralised areas: the southern Massif Central (Les Malines district), the Poitou ridge between the Central and Armorican Massifs (Pb-Zn vein type and disseminated mineralisation in lower Jurassic dolomite), southern Tuscany, Lavrion in Greece, and historical ore districts in central and eastern Slovakia (with Pb contamination produced mainly by smelters which processed polymetallic ore; this effect is even more pronounced in topsoil).

The topsoil compared to subsoil Pb pattern shows some distinct differences. In the ice-divider area of northern Finland Pb concentrations tend to be higher in old regolith subsoil compared to young till in topsoil. However, in many areas the Pb background is higher. The ratio topsoil/subsoil is on average 1.364 (ICP-MS analysis) and 1.489 (*aqua regia* digestion, ICP-AES analysis). After Hg and Cd, Pb shows the strongest enrichment in topsoils with respect to subsoil (Map 11). In addition to geology, anthropogenic influence is apparent in topsoils, especially in old mining areas (where it may be difficult to distinguish from natural mineralisation), but there is also enrichment in industrial areas such as northern Italy, the German Ruhr Basin, northern England and Glasgow, pointing to industrial or urban pollution. Southern Sardinia (mining) and Calabria have anomalies in topsoil.

In subsoil, Pb is strongly correlated with Zn (0.64), and it has a good correlation (>0.4) with Be, Th, Rb, Cs, Tl, Nb, Ta, Al, Ga, In, Y and the REEs. In topsoil, there is still a strong correlation with Zn, and a good correlation with Cd, Sb, Tl, Hg, Th, and most of the REEs. The different pattern of correlations (in top and subsoil) and the association with Cd and Hg in topsoil points to significant anthropogenic contamination.

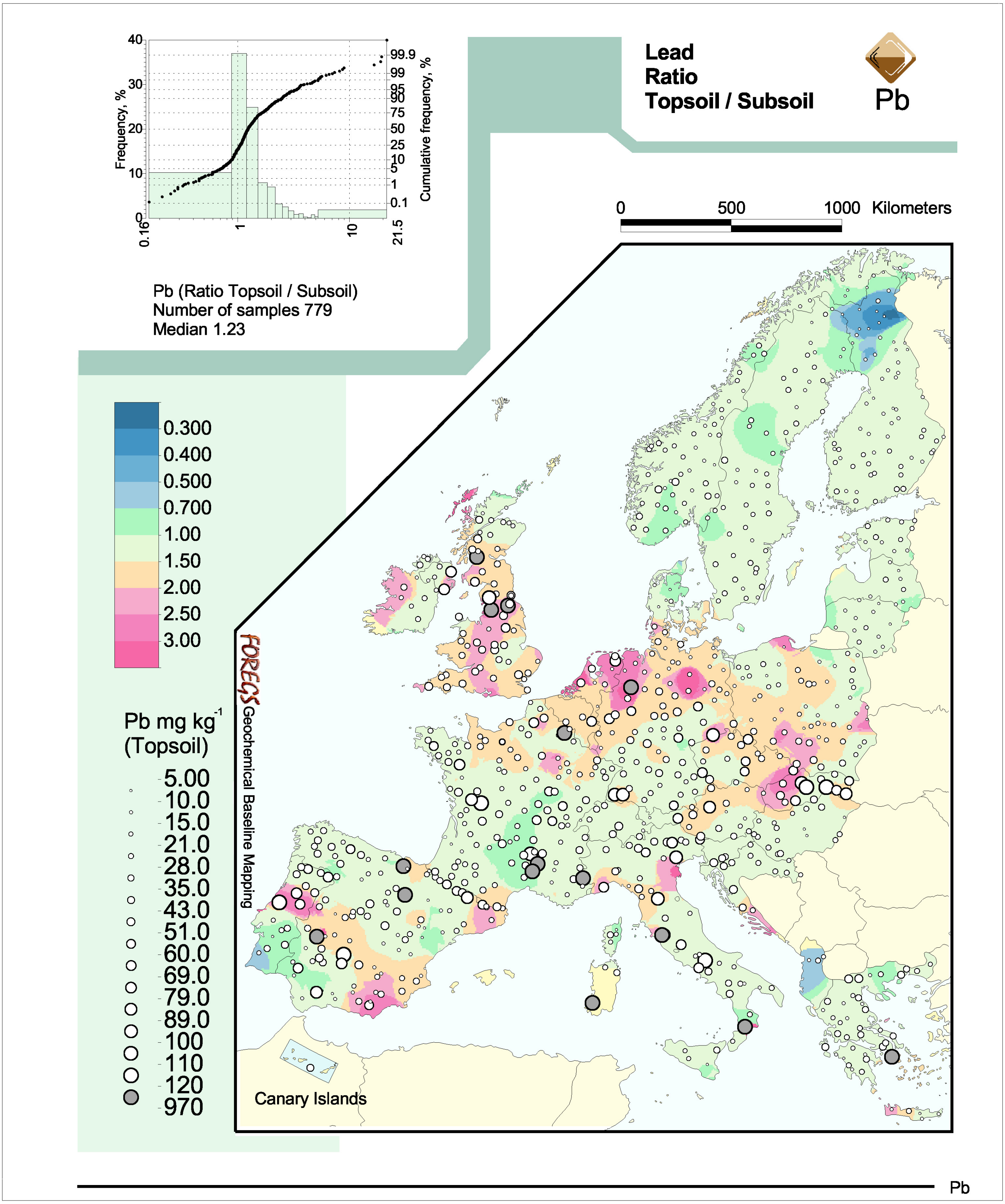
The median Pb content after *aqua regia* extraction (ICP-AES analysis) is 10 mg kg^{-1} in subsoil and 15 mg kg^{-1} in topsoil, with a range from <3 to 749 and from <3 to 886 mg kg^{-1} respectively. This means that about 60% of the Pb is extractable with *aqua regia*. Distribution patterns of extractable Pb are quite similar to total Pb, both in subsoil and topsoil, but there seems to be a relative decrease of extractable Pb in Fennoscandia. This points to a relatively higher metal fraction contained in silicates in Fennoscandia, as opposed to oxidic material and other secondary phases. In fact, it indicates a relative scarcity of secondary phases in Fennoscandia, compared to more southerly latitudes. Lower extractable lead concentrations in northern Europe are the result of leaching, dilution and transportation of soil material during the last deglaciation phase. In southern and central Europe the higher topsoil Pb values (in large part extractable) are often explained by contamination. In topsoil, in Britain, relatively more Pb is extractable.

Pb in humus

The median Pb content in humus is 41.0 mg kg^{-1} and the range varies from 0.80 to 536 mg kg^{-1}.

The Pb distribution map shows low Pb values in humus (<25 mg kg^{-1}) occurring in most of northern Fennoscandia, Denmark, northern Germany, northern Ireland and western France.

High Pb values in humus (>66 mg kg^{-1}) occur throughout most of Britain apart from the Scottish Highlands, Normandy in France, parts of southern Norway and Sweden, and north-western Germany; an area extending across western and



Map 11. Ratio of Pb in topsoil vs subsoil.

southern Poland, Czech Republic and central-eastern Germany, northern Italy and adjacent Switzerland. Anomalies in southern Poland and northern Italy are also seen on moss geochemical maps reflecting recent Pb deposition from probable airborne sources (Rühling and Steinnes 1998). Isolated anomalies are encountered in Belgium (Vesdre basin pollution), southern Finland (earlier lead emissions from industry) and central Sweden.

The high Pb values in humus are probably related to anthropogenic contamination, specifically the use of leaded gasoline in the twentieth century, but also a range of industrial and mining activities. However, the discontinuous and limited data make the interpretation of these patterns difficult, the rather incongruous low levels over Denmark and northern Germany being a prime example of this.

Lead in humus shows only weak correlations with Zn (0.33), Cd (0.36), Cu (0.28), Hg (0.25) and Ga (0.22).

Pb in stream water

Lead values in stream water range over three orders of magnitude, from <0.005 to 6.37 µg l^{-1} (excluding an outlier of 10.6 µg l^{-1}), with a median value of 0.093 µg l^{-1}.

Lowest Pb values in stream water (<0.029 µg l^{-1}) are found throughout northern and western parts of Fennoscandia, in south-eastern Spain, north-eastern Italy, most of Austria, part of southern Germany, Albania and most of Greece. Some of these areas have alkaline stream water, with low solubility of Pb, even when Pb mineralisation is present, as in south-eastern Spain.

Enhanced Pb concentrations in stream water (>0.35 µg l^{-1}) are found in southern Fennoscandia, parts of Lithuania and Latvia, central Britain and Northern Ireland, Brittany and the Massif Central in France, the Sierra Morena in south-central Spain (caused by Pb-Zn veins in the Azuaga district and the Pedroches batholith), and the areas north of Tuscany and Apulia in Italy. Isolated highly anomalous Pb data in south-eastern France are related to previously mined Pb-Zn districts in the Bruche Valley and Moncoutan regions; similarly the anomaly in southern Sardinia (Iglesiente district). Industrial pollution is the most likely cause of the isolated Pb anomalies in Belgium and the area north of Napoli. High values of Pb in Lithuania and Latvia may be related to anthropogenic sources. The highly anomalous Pb value in western Sweden is located in a Pb mining area. In north Portugal, anomalous values are probably anthropogenic. A point anomaly in central Spain near Guadalajara is related to Pb-Ag veins in the Prádena district in the Cordillera Central.

Lead in stream water is distributed according to two important pattern types. The pattern of REEs and associated elements in acid, high-DOC and low-mineralisation stream water comprises high Pb concentrations in southern Fennoscandia, in Lithuania and Latvia, north England and north Ireland, in Brittany and the Massif Central in France. The high Pb present in these stream water types as organic complexes, chloride and hydroxide, mostly does not relate to high Pb concentrations in soil or sediments. The pattern of Base metals elements numbers several important high Pb areas, in the Erzgebirge, Germany, Czech Republic, Switzerland, France, north England, smaller areas in Portugal and Spain, Italy with Sardinia. They mostly correspond to high Pb areas in solid sample media, and reflect higher lead contents in ore districts or polluted regions. But, in general, Pb patterns in stream water are not related to those in soil and sediments.

Pb in stream sediment

The median total Pb content in stream sediment (XRF analysis) is 20.5 mg kg^{-1}, and the range of values varies from <1 to 5760 mg kg^{-1}.

The Pb distribution map shows low values in stream sediment (<14 mg kg^{-1}) occurring throughout northern Fennoscandia including most of Finland, parts of central Norway, the northern European lowlands including the Netherlands and Denmark, but excluding northern Germany, most of the Baltic states, southern and eastern Spain, south-west France, the Rhône valley, north-easternmost Italy and central Austria, central Hungary, western Greece and Crete.

High Pb values in stream sediment (>31 mg kg^{-1}) are found throughout most of Britain (especially in the Pennines and the Tyne valley with vein-type mineralisation mined for a long period of time); southern Norway; the Massif Central in France with a westerly extension into the Poitou area; the eastern Pyrenees (massive sulphides of stratiform Sedex type, such as Margalida, Victoria, hosted by schist and limestone of Cambro-Ordovician age, and also Silurian black shale); the western Iberian Peninsula, including the Iberian Pyrite Belt in the south, rich in base metals sulphides; the Black Forest in south-west Germany and adjacent Alsace; the Roman Alkaline Province. High Pb values in the northern Czech Republic are caused by a combination of atmospheric precipitation (fly ash from power plants) and emissions from industry; the medieval mining areas of Příbram and Kutná Hora in the Erzgebirge are too far removed from the sampling locations to exert any influence.

Smaller Pb stream sediment anomalies occur in the mining districts of Lavrion (Pb-Ag mineralisation) in Greece, southern Sardinia, Silesia-Kraków in southern Poland, and the Rheno-Hercynicum across the Belgian-German border (known Pb-Zn district) (De Vos *et al.* 2005). Point anomalies occur in Donegal (base metal vein-type mineralisation) and over the Mourne granite in Ireland; although Ireland is a major Pb-Zn producer, the deposits are concealed and do not show up in the stream sediments. Other point anomalies occur in Finland, central west Sweden, north-east Greece (mineralisation), and in the Harz in Germany (also mineralisation). Higher background and anomalous Pb values thus seem mostly influenced by mineralisation or old mining and smelting activities, but in some areas other anthropogenic pollution is apparent.

Lead in stream sediment shows a good correlation (>0.4) with Zn, As and Sb, and a weak correlation (>0.3) with Cd, Tl, Cu, Rb and Ba.

Analysis of Pb in stream sediment by ICP-AES after dissolution with *aqua regia* results in a median content of 14 mg kg^{-1}, and a range from <3 to 4880 mg kg^{-1}. This means that about 65% of Pb is extracted. The distribution pattern of aqua-regia extractable lead is almost identical to the total-content Pb distribution, and correlation between both is 1.00.

Pb in floodplain sediment

Total Pb values in floodplain sediment, determined by XRF, vary from 4 to 7084 mg kg^{-1}, with a median of 22 mg kg^{-1}, and *aqua regia* extractable Pb concentrations range from <3 to 5200 mg kg^{-1}, with a median of 16 mg kg^{-1}, meaning that about 72% of Pb is extracted. Overall, geochemical patterns shown by total XRF and *aqua regia* extractable Pb are very similar.

Low total Pb values in floodplain sediment (<15 mg kg^{-1}) occur over most of Finland, central and northern Norway, Latvia, Lithuania, most of Poland, northern Sweden, north-west part of Ireland and eastern and southern Spain, southern half of Italy, and western Greece, including the island of Crete.

High total Pb values in floodplain sediment (>35 mg kg^{-1}) occur throughout England, Wales and southern Scotland, related to extensive Pb-Zn mineralisation (*e.g.,* Scotland: Leadhills Pb-Zn; Pennines: Alston-Greenhow Pb-Zn; Derbyshire ore district, Wales: Shelve Pb-Zn, Cardigan-Montgomery Pb-Zn; Mendips Pb-Zn), but also to anthropogenic contamination in industrial areas, and leaded petrol. High total Pb values occur in France in a large area in western-central France, and a belt from Massif Central to the Mediterranean coast, which include mineralised areas (*e.g.,* Largentiere Pb-Zn, Les Malines Pb-Zn; Brittany: Pontpean Pb-Zn), but also industrial areas and leaded petrol.

Another extensive belt with high total Pb values in floodplain sediment stretches from eastern Belgium over most of central Germany to the Czech Republic and southern Poland, which includes many Pb-Zn mineralised areas (*e.g.,* Mechernich Pb-Zn, Meggen Pb-Zn, Rammelsberg Pb-Zn, Bad Grund Pb-Zn, Freiberg Pb-Zn, Kutna Hora Pb-Zn), and industrialised areas.

High total Pb values in floodplain sediment occur in southern Spain and Portugal associated with the Iberian Pyrite Belt and the Linares and Pedroches- La Alcudia mineralised districts in the Sierra Morena (*e.g.,* Rio Tinto Zn-Cu-pyrite, Linares Pb-Zn-Ag, La Carolina Pb-Zn and Horcajo Pb-Ag deposits), Sardinia (*e.g.,* Montponi Pb-Zn, Arburese Pb-Zn, Silius Pb-Ba and Funtana Raminosa Pb-Zn); the Roman alkaline magmatic province; the base-metal mineralised district of central Macedonia in Greece; the mineralised districts of south-western Norway and Stockholm area in Sweden, which may also be due to industrial-urban activities.

Point total Pb anomalies in floodplain sediment occur in the French Pyrenees (Pierrefitte Pb-Zn), north-western Poland (possibly anthropogenic pollution), in southern and eastern Slovakia (Banska Stiavnica Pb-Zn, Rudnaňy Fe-Cu-Hg-Ba), and the Lavrion polymetallic mineralised area in Attika, Greece (De Vos *et al.* 2005).

The highest total Pb values in floodplain sediment are found in Greece at Lavrion (an outlier with 7084 mg kg^{-1}), because of mining and smelting activities, Belgium in the Vesdre basin (an outlier with 3614 mg kg^{-1}), due to metallurgical pollution, in north-east England in the Northumberland mineralised area (one outlier with 2075, and further values of 1190, 791 and 654 mg kg^{-1}) due to mining activities, in Spain in the Linares mineralised district (934 mg kg^{-1}) and in the Slovakia Pb-Zn mineralised area (649 mg kg^{-1}).

Total Pb in floodplain sediment shows a strong correlation with Zn (0.71), a good correlation with Cd (0.55) and Ba (0.52), and a weak correlation with Cu (0.35). This association points to mineralisation and possibly contamination by mining.

In conclusion, the patterns of high Pb values in floodplain sediment map mineralised areas, and the pollution caused by mining and metallurgical processing, urban and other polluting anthropogenic activities. Lead anomalies reach more extreme values in floodplain sediment. This illustrates the importance of human induced enrichment: lead contents in soil are enhanced from the anthropogenic activities of mining and smelting, as well as other polluting activities (such as the use of leaded petrol), and the subsequent erosion and deposition of contaminated alluvium on floodplains. In support to these observations, it is interesting to note that the median of total Pb is higher in floodplain sediment (22 mg kg^{-1}) than in subsoil (17.2 mg kg^{-1}), but comparable to topsoil (22.6 mg kg^{-1}) and stream sediment (21 mg kg^{-1}). Similary, the aqua regia extractable Pb shows a higher median in floodplain sediment (16 mg kg^{-1}) than in subsoil (10 mg kg^{-1}), but again comparable to topsoil (15 mg kg^{-1}) and stream sediment (14 mg kg^{-1}).

Pb comparison between sample media

In general there are some broad similarities in the Pb distribution between all solid sample media, although there are a number of significant differences. Topsoil is generally enriched in Pb by an average factor of 1.4 relative to subsoil. Main areas of Pb enrichment occur in Britain, south-eastern Spain, north-eastern Italy and adjacent western Austria and in a belt extending from Belgium through central Germany and southern Poland into the Czech Republic (see map of ratio of Pb in topsoil and subsoil), although topsoil are depleted in Pb relative to subsoil in Albania, northern Greece and northern Finland. In stream and floodplain sediments, trends in Pb data are higher in Britain. In stream sediment, the pyrite belt of southern Portugal and Spain is enhanced with respect to the other solid sample media. In the floodplain sediment of the north-west Iberian Peninsula, Pb is lower than in other solid sample media. The belt extending from Belgium through central Germany and southern Poland into the Czech Republic is higher in floodplain sediment and topsoil and lower in stream sediment and subsoil.

A boxplot comparing Pb variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 34.

There is little difference in distribution patterns between total and leachable (*aqua regia*) Pb concentrations.

The pattern in humus Pb is most similar to that found in floodplain sediment and topsoil, especially in Britain and in the belt extending from Belgium through central Germany and southern Poland into the Czech Republic, and is probably related to anthropogenic input. Lead in humus is high in northern Italy and parts of southern Fennoscandia, also related to anthropogenic pollution.

Trends in stream water Pb are complex, and quite often opposite to those observed in all solid sample media. Lead is strongly controlled by pH, and tends to low concentrations in the alkaline environments of central Spain, Greece, Albania and throughout the Alps. It is also solubilised by the presence of organic carbon, and is, hence, quite high in the organic rich areas in parts of southern Fennoscandia. Especially throughout Scandinavia, stream water Pb correlates quite well with trends observed in humus data.

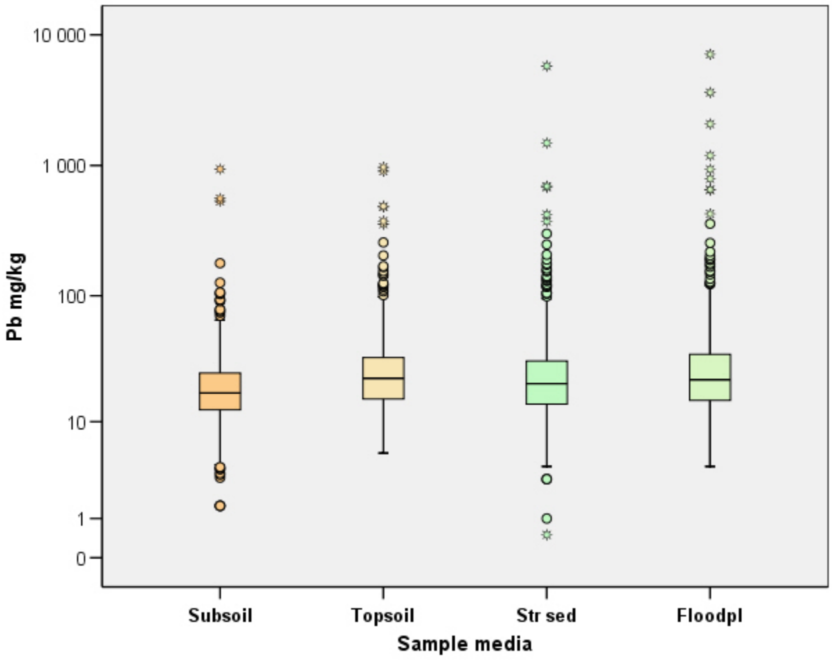


Figure 34. Boxplot comparison of Pb variation in subsoil, topsoil, stream sediment and floodplain sediment.