

## Introduction

Zinc is the heaviest member of the first row transition series of elements, consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 12 of the periodic table, along with Cd and Hg. The element has an atomic number of 30, an atomic mass of 65, one main oxidation state (+2) and five naturally occurring isotopes ( $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$ ,  $^{67}\text{Zn}$ ,  $^{68}\text{Zn}$  and  $^{70}\text{Zn}$ ), of which  $^{64}\text{Zn}$ ,  $^{66}\text{Zn}$  and  $^{68}\text{Zn}$  are the most abundant at 48.6%, 27.9% and 18.8% respectively of the total mass. The chemistry of Zn is most similar to that of Cd.

Zinc is a chalcophile metallic element and forms several minerals, including sphalerite  $\text{ZnS}$ , the commonest Zn mineral, smithsonite  $\text{ZnCO}_3$  and zincite  $\text{ZnO}$ , but is also widely dispersed as a trace element in pyroxene, amphibole, mica, garnet and magnetite.

During magmatic processes, Zn, like most other first-row transition metals, shows compatibility during early fractionation and thus becomes enriched in mafic relative to felsic rocks. The principal Zn carrier in mafic rocks is magnetite, while biotite is generally the most important in granite (Ure and Berrow 1982). Mielke (1979) quotes Zn contents of some igneous rock types: ultramafic  $50 \text{ mg kg}^{-1}$ ; basaltic  $105 \text{ mg kg}^{-1}$ ; granitic  $39\text{--}60 \text{ mg kg}^{-1}$ ; syenite  $130 \text{ mg kg}^{-1}$ , and a crustal average of  $76 \text{ mg kg}^{-1}$ . Zinc is readily partitioned into oxide and silicate minerals by substitution for  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$ , both of which have similar ionic radii to  $\text{Zn}^{2+}$  (74 pm).

The distribution of Zn in sedimentary rocks is primarily controlled by the abundance of ferromagnesian silicates, detrital oxides, *e.g.*, magnetite, and clay minerals (Wedepohl 1978). Carbonate rocks (*ca.*  $50 \text{ mg kg}^{-1}$ ) and quartzofeldspathic sand ( $30\text{--}50 \text{ mg kg}^{-1}$ ) are generally depleted in Zn compared with greywacke ( $70\text{--}100 \text{ mg kg}^{-1}$ ) and shale ( $50\text{--}90 \text{ mg kg}^{-1}$ ). Zinc is readily adsorbed onto ferric oxides (Robinson 1981), although when Fe is absent it is often associated with carbonate and silicate phases (Carroll *et al.* 1998). It has a greater affinity for organic matter than  $\text{Cd}^{2+}$  (Tipping and Hurley 1992), and high values of Zn occur in oil shale (Wedepohl 1978). Elevated levels of Zn, up to 1%, have also been recorded in oolitic ironstone and recent ferro-manganese nodules (Jenkyns

1977).

Zinc is used in geochemical prospecting as a pathfinder for various types of Zn mineralisation, and is normally accompanied by Cd. Zinc in association with Cd, Pb, *etc.* strongly suggests the presence of Sedex or VHMS mineralisation. Because of its strong chalcophile character, Cd may be used to validate a questionable Zn anomaly. Elevated Zn values more likely indicate mafic rocks, or Fe/Mn co-precipitation.

The Zn content in soil depends on the nature of parent rocks, texture, organic matter and pH, and ranges from 10 to  $300 \text{ mg kg}^{-1}$  (Mihaljevic 1999b) with an estimated global average of  $64 \text{ mg kg}^{-1}$  (Kabata-Pendias 2001). The different forms of Zn in soil may include: (1) water soluble; (2) exchangeable and extractable from soil surfaces; (3) occluded by soil hydrous oxides; (4) precipitates; (5) immobilised in living organisms and biological residues, and (6) constituents in the lattice of primary and secondary minerals (Mihaljevic 1999b). Several soil profile studies have shown that extractable Zn generally decreases with depth, while total Zn is uniformly distributed throughout the profile. Extractable Zn usually correlates positively with total Zn, organic matter, clay content and cation exchange capacity. An inverse correlation has been observed between the amount of extractable Zn and free  $\text{CaCO}_3$ , soil pH, and base saturation (Mihaljevic 1999). Since Zn is easily adsorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons (Kabata-Pendias 2001).

The concentration of Zn in weathering solutions is controlled rather by adsorption (on clay minerals Fe, Mn Al hydroxides and organic matter) than by solubility of Zn carbonates, hydroxides and phosphates (Mihaljevic 1999b). Zinc mobility in the environment is greatest under oxidising, acidic conditions and more restricted under reducing conditions. Weathering of sulphide minerals in oxidising conditions may give rise to high concentrations ( $>100 \mu\text{g l}^{-1}$ ) of dissolved Zn sulphates and carbonates (Massey and Barnhisel 1972). Below pH 7.5–8.0, Zn occurs predominantly in the  $\text{Zn}^{2+}$  form. At higher pH values, it forms low solubility complexes with carbonate and hydroxyl ions (Brookins 1988).

Under reducing conditions, particularly in conjunction with low pH, sphalerite may form. Zinc may exhibit amphoteric behaviour at pH>11, but these values are rarely found in nature. It is rapidly sorbed to secondary oxides, clay minerals and organic matter (Jenne 1968, Robinson 1981, Ure and Berrow 1982) in all but the most acid conditions (pH<4.5). Typical Zn concentrations in river water are about 10 to 50 µg l<sup>-1</sup> (Hem 1992).

Anthropogenic sources of zinc are significant, arising mainly from industrial activities such as mining, coal and waste combustion, and steel processing. A major use of Zn is as an anti-corrosion coating. It is also used as a constituent of brass, as a white pigment (ZnO) in paint and rubber products, and in the manufacture of dry batteries. The world's Zn production is still rising, and industrial applications tend to disperse Zn widely in the natural environment, leading to

levels above pre-industrial concentrations in air, soil and water.

Zinc is an essential trace element for humans, animals and higher plants. A recommended intake of 11.4 mg per day is suggested for adults (WHO 1996). Symptoms of deficiency include growth retardation, dermatitis and slow wound healing, defective immune system and, in extreme cases, birth defects. In general, Zn toxicity is not so much a problem as deficiency, although excess Zn can still cause health problems such as stomach cramps, skin irritations, vomiting, nausea and pancreas damage. Fish can accumulate Zn, causing biomagnification up the food chain, and plants often take up more Zn than their systems can handle.

Table 76 compares the median concentrations of Zn in the FOREGS samples and in some reference datasets.

Table 76. Median concentrations of Zn in the FOREGS samples and in some reference data sets.

<b>Zinc (Zn)</b>	<b>Origin – Source</b>	<b>Number of samples</b>	<b>Size fraction mm</b>	<b>Extraction</b>	<b>Median mg kg<sup>-1</sup></b>
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	67
<b>Subsoil</b>	<b>FOREGS</b>	<b>788</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>47.0</b>
<b>Subsoil</b>	<b>FOREGS</b>	<b>784</b>	<b>&lt;2.0</b>	<b>Aqua regia (ICP-MS)</b>	<b>44.0</b>
<b>Topsoil</b>	<b>FOREGS</b>	<b>845</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>52.0</b>
<b>Topsoil</b>	<b>FOREGS</b>	<b>837</b>	<b>&lt;2.0</b>	<b>Aqua regia (ICP-MS)</b>	<b>48.0</b>
Soil <sup>2)</sup>	World	n.a.	n.a.	Total	70
Soil, C-horizon <sup>3)</sup>	Barents region	1357	<2	Aqua regia (ICP-AES)	20.0
<b>Humus</b>	<b>FOREGS</b>	<b>367</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>45.5</b>
Humus <sup>3)</sup>	Barents region	1357	<2	Total (HNO <sub>3</sub> , ICP-MS)	44.0
<b>Water</b>	<b>FOREGS</b>	<b>807</b>	<b>Filtered &lt;0.45 µm</b>		<b>2.68 (µg l<sup>-1</sup>)</b>
Water <sup>4)</sup>	World	n.a.	n.a.		20 (µg l <sup>-1</sup> )
<b>Stream sediment</b>	<b>FOREGS</b>	<b>852</b>	<b>&lt;0.15</b>	<b>Total (XRF)</b>	<b>71.0</b>
<b>Stream sediment</b>	<b>FOREGS</b>	<b>845</b>	<b>&lt;0.15</b>	<b>Aqua regia (ICP-AES)</b>	<b>60.0</b>
<b>Floodplain sediment</b>	<b>FOREGS</b>	<b>747</b>	<b>&lt;2.0</b>	<b>Total (XRF)</b>	<b>65.0</b>
<b>Floodplain sediment</b>	<b>FOREGS</b>	<b>747</b>	<b>&lt;2.0</b>	<b>Aqua regia (ICP-AES)</b>	<b>56.0</b>
Stream sediment <sup>5)</sup>	Canada	82 464	<0.18	Aqua regia (ICP-AES)	70

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

## Zn in soil

The median total Zn content (XRF analysis) is 47 mg kg<sup>-1</sup> in subsoil and 52 mg kg<sup>-1</sup> in topsoil; the range of values varies from <3 to 3060 in subsoil and from <3 to 2900 mg kg<sup>-1</sup> in topsoil. The average ratio topsoil/subsoil is 1.075.

The subsoil Zn distribution map shows low values (<26 mg kg<sup>-1</sup>) over northern Europe, especially the Netherlands, Poland, northern Germany, central Finland and southern Sweden. A few values in Scandinavia are locally higher than average, probably caused by Mn-coprecipitation.

High Zn values in subsoil (>76 mg kg<sup>-1</sup>) occur in the crystalline basement of the Iberian Massif in north-western Spain and northern Portugal, the Pyrenees (black shale), in France from Brittany over Poitou to the southern Central Massif, in northern Italy, Tuscany, karstic Slovenia and Dalmatian Croatia, Sardinia, Calabria, the Attica peninsula in Greece (Lavrion), an area from the northern Central Massif to the Jura Mountains, northern Bavaria, and near Glasgow and Newcastle in Britain. The highest subsoil Zn values apparently occur in mineralised regions, mining and smelting areas (Northern France, north-west Germany, Sierra de la Demanda in north-central Spain).

The topsoil Zn map likewise shows low values over northern Europe. High Zn values occur in the Canary Islands (basalt), west-central Spain,

the Pyrenees, the Poitou region in France, the southern Central Massif, the east part of northern Italy, Slovenia, Sardinia (associated with Pb-Zn mineralisation near the Iglesias-Sulcis mining district), Calabria (local sulphide mineralisation), the Lavrion polymetallic mineralisation in Greece, an area from the Rheno-Hercynian to the Vosges, Schwarzwald and Jura, and the Erzgebirge region. In Brittany (France), the poor correlation between Zn and Pb may indicate Zn-pollution of the topsoil by liquid manure spreading.

The average ratio topsoil/subsoil for Zn is 1.075, expressing a slight enrichment in topsoils.

A few isolated Zn anomalies occur in either subsoil or topsoil, and should be investigated locally.

Zinc in subsoil shows a strong correlation (>0.6) with Pb and In, and a good correlation (>0.4) with Cd, Cu, Te, Co, Ti, Mn, Fe, Sc, V, Al, Ga, Nb, Tl, Y and the REEs. In topsoil, many correlations of Zn are enhanced, and a good correlation also exists with Th and P<sub>2</sub>O<sub>5</sub>.

Analysis with ICP-AES after *aqua regia* dissolution results in a median Zn content of 44 mg kg<sup>-1</sup> in subsoil and 48 mg kg<sup>-1</sup> in topsoil, with a range from 5 to 2280 and from 4 to 2270 mg kg<sup>-1</sup> respectively. These values are similar to total Zn content, so most of the Zn is extracted by *aqua regia*. The distribution maps for both analytical methods are almost identical.

## Zn in humus

The median Zn content in humus is 46.0 mg kg<sup>-1</sup>, and the range varies from 1.00 to 1860 mg kg<sup>-1</sup>.

The Zn distribution map shows that low values in humus (<30 mg kg<sup>-1</sup>) prevail over western France, Ireland, northern and south-west England and northern Scotland, the glacial drift area from Denmark over north-eastern Germany to most of Poland and southern Lithuania, and west-central Norway.

High Zn values in humus (>63 mg kg<sup>-1</sup>) are mainly found in an area from Belgium and adjacent northern France over central Germany into north-western Czech Republic; southern Poland and Slovakia; northern Italy and adjacent

Switzerland and Austria; central Sweden; northern Norway; a small area in eastern Finland. An isolated Zn anomaly in humus occurs in south-western Norway. The same anomaly point is shown on the moss geochemical map reflecting deposition from the air (Rühling and Steinnes 1998). Moss maps suggest deposition as an explanation also for southern Poland, the Netherlands and central Germany (Siewers *et al.* 2000).

The Zn distribution in humus is somewhat similar to that in topsoil, and is at least in part geogenic, as it follows the pattern of Ga and Co in central Europe (southern Germany having intermediate values, surrounded by areas with

high values). Some anthropogenic pollution is also present, as testified by the anomaly in the Vesdre basin in Belgium (humus here contains  $1863.4 \text{ mg kg}^{-1}$  Zn, an outlier), known for its past industrial activity, specifically brass working (see Cd description in humus).

When discarding the single outlier of the Vesdre basin, Zn has a good correlation with Cd (0.53), which could represent a natural association, and weak correlations (0.3 to 0.4) with Ga, Rb and Ba, pointing to its geogenic distribution.

### Zn in stream water

Zinc values in stream water range over four orders of magnitude, from  $<0.01$  to  $181 \mu\text{g l}^{-1}$  (excluding an outlier of  $310 \mu\text{g l}^{-1}$ ), with a median value of  $2.68 \mu\text{g l}^{-1}$ . Zinc distribution in stream water resembles that of Cd and Pb.

Lowest Zn values in stream water ( $<1.17 \mu\text{g l}^{-1}$ ) are found in north and north-east of Finland, in central and northern Sweden on Precambrian Shield rocks, and in Caledonian terrains of west central Norway, north (partly Laurentian) and central Scotland and in small areas of western and southern England. In the Variscan part of Europe is a large area in southern Germany, two small areas in France, several small areas in Spain, and in Corsica. A low Zn belt occurs on Quaternary glacial deposits in central south-east Poland. On the Alpine Orogen, a low Zn stream water area stretches from south-east France across northern Italy to central Austria. Low Zn values in stream water are found in southern Hungary and north-east Croatia, in southern Albania and entire Greece, including Crete.

High Zn concentrations in stream water ( $>8.3 \mu\text{g l}^{-1}$ ) are found in countries bordering the Baltic Sea, on Precambrian Shield in southern Sweden, partly south-eastern Norway, and in south-eastern and south-western Finland, and on Precambrian Shield derived glacial drift in Denmark, Estonia, Latvia (partly anthropogenic in origin, but partly linked to increased extractability from sulphate-bearing Devonian deposits (see subsoil map; and high mobility in alkaline humid conditions) and Lithuania, northern Poland and east central Germany bordering on Czech Republic (here on Variscan rocks), and in Netherlands on Quaternary deposits. In south-western Finland, as for Cu, some relatively high Zn values in stream water may be influenced by some anthropogenic contributions. On Variscan terrains high Zn in stream water occurs in Brittany, in northern Portugal, central and southern Spain (mostly

associated with Zn mineralisation), and on Sardinia where it is related to Pb-Zn mineral deposits. In France (Brittany), high Zn concentrations in stream water are not related to some Hercynian mineralisation, but most probably to the contribution of a high density pigs (liquid manure) and chicken farms. An isolated high Zn stream water value in Belgium (Vesdre basin) is ascribed to industrial pollution (mining, metallurgical, textile, paper industry). On the Alpine Orogen high Zn values in stream water occur in Switzerland and at its borders in France, Germany and Austria, in southern Italy with Sicily (mineralisation) and in Baetics of southern Spain. Very high Zn and Cu values in Switzerland are probably the result of batch contamination during acidification. In Slovenia, the isolated Zn stream water anomaly is related to industrial pollution. The anomalous isolated Zn value observed on the border between northern Sweden and Finland is most likely related to contamination of the stream water sample during collection. An anomalous Zn value in stream water is found in the vicinity of the iron smelter at Czeřochowa. A point anomaly in eastern Slovakia is due to the mining and processing of metamorphic-hydrothermal vein mineralisation (complex siderite-sulphide ores). The point Zn anomaly northeast of Hannover (Germany) is located in the surroundings of sedimentary iron-ore deposits and can be related to anthropogenic sources. The Zn anomalies in north-western Germany correlate with high DOC waters; they are related to environmental conditions.

Zinc is in general distributed in stream water according to two models. The pattern of REEs-containing acid high-DOC low-mineralisation stream water comprises high Zn areas in southern Fennoscandia, Denmark, northern Poland, Baltic states and Brittany. The high Zn, present in these stream water samples as ionic and soluble organic species, does not generally correspond to Zn

anomalies in soil or sediments, except for Brittany and two small areas in Fennoscandia, but is most probably generated by the acidity and high DOC of stream water, which resulted from exogenic - climatic factors. The second pattern, that of Base metals, comprises high Zn in the Erzgebirge,

Germany, Switzerland, smaller areas in Portugal and Spain, southern Italy with Sicily and Sardinia, mostly corresponding to high Zn values in solid sample media. Zinc patterns in stream water are complex and often opposite to those of solid sampling materials.

### Zn in stream sediment

The median total Zn content in stream sediment is 71 mg kg<sup>-1</sup> (XRF analysis), and the range of values varies from 4 mg kg<sup>-1</sup> to 13900 mg kg<sup>-1</sup> or 1.39%. Analysis with ICP-AES after dissolution with *aqua regia* resulted in a median content of 60 mg kg<sup>-1</sup>, and a range between 7 mg kg<sup>-1</sup> and 11400 mg kg<sup>-1</sup> (1.14%), pointing to an almost complete extraction.

Low Zn values in stream sediment (<45 mg kg<sup>-1</sup>) occur over central Finland, southern Sweden, northern Norway, south-central Norway, the Baltic states, most of the northern European plain (not in western Germany), the Netherlands, the whole of eastern Iberia, south-west France, east-central France and north-west Switzerland, north-easternmost Italy, central Austria and adjacent Germany; central Hungary, part of central Italy; western Greece and Crete.

High Zn values in stream sediment (>109 mg kg<sup>-1</sup>) occur in southern Finland, northern Sweden (the mineralised Skellefte district), the central Pyrenees, and a point anomaly in northern Italy. The highest point stream sediment Zn anomaly is in the old mining district of southern Sardinia with 1.38% Zn, 5758 mg kg<sup>-1</sup> Pb, 5000 mg kg<sup>-1</sup> Ba, 43 mg kg<sup>-1</sup> Cd, 13.5 mg kg<sup>-1</sup> Hg, 3.5 mg kg<sup>-1</sup> Ag, 6 mg kg<sup>-1</sup> Sb, and also elevated values for *aqua regia* extractable Zn, Pb, Ba. A point stream sediment anomaly in Attica in Greece has 1.0% Zn, 1484 mg kg<sup>-1</sup> Pb, 220 mg kg<sup>-1</sup> Cu, 170 mg kg<sup>-1</sup> Cr, 104 mg kg<sup>-1</sup> Ni, 92 mg kg<sup>-1</sup> As, 23 mg kg<sup>-1</sup> Sn, 15.8 mg kg<sup>-1</sup> Cd, 8.3

mg kg<sup>-1</sup> Sb, 7.9 mg kg<sup>-1</sup> Tl, and 2.7 mg kg<sup>-1</sup> Ag; this sample also has 31% CaO and occurs in an area with no known mineralisation. Mineralisation-related stream sediment Zn anomalies occur also in the Czech Republic and Germany (Mansfeld district), Poland and Slovakia, the Pennines in England, Wales, the German-Belgian border area, and the Iberian Pyrite Belt of southern Portugal and Spain (Tharsis Cu-Zn-Pb-pyrite and Rio Tinot Cu-Zn-Pb-Au-pyrite massive sulphide deposits). The strongest stream sediment Zn anomalies are related to mineralisation or mining pollution; generally, they show an association of several metals. Lithologically high Zn stream sediment values are present in northern Ireland (Antrim plateau basalt). In Brittany, and probably also in central Britain, Zn enrichment is most likely the result of agricultural pollution through liquid manure spreading (no Pb anomaly), but the point anomaly in south Brittany lies near a stratabound volcanic-hosted massive sulphides mineralisation.

Zinc in stream sediment shows a strong correlation with Cd (0.69), a good correlation with Mn, Fe, V, Co, Cu, Ga and Pb, and a weak correlation with As, Sb, Li, Ba, Al, P and Ti. The association with Mn, Fe, V and Co in the secondary environment is attributed to co-precipitation, whereas the association with Cd, Pb, Cu, As and Sb can be explained by mineralisation, mining and metallurgical contamination.

### Zn in floodplain sediment

Total Zn in floodplain sediment, determined by XRF, varies from 6 to 4911 mg kg<sup>-1</sup>, with a median of 65 mg kg<sup>-1</sup>, and by *aqua regia* extraction ranges from 7 to 2832 mg kg<sup>-1</sup> with a median of 56.0 mg kg<sup>-1</sup>, which indicates that on average 80% of Zn has been extracted by *aqua regia*. The spatial distribution of Zn values in

floodplain sediment, determined by the two analytical methods, is very similar.

Low Zn values in floodplain sediment (<42 mg kg<sup>-1</sup>) are found mainly in northern and southern Europe. They cover most of Finland, northern Sweden and Norway on gneiss, leptitic gneiss and granite of Precambrian age; central and

southern Sweden and parts of south Norway on Precambrian gneiss and granite, and in Norway also on mostly Caledonian metamorphic rocks, and northern Scotland on schist, gneiss and sandstone. Low Zn values are also found on the glacial drift extending from north-east Germany, over most of Poland, Lithuania and Latvia. In the south, they cover large parts of central and eastern Spain on mostly clastic, partly carbonate and also crystalline rocks; the Garonne estuary on fluvial deposits; the molasse basin of central-north Austria, and southern Italy.

High total Zn values in floodplain sediment ( $>100 \text{ mg kg}^{-1}$ ) occur roughly in a NW-SE oriented belt extending from eastern Ireland to Southern Uplands of Scotland and much of England, central and northern France, eastern part of Belgium across to central Germany, the Czech Republic, southern Poland, Slovakia, Hungary, and Croatia. In this area there are many Pb-Zn deposits (*e.g.*, Ireland: Navan Pb-Zn, Lisheen Zn-Pb; Scotland: Leadhills Pb-Zn-Ag; Wales: Halkyn-Minera Pb-Zn, Shelve Pb-Zn-Ba, Cardigan-Montgomery Pb-Zn; England: Alston-Greenhow Pb-F-Zn-Ba, Derbyshire Pb-Zn-Ba-F; Shropshire Pb-Zn; Mendips Pb-Zn-Ba; France: Porte-aux-Moines Zn-Cu-Pb, Pontpean Pb-Zn, Rouez Zn-Pb; Massif Central: Chessy Cu-Zn-Ba-Ag, Largentiere Pb-Ag-Zn, Les Malines Zn-Pb; Germany: Meggen Zn-Pb-Ba, Rammelsberg Zn-Pb-Ba-Cu-Ag, Bad Grund Zn-Pb-Ag; the Czech Republic: Příbram Ag-U-Pb-Zn, Kutná Hora Ag-Pb-Zn, Zlaté Hory Au-Cu-Pb-Zn; southern Poland: Silesia-Kraków Cd-Zn-Pb; Slovakia: Banská Štiavnica Pb-Zn-Cu-Au-Ag, Zlata Bana Zn-Pb; Hungary: Recsk Cu-Zn; Slovenia: Mežica Pb-Zn (De Vos *et al.* 2005). The elevated floodplain sediment Zn values in Croatia are related to industrial pollution due to coal combustion.

In southern Spain high total Zn values in floodplain sediment are located in the Iberian Pyrite Belt and the Castuera and Los Pedroches mineralised districts in the Sierra Morena (Linares Pb-Zn-Ag, La Carolina Pb-Zn and Horcajo Pb-Ag deposits); in south Portugal, there may be a relation with volcanosedimentary Zn mineralisation, and in north Portugal with sulphides in vein mineralisation and also anthropogenic influence; in northern Spain, in the

eastern part of the Cantabrian Mountains, south of Bilbao, the anomalous Zn values in floodplain sediment are accompanied by high Cd, S, Pb and Cu (Peñas de Aya district with Pb-F-Zn veins, near Cinco Villas). High total Zn values occurring in the Po River ( $811 \text{ mg kg}^{-1}$ ) are possibly associated with the Gorno Pb-Zn-Ag-F deposit. The moderately high Zn value ( $198 \text{ mg kg}^{-1}$ ) in south Sardinia appears to be related to the Gena Ureu Pb-Zn-Ag and Silius F-Pb-Ba deposits. Minor enhanced Zn values in floodplain sediment occurring in south-west Finland and in the Stockholm region of Sweden are associated with gneiss, granite and base metal mineralization (*e.g.*, Orijärvi Cu-Zn-Pb deposit in Finland; Saxberget Zn-Cu-Pb deposit in Sweden).

Point total Zn anomalies in floodplain sediment occur in the Lavrion mining area in Greece ( $4911 \text{ mg kg}^{-1}$ ), in the Vesdre basin in Belgium ( $3643 \text{ mg kg}^{-1}$ ) due to metallurgical pollution, in the French Pyrenees ( $1478 \text{ mg kg}^{-1}$ ) ascribed to the Pierrefitte Zn-Pb deposit (De Vos *et al.* 2005). In Slovakia the high total Zn value ( $1764 \text{ mg kg}^{-1}$ ) is possibly related to the Zn-Pb deposit and smelter of Banská Štiavnica. There are two point Zn anomalous values in Poland, one on the Oder River near Lubin ( $636 \text{ mg kg}^{-1}$ ) possibly caused by the mining pollution of the Legnica-Głogów Cu-Ag deposit, and the second one on the Gwda River near Piła ( $1251 \text{ mg kg}^{-1}$ ) most likely related to anthropogenic pollution; in north-east England the high Zn values ( $1221$  &  $915 \text{ mg kg}^{-1}$ ) are caused by mining in the Northumberland mineralised area; in east Germany the high total Zn anomalous value ( $869 \text{ mg kg}^{-1}$ ) is associated with the mineralisation from the Erzgebirge (*e.g.*, Freiberg Pb-Zn).

Zinc in floodplain sediment shows a strong positive correlation with Pb (0.71) and Cd (0.71), a good correlation with Cu, and a weak correlation with As, Hg, Ba and  $\text{P}_2\text{O}_5$ . This correlation pattern points to mineralisation, possible related contamination by mining and smelting, and other human activities.

In conclusion, the patterns of high Zn values in floodplain sediment map mineralised areas, and the pollution caused by mining and metallurgical processing, urban and other polluting anthropogenic activities.

### Zn comparison between sample media

In general, there are some broad similarities between all solid sample media, although there are a number of significant differences. In stream and floodplain sediments, the northern Iberian Peninsula is depleted in Zn, although it is enhanced in the southern Iberian Pyrite Belt. In stream sediment and, to a lesser extent, floodplain sediment, Britain and Ireland have higher Zn compared to soil. In a belt extending from Belgium through central Germany and southern Poland into the Czech Republic, Zn is higher in floodplain and stream sediments compared to topsoil and, especially, subsoil. In coastal southern Finland, Zn is much higher in sediments. Lower Zn is present in stream sediment throughout the coastal region of Croatia and Slovenia and the adjacent areas of western Austria (possibly explained by removal of fine-grained material from residual soil and karst). A boxplot comparing Zn variation in subsoils, topsoils, stream sediments and floodplain sediments is presented in Figure 54.

The pattern in humus Zn is most similar to that found in subsoil, and is most probably related to geogenic effects and reflects the mineral content. There are, however, some major unexplained differences in the humus Zn distribution, particularly throughout parts of Fennoscandia.

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

Patterns in stream water Zn are complex, and quite often opposite to those seen in all solid sample media. Zinc is strongly controlled by pH, and tends to lower concentrations in the alkaline environments of central Spain, Greece, Albania and throughout the Alps, and higher concentrations occur in the more acidic environments in southern Sweden, Denmark, the Baltic states, parts of northern Poland (also associated with high DOC) and Brittany. High Zn is also observed in southern Italy, Sardinia, Sicily and, especially, Switzerland.

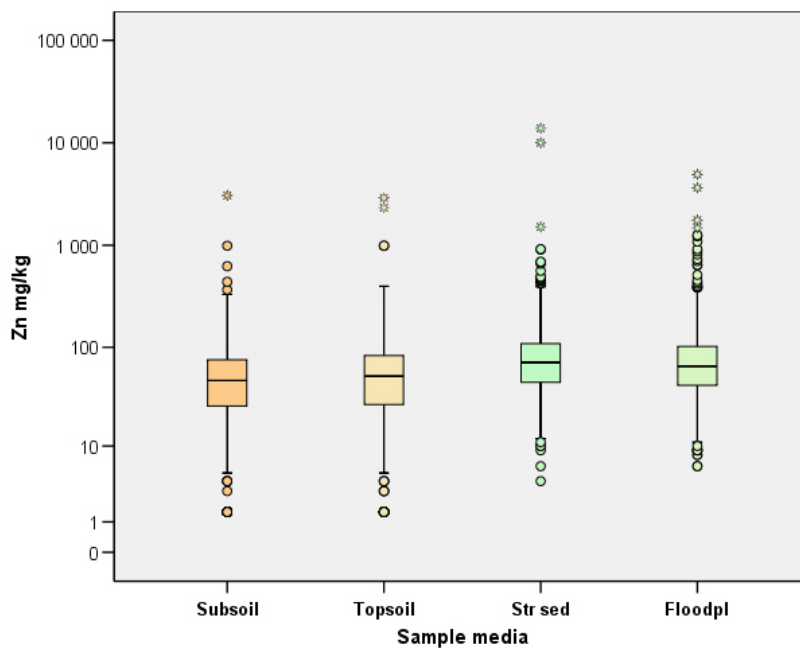


Figure 54. Boxplot comparison of Zn variation in subsoil, topsoil, stream sediment and floodplain sediment.