Introduction

Mercury is a heavy metal from group 12 of the periodic table, along with Zn and Cd. Gold and Tl are its period neighbours. The element has an atomic number of 80, an atomic mass of 201, two main oxidation states (+1 and +2) and seven stable isotopes (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg and ^{204}Hg) of which ^{202}Hg is the most abundant at 29.6% of the total mass, followed by ^{200}Hg and ^{199}Hg at 23.3% and 17.0% respectively. Mercury has a very different chemistry from its group and period neighbours, and is the only metal that is liquid at room temperature.

Mercury is a very rare chalcophile element, despite being known from antiquity, because of its occasional appearance as the distinctive native metal, and its relative ease of preparation from its main ore. Volcanic hot springs and sedimentary rocks altered by phreatic activity are the main sources of Hg mineralisation. The principal mineral is cinnabar HgS, along with the metacinnabar group of minerals in which variable amounts of Zn and Fe substitute for Hg, and Se substitutes for S. Other primary Hg minerals, include native mercury, corderoite $Hg_3S_2Cl_2$ and livingstonite $HgSb_4S_8$. Secondary Hg minerals, include schuetteite $Hg_3(SO_4)O_2$ and calomel Hg_2Cl_2. Mercury occurs also as a trace constituent in some sulphides such as tetrahedrite $Cu_3SbS_{3.25}$ and sphalerite ZnS.

The large size of the nominal Hg^{2+} ion, together with its low degree of ionic character, precludes its incorporation into many rock-forming silicate minerals. Igneous rocks, basalt and gabbro have generally much lower Hg contents (typically 10 µg kg^{-1}) than granite (average 80 µg kg^{-1}). Much higher Hg levels (up to 1500 µg kg^{-1}) have been found in eclogite and peridotite in inclusions in kimberlite pipes, suggesting that the deep crust and upper mantle may be considerably enriched in Hg compared to the upper crustal rocks. In sedimentary rocks, average Hg levels are higher in shale (400 µg kg^{-1}) than in carbonate rocks (40 µg kg^{-1}) and sandstone (30 µg kg^{-1}) (Wedepohl 1978). The relative enrichment of Hg in shale is even more marked in some organic-rich black shale, which may hold several mg kg^{-1} Hg bound to clay minerals, organic residues and sulphides. Coal shows very variable Hg levels, from <10 µg kg^{-1} to >1000

µg kg^{-1}, and some very high levels, up to 30 mg kg^{-1}, have been recorded in crude oils (Hutchinson and Meema 1987). Its average content in crustal rocks is probably less than 80 µg kg^{-1} (Greenwood and Earnshaw 1984), although there is considerable disagreement on the actual value (Wedepohl 1978).

Mercury is used in geochemical prospecting as a pathfinder element for its deposits, and also for Au, Ag, Sb and massive sulphide mineralisation. High Hg levels occur in rocks and soil near fault zones.

The behaviour of Hg in soil is highly dependent on its form, which is a function of several parameters including its initial concentration in soil solution, the presence of other ions, such as Cl, organic complex formation and precipitation. The presence of an excess of Cl$^-$ ions in soil appears to decrease the sorption of Hg$^+$ onto mineral particles, including Mn oxides, and organic matter because highly stable Hg-Cl complexes are rather poorly sorbed (Kabata-Pendias 2001). The sorption of Hg by clay in soil seems to be very limited, and to vary slightly with pH, the highest being at pH values from 4 to 5. However, in acid gley soil, the formation of HgS, and even of metallic Hg may occur. The accumulation of Hg in soil is, therefore, controlled by organic complexes and rainfall. Thus, the mobility of Hg requires dissolution processes, as well as biological and chemical degradation of organometallic compounds (Kabata-Pendias 2001). The transformation of organomercury compounds, especially the methylation of elemental Hg, plays the most important role in the Hg-cycle in the environment. Normal soil typically contains 20-150 µg kg^{-1} Hg (Mihaljevic 1999a), and surface soil values do not tend to exceed 400 µg kg^{-1} (Kabata-Pendias 2001). The accumulation of Hg is related mainly to the levels of organic C and S in soil, and higher concentrations occur in surface soil than subsoil; organic soil has a higher Hg content than mineral soil, which is due to the binding capacity of raw humus. In acid environments, Hg bound to organic matter may be leached in a form bound to organic compounds, whereas in neutral and alkaline soil, it is leached out in an inorganic active fraction. The amount of mobilised Hg

decreases at pH<3 and at pH>12, due to the extremely high buffering capacity of humus in both acidic and alkaline environments (Kabata-Pendias 2001).

Mercury occurs in natural water in several forms including elemental Hg (Hg^0), which is rare in unpolluted waters, ionic Hg (Hg^+ and Hg^{2+}) and methylated Hg (CH_3Hg^+, CH_3Hg). There is increasing evidence that natural organic materials form strong complexes with mercury, via sulphidic functional groups, which influence the concentration, speciation and subsequent bioaccessibility of mercury in the aquatic environment (Ravichandran 2004). Background levels of Hg in surface water are usually very low, typically <0.1 µg l^{-1}. Mercury minerals, such as cinnabar and metacinnabar, are insoluble under normal conditions, and metallic mercury will not react with stream water directly (Brookins 1988). However, this apparently inert behaviour can be of concern, since spills of metallic mercury may persist within the stream sediment for many years, and may still be mobilised in small, but significant quantities, by microbial methylation under favourable conditions.

Most mercury is derived from natural sources, although Hg concentrations in the environment are increasing as a result of human activity, mainly through fossil fuel combustion, mining, smelting and solid waste combustion. Nriagu and Pacyna (1988) estimated that 11,000 tons of Hg per year from anthropogenic sources enter the biosphere. The metal is widely used in the manufacture of thermometers, barometers, diffusion pumps, mercury-vapour lamps, advertising signs, mercury switches and other electronic apparatus. Other uses include pesticides, fungicides, dental preparations, anti-fouling paint, batteries and catalysts.

Mercury is highly toxic to most forms of life. Metallic Hg is relatively inert and not readily taken up by organisms, but it is volatile and its vapour is toxic. Mercuric salts are also highly toxic, but of even greater concern is the ability of micro-organisms to methylate Hg and its salts to create fat-soluble species, such as methylmercury (CH_3Hg^+) and dimethylmercury [$(CH_3)_2Hg$]. These compounds are readily taken up by aquatic organisms, and may be concentrated by higher members in the food web, such as fish and shellfish, to several mg kg^{-1}. Chronic exposure to dietary methylmercury and Hg vapour leads to the typical neurotoxic symptoms associated with Hg poisoning, including disruption of the nervous system, damage to brain functions, DNA and chromosomal damage and negative reproductive effects, such as sperm damage, birth defects and miscarriages.

Table 35 compares the median concentrations of Hg in the FOREGS samples and in some reference datasets.

Table 35. Median concentrations of Hg in the FOREGS samples and in some reference data sets.

Mercury (Hg)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg^{-1}
Crust[1]	Upper continental	n.a.	n.a.	Total	0.05
Subsoil	**FOREGS**	**779**	**<2.0**	**Total (CVAAS)**	**0.022**
Topsoil	**FOREGS**	**833**	**<2.0**	**Total (CVAAS)**	**0.037**
Soil[2]	World	n.a.	n.a	Total	0.05
Humus	**FOREGS**	**377**	**<2.0**	**Total (CVAAS)**	**0.202**
Humus[3]	Barents region	1357	<2	Total (CVAAS)	0.18
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (CVAAS)**	**0.038**
Floodplain sediment	**FOREGS**	**696**	**<2.0**	**Total (CVAAS)**	**0.045**
Stream sediment[4]	Canada	72 163	<0.18	Total (CVAAS)	0.040

[1]Rudnick & Gao 2004, [2]Koljonen 1992, [3]Salminen *et al.* 2004, [4]Garret 2006.

The median Hg content is 0.022 mg kg^{-1} in subsoil and 0.037 mg kg^{-1} in topsoil, with a range from 0.002 to 0.93 mg kg^{-1} in subsoil and 0.005 to 1.35 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 1.660.

A notable feature in both subsoil and topsoil is the low Hg values (<0.011 mg kg^{-1}) in Poland, Denmark and the Baltic states due to the glacial drift, and throughout the metamorphic basement and till covered Fennoscandia. Low values are also found throughout parts of central and eastern Spain and north-eastern Greece with granite, gneiss, schist and sedimentary rocks.

The highest mercury values in subsoil are point anomalies, which occur in southern Spain (caused by Hg mineralisation in the Almadén district, stratabound Hg in Permo-Triassic limestone near Granada, and by Zn-Pb mineralisation in the Baetic Range), the western Pyrenees (related to Zn-Pb veins), Asturias (Hg mineralisation hosted by Carboniferous limestone), northern Italy in Val Lodrino, and in the eastern-central part of Germany. High values (>0.041 mg kg^{-1}) also occur in Tuscany (sulphide mineralisation), the Roman alkaline Province (including the Monte Amiata Hg deposit), northern Italy (possible sulphide mineralisation), in karstic soil of Slovenia and Croatia, Lavrion in Greece (polymetallic mineralisation), western Austria, southern and western Germany, eastern Slovakia, Cornwall in south-west England, Ireland, and western Scotland.

Figure 21. Scattergram of Hg and TOC concentrations in topsoils.

In topsoil, there is a striking continuous pattern with high Hg values (>0.07 mg kg^{-1}) extending from the Netherlands down through the western part of Germany, western Austria, central Switzerland and into northern Italy, western Slovenia and Croatia, and central Italy with the Roman Alkaline Province. This high Hg area probably points to anthropogenic contamination. However, as Hg is adsorbed on organic matter, there could be a relation to organic matter content of soil in central Europe (very often in western Germany, agricultural soil was sampled). The scattergram Hg-TOC in topsoil does not, however, reveal a clear tendency (Figure 21). In Spain,

Britain, Ireland and the Erzgebirge, the Hg pattern in topsoils and subsoils is rather similar with high values in mineralised areas. Several point Hg anomalies occur in southern Italy (including the Roman, Neapolitan and Mount Vulture Alkaline Provinces), near Cagliari in Sardinia (mining district), in Calabria (sulphide mineralisation), and in western Slovakia (fossil fuel combustion, metallurgical works and application of soil chemicals), and a point anomaly in the Spišsko-gemerské Rudohorie ore district in eastern Slovakia. It is noted that the topsoil does not show an anomaly in Attica, Greece.
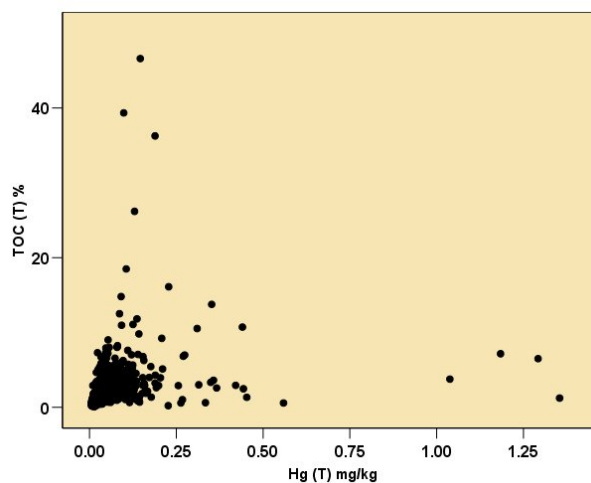

Figure 21. Scattergram of Hg and TOC concentrations in topsoils.

The average ratio topsoil/subsoil is 1.66 for Hg, the highest of all the analysed elements (Map 7). This probably points to major anthropogenic Hg contamination in Europe, but a natural affinity of Hg to organic matter (more abundant in topsoil) may be partly responsible.

In subsoil, Hg shows a good correlation (>0.4) with TOC, and a weak correlation (>0.3) with Co, V, Ti, Fe, In, I, Nb, Pb, Zn, Sb and Te.

In topsoil, Hg has a good correlation with Pb, Sb, TOC, and a weak correlation with Ce, La, Gd, Nd, Pr, Sm, Th, U, Cd, Zn and S.
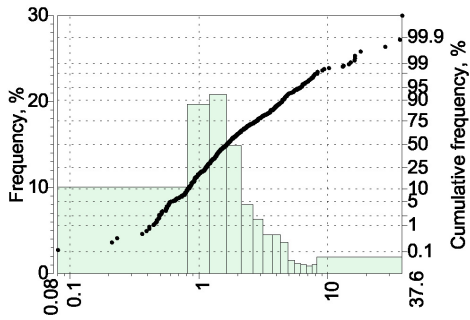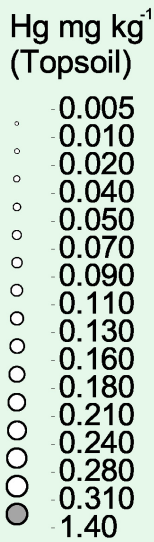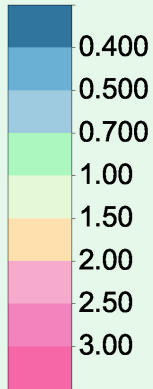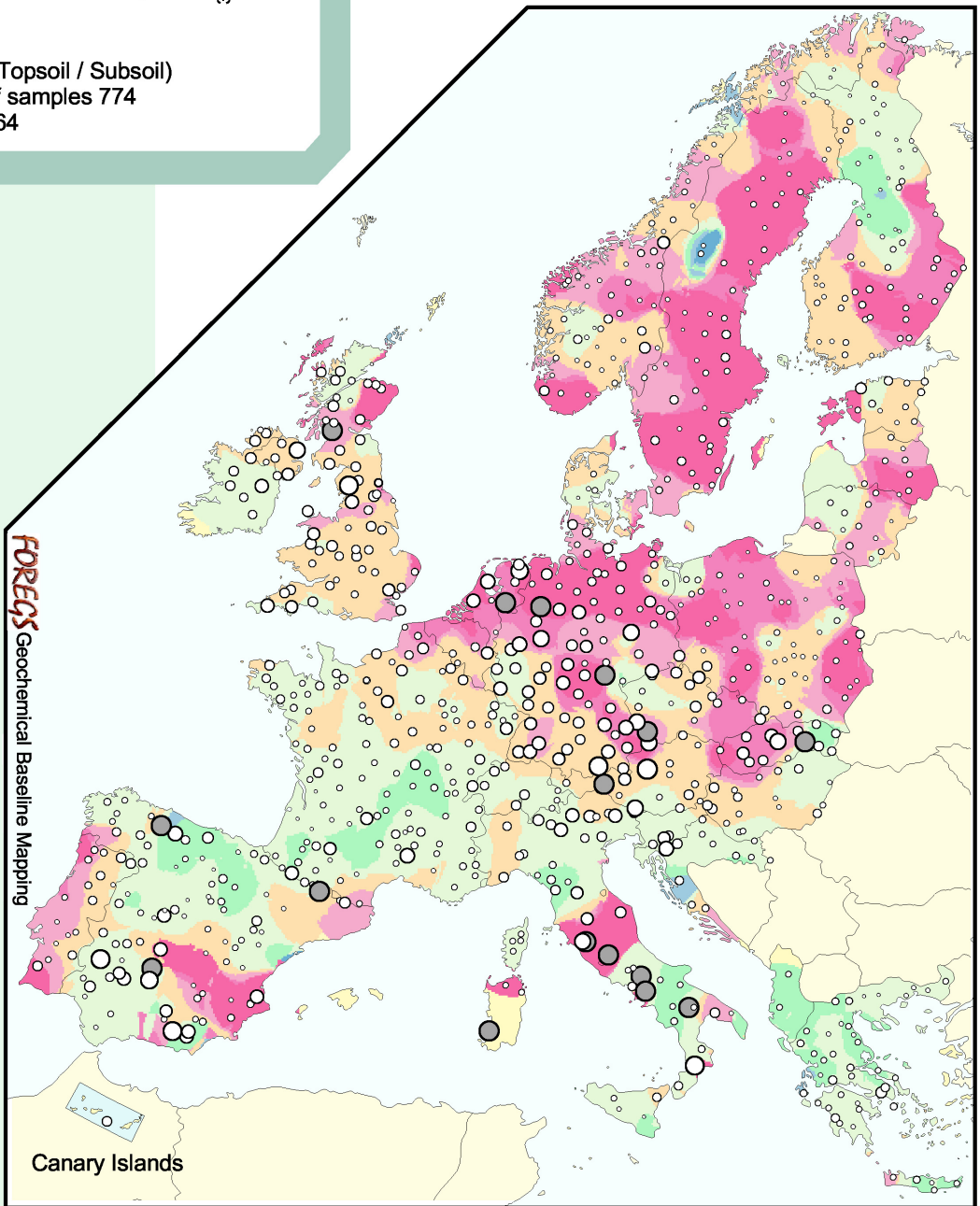
Map 7. Ratio of Hg in topsoil vs subsoil.

Hg in humus

The median Hg content in humus is 0.200 mg kg^{-1}, and the range varies from 0.020 to 3.75 mg kg^{-1}.

The Hg distribution map shows low values in humus (< 0.15 mg kg^{-1}) occurring mainly in north-eastern Germany, parts of France, northern Ireland and northern Scotland, central-western Norway, Hungary and northern Croatia.

High Hg values in humus (>0.27 mg kg^{-1}) occur mainly throughout most of central England and southern Scotland, north-western and south-eastern Germany, Austria and adjacent north-eastern Italy and southern Czech Republic, south-western Poland and southern Sweden. Isolated anomalies occur in eastern Belgium (industrialised Vesdre basin) and southern Switzerland.

This pattern of Hg in humus is unrelated to geology. There is a noticeable similarity with the Hg pattern in topsoil, especially in Germany. This points to pollution, in this case of possible atmospheric origin. As Hg is released in gaseous form through a number of industrial processes, among them coal combustion, it is redeposited in the wider environment of industrialised areas, and forms complexes with organic molecules in humus. Agricultural input through mineral fertilisers and pesticides is also a possible source.

The only significant correlation of Hg in humus is a very weak correlation with Pb (0.25). Contamination from anthropogenic airborne sources is the probable link between Hg and Pb.

Hg in stream sediment

The median Hg content in stream sediment is 0.040 mg kg^{-1}, with a range from 0.003 to 13.6 mg kg^{-1}.

Low Hg values in stream sediment (<0.02 mg kg^{-1}) are present in Finland, a small part of central Norway, parts of the Baltic States and northern Poland, the central Alps, south-west France, east-central Spain, Calabria and Sicily, and most of Greece with calcareous and mafic-ultramafic rocks.

High Hg values in stream sediment (>0.07 mg kg^{-1}) are found throughout southern Spain (including the well-known Almadén Hg district, but also related to Zn-Pb veins in the Pedroches, Linares and Valle de Alcudia districts, stratabound Pb-Zn-F ores in the Baetic Cordillera, and stratabound Hg mineralisations in carbonate Permo-Triassic rocks in the Alpujárrides Unit of the Baetic Cordillera), in north-west Spain related to diverse Zn-Pb mineralisation, in southern Sardinia (polymetallic mineralisation), Corsica, south-western and southern Italy (alkaline volcanic district), Lorraine in France, south-west England (Cornwall mineralisation), south-east England (possible pollution), the northern part of the Czech Republic with adjacent areas in Germany and Poland, eastern Slovakia, Slovenia, and point anomalies in northern Spain, and in Lavrion in Greece. The anomalous Hg value in eastern Slovakia is related to mineralisation where Hg ore is linked to neogenic andesite. High values in the Czech Republic and adjacent Poland are explained by contamination caused by atmospheric deposits from the coal-fired power plants in the area.

There is one real outlier in stream sediment, with 13.5 mg kg^{-1} Hg, in the old mining district of Iglesiente-Sulcis in southern Sardinia; this sample is also the richest outlier for Zn, Pb, Cd and Ba, and anomalous for Ag, Sb, S, Tl and Mn (see Zn description). The second richest sample is in the silver mining district of Lavrion, Greece, and contains 1.28 mg kg^{-1} Hg (a factor 10 below the richest sample), and also anomalous amounts of Zn, Pb, Cd, Ag, As, Sb, Cu, Cr, Ni, Mn, S, Sn and Tl. Owing to the widely spaced random distribution of sampling sites, the highly anomalous and wide mercury signature of the Idrija mercury mine in Slovenia was missed.

After removing the outlier, according to the procedure followed for all the elements (see introduction), mercury in stream sediment shows only a very weak correlation with Sb (0.25) and Zn (0.22).

Hg in floodplain sediment

The total Hg distribution in floodplain sediment varies from 0.002 to 4.39 mg kg^{-1}, with a median of 0.045 mg kg^{-1}.

Low total Hg values in floodplain sediment (<0.02 mg kg^{-1}) occur over the crystalline rocks of most of Finland, Norway, glacial drift covered central Poland; low Hg values also are found in north-east Scotland, central and eastern Spain (Iberian Central Meseta, Ebro basin and Iberian Cordillera), southern Italy, Sicily and northern Sardinia, and parts of Greece.

High Hg values in floodplain sediment (>0.09 mg kg^{-1}) occur in river basins draining mineralised areas of Scotland (*e.g.,* Leadhills Pb-Zn) and central Ireland (Gortdrum Hg deposit); mineralised and industrialised England (*e.g.,* Alston-Greenhow Pb-Zn, Greenside Pb-Zn, Pennine ore field, English Midlands); in France there is a belt covering the lower Paris Basin to Normandy, Poitou to the coastal part of the Aquitaine Basin, where some of the anomalies are due to mineralisation (*e.g.,* Pontpean Pb-Zn, Salsigne Au-As), and others to possible anthropogenic contamination; northern Spain (Hg mineralisations in the Cantabrian Mountains in Asturias, Zn-Pb-Cu veins in Sierra de la Demanda); southern Spain (related to Pb-Zn veins in the Valle de Alcudia and Linares districts, somewhat weaker in the Guadiana River basin with the Almadén Hg deposit, and in the Iberian Pyrite Belt with the Rio Tinto pyrite-Cu-Zn and Tharsis pyrite-Cu deposits); southern Portugal (Sado River); Italy (northern Italy Gorno Pb-Zn-Ag deposit; Roman Alkaline Province with Monte Amiata (Hg); Sardinia with Monteponi Zn-Pb-pyrite and Silius F-Pb-Ba deposits); a north-west to south-east trending belt with high Hg values extends from Belgium (polluted Vesdre basin), through most of Germany, the Czech Republic, Slovakia to Hungary, including mineralised areas (*e.g.,* Harz Mountains; Erzgebirge; Bohemian Massif; eastern Slovakia Zlata Bana Zn-Pb-Ag-Au-Hg), but part may be ascribed to anthropogenic activities (De Vos *et al.* 2005). The enrichment in the Czech Republic is attributed to atmospheric deposits from the coal-fired power plants in the area.

Highly anomalous Hg values in floodplain sediment are found in the Roman Alkaline Province (4.4 mg kg^{-1}), in Slovakia related to the Banska Stiavnica (3.6 mg kg^{-1}) and Rudnamy (2.2 mg kg^{-1}) mineralisation; in Spain (1.9 mg kg^{-1}) is associated with the Linares Pb-Zn mineralisation, in central Macedonia of Greece is connected with Au mineralisation (1.9 mg kg^{-1}), and in north-western France (1.9 mg kg^{-1}) occurs in the a mineralised shear zone.

Mercury in floodplain sediment shows a good correlation (>0.4) with Cu and Cd, and a weak correlation with Zn and P$_2$O$_5$. This association points to mineralisation (Cu, Zn, Cd) and possible anthropogenic influence (phosphate fertilisers).

In conclusion, the Hg distribution in floodplain sediment shows the geochemical differences of the geological substratum and mineralised areas quite well, and also pollution from mining and other anthropogenic activities, *e.g.*, atmospheric deposits from coal-fired power stations in Czech Republic. The possibility of Hg pollution by phosphate fertilisers warrants further investigation.

Hg comparison between sample media

There are broad similarities, but also significant differences, between the different solid sample media. A boxplot comparing Hg variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 22.

Topsoil is enriched by an average factor of 1.673 relative to subsoils, although patterns in distribution between topsoil and subsoil are broadly the same. The enhancement is particularly noticeable throughout central and southern Fennoscandia, and most parts of central and northern mainland Europe. In mainland Europe the enhancement is probably related to anthropogenic influences (see map of difference between Hg in topsoil and subsoil), but in Fennoscandia the major cause of higher Hg in topsoil may be related to its preferential association with organic material (see map of ratio of Hg in topsoil and subsoil). There is close agreement between the general distribution patterns of Hg and organic carbon content of soil (especially topsoil) throughout all of Europe,
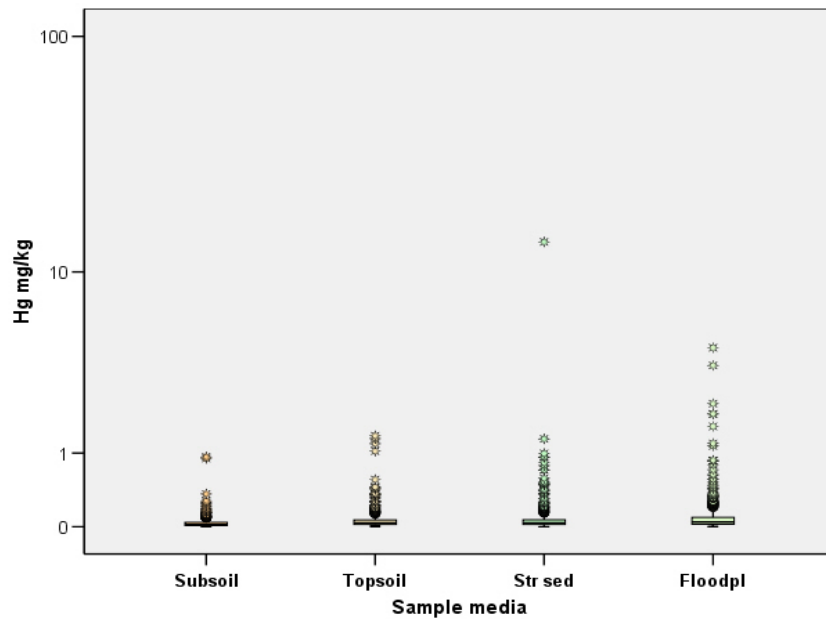
Figure 22. Boxplot comparison of Hg variation in subsoil, topsoil,
stream sediment and floodplain sediment.

except parts of the west and central Iberian Peninsula. Patterns in floodplain sediment are broadly similar to those seen in the soil samples, except for higher Hg content in north and western France and throughout parts of south-east England. Mercury concentrations in stream sediment are much lower in central mainland Europe and Ireland compared to other solid sample media. This is possibly related to the fact that Hg in soil is mainly associated with organic complexes that are attached to the fine clay fraction. This clay fraction is adsorbed on clay in the finer-grained floodplain sediment, but is not

subsequently deposited in the relatively coarser grain stream sediment. The Hg distribution in humus most closely resembles the pattern of distribution in floodplain sediment and topsoil, although Hg in humus is generally higher throughout Fennoscandia.

There is no map of stream water distribution for Hg because of problems with contamination of samples during collection and preservation.

There is a close similarity in the distribution patterns of high Cd, Hg and Zn levels in the floodplain sediment of central Europe and Britain, suggesting a significant anthropogenic influence.

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