Introduction

Copper is a member of the first row transition series of elements, which consists of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, and belongs to group 11 of the periodic table, along with Ag and Au. The element has an atomic number of 29, an atomic mass of 63, two main oxidation states (+1 and +2) and two naturally occurring isotopes (^{63}Cu and ^{65}Cu), with abundances of 69.17% and 30.83% respectively. In spite of a similarity in electronic structure, there are few resemblances between the chemistry of the three elements in group 11, although certain complexes of Cu^{2+} and Ag^{2+} are isomorphous (Cotton and Wilkinson 1972).

Copper is a chalcophile element forming several minerals, including chalcopyrite $CuFeS_2$, covellite CuS, and malachite $Cu_2CO_3(OH)_2$, but is more widely dispersed at trace levels in mica (biotite), pyroxene and amphibole, thus showing a greater affinity for mafic than for felsic igneous rocks. Copper can occur in its metallic form in nature (*i.e.,* native copper), and is one of the seven metals known in antiquity. Copper may be redistributed during low-grade metamorphism and metasomatism (Senior and Leake 1978), but its mobility is more restricted at higher metamorphic grades (Nicollet and Andriambololona 1980). In common with other chalcophile elements, Cu is strongly concentrated into sulphide minerals during hydrothermal mineralisation.

Average Cu values for silicate minerals are given by Ure and Berrow (1982) as 115 mg kg^{-1} for olivine, 120 mg kg^{-1} for pyroxene, 78 mg kg^{-1} for amphibole, 86 mg kg^{-1} for biotite and 62 mg kg^{-1} for plagioclase. Chalcopyrite is a common accessory mineral and primary Cu carrier in mafic igneous rocks. Basalt and gabbro (40–60 mg kg^{-1}) and ultramafic rocks (40 mg kg^{-1}) typically contain more Cu than intermediate (*ca.* 20 mg kg^{-1}) and granitic (*ca.* 12 mg kg^{-1}) rocks (Wedepohl 1978). The crustal average for Cu is 68 mg kg^{-1} (Mielke 1979). In unmineralised sediments, Cu concentrations are principally determined by mafic detritus, secondary Fe and Mn oxides (Forbes *et al.* 1976), clay minerals (Heydemann 1959) and organic matter (Stevenson and Ardakani 1972). Fine-grained clastic rocks, particularly black shale, are typically enriched in

Cu (*ca.* 50 mg kg^{-1}) relative to quartzo-feldspathic and carbonate sediments (5–15 mg kg^{-1}). McLennan and Murray (1999) quote average values for river particulates and loess as 100 and 18 mg kg^{-1} Cu respectively.

Copper is used in geochemical prospecting as an indicator of all types of copper mineralisation and is an important pathfinder for many types of gold deposit. Elevated Cu values are, however, more likely to indicate the presence of mafic rocks, although Cr and Ni are less ambiguous indicators. In the search for ultramafic-hosted magmatic nickel deposits, elevated Cu values may enable the discrimination of Ni anomalies associated with sulphide from those derived from unmineralised ultramafic rocks.

Copper is mobile under oxidising, acidic conditions, especially at pH values in the range 5.0 to 6.0. The more oxidised Cu^{2+} species predominates. The affinity of Cu for natural organic matter has been widely documented (Rashid 1974, Rippey 1982) and may explain the significant amounts of non-detrital Cu in stream water in areas of peaty drainage or high algal productivity. Copper, along with Ag and Pb, is often bound to the coarser sediment fraction, but since Cu is more soluble, it is often transported further downstream (Lottermoser *et al.* 1999). Co-precipitation of Cu and Zn occur in the presence of Fe hydrous oxides (Lottermoser *et al.* 1999).

Average Cu levels in soil vary from 13 to 24 mg kg^{-1} (Kabata-Pendias 2001). Copper normally accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources (Kabata-Pendias 2001). Copper ions are held very strongly by both inorganic and organic exchange sites. The processes controlling its fixation by soil constituents are: (a) adsorption, (b) occlusion, coprecipitation and substitution, (c) organic chelation and complexing and (d) microbial fixation. All soil minerals are capable of absorbing Cu ions from solution, and these properties depend on the surface charge of the adsorbents. The surface charge is strongly controlled by pH and, therefore, the adsorption of Cu ion species is a function of pH. This type of

Cu adsorption is considered to be the most important in soil with a large content of variable-charge minerals. Occlusion, coprecipitation, and substitution are involved in non-specific adsorption of Cu, *e.g.,* Al and Fe hydroxides, carbonates, phosphates and, to some extent, clay minerals, have a great affinity to bind part of the soil Cu in a nondiffusible form. The affinity of Cu to chelation and complexing by organic matter has already been mentioned; it suffices to note that humic and fulvic acids form relatively stable complexes when Cu is present in small amounts. Microbial fixation is a prominent process governing the binding of Cu in certain soil types. Although Cu is one of the least mobile heavy metals in soil, it is abundant as free and complexed ions in soil solutions of all soil types (Kabata-Pendias 2001).

Copper levels of around 10 μg l^{-1} are fairly typical in uncontaminated and natural water, although concentrations as high as a few hundred μg l^{-1} may be present in acid drainage from mines (Hem 1992).

Anthropogenic sources of copper include copper mining and smelting, the electrical industry, agriculture, sewage sludge and steel works. Copper compounds are widely used in agriculture and are a possible source of drainage anomalies.

Copper is an essential trace element for all organisms, and humans can tolerate levels up to 12 mg per day (WHO 1996), although the element can be toxic at extremely high levels. For example, Reimann and de Caritat (1998) report examples of kidney failure in small children resulting from drinking water from new copper pipes in low pH environments containing high concentrations of Cu up to about 1 mg l^{-1}.

Table 23 compares the median concentrations of Cu in the FOREGS samples and in some reference datasets.

Table 23. Median concentrations of Cu in the FOREGS samples and in some reference data sets.

Copper (Cu)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg^{-1}
Crust[1]	Upper continental	n.a.	n.a.	Total	28
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**13.9**
Subsoil	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**13.0**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**13.0**
Topsoil	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**12.0**
Soil[2]	World	n.a.	n.a	Total	25
Soil, C-horizon[3]	Barents region	1357	<2	*Aqua regia* (ICP-AES)	9.21
Humus	**FOREGS**	**367**	**<2.0**	**Total (ICP-MS)**	**7.90**
Humus[3]	Barents region	1357	<2	Total (HNO$_3$, ICP-MS)	7.88
Water	**FOREGS**	**808**	**Filtered <0.45 μm**		**0.88 (μg l^{-1})**
Water[4]	World	n.a.	n.a.		7 (μg l^{-1})
Water[3]	Barents region	1364	Filtered <0.45 μm		0.50 (μg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**17.0**
Stream sediment	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**14.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**17.0**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**16.0**
Stream sediment[5]	Canada	82 465	<0.18	*Aqua regia* (ICP-AES)	22

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

Cu in soil

The median total Cu content (ICP-MS analysis) is 13.9 mg kg^{-1} in subsoil and 13.0 mg kg^{-1} in topsoil, with a range from 0.86 to 125 mg kg^{-1} in subsoil and 0.81 to 256 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 0.967.

The subsoil map shows lowest Cu areas (<7.35 mg kg^{-1}) throughout the Quaternary plain of northern Central Europe, parts of southern Fennoscandia and the Baltic states, north-eastern Italy, central Hungary and central Portugal. The southern limit of the glacial drift area is well marked on the map.

High Cu values in subsoil (>22.2 mg kg^{-1}) are found in Galicia and adjacent north-western Spain (crystalline Iberian Massif including schist, amphibolite, and igneous intermediate to ultramafic rocks, with local Cu mineralisation), southern Spain in the Cádiz-Málaga area (clastic Triassic sediments with Cu-Fe mineralisation in olisthostromic units, and ultramafic rocks in Ronda and Ojén massifs), the western Pyrenees (Silurian black shale and mineralised veins), a crystalline area in France from Brittany to the Massif Central, the northern Apennines from Liguria to Tuscany, Corsica, the southern tip of Italy, all over Greece except Attica and Crete, where it is associated with mafic-ultramafic rocks, mineralisation, shale and schist, the Dalmatian coast, south-central Austria, north-eastern Slovakia, the Harz Mountains and Thuringia, south-west England, northern Wales, eastern and northern Ireland, western Norway near Bergen, an area near Narvik and in central Sweden. Isolated anomalies near Avila in central Spain are related to Cu-bearing veins in the Cordillera Central.

It is clear that the distribution of copper in subsoil is mainly related to regional and local geology, and to mineralisation. There are strong positive correlations (>0.6) with Fe, V and Sc and Co, reflecting the fact that intermediate to mafic igneous rocks contain more Cu. Good correlations (between 0.4 and 0.6) exist with Al$_2$O$_3$, Ga, In, Te, Ni, Cr, Mn, Zn, TiO$_2$ and some light REEs. Correlations in the same range with MnO and Co point to coprecipitation with (hydro)oxides in soil material. There is a weak negative correlation (-0.38) with SiO$_2$, pointing to natural Cu-enrichment in mafic and intermediate rocks, shale and clay, which are relatively poor in silica.

The Cu topsoil distribution map shows a somewhat different pattern, especially in Fennoscandia, where Cu content is generally very low in topsoils (one exception is near Bergen). This is probably a leaching effect in northern humid climates in combination with acid pH in water. In contrast, most of the Mediterranean topsoil is enriched in Cu; weathering in dry climates causes more precipitation of (hydro)oxides, sulphate and carbonate, and adsorption by Fe-Mn oxides. In Gran Canaria high Cu is related to basaltic rocks.

Topsoil is also vulnerable to anthropogenic contamination. In France, a north-west-south-east oriented Cu enriched belt from Brittany to Montagne Noire may indicate partly a natural contribution from amphibolite, but also pollution by agricultural sewage enriched in Cu (pig farm manure in Brittany) or the use of copper sulphate as a fungicide in fruit cultivation and vineyards. The latter practice may be widespread in Europe, and was confirmed in former Yugoslavia (Prohic *et al.* 1995).

The average ratio topsoil/subsoil for Cu is 0.97, but the correlation between topsoil and subsoil is only 0.666, a low figure expressing the contrasting behaviour of Cu in northern and southern Europe and regionally different anthropogenic influences (Map 5).

The correlation pattern of Cu with other elements in topsoil is similar to that for subsoil.

The median Cu content after *aqua regia* extraction (ICP-AES analysis) is 13 mg kg^{-1} in subsoil and 12 mg kg^{-1} in topsoil, with a range from <1 to 118 mg kg^{-1} in subsoil and from 1 to 239 mg kg^{-1} in topsoil. This means that nearly all Cu is extracted with *aqua regia*. The distribution pattern of extractable Cu is almost the same as the one for total Cu, showing some small differences for individual point values, *e.g.,* in Greece and southern Italy.
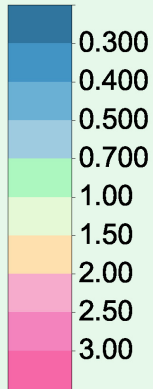
Copper Ratio Topsoil / Subsoil

Cu
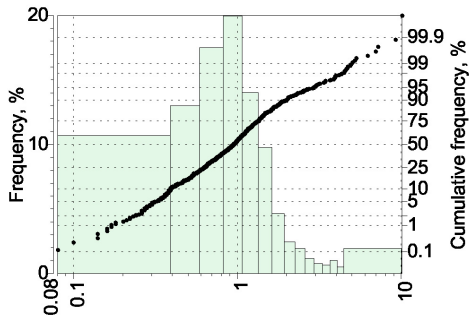
Cu (Ratio Topsoil / Subsoil)
Number of samples 777
Median 0.940

0   500   1000   Kilometers

0.300
0.400
0.500
0.700
1.00
1.50
2.00
2.50
3.00
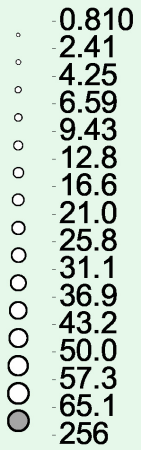
FORECS Geochemical Baseline Mapping

Cu mg kg^{-1}
(Topsoil)

0.810
2.41
4.25
6.59
9.43
12.8
16.6
21.0
25.8
31.1
36.9
43.2
50.0
57.3
65.1
256
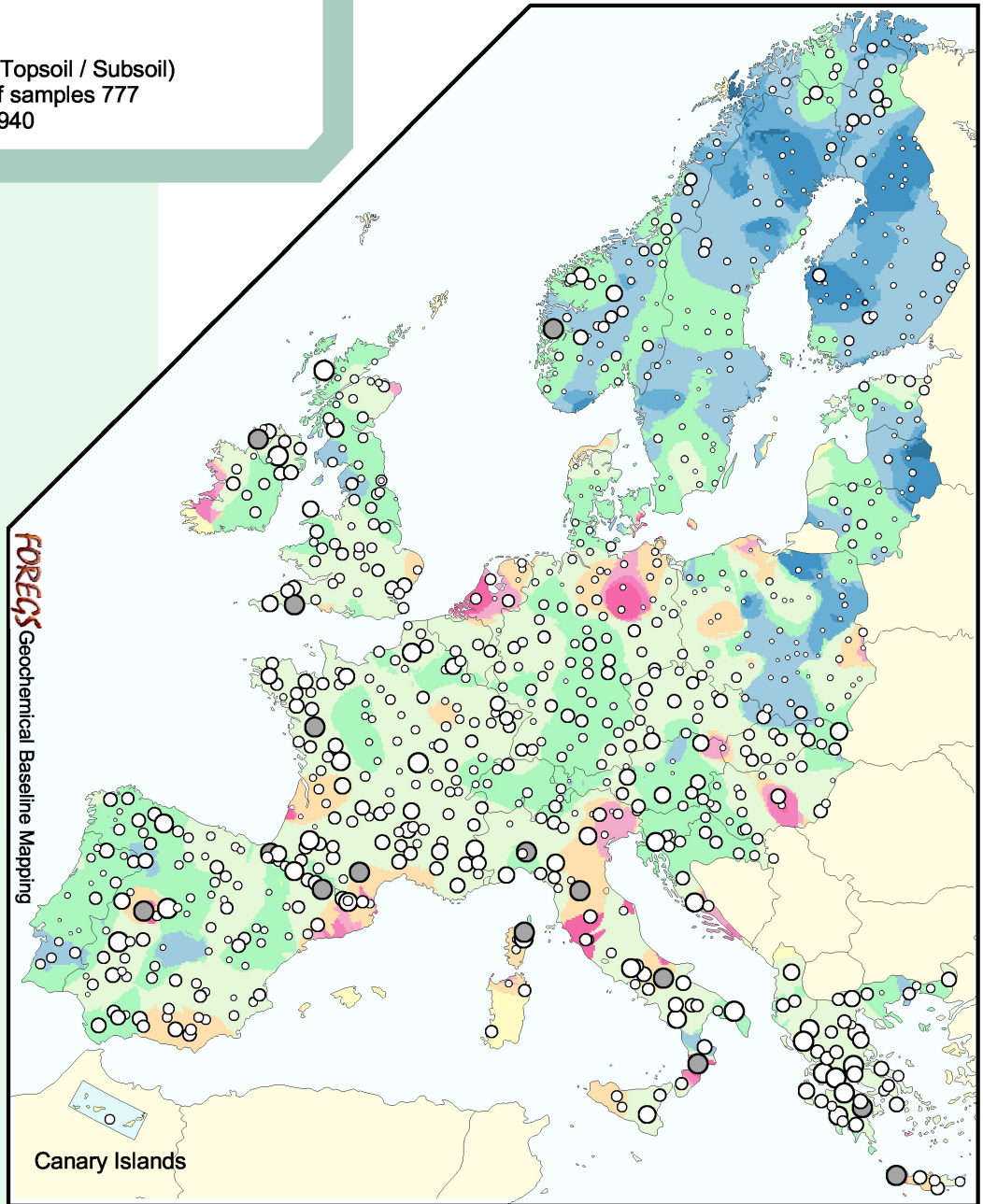
Canary Islands

Cu

Map 5. Ratio of Cu in topsoil vs subsoil.

Cu in humus

The median Cu content in humus is 7.90 mg kg^{-1}, with a range from <0.3 to 296 mg kg^{-1}.

The humus Cu distribution map shows low values (<5.30 mg kg^{-1}) are present in most of Sweden, Denmark, part of northern Germany and Poland, Scotland, north-eastern Ireland and western France.

High Cu values in humus (>15 mg kg^{-1}) are found in an arc from Belgium to central-eastern Germany, south-western Poland (Legnica-Głogów copper mining and smelting area), Czech Republic, Austria, northern Italy and one sample in Slovakia; also in central Britain, a large area in southern Norway and eastern Estonia. Isolated anomalies occur in northern Ireland (basalt).

The Cu distribution in humus is probably partly geogenic, and partly anthropogenic, with contamination present in some industrial and mining areas, through use of agricultural fertilisers and as a fungicide in fruit cultivation and vineyards. Airborne Cu deposition is reflected in moss samples in south-western Poland, Slovakia, the Netherlands and central Germany (Rühling and Steinnes 1998, Siewers et al. 2000).

Copper in humus has a weak but significant correlation with Pb (0.28) pointing to common contaminated sites. Further, Cu is very weakly correlated to Ga, Co and Ni (about 0.20), which possibly suggests a relation to the proportion of mineral soil contained in the humus sample.

Cu in stream water

Copper values in stream water range over two orders of magnitude, from 0.08 to 14.6 µg l^{-1}, with a median value of 0.88 µg l^{-1}.

Lowest Cu values in stream water (<0.38 µg l^{-1}) are found in northern Scotland and throughout most of Fennoscandia on both Precambrian and Caledonide terrains, in eastern Poland, throughout Spain in Variscan terrains, in north-eastern Italy and adjacent western Austria and southern Germany, in Albania and most of Greece on Alpine Orogen terrains.

Enhanced Cu concentrations in stream water (>1.97 µg l^{-1}) are found in parts of western, southern and eastern Finland, Denmark and the Netherlands, throughout south-east Ireland and eastern England, in parts of Brittany, areas of southern Spain on Variscan terrains (Cu-bearing Iberian Pyrite Belt with acid pH, and minor mineralisation in the Cádiz-Málaga area; Fe mineralisation near Alicante in Triassic sediments), and in southern Italy (De Vos *et al*. 2005). Very high values are found throughout Switzerland and adjacent areas in France and Germany; these samples were taken by the same field team and were probably contaminated during acidification by acid containing Cu, Pb and Zn. In western Finland, the enhanced Cu values are probably associated with clay-rich soil; in the east, they are possibly associated with black schist and sulphide deposits. The point anomaly in southern Sweden is close to an area of historic gold mines.

The Cu enhanced values of Brittany might have an anthropogenic source related to liquid manure from pigs and chicken farms. The highly anomalous Cu value in eastern Slovakia (9.88 µg.l^{-1}) is related to the mining and processing of metamorphic-hydrothermal vein mineralization in the Spišsko-gemerské rudohorie Mountains (mainly complex siderite-sulphide ores). Highly anomalous values in south-west Spain may be related to the Rio Tinto and Aznalcollar mineralised area of the Iberian Pyrite Belt.

The distribution of copper in stream water follows several models, each characterised by its typical speciation. In Major-ions high-mineralisation stream water it is transported in ionic form, in REEs high-DOC acid stream water probably on organic ligands, and the Heavy metals pattern is connected to weathering of Cu-containing ores and Cu pollution. There are similarities, but also major differences, between the Cu distribution in stream water and in the solid sample media. *For example*, much higher values are found in stream water in the Netherlands and Denmark (perhaps related to DOC) and Sicily and Sardinia; much lower values are found in stream water throughout Albania and Greece (perhaps related to higher pH) and north-eastern Italy and adjacent areas (again probably related to alkaline pH).

A more detailed description on the chemistry of Cu in stream water is given in Annex 1 in this

volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see section on Cu speciation).

Cu in stream sediment

The median total Cu content (XRF analysis) is 17 mg kg^{-1}, with a range from 1.0 to 877 mg kg^{-1}. The median content for Cu determined after partial dissolution with *aqua regia* (ICP-AES analysis) is 15 mg kg^{-1}, with a range between 1 and 998 mg kg^{-1}, indicating that most of the copper is extracted.

Copper in stream sediment shows low values (<11.0 mg kg^{-1}) across the northern European plain, the Baltic states, western Finland, south-eastern Norway, central and northern Sweden, the Garonne area in France, central Spain, north-western Austria, and central Hungary.

High Cu values in stream sediment (>27 mg kg^{-1}) are found in Albania and most of Greece (in relation to ophiolitic rocks and mineralisation, but also agricultural pollution), northern Italy and adjacent France, south Sardinia, the Iberian Pyrite Belt in southern Spain and Portugal, north Portugal (sulphides in vein mineralisation, possibly accompanied by agricultural pollution related to vineyards), near Málaga in south Spain (reflecting ultramafic Ni-Cr-Cu occurrences), the eastern Pyrenees and a point anomaly in the western Pyrenees (Silurian and Cambro-Ordovician black shale, with Pb-Zn and Cu-veins in the west and skarn in the central Pyrenees), most of Britain (possibly coprecipitation with Fe and Mn oxides), north-eastern Ireland including an anomaly near the Antrim basalt, coastal southern Finland (over clay-rich marine sediments), south-western Poland (Kupferschiefer), a point anomaly in southern Poland (Cu-Pb mineralisation at Miedzianka in the Góry Świętokrzyszkie (Holy Cross Mountains), a point anomaly in Slovakia, and an enriched area in the Czech Republic, especially in the north-west (combined contamination by industry, herbicide and fertiliser use in agriculture).

Copper in stream sediment has a good correlation (>0.4) with Fe, V, Co, Ni, Zn, Al, Ga and Li, and a weak correlation with As, Sb, Pb, Cr and Ti.

Cu in floodplain sediment

Total Cu values in floodplain sediment, determined by XRF, vary from 2 to 495 mg kg^{-1}, with a median of 17 mg kg^{-1}, and *aqua regia* extractable concentrations range from 1 to 421 mg kg^{-1}, with a median of 16 mg kg^{-1}, suggesting that almost all Cu is present in *aqua regia*-extractable mineral phases. Geochemical patterns of total XRF and *aqua regia* extractable Cu are very similar.

Low total Cu values in floodplain sediment (<11 mg kg^{-1}) occur over the granitic, granodioritic and gneissic areas of the Fennoscandian countries, parts of southern, central and northern Sweden, and eastern and western Finland, the glacial drift covered plain of north Germany, Poland, and the Baltic countries; the sandstone, metamorphic, and granitic rocks of northern Scotland; the calcareous, clastic and crystalline rocks of central and eastern Spain, and the molasse basin of Austria. The southern limit of the glacial drift covered area, through Germany and Poland, is well marked on the map, with low values north of it.

High total Cu values in floodplain sediment (>28 mg kg^{-1}) are found over the amphibolite of central and northern Norway but also attributed to mineralisation and its exploitation through mining (*e.g.,* Killingdal Cu-Zn-pyrite, Tverrfjellet Cu-Zn-pyrite, Løgen Cu-Zn-pyrite); in the Stockholm region in Sweden (Saxberget Zn-Cu-Pb); the mineralised areas of south-west Finland (*e.g.,* Vammala Ni-Cu, Kylmäkoski Ni-Cu); the shale, mafic volcanics in the Scottish Midland Valley; the Cu anomalies in Wales (*e.g.,* Parys Mountain Cu), Midlands and south-west England are attributed to lithology, base metal, iron mineralisation, and possibly industrial pollution; the same applies to an extensive arcuate belt extending from Belgium through central Germany to the Harz Mountains (*e.g.,* Rammelsberg Zn-Pb-Ba-Cu-Ag, Mansfeld Cu), Thuringian Forest, Erzgebirge, the Bohemian Massif, the Czech

Republic (*e.g.,* Ransko Ni-Cu, Zlate Hory Au-Cu-Pb-Zn), Slovakian Ore Mountains (*e.g.,* Banska Stiavnica Pb-Zn-Cu-Au-Ag), almost the whole of Hungary (*e.g.,* Recsk Cu-Zn), Slovenia, Croatia, the mineralised Southern Alps of Austria, and northern Italy, caused in part by mafic rocks and mineralisation (*e.g.,* Vignola F-Cu-Pb-Zn, Vigonzano Cu-Fe), but also possibly by copper sulphate used in viticulture (De Vos *et al.* 2005).

Copper anomalies occur in other mineralised areas, such as in the eastern Pyrenees (*e.g.,* Salsigne Au-As-Bi-Cu-Ag). In southern Spain and Portugal high total Cu values are located in the Iberian Pyrite Belt (*e.g.,* Spain: Rio Tinto, Tharsis Cu-pyrite, La Zarza Cu-Zn-Pb-Au-pyrite) and the Linares mineralised district in the Sierra Morena (Pb-Zn-Ag); northern Portugal mineralised district; in Galicia near the Arinteiro and Fornás Cu-Fe ores hosted by metabasites of an ophiolitic complex (De Vos *et al.* 2005). In the western Pyrenees and Basque Country high Cu values are linked to Pb-F-Zn (Cu) veins of Peñas de Aya and Cinco Villas district, and to the Zn-Pn stratabound mineralisation in Lower Cretaceous limestone in the Nervión basin, but an anthropogenic influence of the industrial region of Bilbao is very probable. The extensive belt with high Cu values stretching from Albania to almost the whole of Greece is possibly due to the ophiolites, and base metal mineralisation; it is worth noting that this region has high values in Ni, Co, Cr, Mn and MgO.

The highest Cu anomalous values in floodplain sediment occur in Spain and are related to the Linares mineralisation (495 mg kg^{-1}) and to Rio Tinto (212 mg kg^{-1}). In eastern Slovakia a high point anomaly (495 mg kg^{-1}) is attributed to the Rudnany Fe-Cu-Hg-Ba mineralisation. The high Cu anomaly in southern Portugal (435 mg kg^{-1}) is in the Iberian Pyrite Belt, whereas the Cu point anomaly in central Portugal (118 mg kg^{-1}) can be related to drainage of the Panasqueira W-Sn-Cu deposit (De Vos *et al.* 2005). The two Cu point anomalies in central England (267 and 143 mg kg^{-1}) may be due to copper mineralisation in the southern Pennines orefield. The point anomaly in the Vesdre basin of Belgium (160 mg kg^{-1}) is attributed to metallurgical pollution. The point anomaly to the west of Genova in Italy (170 mg kg^{-1}) may also be due to industrial pollution.

Copper in floodplain sediment shows a good correlation (>0.4) with As, Hg, Zn, Cd, Fe$_2$O$_3$, V and Co, and a weak correlation (>0.3) with P$_2$O$_5$, Pb, Ti and Ga. The association with Fe, V and Co points to coprecipitation processes in the secondary environment, whereas association with As, Hg, Zn, Cd, Pb and P$_2$O$_5$ seem to suggest that lithology and mineralisation are important factors influencing Cu distribution, whereas industrial activities and the application of agricultural fertilisers and fungicides are of minor importance.

In conclusion, the Cu distribution in floodplain sediment maps areas with mafic and ultramafic lithologies, and ophiolite masses, together with their metamorphic equivalents (greenstone) and also mineralisation. It shows, therefore, the geochemical differences of the geological substratum and mineralised areas quite well, and influences from anthropogenic activities are masked by the stronger signal of the natural distribution.

Cu comparison between sample media

Patterns in Cu distribution between all solid sample media are broadly similar. There is very little difference between total and leachable (*aqua regia*) Cu distributions. The patterns in the humus distribution is difficult to explain, but in central Europe there is a similarity with those observed in floodplain sediment. The main differences are throughout most of England, where high Cu values observed in stream sediments are overall much lower in the corresponding floodplain sediments and soil samples. A similar effect is observed in Mn and Co data. A possible explanation for the stream sediment Cu pattern is coprecipitation with Fe and Mn, and dilution for the comparatively lower values in floodplain sediment. A zone of polymetallic mineralisation, which extends from the Massif Central to Brittany is evident in the soil maps for Cu, but not in the stream and floodplain sediment. A similar situation occurs in the Baetics of southern Spain, although the southern Spanish pyrite belt shows high Cu in stream and floodplain sediment, but not in soil. High Cu associated with mineralisation in south central Austria is visible in subsoil, but not in the other solid sample media.

A boxplot comparing Cu variation in subsoil,

topsoil, stream sediment and floodplain sediment is presented in Figure 16.

There are a few similarities, but some major differences, between the Cu distribution in stream water and in solid sample media. *For example*, much higher values are found in stream water in Switzerland and surrounding areas (but these probably result from contamination during acidification of the samples). Higher values in stream water are also found in the Netherlands, Denmark, Sicily and Sardinia, possibly related to DOC and anthropogenic sources of soluble copper. Much lower values occur in stream water throughout Albania and Greece, perhaps related to insoluble copper minerals in ophiolite and alkaline pH, and north-eastern Italy and adjacent areas (stream water pH is in the alkaline range).
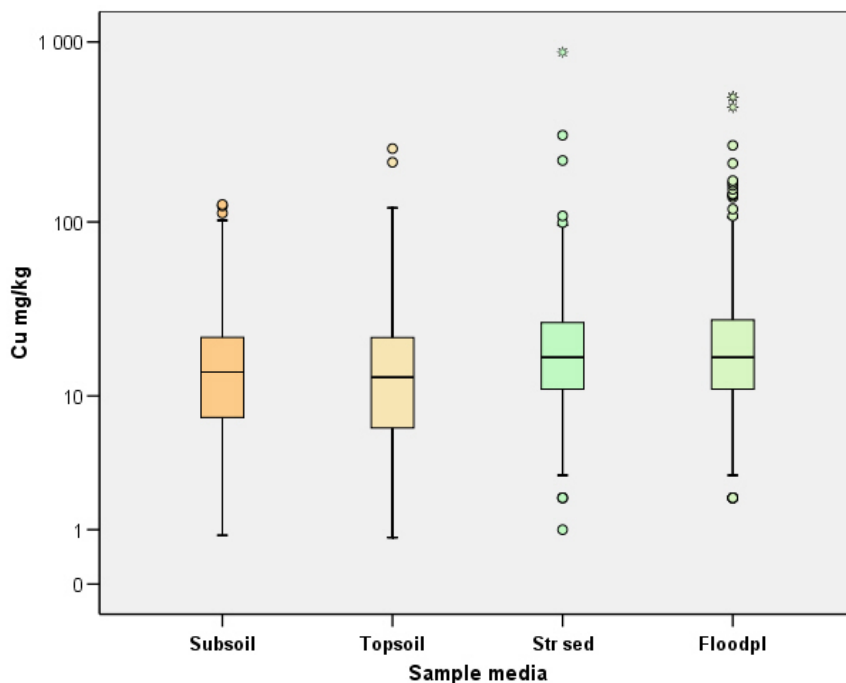

Figure 16. Boxplot comparison of Cu variation in subsoil, topsoil, stream sediment and floodplain sediment.