Introduction

Cadmium is a second row transition metal belonging to group 12 of the periodic table, along with Zn and Hg. The element has an atomic number of 48, an atomic mass of 112, one main oxidation state (+2) and eight naturally occurring isotopes (¹⁰⁶Cd, ¹⁰⁸Cd and ¹¹⁰Cd to ¹¹⁶Cd), of which ¹¹⁴Cd, ¹¹²Cd, ¹¹¹Cd, ¹¹⁰Cd and ¹¹³Cd have abundances of 28.73%, 24.13%, 12.80%, 12.49% and 12.22% respectively (Smith 1999b). The chemistry of cadmium is most similar to that of Zn.

Cadmium is a low-abundance, chalcophile element that most commonly occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals, especially sphalerite ZnS, and, to a lesser extent, in other Zn minerals such as smithsonite ZnCO3. The Cd content of sphalerite varies widely, but is normally in the range 0.02 to 1.5%, with a median value of around 0.3%, although contents up to 5% have been reported (Fergusson 1990). It is also found in trace amounts in some silicate minerals, such as biotite and amphibole. Cadmium occasionally forms minerals in its own right, most notably greenockite CdS, but also the rarer octavite CdCO₃ and monteponite CdO (Reimann and de Caritat 1998). There is also evidence of an affinity with organic matter; some types of coal, peat, and crude oil contain relatively high Cd levels, which may be due to selective adsorption and complexation by humic compounds.

The average crustal abundance of Cd is rather low, between 0.1 and 0.2 mg kg⁻¹ (Smith 1999b). Generally lower levels occur in igneous and metamorphic rocks (granite typically 0.09 mg kg⁻¹, basalt 0.13 mg kg⁻¹), sandstone and limestone, but higher levels are found in shale (0.8 mg kg⁻¹), especially organic-rich sediments, and in marine manganese nodules and phosphorite (Fergusson 1990). The concentration of Cd in river particulates has been estimated as 1 mg kg⁻¹ (McLennan and Murray 1999).

Elevated Cd values are generally indicative of sulphide mineralisation. When Cd is associated with Pb and, especially, Zn, it strongly suggests the presence of Sedex or VHMS mineralisation. Since Cd has strong chalcophile affinities, it may be used to validate a questionable Zn anomaly.

In the surface environment, Cd is most mobile under oxidising conditions at pH levels below 8. Consequently, the mobility of Cd released from minerals is likely to be high, especially during conditions of elevated flow, when pH is lower and Cd more readily leached. Since Cd^{2+} is the only stable oxidation state, the solubility of Cd is largely unaffected by changes in Eh (Fergusson 1990, Brookins 1988). However, the sulphate and carbonate of Cd are less soluble than those of Zn (Rubin 1976), so Cd^{2+} mobility is more restricted in carbonate-rich sediment and soil (Bowen 1982). Although cadmium sulphate is relatively insoluble, concentrations are generally well below saturation (Hem 1992). Cadmium readily forms complexes in solution with halides, cyanides and ammonium species, and has a strong affinity for organic matter. Humic substances bind Cd²⁺ to a greater extent than the major inorganic ligands, especially at high pH levels (Reuter and Perdue 1977). Clay minerals and iron oxyhydroxide coatings adsorb Cd, and the metal also coprecipitates with manganese oxide (Hem 1992). The soil clay fraction is not, however, the major soil factor controlling Cd distribution since its contribution only accounts for up to 10%; a stronger relationship appears to exist with the Fe and Mn contents of soil (Kabata-Pendias 2001). In all soil types, Cd activity is strongly affected by pH; it is more mobile in acidic soil within the pH range of 4.5 to 5.5, and its solubility is largely controlled by organic matter and sesquioxides. In alkaline soil, Cd is rather immobile and precipitation of Cd compounds occur. The critical acidity in mineral soil is between pH 4.0 to 4.5, at which a drop in pH of merely 0.2 units results in a 3 to 5 times increase of Cd concentration in soil solutions.

The average content of Cd in soil varies between 0.06 to 1.1 mg kg⁻¹, whereas the global mean for surface soil has been estimated to be 0.53 mg kg⁻¹, and apparently all higher values may reflect anthropogenic influences (Kabata-Pendias 2001).

Cadmium concentrations in river water are typically <0.5 μ g l⁻¹ (Neal and Robson 2000), although Hem (1992) reports that about 4% of surface water has concentrations as high as 10 μ g l⁻¹Cd.

In industrialised countries there is concern over anthropogenic accumulations of Cd in the

environment, and it is classified as a potentially harmful element with respect to soil biological activity, plant metabolism and the health of humans and animals (Kabata-Pendias 2001). Percentage level cadmium loadings in sewage sludge are a concern for disposal and limit or prevent sludges being applied to land as fertilisers. Cadmium is used extensively in industrial processes. Of these, electroplating and battery, paint, ink and plastic manufacture are of greatest Leaching of waste from these importance. processes may have an impact on surface water chemistry. Cadmium tends to volatilise at high temperatures, providing a mechanism for its entry into the hydrological cycle via atmospheric deposition downwind of industrial regions. The increasing use of Zn in fertilisers may lead to Cd contamination. Phosphate fertilisers contain between 5 and 100 mg kg⁻¹ Cd and up to 300 mg

kg⁻¹ Cd may be present in sewage sludge. According to EU recommendations, soil treated with sewage sludge should not contain more than 3 mg kg^{-1} Cd (86/278/EC/12-6-1986).

Cadmium has no essential biological function, but it tends to accumulate in plants and aquatic biota, with consequent problems of toxicity. It is toxic to humans through the inhalation of dust, causing lung damage, and may cause cancer from long-term exposure (WHO 1996); it is also teratogenic and embryocidal (Smith 1999b). The maximum tolerable intake of Cd is regarded as 7 μ g kg⁻¹ of body weight (WHO 1996). Uptake by some invertebrates may show a complicated relationship with pH, showing a maximum in bioaccumulation at pH 5.5 (Vesely 1994).

Table 17 compares the median concentrations of Cd in the FOREGS samples and in some reference datasets.

Cadmium (Cd)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg ⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	0.09
Subsoil	FOREGS	783	<2.0	Total (ICP-MS)	0.09
Topsoil	FOREGS	840	<2.0	Total (ICP-MS)	0.15
Soil ²⁾	World	n.a.	n.a	Total	0.3
Humus	FOREGS	367	<2.0	Total (ICP-MS)	0.40
Humus ³⁾	Barents region	1357	<2	Total (HNO ₃ , ICP-MS)	0.34
Water	FOREGS	807	Filtered <0.45 µm		0.01 (μg Γ ¹)
Water ⁴⁾	World	n.a.	n.a.		0.2 (µg l ⁻¹)
Stream sediment	FOREGS	848	<0.15	Total (XRF)	0.28
Floodplain sediment	FOREGS	743	<2.0	Total (XRF)	0.30
Stream sediment ⁵⁾	Canada	52 112	<0.18	Total (INAA)	0.2

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

Cd in soil

The median Cd content is 0.09 mg kg⁻¹ in subsoil and 0.145 mg kg⁻¹ in topsoil; the range varies from < 0.01 to 14.2 mg kg⁻¹ in subsoils and up to 14.1 mg kg⁻¹ in topsoils. The average ratio topsoil/subsoil is 1.477.

Low Cd values in subsoil (<0.05 mg kg⁻¹) occur especially in Denmark, northern Germany, Poland, Lithuania, Latvia, Finland, southern

Sweden, Scotland, central France, Portugal and adjacent parts of Spain. The distribution pattern of low Cd values in topsoil ($<0.08 \text{ mg kg}^{-1}$) is overall similar, but not in Poland, northern Germany and Lithuania (partly left over from Soviet-time agricultural use of poor-quality fertilisers and herbicides), where Cd contents in topsoils are overall slightly higher than in subsoil.

In subsoil, high Cd values ($>0.15 \text{ mg kg}^{-1}$) are found throughout northern Spain: in Cantabria and Basque country they can be related to dolomitised limestone of Mesozoic age hosting Zn-Pb strata bound mineralisation; in the central-western Pyrenees, they are related to Silurian and Cambro-Ordovician black shale, and in Asturias, to widespread vein mineralisation. High Cd values are also found in southern Italy, central Greece on terra rossa soil, the karstic soil of Slovenia and Dalmatian Croatia (probably anthropogenic contamination), the western Alps and southern France, the Poitou region, the northern and eastern Paris basin, Ireland; and to a smaller degree the Pennines in England, the area between the Vesdre in Belgium and the German Meggen region (former mining and smelting district of La Calamine-Eifel), the Erzgebirge, and a few points in central Sweden. The distribution of high values is related to sulphide ore occurrence and ancient mining. The highest subsoil Cd value (14.2 mg kg⁻¹) occurs on the Greek Ionian island of Kefallinia in terra rossa soil, and the second one (6.2 mg kg^{-1}) near the mining town of Alès in southern France.

The topsoil map shows some shifts in Cd levels, with enrichment in the area from Belgium through to Germany, probably arising from contamination, and also in Slovakia, the Pyrenees, and southern Sardinia. Cadmium anomalies in topsoil compared to subsoil are slightly weaker in Greece and in the karstic soils of Slovenia and Dalmatian Croatia.

Cadmium is one of the elements that show systematic enrichment in topsoil, similar to Pb, Hg, P_2O_5 , and Sb. For Cd the ratio topsoil/subsoil

is 1.477, and correlation between topsoil and subsoil is 0.819. The good correlation means that the pattern of enrichment in topsoils is valid for the population as a whole. The topsoil enrichment may be masked on the maps because the colours are laid out relative to the median, and this is substantially higher in topsoils than in subsoils. But the map of the topsoil/subsoil ratio (Map 4) shows that substantial enrichment occurs in most of Britain, northern Ireland, Belgium, Germany, Poland and Portugal.

This enrichment of Cd in soil has several possible causes: (1) anthropogenic pollution due to mining, chemical and other industries; (2) fertiliser use in agriculture; (3) possibly upward movement in soils by repeated reprecipitation, and (4) association with organic matter, which is more abundant in topsoil.

The highest topsoil Cd value (14.1 mg kg⁻¹) is again in Kefallinia (Greece). This sample is an outlier for cadmium and phosphorus, and the highest value for I, in both subsoil and topsoil; it is in *terra rossa* soil developed over Cretaceous limestone, which hosts low grade phosphate deposits as elsewhere in the Cretaceous, providing a lithological cause for the anomaly. The second richest Cd value (7.1 mg kg⁻¹) occurs near Nyons in the French Provence (probably pollution of an iron rich palaeosol recently reworked for installing a tree nursery).

In subsoil, Cd shows a good correlation (>0.4) with Te and Zn, and a weak correlation (>0.3) with Pb, Mn, Y, Co, Ni and some REEs.

In topsoil, it has a good correlation with Zn, Te, Mn, Pb, Y and Ho, and a weak correlation with Co, Cu, Sb, Hg and most REEs.

Cd in humus

The median Cd content in humus is 0.40 mg kg⁻¹ and the range varies from <0.1 to 18.3 mg kg⁻¹.

The humus Cd distribution map shows low values (<0.25 mg kg⁻¹) occurring in parts of Britain, north-western Ireland, central Norway, northern Sweden and Norway, north-eastern Germany, and western France.

High Cd values in humus (>0.60 mg kg⁻¹) occur throughout Belgium and southern Netherlands (metallurgical Zn smelters are present in this area); the industrial Glasgow area in Scotland; central Ireland; south-western Norway; south-eastern Poland; parts of Austria, northern Italy and Switzerland and the French Jura. The highest value occurs in the Vesdre basin in Belgium, it is an outlier with 18.3 mg kg⁻¹ Cd and 1863.4 mg kg⁻¹ Zn. Also topsoil, floodplain and stream sediment are anomalous at this location, and the cause has been traced to industrial pollution (De Vos *et al.* 1996); specifically brass metallurgy is responsible for the Zn-Cd anomaly.

The pattern of high Cd values in humus probably reflects anthropogenic contamination.



Map 4. Ratio of Cd in topsoil vs subsoil.

Recent deposition of Cd is found in moss samples in south-eastern Poland, in northern Italy and in the Netherlands (Rühling and Steinnes 1998), and in Germany (Siewers *et al.* 2000). In the intermediate and low values, some geogenic variation is probably present.

Cadmium in humus has a very strong correlation with Zn (0.93), but discarding the one outlier this is reduced to a good correlation (0.53). Cadmium also weakly correlates with Pb (0.36).

Cd in stream water

Cadmium values in stream water range over more than two orders of magnitude, from <0.002to 0.53 μ g l⁻¹ (excluding three outliers up to 1.25 μ g l⁻¹), with a median of 0.01 μ g l⁻¹. In stream water, cadmium patterns are similar to that of REEs and associated elements in acid, low mineralisation, high DOC water of the southern part of Fennoscandia, in Denmark and part of north Germany, and in the Armorican Massif in France. However, the association with heavy metals patterns could explain the highest concentrations in stream waters situated in Slovakia, in the Erzgebirge in Germany, in north Germany, on Sardinia, and in Slovenia, Lithuania and Latvia, by pollution and partly by mineral deposits.

Low Cd values in stream water ($<0.007 \ \mu g \ l^{-1}$) are found in northern Fennoscandia, across central Sweden and Norway, on Precambrian Shield, and, in Norway and north-western Scotland (also on Laurentian terrains) on Caledonian rocks. In Estonia, low values occur on Precambrian Shield derived glacial drift. The low values in southern England, north and east central France, west central Germany and on most of the Iberian Peninsula all belong to Variscan terrains, with the exception of the Alpidic Pyrenees and part of the Baetic Cordillera. The low values in the Alpidic realm appear in north Italy and bordering France and Switzerland, and in Austria extending to southern Variscan Germany, and in south-eastern Hungary and eastern Croatia on clastic deposits of the Pannonian Basin, central and southern Italy and throughout all of Albania and Greece on the Alpidic Orogen.

Enhanced Cd concentrations in stream water $(>0.022 \ \mu g \ l^{-1})$ are found in areas of east, west and

south Finland, in southern Sweden and southernmost Norway on Precambrian Shield rocks. High values in Latvia, Lithuania, Denmark and parts of north Germany appear on glacial drift from Fennoscandia, although the values in Latvia and Lithuania may arise partly from contamination during collection and handling of samples, and partly from agricultural contamination. High values in east central and south-east England are on sedimentary cover rocks of Caledonian terrains. High Cd levels on the Variscan appears in large parts of Germany (partly on glacial drift), west and east Czech Republic, in Armorican Massif of France (Brittany), in northern Portugal, and on Sardinia, where they are connected to Pb-Zn ore deposits. On the Alpidic Orogen, high Cd occurs in Slovakia and north-east Hungary, north central Italy and on west Sicily. The Cd anomaly in central Slovakia could be related to a mineralised zone. The high Cd value in Belgium (Vesdre basin) is related to industrial pollution (mining, metallurgical, textile, paper industry). The anomalous Cd value in south-west France near the border with Spain is related to a previously mined Pb-Zn district (Moncoutan) enclosed in carbon rich Ordovician black shale. The distribution of Cd closely resembles that of Zn and Pb, the latter especially throughout Fennoscandia and the Baltic countries, Britain and the Armorican Massif in France. Anomalously high isolated Cd values in Germany and Slovakia could be the result of pollution by industry, mining, agricultural practice (fertilisers) or a combination of these sources; the same areas are anomalous in stream sediment and enriched in topsoil.

The median Cd content in stream sediment is 0.29 mg kg^{-1} , and the range varies from <0.02 to 43.1 mg kg⁻¹.

The Cd distribution map shows low values in stream sediment (<0.18 mg kg⁻¹) occur throughout most of Finland, Estonia, central Norway, Poland, Lithuania, most of Iberia, south-west France, the western Alps and Rhône valley, north-easternmost Italy and central Austria, Sicily, eastern Pannonian Croatia.

High values in stream sediment (>0.51 mg kg⁻¹) occur in large parts of Britain, Belgium, the Netherlands, northern and central Germany, Czech Republic, south-western Poland and Latvia (also rich in Ag). The broad high Cd zones extending across the central-northern European lowlands and much of Britain, may reflect a significant anthropogenic contribution. As phosphate is enriched in these same zones, it may point to agricultural practices (spreading of sewage sludge); the scattergram P-Cd reveals a

common tendency in the intermediate values. High Cd values also occur in Brittany, southern France, Slovenia and western Croatia (industrial pollution) and north-east Portugal. A clear link with ancient and recent mining can be established at point anomalies in Sardinia and Lavrion (Greece), where Cd values define strong outliers, in common with Pb, Zn and Hg (see Hg description); a second high value in Attica to the north-west of Lavrion is possibly the result of industrial pollution, although the occurrence of unknown mineralisation cannot be precluded. A link with former mining can also be observed in Britain, the Belgian-German border area, the Harz Mountains, western Bohemia (Zlaté Horv district), Silesia in south-west Poland (Kupferschiefer) and Hungary (De Vos et al. 2005).

Cadmium in stream sediment has a strong correlation with Zn (0.69), and a weak correlation (between 0.3 and 0.4) with Pb, Sn and Mn.

Cd in floodplain sediment

The total Cd distribution in floodplain sediment varies from <0.01 to 23.6 mg kg⁻¹, with a median of 0.3 mg kg⁻¹. The Cd median in floodplain sediment (0.30 mg kg⁻¹) is much higher than in subsoil (0.09 mg kg⁻¹) and topsoil (0.14 mg kg⁻¹), but similar to stream sediment (0.29 mg kg⁻¹).

Low Cd values in floodplain sediment (<0.17 mg kg⁻¹) occur over most of the crystalline rocks of Finland, central Norway, and northern Scotland, the glacial drift covered eastern Poland, most of central Spain and Portugal with calcareous, clastic and crystalline rocks, and southern Italy with calcareous, clastic and volcanic rocks.

High Cd values in floodplain sediment (>0.44 mg kg⁻¹) occur in a north-west to south-east belt extending from Ireland through England, Germany, the Czech Republic, Slovakia and eastern Hungary. The spreading of sewage sludge and phosphate fertilisers, both of which may contain high levels of Cd, is prevalent in this whole area. In this region there are also known Pb-Zn ore deposits, which contain enhanced Cd levels (*e.g.*, Tynagh, Silvermines and Navan in Ireland, the Pennines mineralised district in

England, Ruhr, Meggen Mechernich, Rammelsberg and Freiberg in Germany, Kutna Hora in the Czech Republic, Banska Stiavnica in Slovakia, and Recsk in Hungary). In addition, anomalous Cd values are found in mineralised areas in south-west Sweden, south-west Norway, France (Brittany, Poitou, Normandy, and the southern part of Massif Central), Sardinia, Italian Alps (Gorno), and Croatian coast.

Point anomalies in floodplain sediment occur in the Lavrion mining area in Greece (23.6 mg kg⁻¹), in Slovakia (15.2 mg kg⁻¹), which is possibly related to the Banska Stiavnica Pb-Zn mineralisation, in the Vesdre basin in Belgium (13 mg kg⁻¹), caused by metallurgical pollution, eastcentral Germany (12.0 mg kg⁻¹) downstream of the mineralised Erzgebirge region, in north-east England (11.7 mg kg⁻¹) with mining activities, in northern Germany (10.4 mg kg⁻¹) possibly caused by the mining activities in the Harz Mountains, and in south-west England in Devon (9.54 $mg kg^{-1}$) associated with the mineralisation related to the Dartmoor granite. In the Extremadura-Córdoba region in southern Spain, two high values correspond to catchment basins containing important Pb-Zb mining districts (Valle de

Alcudia-Pedroches and Azuaga). A high value in northern Spain is in a basin containing Zn-Pb stratabound mineralisation in the Lower Cretaceous of Basque country.

Cadmium in floodplain sediment has a strong correlation with Zn (0.71), a good correlation (>0.4) with Pb, Cu and Hg, and a weak correlation

with P_2O_5 .

In conclusion, the patterns of high Cd values in floodplain sediment map mineralised areas, and the pollution caused by mining and metallurgical processing, but also the spreading of sewage sludge and phosphate fertilisers in agricultural areas.

Cd comparison between sample media

There are large differences between the different solid sample media. Topsoil is generally enriched by an average factor of 1.45 relative to subsoil (see ratio map of Cd in topsoil and subsoil). Patterns in distribution between topsoil and subsoil are broadly the same, but there is a general increase in topsoil Cd throughout northern mainland Europe. The same trend is enhanced in stream and floodplain sediments with particular enrichment over the Czech Republic, southern Poland and northern England. In the Czech Republic, no significant natural sources of Cd are known. Its higher values originate mainly from industrial activities (floating, production of batteries, paints and plastics). Brown coal has been burnt in large quantities in industrial areas in power plants and other factories; Tertiary coal from the nearby deposits sometimes contains high concentrations of trace elements including Cd; in the south-western Czech Republic Cd contamination probably results from а combination of industrial pollution and agricultural activities. In Latvia, high Cd is observed in stream sediments, compared to other solid sample media. In Ireland, floodplain sediment is particularly high in Cd compared to other solid sample media. Greece, Albania, Slovenia, coastal Croatia, southern Italy and Sicily show lower Cd in stream and floodplain

sediments compared to soil.

A boxplot comparing Cd variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 11.

Patterns in stream water Cd are complex, and quite often opposite to those seen in total Cd content in solid sample media. Cadmium is strongly controlled by pH, and tends to low concentrations in the alkaline environments of central Spain, Greece and Albania, and higher concentrations in the more acidic environments in southern Sweden, Denmark, Latvia, Lithuania, and Brittany in France; the high Cd concentrations in stream water are not accompanied by high values in soil or sediments. On the other hand, high Cd is also observed in stream water and some solid sample media throughout eastern Germany, in Slovakia and on Sardinia, but in these regions they probably result from pollution or mineralisation.

The pattern in humus Cd is quite complex and is probably related to anthropogenic effects.

Whereas the distribution pattern of Cd in subsoil can be easily explained by geogenic causes, this is not the case for Cd in stream and floodplain sediments, which show apparent contamination from anthropogenic sources, including industry and application of sewage sludge and fertilisers to land.



Figure 11. Boxplot comparison of Cd variation in subsoil, topsoil, stream sediment and floodplain sediment.