## Introduction

Iron is a 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 8 of the periodic table, along with Ru and Os. The element has an atomic number of 26, an atomic mass of 56, two main oxidation states (+2 and +3) and four naturally occurring isotopes (<sup>54</sup>Fe, <sup>56</sup>Fe, <sup>57</sup>Fe and <sup>58</sup>Fe), although <sup>56</sup>Fe is the major isotope at 92% of the total mass.

Iron is the fourth most abundant element and second most abundant metal in the Earth's crust (after aluminium). It is one of the seven metals known in antiquity (along with gold, silver, copper, mercury, tin and lead). It has both lithophile and chalcophile properties, forming several common minerals, including pyrite FeS<sub>2</sub>, magnetite Fe<sub>3</sub>O<sub>4</sub>, haematite Fe<sub>2</sub>O<sub>3</sub> and siderite FeCO<sub>3</sub>. It is also present in many rock-forming minerals, including mica, garnet, amphibole, pyroxene and olivine. Iron becomes concentrated in mid-stage fractionates during magmatic processes and is generally enriched in mafic rocks relative to felsic, intermediate or ultramafic types. There is a wide range of Fe concentrations within different rock classifications depending on their mineralogical composition but, as a guide, Mielke (1979) and Williamson (1999) report Fe values as: ultramafic 9.6%; basaltic 8.6%; granitic 2.2% (1.4-3.0%); syenite 3.7%; and a crustal average of 7%.

The abundance of Fe in sedimentary rocks is determined by various factors. including provenance, pH-Eh conditions, the extent of diagenetic alteration and grain size. In most instances, secondary hydrous oxides are the dominant Fe phases, although primary oxides may account for some of the iron. The tendency for hydrous Fe phases to form surface oxide coatings can be reflected in a direct relationship between total Fe content and the specific surface areas of sedimentary particles (Ure and Berrow 1982). Hence, clay, shale and greywacke (>6% Fe) are generally enriched relative to arkose (ca. 3% Fe), quartz-feldspathic sandstone (ca. 0.5% Fe) and carbonate rocks (ca. 0.5% Fe). Sedimentary ironstone, where the dominant iron minerals are siderite, ankerite or oxides of the goethitelimonite type, may contain >30% Fe<sub>2</sub>O<sub>3</sub>. Typical

levels for Fe in sedimentary rocks are given by Williamson (1999) as: limestone 0.33%; sandstone 0.98%, shale 4.7%, and banded iron formation 28%. McLennan and Murray (1999) cite average values for river particulates and loess as 4.8% and 2.4% Fe respectively.

Iron is a major element in soil with a median value of 2.1% (Rose et al. 1979). It is present mostly as Fe<sup>2+</sup> in ferro-magnesian silicates, such as olivine, pyroxene, amphibole and biotite, and as  $Fe^{3+}$  in iron oxides and hydroxides, as the result of weathering. The reactions of Fe in weathering processes are dependent largely on pH-Eh, and on the oxidation state of the Fe compounds involved. In general, oxidising and alkaline conditions promote Fe precipitation, whereas acid and reducing conditions favour the solution of Fe compounds; therefore, acid soil tends to have higher levels of soluble inorganic Fe compounds than neutral and calcareous soil types (Kabata-Pendias 2001). When soil is waterlogged,  $Fe^{3+}$  is reduced to  $Fe^{2+}$ , and this is reflected in an increase in Fe solubility. Overall, ion  $Fe^{2+}$  is moderately mobile in the secondary environment, whereas  $Fe^{3+}$  has a very low mobility. It is noted that the mobility of Fe in soil is largely controlled by the solubility of Fe<sup>3+</sup> and Fe<sup>2+</sup> amorphous hydrous oxides, although the formation of other Fe compounds, such as phosphates, sulphides and carbonates, may greatly modify Fe solubilities (Kabata-Pendias 2001). Precipitation of Fe<sup>3+</sup> hydrous oxides often leads to formation of coatings on other mineral phases and causes coprecipitation of metals, such as Mn, Ti, V, Sc, Cu, Co and many others in limonitic or haematitic phases. Soil Fe exhibits a strong affinity to form mobile organic complexes and chelates, which are responsible for its migration between soil horizons and its leaching (Kabata-Pendias 2001). Areas with Fe deficiency in soil occur under arid climatic conditions, and are related to calcareous, alkaline, or other specific soil types (e.g., manganiferous soil), and in temperate climates with humic acid soil (Kabata-Pendias 2001).

The controls on dissolved Fe concentrations in stream water are complex. Iron is relatively immobile under most environmental conditions, mainly due to the very low solubility of iron (III)

hydroxide in its various forms. Its solubility is strongly influenced by redox conditions. The  $Fe^{2+}$ ion is much more soluble in strong acid or reducing conditions, so higher concentrations are found in reducing groundwater (Hylander et al. However, dissolved Fe is generally 2000). precipitated rapidly with increasing pH or Eh, and this is responsible for the presence of hydrous oxide coatings, e.g., goethite, limonite and lepidocrocite, on stream clasts in aerobic environments. Iron is also soluble in acid mine drainage where pH levels below 2 stabilise  $Fe^{3+}$  in solution (Wedepohl 1978). Significant levels of H<sub>2</sub>S and CO<sub>2</sub> in solution influence the pH-Eh conditions for mineral stability, decreasing the solubility of Fe under more reducing conditions (below +200 mV) particularly at near-neutral pH. The abundance of complexing agents in solution, notably Cl<sup>-</sup>, F<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and natural organic materials, also influences the Fe content of stream water. Iron concentrations in surface water are highly variable; Neal and Robson (2000) quote values from <10 to over 1000  $\mu$ g l<sup>-1</sup> Fe for United Kingdom river water; Lahermo *et al.* (1996) give Fe values ranging from <5 to over 3600  $\mu$ g l<sup>-1</sup> for Finnish stream water.

Anthropogenic sources of iron include the iron and steel industry, sewage and dust from iron mining (Reimann and de Caritat 1998). Iron sulphate is also used as a fertiliser and herbicide (Reimann *et al.* 2003).

Iron is an essential nutrient for plants and animals. Between 10 and 18 mg per day is needed for adults (Mertz 1987) and iron deficiency is a common medical condition. Its main role in humans is in the production of haemoglobin in red blood cells (WHO 1996). High intakes of cobalt, zinc, cadmium, copper and manganese interfere with iron absorption in the human body, which can lead to anaemia (Mertz 1987).

Table 29 compares the median concentrations of Fe in the FOREGS samples and in some reference datasets.

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Iron (Fe <sub>2</sub> O <sub>3</sub> )	Origin – Source	Number of samples	Size fraction mm	Extraction	Median %
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	5.04
Subsoil	FOREGS	788	<2.0	Total (XRF)	3.75
Subsoil <i>(Fe)</i>	FOREGS	784	<2.0	Aqua regia (ICP-MS)	2.11
Topsoil	FOREGS	845	<2.0	Total (XRF)	3.51
Topsoil <i>(Fe)</i>	FOREGS	837	<2.0	Aqua regia (ICP-MS)	1.96
Soil <sup>2)</sup>	World	n.a.	n.a	Total	5.0
Soil, C-horizon (Fe) <sup>3)</sup>	Barents region	1357	<2	Aqua regia (ICP-MS)	1.26
Water (Fe)	FOREGS	807	Filtered <0.45 μm		67.0 (μg l <sup>-1</sup> )
$Water(Fe)^{4}$	World	n.a.	n.a.		40 (µg l <sup>-1</sup> )
Stream sediment	FOREGS	852	<0.15	Total (XRF)	3.57
Stream sediment (Fe)	FOREGS	845	<0.15	Aqua regia (ICP-AES)	1.97
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	3.33
Floodplain sediment (Fe)	FOREGS	747	<2.0	Aqua regia (ICP-AES)	1.95
Stream sediment $(Fe)^{5}$	Canada	26 227	<0.18	Total (INAA)	4.9
Stream sediment $(Fe)^{5}$	Canada	82 464	<0.18	Aqua regia (ICP-AES)	2.2

<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

The median total iron content expressed as  $Fe_2O_3$  (XRF analysis) is 3.75% in subsoil and 3.51% in topsoil, with a range varying from 0.11 to 15.6% in subsoils and 0.16 to 22.3% in topsoils. The average ratio topsoil/subsoil is 0.923.

The Fe<sub>2</sub>O<sub>3</sub> subsoil distribution map shows low values (<2.40%) throughout the glacial drift sandy plains from Poland to the Netherlands, much of the Baltic states, large parts of southern Finland and Sweden, and limestone areas in southern Spain and north-central France.

 $Fe_2O_3$  in subsoil is high (>5.44%) in northwestern Spain (mafic and ultramafic lithologies of the Ordenes ophiolite), the western Pyrenees (siderite replacement deposits in Lower Cretaceous), Brittany, Central Massif (soil over Quaternary basalt), a north-south band in Italy from north of the Garda Lake to the Roman Alkaline Province, southern Sicily, Greece north of the Gulf of Corinth (*terra rossa* soil, ophiolite, bauxite, Fe-Ni mineralisation), Croatia, Slovenia and southern Austria (karstic residual soil), eastern Slovakia (soil over volcanic rocks and Palaeogene flysch with ultramafic clasts), eastern Latvia (related to iron concretions due to changes oxidation-reduction conditions close to in groundwater level in poorly drained soil), parts of Norway (amphibolite), the ice divide area of northern Finland (which is rich in mica), the west coast of Wales and Scotland, and northern Ireland (over the Antrim basalt). What most of these areas have in common is crystalline rocks of intermediate to mafic or alkaline affiliation, including greenstone belts, and also karst with soils on carbonate rocks (Greece, Croatia, Slovenia). In northern Finland iron ores are present, and magnetite has a tendency to be enriched during weathering. Weaker iron enrichment occurs in southern Portugal, and the French-Belgian Ardennes and parts of central England where Mesozoic red-beds and sedimentary iron ores are present.

The topsoil  $Fe_2O_3$  map exhibits many differences compared to the subsoil map. In Latvia and eastern Slovakia, the subsoil anomaly disappears completely in the topsoil. In northern Finland, there is enrichment in podzolic topsoil,

because metals are enriched in the illuvial horizon. In Spain, several areas show high iron content in topsoil, but lower background values on the subsoil map are clearly caused by a sampling bias, because fewer subsoil were collected; this is the case in the Spanish Pyrenees, where a continuous Fe<sub>2</sub>O<sub>3</sub> anomaly is present in the topsoil (linked to Silurian black shale), in the Sierra Nevada (amphibolite and schist with Fe mineralisation of Las Piletas), Sierra Morena, Gran Canaria, and western Spain along the Portuguese border (iron skarn and stratabound mineralisation). In parts of France, Fe V, Co, Mn enrichment in both subsoil and topsoil reflects iron-rich palaeosurfaces (Permo-Triassic boundary, siderolithic Eocene). In the western part of Brittany (France) a Fe-Sc anomaly is clearly related to the well known Segre Ordovician oolitic stratabound iron ore deposit.

Two trace elements, V and Sc, have a distribution which is very similar to  $Fe_2O_3$ . The correlation coefficient Fe-V is very strong: 0.91 in both subsoil and topsoil; the correlation with Sc is 0.89 in subsoil and 0.92 in topsoil.

In subsoil, iron also shows a very strong correlation with Ti (0.80), a strong correlation (>0.6) with Co, Al, Ga, In, Mn, Cu and some of the REEs, and a good correlation (>0.4) with Nb, Ta, Ni, Cr, Zn, As, Te,  $P_2O_5$  and the remaining REEs.

In topsoil, there is a strong correlation with Co, Al, Ga, In, Ti, Mn, Cu, Zn and some of the REE, and a good correlation with Nb, Ni and Te, and a good negative correlation with  $SiO_2$  (-0.50), verifying statistically the inverse geochemical relationship that exists between Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

The median Fe content after *aqua regia* extraction (ICP-AES analysis) is 2.11% Fe-metal in subsoil and 1.96% Fe-metal in topsoil, corresponding to 3.0% and 2.8% Fe<sub>2</sub>O<sub>3</sub> respectively. This is about 80% of the total Fe<sub>2</sub>O<sub>3</sub> values. The range is from 0.07 to 9.42 in subsoils and from 0.07 to 15.2% in topsoil. This means that about 80% of the iron is extracted with *aqua regia*. The distribution pattern of extractable Fe in soil is almost the same as the one for total Fe, but values are generally higher in Britain, and somewhat lower in Norway.

Iron values in stream water range over three orders of magnitude, from <1.0 to  $4820 \ \mu g \ l^{-1}$ , with a median value of 67  $\ \mu g \ l^{-1}$ . Iron has a very close inverse correlation with pH and a close positive correlation with Al, except over western Norway.

Lowest Fe values in stream water (<11  $\mu$ g l<sup>-1</sup>) are predominantly found in parts of central and west Norway, west-central France near Bordeaux, eastern Iberian Peninsula (alkaline stream water), northern half and parts of southern Italy and Sicily, parts of Hungary, eastern Croatia, and throughout Albania and Greece. Iron is not solubilised because of the relatively high pH in these areas, which is predominantly controlled by carbonates, but is also controlled by geology, *e.g.*, in Norway.

Highest Fe concentrations in stream water  $(>1000 \ \mu g \ l^{-1})$  are predominantly found throughout most of central and southern Finland, eastern and southern Sweden, Denmark, northern Netherlands, north-east Scotland and northern Ireland. These regions have base-poor buffering capacity because of their geology, and Fe is controlled mainly by low pH and the presence of dissolved organic matter (see DOC map). The isolated Fe anomaly north of Naples in Italy is

possibly related to industrial pollution. Highly anomalous isolated values in eastern Poland are related to different sources (metallurgical industry in the south-eastern part of the country and peat lands with high DOC concentration in the northeast). A high Fe value in central Spain is related to Fe-oxide enrichment in Ordovician quartzite, close to old Pb mines.

The Fe distribution in stream water follows closely the pattern of REEs and associated elements in acid, low-mineralisation and high-DOC stream water type. The pattern is primarily exogenic, in the first instance climate-dependent. Dissolved species in these stream water types may be dissolved organic materials, and possibly also common anions, such as chloride, in the south, in Brittany and Alentejo, Portugal. The association with Mn and DOC may explain the high Fe waters in Latvia and eastern Poland. Patterns of Fe in stream water are entirely different from those in soil and sediment.

A more detailed description on the chemistry of Fe in stream water is given in Annex 1 by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see section on Fe speciation).

## Fe<sub>2</sub>O<sub>3</sub> in stream sediment

The median total iron content in stream sediment, expressed as  $Fe_2O_3$  (XRF analysis), is 3.58%, with a range varying from 0.11 to 18.3%.

Low Fe values in stream sediment (<2.24% Fe<sub>2</sub>O<sub>3</sub>) occur mainly in the glacial drift area from Poland to the Netherlands, in Latvia, Estonia, north-western and south-western France, the Jura Mountains, parts of eastern Spain, and central Austria.

High  $Fe_2O_3$  values in stream sediment (>5.15%) are found throughout southern and northern Finland (iron ores), northern and central Sweden, northern Norway (Caledonian layered mafic intrusions such as Sulitjelma), and the Caledonides of Norway generally. The North-Atlantic Tertiary volcanic province shows high Fe values in western Scotland (central complexes of Skye, Mull, Rhum and Ardnamurchan) and in northern Ireland (Antrim plateau basalt). In north-western Ireland a base-metal mineralisation

causes an anomaly in Fe, Pb, Cu, Mn, Sb, As, Ge, Co, Ba. Most of Britain shows high Fe values, which may be caused by secondary precipitation in stream sediment.

In central and southern Europe, in contrast, Fe anomalies in stream sediment are scarce, limited to southern Portugal and adjacent Spain (Iberian Pvrite Belt and Ossa Morena metamorphic zone with Fe mining), north-western Spain (Ordovician quartzite with Fe-oxides and Fe-oolithic mineralisation), the Central Pyrenees (supergene Fe-oxide precipitation, with Fe coming from Silurian black shale with pyrite), the Roman Alkaline Province in Italy, point anomalies on basaltic rocks of the Canary Islands, the Etna volcanic area in Sicily. Roccamonfina in Campania, and eastern Greece (ophiolite, Fe-Ni deposits, bauxite and polymetallic mineralisation). In addition, scattered point anomalies throughout Europe could be caused by local geological

substrate or by oxidising precipitation conditions in stream sediment, and should be investigated locally.

Iron in stream sediment shows a very strong correlation with V (0.87), a strong correlation (>0.6) with Co, Ti and Ga, and a good correlation (>0.4) with Eu, Al, Mn, Cu, Ni, Zn and Nb.

Aqua regia extractable Fe (ICP-AES analysis) in stream sediment yields a median value of 1.97% Fe-metal, corresponding to 2.8% Fe<sub>2</sub>O<sub>3</sub>, or about 80% of total iron content. The correlation

coefficient between both analytical methods is 0.88, suggesting that overall a similar proportion from each stream sediment sample is extracted by this method. The distribution patterns of total and extractable  $Fe_2O_3$  are almost the same throughout most of Europe, except in Norway and northern Finland where leachable Fe content is relatively lower. In Precambrian areas of Fennoscandia, Fe is mainly present in the mineral magnetite, which is insoluble in *aqua regia*.

## Fe<sub>2</sub>O<sub>3</sub> in floodplain sediment

Total Fe<sub>2</sub>O values in floodplain sediment show considerable variation ranging from 0.25 to 35.8%, with a median 3.33%, and *aqua regia* extractable Fe-metal concentrations vary from 0.16% to 19.5% with a median of 1.95%, corresponding to 0.29% to 27.9% Fe<sub>2</sub>O<sub>3</sub> and a median of 2.79% Fe<sub>2</sub>O<sub>3</sub>. On average the *aqua regia* extracts about 80% of total iron. Hence, the geochemical patterns shown by total XRF and *aqua regia* extractable Fe are approximately similar, but with minor differences in some areas.

Low total Fe<sub>2</sub>O<sub>3</sub> values in floodplain sediment (<2.12%) extend over the glacial drift covered plain from north-east Germany, Poland to Lithuania and Latvia. Other areas with low total Fe<sub>2</sub>O<sub>3</sub> values are the felsic and metamorphic basement rocks of central and southern Sweden; the metagreywacke, mica schist and phyllite of south-east Finland; part of north-east Scotland with gneiss, schist, granite and sandstone; the glacial drift covered carbonate rocks of Ireland; the alluvial plain of the lower Garonne-Dordogne rivers in France; the crystalline basement and clastic rocks of the Iberian Meseta, and the limestone and clastic cover of eastern and southwest Spain, the molasse basin in Austria, and Dalmatian Croatia with karst and flysch.

High total Fe<sub>2</sub>O<sub>3</sub> values in floodplain sediment (>4.53%) are found in areas with mafic rocks and mineralisation, as for example, in most of Norway (*e.g.*, Ofoten-N. Trams Fe-Mn, Rana Fe, Fosdalen Fe, Rodsand Fe-V-Ti), central and northern Sweden (*e.g.*, Norrbotten mineralised district with Ruoutevare V-Ti-Fe, Tjerrojekka Fe-Cu, Ekströmsberg Fe-P, Pattok Fe-P, Kiirunavaara Fe-P, Mertainen Fe-P, Leveaniemi Fe-P, Malmberget Fe-P, Sahavaara Fe), and extending into northern to central Finland with paragneiss, granulite, felsic metavolcanics, mica schist and amphibolite and mineralisation (e.g., Rautuvaara Fe-Cu-Au, Misi Fe, Mustavaara Fe-V-Ti, Otanmaki Fe-V-Ti). Other areas with high total Fe<sub>2</sub>O<sub>3</sub> values include the mineralised south-west Finland with metagraywacke, mica schist, phyllite, felsic and ultramafic rocks (e.g., Jussarö Fe, Stormi Ni, Vammala Ni-Cu, Kylmakoski Ni-Cu); the high total  $Fe_2O_3$  values in south-east Sweden occur in the mineralised Stockholm hinterland (e.g., Striberg Fe, Stripa Fe, Stressa Fe, Norberg Fe) with granite, granodiorite, tonalite and some gneiss, and the Lagan River basin with the Smelands Taberg V-Ti-Fe in its upper reaches; in the Midland Valley of Scotland on the Clyde River draining alkaline basaltic volcanics, Wales with Ordovician mafic volcanics, shale, slate, schist and mineralisation (e.g., Shelve Pb-Ba-Zn-Cardigan-Montgomery Pb-Zn-pvrite. pyrite, Coed-y-Brenin Cu-pyrite), central and eastern England (*e.g.*, the sources may be the sedimentary iron ore deposits of the Nottingham-Corby-Northampton, and adsorption on clay); the Armorican Massif in Brittany (island arc lavas, shale, mineralisation including the Segre Fe-ore deposit), and the Iberian Pyrite Belt in southern Spain Portugal with base and metal mineralisation, including the Tharsis deposit in the Odiel basin (De Vos et al. 2005); the Sierra Morena in south Spain with the Córdoba and Linares mining districts; the upper reaches of the Po River basin draining the Italian-French-Swiss Alps with mineralisation including the Cogne Fedeposit hosted in serpentinite and calc-schist; Corsica (mafic and ultramafic rocks), and the Roman Alkaline Province in Italy. High total Fe<sub>2</sub>O<sub>3</sub> values extend from the Austrian part of Alps into Slovenia, Croatia, Hungary, western

Slovakia, southern Czech Republic and ending at the Bohemian Massif and Erzgebirge; the similarity of the patterns with high TiO<sub>2</sub> and V and Al<sub>2</sub>O<sub>3</sub> possibly suggests accumulation of mafic minerals in the fine clay fraction. In the karst region of Slovenia and Croatia the high Fe<sub>2</sub>O<sub>3</sub> values may be explained by their accumulation in residual soil, and its subsequent erosion and deposition on the floodplains. Another belt with high Fe<sub>2</sub>O<sub>3</sub> values extends from Albania (ophiolite) and into Greece (Epirus, central Macedonia, Thrace and eastern coastal region) with ophiolite, chromite, bauxite, Fe-Ni and base metal deposits. A high total Fe<sub>2</sub>O<sub>3</sub> value (9.18%) occurs over basalt in Gran Canaria in the Canary Islands.

The point anomaly of total  $Fe_2O_3$  in floodplain sediment (8.45%) in the Vesdre basin in Belgium is caused by industrial pollution; the one in eastern Slovakia is possibly related to the Rudnany Fe-Cu-Hg-Ba deposit; in the Pyrenees (8.95% Fe<sub>2</sub>O<sub>3</sub>) to the Pierrefitte Zn-Pb-pyrrhotitemagnetite deposit, and in the Bilbao area in northern Spain (8.4% Fe<sub>2</sub>O<sub>3</sub>) to the Gallarta and Primitiva Fe deposits, but with additional industrial contamination in the Nervión basin; in northern Germany the point Fe<sub>2</sub>O<sub>3</sub> anomaly (35.82% Fe<sub>2</sub>O<sub>3</sub>) is possibly related to iron-ore mineralisation; another point anomaly in northern Sweden in the Skelefte mineralised belt (32.85% Fe<sub>2</sub>O<sub>3</sub>) is probably related to iron-ore mineralisation.

It is quite apparent that the Fe<sub>2</sub>O<sub>3</sub> geochemical patterns in floodplain sediment are similar to those of TiO<sub>2</sub> and V, and in some areas with Al<sub>2</sub>O<sub>3</sub>. Iron has a very strong correlation with V and Co, a strong correlation with Al, Ga, Nb, Ti, Eu and Y, and a good correlation with Mn, Cu, Li, Th and the REEs.

The *aqua regia* Fe distribution map of floodplain sediment shows some similarity with the total  $Fe_2O_3$  map, but with more widespread high values in England, and the Po River basin in northern Italy. *Aqua regia* extractable Fe is relatively higher in northern Portugal, northwestern Spain (ophiolitic complex in Galicia) and the French Pyrenees. On the other hand in northern Fennoscandia *aqua regia* extractable Fe is much lower than the total  $Fe_2O_3$  content, meaning that possibly more magnetite is present in the floodplain sediment of Fennoscandia (magnetite is more resistant to dissolution in *aqua regia*).

In conclusion, the distribution of  $Fe_2O_3$  in floodplain sediment is related mainly to the geological substratum and mineralised areas, and particularly to areas with mafic and ultramafic rocks, and mineralisation. However, pollution from industrial activities is evident in some areas as in the Vesdre basin in Belgium.

## Fe comparison between sample media

Patterns in Fe distribution between all solid sample media are broadly similar, although stream sediment concentrations are slightly higher than in other sample media throughout most of Britain and Ireland, southern Norway and southern Finland (Fe and Mn oxide precipitation), southern Poland and northern Germany, and lower throughout Croatia, Slovenia and southern Austria (removal of fine-grained material from residual soil is a possible explanation). Trends between total and *aqua regia* leachable Fe concentrations in soil samples are broadly similar. For stream and floodplain sediments, trends are broadly similar between total and leachable Fe contents except throughout northern and western Fennoscandia, where extractable Fe data are significantly lower due to the occurrence of insoluble magnetite grains in the sediment, and throughout southern England and over the Pyrenees, in which leachable floodplain Fe data (but not stream sediment data) are higher (no explanation). A boxplot comparing  $Fe_2O_3$  variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 18.

Stream water Fe data show almost exactly the opposite trends to those observed in solid sample media, with highest concentrations found in central and southern Finland and eastern and southern Sweden, northern Ireland and north-east Scotland, and lowest concentrations in western and southern Norway and throughout the Mediterranean. Iron in stream water is controlled by the DOC content throughout northern Europe, and by pH in Mediterranean Europe.



Figure 18. Boxplot comparison of  $Fe_2O_3$  variation in subsoil, topsoil, stream sediment and floodplain sediment.