Mn – Manganese

Introduction

Manganese 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 7 of the periodic table, along with Tc and Re. The element has an atomic number of 25, an atomic mass of 54, several oxidation states (+2, +3, +4, +6 and +7) and one naturally occurring isotope (^{55}Mn).

Manganese is relatively abundant with an average upper crustal abundance of 600 mg kg^{-1} and a bulk continental crust average of 1400 mg kg^{-1} (McLennan and Taylor 1999). Of the transition metals, only Fe occurs at higher concentrations in the Earth's crust. It is a common lithophile element forming several minerals including pyrolusite MnO_2, rhodochrosite $MnCO_3$ and manganite MnO(OH), and less well-characterised oxides in sedimentary rocks. It is widely distributed as an accessory element in garnet, olivine, pyroxene, amphibole and calcite.

Divalent manganese (Mn^{2+}) is the most stable oxidation state for Mn during magmatic processes. The ionic radius of Mn^{2+} (67 pm) is comparable to that of Fe^{2+} and Mg^{2+} (61 and 72 pm respectively) and Mn readily substitutes for Fe^{2+} and Mg^{2+} in minerals (Ure and Berrow 1982). Manganese is partitioned into ferromagnesian silicates and Fe-Ti oxides, becoming enriched in mafic and ultramafic rocks relative to felsic lithologies. This is demonstrated by the values reported by Mielke (1979) for igneous rocks: ultramafic 1600 mg kg^{-1}; basaltic 1500 mg kg^{-1}; granitic 390-540 mg kg^{-1}, and syenite 850 mg kg^{-1}. There is a close correlation between Mn and ferrous iron in most igneous rocks, with Mn:Fe ratios generally lying in the range 0.015-0.02.

The Mn content of sedimentary rocks is controlled by the geochemistry of the source rock and the redox conditions of the depositional environment (Wedepohl 1978). Manganese may occur in detrital phases such as mafic silicates, magnetite and ilmenite, but the largest proportion is typically held in secondary Mn^{4+} oxides that form either discrete concretions or surface coatings on primary minerals and lithic fragments. Shale and greywacke generally have higher levels of Mn (*ca.* 700 mg kg^{-1}) relative to coarser quartzitic sandstone and grits (*ca.* 170 mg kg^{-1}). Carbonate rocks, particularly dolomite, may also contain high concentrations of Mn, on average *ca.* 550 mg kg^{-1} (Wedepohl 1978). Loess has an average concentration of 560 mg kg^{-1} Mn (McLennan and Murray 1999).

High Mn values in association with Cr, Ni, V, *etc.*, are indicative of mafic rocks. In association with iron, Mn may denote the effects of co-precipitation in soil and stream or lake sediments and allow the screening of false anomalies of other elements.

The behaviour of Mn in soil is very complex and is controlled by different environmental factors, of which pH-Eh conditions are the most important (Kabata-Pendias 2001). Under cold climatic conditions, Mn is removed from the weathering zone and soil by acid solutions as bicarbonate or as a complex with organic acids derived from decaying plants. The physical properties of Mn oxides and hydroxides, such as small crystal size and, consequently, large surface area, have important geochemical implications. The negatively charged $Mn(OH)_4$ and MnO_2 are responsible for the high degree of association of Mn concretions with some transition metals, in particular with Co, Ni, Cu, Zn, Pb, Ba, Tl, W and Mo; in addition, the oxidation of As, Cr, V, Se, Hg and Pu by Mn oxides may control the redox behaviour of these elements in soil (Kabata-Pendias 2001). The global average for Mn in soil has been estimated as 437 mg kg^{-1}.

Although the $Mn^{2+}(aq)$ ion is readily soluble, manganese is not very mobile, especially under oxidising conditions, because Mn^{3+} and Mn^{4+} ions form insoluble hydrous oxides. Manganese is greatly influenced by redox conditions and is easily mobilised as Mn^{2+} under anoxic conditions (Hylander *et al.* 2000). Its chemistry is similar to that of Fe as both metals participate in redox reactions. Recent studies have suggested that Mn^{2+} has a low affinity for organic ligands (Lazerte and Burling 1990, Chiswell and Zaw 1991). Manganese concentrations in streams, receiving contributions from acid mine drainage can exceed 1 mg l^{-1}, although a more typical mean concentration is 7 µg l^{-1} (Wedepohl 1978). The average abundance of Mn in river particulates is 1050 mg kg^{-1} (McLennan and Murray 1999).

Anthropogenic sources of manganese include mining and smelting, engineering, traffic and agriculture. It is also used in the manufacture of steel, glass, dry batteries and chemicals. Permanganate is a powerful oxidising agent and is used in quantitative analysis and medicine. Manganese can be an undesirable impurity in water supplies, forming black oxide precipitates on pipes that may slough off, giving rise to staining, taste and odour problems. Geogenic sources of Mn are generally considered to be much more important than anthropogenic ones in the environment (Yang and Sanudo–Wilhelmy 1998).

Manganese is an essential element in plant and animal nutrition (Hurley and Keen 1987), although it is toxic at high concentrations. Many foods in the human diet contain Mn, including spinach, tea, herbs, grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. Manganese toxicity in humans mainly affects the respiratory tract and the brain; symptoms include hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson's disease, lung embolism and bronchitis. Manganese deficiency, considered to be less than 0.11 mg Mn day^{-1} for adults, is more common than toxicity, and causes impaired reproduction and growth (Reimann and de Caritat 1998). Symptoms of Mn deficiency include weight gain, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects and neurological symptoms.

Plants can also suffer from Mn toxicity and deficiency; the latter is more common when the pH of the soil is low. Highly toxic concentrations of manganese in soil can cause swelling of cell walls, withering of leafs and brown spots on leaves; symptoms of Mn deficiency are quite similar. There is only a narrow concentration range of Mn for optimal plant growth.

Table 44 compares the median concentrations of MnO in the FOREGS samples and in some reference datasets.

Table 44. Median concentrations of MnO in the FOREGS samples and in some reference data sets.

Manganese (MnO)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median %*
Crust[1]	Upper continental	n.a.	n.a	Total	0.10
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (ICP-MS)**	**0.06**
Subsoil *(Mn)*	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**337 *mg kg^{-1}***
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (ICP-MS)**	**0.065**
Topsoil *(Mn)*	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**382 *mg kg^{-1}***
Soil[2]	World	n.a.	n.a	Total	0.07
Soil, C-horizon*(Mn)*[3]	Barents region	1357	<2	*Aqua regia* (ICP-AES)	167 *mg kg^{-1}*
Water *(Mn)*	**FOREGS**	**804**	**Filtered <0.45 µm**		**15.9 (µg l^{-1})**
Water *(Mn)*[4]	World	n.a.			10 (µg l^{-1})
Stream sediment	**FOREGS**	**850**	**<0.15**	**Total (XRF)**	**0.079**
Stream sediment *(Mn)*	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**452 *mg kg^{-1}***
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**0.071**
Floodplain sediment *(Mn)*	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**446 *mg kg^{-1}***
Stream sediment *(Mn)*[5]	Canada	82 462	<0.18	*Aqua regia* (ICP-AES)	430 ***mg kg^{-1}***

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

MnO in soil

The median total MnO content (XRF analysis) is 0.060% in subsoil and 0.065% in topsoil, with a range from 0.003 to 0.604% in subsoil and 0.004 to 0.778% in topsoil. The average ratio topsoil/subsoil is 1.075.

The MnO subsoil distribution map shows low MnO values (<0.040%) throughout southern Sweden and southern Finland, the northern European plain from Poland to the Netherlands, the eastern part of Hungary, the extreme north-east of Scotland, and throughout Portugal and most of Spain, especially the calcareous southern half.

High MnO values in subsoil (>0.090%) occur in the Norwegian Caledonides, central and south-west England, Wales and Ireland (over Carboniferous shaly strata); a belt through central Germany from the Rhenish Schiefergebirge to Bavaria and into the eastern Alps, karst soil of Slovenia and coastal Croatia, Italy (hydrothermal activity in southern Italy especially near Naples), Greece and some scattered anomalies in Spain, among them an area from Asturias to north-east-Portugal (numerous Mn-Fe mineralisations associated with Middle Cambrian limestone, remobilised and precipitated in karstic spaces and fractures; volcanosedimentary Mn in Silurian and Devonian near Zamora on Spain-Portugal border). In Greece, MnO is associated with *terra rossa* soil (Kefallinia), base-metal mineralisation (Lavrion in Attica), Mn, Fe and Fe-Ni mineralisation. From south Brittany towards Poitou and the Massif Central in France, Mn anomalies in soil are linked to Cretaceous unconformity related mineralisation (Fe-Mn-Co karst); iron rich palaeosoil is also anomalous in Mn, Sc, V in the Vaucluse area of Provence.

The topsoil map is less anomalous with respect to MnO in Norway and Croatia, but shows additional enrichment in Sardinia, Gran Canaria and the Peloponnese in Greece. Overall the topsoil shows a slight enrichment in Mn in relation to the subsoil, with an average ratio topsoil/subsoil of 1.075. This contrasts with a slight depletion for Fe, where this ratio is 0.923.

The distribution of MnO in soil is closely related to that of Fe_2O_3, with which it has a strong correlation. In subsoil, the Fe-Mn correlation coefficient is 0.62 and in topsoil 0.63. Manganese precipitates in soil under oxidising conditions, causing local anomalies, in addition to anomalies due to the bedrock. Manganese in subsoil also shows a strong correlation with Co (0.64), and a good correlation (>0.4) with Ti, V, Sc, Al, In, Cu, Zn, Nb, Te, Y and the REEs. In topsoils, the pattern of correlations is the same, but Zn and the REEs have a stronger correlation with Mn, and there is also a good correlation with Cd and P_2O_5.

The median Mn content in soil after *aqua regia* extraction (ICP-AES analysis) is 337 mg kg^{-1} Mn-metal for subsoil and 382 mg kg^{-1} for topsoil, corresponding to 0.043% and 0.049% MnO respectively, with a range from <10 to 4390 mg kg^{-1} Mn-metal in subsoil, and <10 to 6480 mg kg^{-1} in topsoil. This means that on average about 70% of the Mn is extractable, but some extractable values are apparently higher than the total content. The distribution maps of extractable Mn are very similar to those of total content, except in Scandinavia, where extractable Mn is much lower, especially in the Caledonian mountain range.

Mn in stream water

Manganese values in stream water cover a remarkably wide range of five orders of magnitude from <0.05 to 698 µg l^{-1} (excluding three outliers up to 3010 µg l^{-1}), with a median value of 15.9 µg l^{-1}. Manganese data tend to correlate to a certain extent with F.

Lowest Mn values in stream water (<1.7 µg l^{-1}) are found in central and northern Sweden on the Precambrian Shield, and in central and south Norway, in western Scotland and western England on Caledonian terrains. Low Mn concentrations also occur in a small area in east-central France and in a larger one in south and south-west France extending to eastern Spain, and in small areas in northern Spain and Portugal, and on Corsica, in the Variscan part of Europe. Low Mn values are found across most of the Alps in France, northern and north-central Italy, most of Switzerland and west Austria with an extension into southern Germany, and in western Slovenia, in south-central Italy, south Italy and part of Sicily, a belt extending from Albania into north-western and central as well as north-easternmost Greece and Crete, all in the Alpidic region of Europe.

High Mn values in stream water (above 92 μg l^{-1}) occur around the Baltic Sea, on the Precambrian Shield rocks in southern Sweden (located in a Pb mining area), in central, east and south Finland, and on shield derived glacial drift cover in Estonia, Latvia and Lithuania, in most of Poland, in Denmark and northern Germany, with an extension to Netherlands and part of Belgium on Quaternary deposits. In the Caledonides region, enhanced Mn values occur in eastern Scotland and south-east England (in contrast to low Mn levels corresponding to soil and sediments in the latter area). On Variscan terrains, high Mn concentrations are found in south-west Poland (associated with glacial boulder clay) and central Czech Republic with an extension to Alpidic easternmost Austria and south-west Slovakia, in southern Portugal and Sardinia, where they are explained by the presence of Mn ore deposits and soluble forms in Mn rich Palaeozoic terrains. On the Alpidic Orogen, enhanced Mn occurs in the Pannonian basin of southern Hungary and north-eastern half of Croatia, in north central and south Italy (derived from recent alkaline volcanism), and in the western half of Sicily. An isolated anomaly in central Spain is related to lenticular Mn deposits associated with Pliocene-Quaternary alkaline basaltic volcanism; in south Spain near Huelva a Mn anomaly is associated with volcanosedimentary Mn ore deposits of the Iberian Pyrite Belt (De Vos *et al*. 2005).

The anomalous Mn concentration in stream water located in south-eastern Slovakia (602 μg l^{-1}) is due to mining and processing of metamorphic-hydrothermal vein mineralisation in the Spišsko-gemerské rudohorie Mountains. The second Mn anomaly in eastern Slovakia (558 μg l^{-1}) probably reflects the primary lithology of the Palaeogene claystone and sandstone. The enhanced content of Mn in the western Slovak lowlands is possibly caused by agricultural and/or industrial contamination (fertilisers, sewage water, organic compounds *etc.*)

The described Mn distribution pattern in stream water is surprising, because it is similar to elemental associations of opposing behaviour: in Fennnoscandia and Scotland to the REEs and associated elements in acid, low mineralisation stream water type; in most of central and southern Europe to the Major-ions group in high mineralisation stream water; and possibly on Sardinia, in Poland and the Baltic states to the Mn-Fe DOC association. The Mn distribution pattern, thus, does not reflect the geological substrate, but surficial factors. The pattern of high Mn concentration in stream water shows only exceptionally some resemblance to patterns in the solid sampling media.

MnO in stream sediment

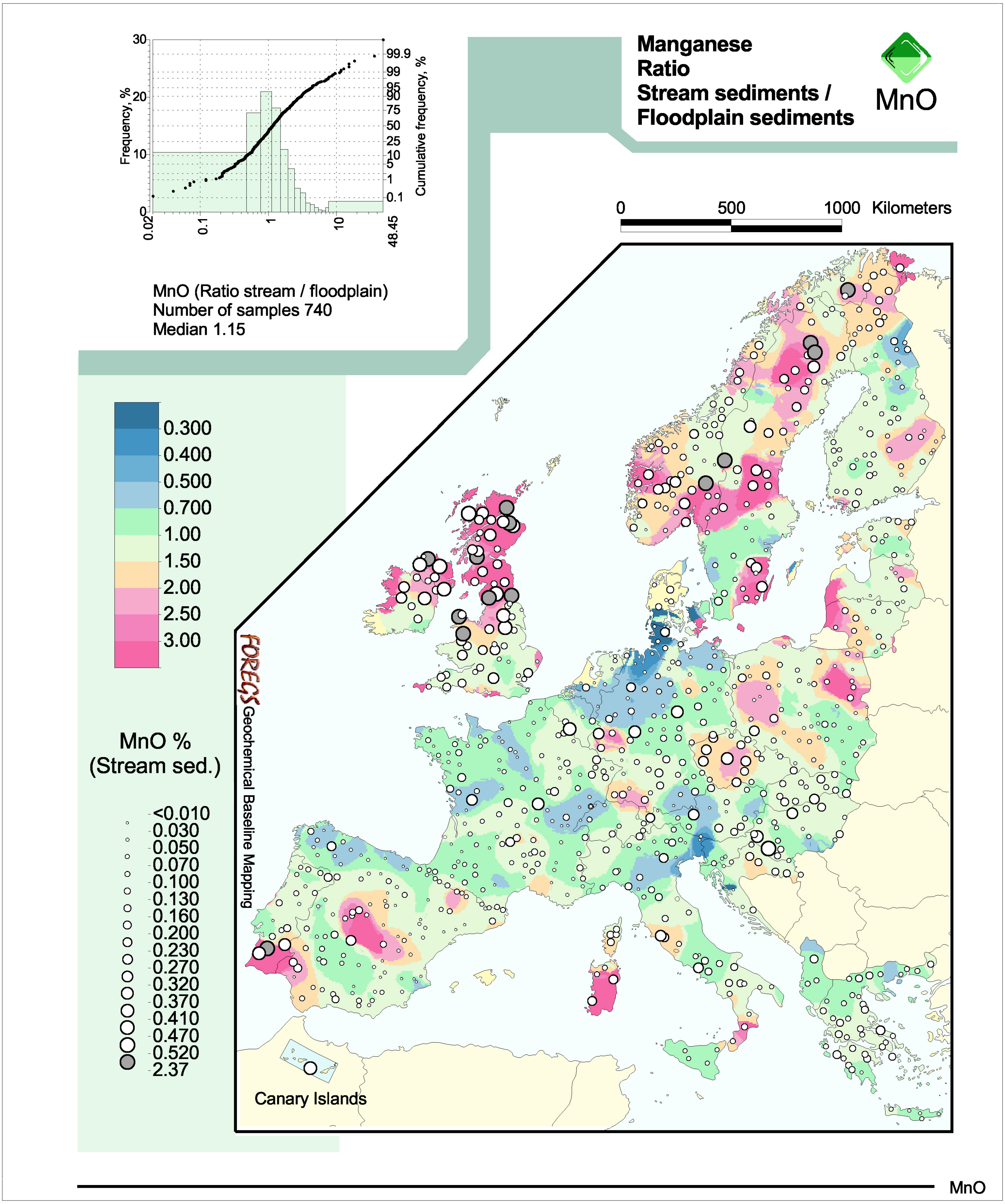
The median total MnO content in stream sediment (XRF analysis) is 0.08%, equivalent to 620 mg kg^{-1} as Mn metal, with a range from <0.01 to 2.37% (<77 to 18372 mg kg^{-1} Mn metal).

Low Mn values in stream sediment (<0.05%) occur in large areas of northern and eastern Spain, south-western and north-western France, the Jura-western Alps area, coastal Croatia and Slovenia with adjacent Austria and Italy, Crete, the Netherlands, parts of Poland and eastern Germany, Latvia, and small areas in eastern Finland and south-eastern Sweden.

The Mn distribution pattern in stream sediment is dominated by anomalously high values (>0.30%) over Britain and Ireland, except in the south-east; the similarity of the distribution patterns for Fe, Co, Mo, Ni, Cu, Pb, Zn, Ge and V in Britain and Ireland, suggests coprecipitation of metals on surface coatings in stream sediment, reflecting surficial processes rather than underlying bedrock signatures. High values (>0.13%) also occur in southern Norway and parts of northern Norway, most of central and northern Sweden, northern Finland, the Czech Republic, the southern Eifel in Germany, Pannonian Croatia and adjacent southern Hungary, alkaline volcanic provinces of central and southern Italy, Sardinia, Corsica and southern Portugal (Mn-rich volcanosedimentary deposits in the Iberian Pyrite Belt and Mn rich terrains).

Manganese in stream sediment shows a good correlation (>0.4) with Fe_2O_3, Co and Zn, and a weak correlation (0.3 to 0.4) with Ti, V and Cd.

Analysis of stream sediment by ICP-AES after dissolution with *aqua regia* results in a median content of 452 mg kg^{-1} Mn-metal, ranging from 24



Map 9. Ratio of Mn in stream versus floodplain sediments.

to 18898 mg kg^{-1}. This indicates that almost all Mn is extracted. Distribution patterns between total and extractable MnO are very similar.

MnO in floodplain sediment

Total MnO values in floodplain sediment, determined by XRF, vary from <0.01 to 6.61%, with a median of 0.070%, which corresponds to a range from <77 to 55193 mg kg^{-1} Mn metal with a median of 542 mg kg^{-1}. *Aqua regia* extractable Mn concentrations in floodplain sediment range from <10 to 49,800 mg kg^{-1} Mn metal with a median of 450 mg kg^{-1} Mn metal, corresponding to a range of 0.0013 to 6.43% MnO, with a median of 0.058% MnO. Generally, Mn values obtained by *aqua regia* extraction are about 30% lower than those with total extraction.

Low total MnO values in floodplain sediment (<0.05%) occur over the granitic, granodioritic and metasediment areas of the Scandinavian countries (southern Norway, southern Sweden and eastern Finland); the glacial drift deposits of north-east Germany, Poland, Lithuania, Latvia and Estonia; the alluvial sediments of the Garonne and Rhône rivers in France; most of the eastern half of the Iberian Peninsula with mainly clastic and calcareous rocks; the molasse basin in Austria, and Calabria in Italy with mainly alkaline volcanics and Tertiary sediments.

High total MnO values in floodplain sediment (>0.10%) occur over a variable lithology in central and northern Norway; southern, central and northern Sweden. In north-eastern Finland high Mn is explained by water-logged sediments containing Fe-Mn-precipitate. A belt of high MnO values extends from north of the Erzgebirge to the Bohemian Massif, the Pannonian basin in Hungary, and border area of Austria, Hungary, Slovenia and Croatia over variable lithology and mineralisation. Another zone with high total MnO values, but of smaller extent, occurs over the Albania and most of mainland Greece, which may be explained by the lithology and mineralisation, but also climatic conditions. Other high total MnO values are found again over variable lithology and mineralisation in north-west and north-east Germany, central and south-west England and Wales, southern half of Ireland, the Poitou and northern Massif Central in France, Galicia in north-west Spain (weathering of ultramafic rocks of the Ordenes complex), western Alps, the lower Po basin, the Roman Alkaline Province and southern Italy.

The highest MnO value in floodplain sediment (6.67%) occurs in northern Sweden in the Skellefte Belt with base metal mineralisation (*e.g.,* Rakkejaur Zn-Cu, Adak Cu-Zn). Another point MnO anomaly in central Sweden is possibly related to the Vassbo Pb-Zn deposit. The point MnO anomaly on the Clyde River near Glasgow in Scotland may be related to mafic volcanics of the Midland Valley.

Manganese in floodplain sediment shows a good correlation (>0.4) with Ti_2O, Fe_2O_3 and Co, and a weaker correlation (>0.3) with P_2O_5, V, Ga and Mo.

Geochemical patterns in floodplain sediment shown by total XRF and *aqua regia* extractable Mn are approximately similar, with differences in some areas, *e.g.,* in central Norway *aqua regia* extractable Mn is lower.

In conclusion, the distribution of MnO in floodplain sediment is related mainly to the geological substratum and mineralised areas, and particularly to areas with mafic and ultramafic rocks, and mineralisation.

Mn comparison between sample media

Although there are general similarities in the distribution of Mn in all solid sample media, there are also many more differences than observed in other elements. The main differences are throughout all but south-east Britain and Ireland, in which very high Mn is observed in stream sediment but much lower concentrations observed in the floodplain sediment and soil. A similar enrichment is observed in southern Portugal, and parts of Sweden and adjacent Norway (see Map 9, ratio of stream sediment to floodplain sediment data for Mn). southern Poland, northern Germany and Denmark. This effect is also found in Co data. Manganese concentrations are also generally higher in subsoil and floodplain sediment throughout most of Norway, but much lower in topsoil and stream sediment . There is good agreement between patterns in total and aqua regia leachable Mn concentrations in soil and sediment with the exception of extreme northern Fennoscandia, where Mn is lower in the leachable fraction.

A boxplot comparing MnO variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 28.

With the exception of the Iberian Peninsula, the general trend for stream water Mn data to show opposite patterns to those generally found in solid sample media, *i.e.,* generally low throughout Scandinavia and in areas adjacent to the Mediterranean, and high throughout Finland and throughout the Quaternary sediments of northern mainland Europe. The higher stream water Mn values (in the reduced Mn^{2+} form) are strongly associated with the presence of DOC; the lower Mn values are more closely associated with rocks in which Mn is more tightly bound in the Mn^{4+} oxidation state.

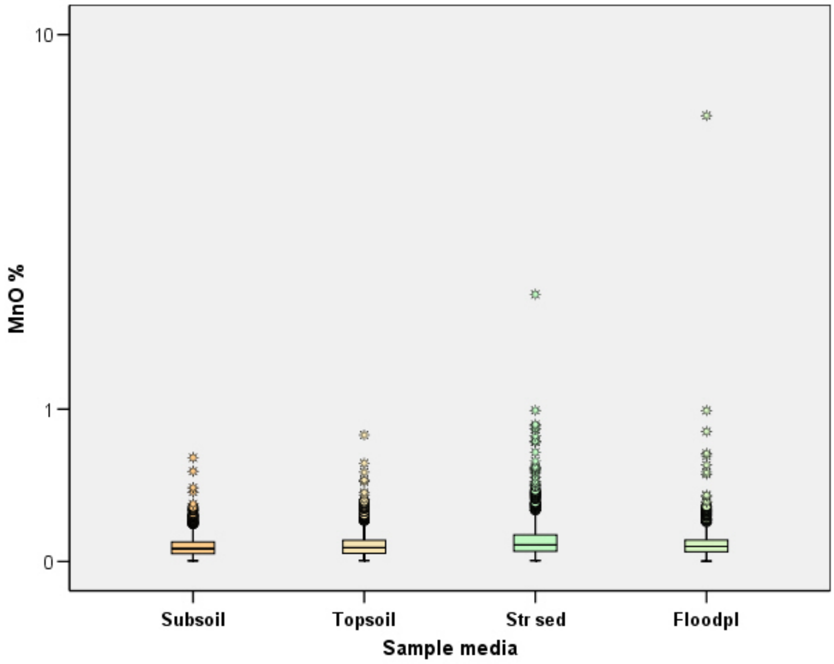


Figure 28. Boxplot comparison of MnO variation in subsoil, topsoil, stream sediment and floodplain sediment.