

Introduction

Chromium 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 6 of the periodic table, along with Mo and W. The element has an atomic number of 24, an atomic mass of 52, two main oxidation states (+3 and +6) and four naturally occurring isotopes (^{50}Cr , ^{52}Cr , ^{53}Cr and ^{54}Cr), of which ^{52}Cr represents 84% of the total mass.

Chromium is a lithophile metallic element forming several minerals, including chromite FeCr_2O_4 and the rare crocoite PbCrO_4 , and is present as an accessory element in several others, such as spinel, amphibole, mica, pyroxene and garnet. The trivalent ion Cr^{3+} has an ionic radius of 62 pm and, like other transition elements with intermediate radii, readily substitutes for Fe and Mg, and is partitioned into spinel and pyroxene during the earliest stages of crystal fractionation. As a result, Cr is enriched in ultramafic rocks (1000–3000 mg kg^{-1}), along with elements such as Ni. While the principal Cr ore mineral, chromite, is generally mined from ultramafic rocks, it is also a major carrier of Cr in basaltic magmas, along with Cr-enriched magnetite and ilmenite (Wedepohl 1978). Olivine is generally poor in Cr, but pyroxene, amphibole and mica may be enriched (Ure and Berrow 1982). Mielke (1979) cites Cr values for igneous rocks as: ultramafic 1600 mg kg^{-1} ; basaltic 170 mg kg^{-1} ; granitic 4–22 mg kg^{-1} ; and an average crustal abundance of 122 mg kg^{-1} (Kabata-Pendias 2001).

Elevated Cr values are indicative of mafic or ultramafic rocks, even in strongly-weathered environments, such as laterite; this apparently holds true even when *aqua regia* digestion is applied, which is incapable of breaking down chromite. Very low Cr contents in association with elevated values of K, Th, U and REEs may indicate the presence of felsic rocks, e.g., kaolinised intrusives.

In sedimentary rocks, Cr may be present in primary detrital phases such as chromite, magnetite and ilmenite. During weathering, the behaviour of Cr^{3+} resembles that of Fe^{3+} and Al^{3+} , leading to widespread accumulation in secondary oxides and clays. The average concentration of Cr in shale is reported to be 90 mg kg^{-1} , with

rather lower mean values in sandstone (35 mg kg^{-1}) and limestone (11 mg kg^{-1}) (Mielke 1979). McLennan and Murray (1999) quote average values for river particulates and loess as 100 and 44 mg kg^{-1} Cr respectively.

Chromium is a low mobility element, especially under moderately oxidising and reducing conditions and near-neutral pH values. In soil, Cr behaviour is governed by pH, Eh and organic matter. Its adsorption by clay is also highly dependent on pH; Cr^{6+} adsorption decreases with increasing pH, and Cr^{3+} adsorption increases with increasing pH. The dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} to Cr^{3+} , the rate of which increases with soil acidity (Kabata-Pendias 2001). Cationic Cr^{3+} , CrOH^{2+} and $\text{Cr}(\text{OH})_2^+$ are the main forms of chromium in reducing environments between pH 5 and pH 9. In alkaline oxidising environments, Cr may be present as the chromate ion, CrO_4^{2-} , although this species is reduced naturally in stream sediment over time (Whalley *et al.* 1999). Trivalent chromium readily substitutes for Fe^{3+} in minerals, and co-precipitates with Fe^{3+} as insoluble $\text{Cr}(\text{OH})_3$ at high pH values. The global average of Cr in surface soil has been estimated to be 54 mg kg^{-1} ; soil on serpentine contains as much as 0.2 to 0.4% Cr, sandy soil and histosols contain on average 47 and 12 mg kg^{-1} Cr respectively.

Concentrations of chromium in uncontaminated natural water are typically less than 10 $\mu\text{g l}^{-1}$ (Hem 1992). The European Commission and US EPA threshold for drinking water is 50 $\mu\text{g l}^{-1}$ Cr (European Commission 1998).

Chromium is a major component of steel alloys (10–26%) and used for coating steel as chrome plating. Chromates and dichromates, containing Cr^{6+} , are sometimes released in industrial effluents, especially from leather tanning and electroplating operations, and are highly poisonous and readily soluble. However, because of their powerful oxidising properties they are rapidly reduced and sorbed by organic residues.

Chromium, once thought to be non-essential, is now known to have at least one important

biological function (Frausto da Silva and Williams 1991). It is needed by the human body in small amounts for insulin action and the metabolism of proteins and carbohydrates. Chromium has a varying toxicity depending on its valency and speciation in the environment. Soluble Cr³⁺ is

considered relatively harmless at levels normally encountered, but Cr⁶⁺ is highly toxic, causing liver and kidney damage and acting as a carcinogen.

Table 21 compares the median concentrations of Cr in the FOREGS samples and in some reference datasets.

Table 21. Median concentrations of Cr in the FOREGS samples and in some reference data sets.

Chromium (Cr)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	92
Subsoil	FOREGS	787	<2.0	Total (ICP-MS)	62.0
Subsoil	FOREGS	784	<2.0	Aqua regia (ICP-MS)	24.0
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	60.0
Topsoil	FOREGS	837	<2.0	Aqua regia (ICP-MS)	22.0
Soil ²⁾	World	n.a.	n.a.	Total	80
Soil, C-horizon ³⁾	Barents region	1357	<2	Aqua regia (ICP-MS)	18.8
Water	FOREGS	806	Filtered <0.45 µm		0.38 (µg l⁻¹)
Water ⁴⁾	World	n.a.	n.a.		1 (µg l ⁻¹)
Stream sediment	FOREGS	852	<0.15	Total (XRF)	63.0
Stream sediment	FOREGS	845	<0.15	Aqua regia (ICP-AES)	21.0
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	59.0
Floodplain sediment	FOREGS	747	<2.0	Aqua regia (ICP-AES)	23.0
Stream sediment ⁵⁾	Canada	26 227	<0.18	Total (INAA)	80
Stream sediment ⁵⁾	Canada	7875	<0.18	Aqua regia (ICP-AES)	49

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

Cr in soil

The median total Cr content (XRF analysis) is 62 mg kg⁻¹ in subsoil and 60 mg kg⁻¹ in topsoil. The range of values varies from 3 to 2140 mg kg⁻¹ in subsoil and <3 to 6230 mg kg⁻¹ in topsoil. The average ratio topsoil/subsoil is 1.096.

Low Cr values in subsoil (<34 mg kg⁻¹) occur in southern Fennoscandia, Estonia, parts of northern Germany and Poland, central Portugal and parts of central and eastern Spain.

The subsoil Cr map shows a strong anomaly over most of Greece and Albania, caused by mineralised ophiolitic rocks, and sedimentary rocks derived from them. There are also high values (>95.0 mg kg⁻¹) over ophiolites in Liguria (Italy) and Corsica, over Slovenia and Croatia

(high values in *terra rossa* over carbonate rocks), the Rheno-Hercynian, the Carpathians, northern Ireland (Antrim basalt), central Norway and a large area with greenstone belts in northern Fennoscandia. In France, in the western Massif Central and southern Brittany, Cr-Ni anomalies in soil are related to amphibolite of the lower gneiss unit. In the core of the Massif Central, soil over Miocene mafic volcanics of the Cantal are also enriched in Cr, Ni and Fe. In Greece, the Cr and Ni anomalies are also associated with bauxite, Fe-Ni and polymetallic sulphide mineralisation. In central England, elevated Cr levels are associated with Mesozoic sedimentary ironstone. Isolated high Cr values in Spain are related to the Peñas de

Aya gabbro in the western Pyrenees, the Ordenes ophiolitic Complex in Galicia (north-west Spain) and other mafic facies in central and southern Spain.

The topsoil map for Cr is very similar to the subsoil map. Gran Canaria shows an anomaly due to basaltic volcanic rocks.

It can be concluded that high Cr contents in European soil is mostly of geogenic origin.

The correlation between Cr and Ni is very strong (0.89 in subsoil and 0.83 in topsoil). In subsoils, there is also a strong positive correlation with Co and a good correlation with Fe, Sc, V and U. In topsoil, Cr only shows a good correlation

with Cu.

The median Cr content after *aqua regia* extraction (ICP-AES analysis) is 24 mg kg⁻¹ in subsoil and 22 mg kg⁻¹ in topsoil, with a range from <1 to 1710 mg kg⁻¹ in subsoil and <1 to 2340 mg kg⁻¹ in topsoil. This is only about a third of total Cr content. Nevertheless, the distribution pattern of extractable Cr is very similar to total Cr, with only small differences: the subsoil of the Ardenne-Rhenish Massif (Belgian-Germany border area) shows no high values for extractable Cr; in topsoil, a point anomaly appears in west-central Spain.

Cr in stream water

Chromium values in stream water range over more than three orders of magnitude from <0.01 to 43.3 µg l⁻¹ with a median value of 0.38 µg l⁻¹.

Lowest Cr values in stream water (<0.21 µg l⁻¹) are found in western, central and northern Norway, central Sweden, central England and Wales on Precambrian Shield and Caledonian terrains, north-western Spain (Iberian Massif with acidic pH), Corsica, Sardinia, and throughout most of central mainland Europe from central France, across Germany and Czech Republic largely on Variscan terrains, and in most of northern and south-central Italy, Switzerland, Austria and Slovenia, western Slovakia and northern Hungary, all on the Alpine Orogen.

Enhanced Cr concentrations in stream water (>1 µg l⁻¹) are found in south-western Sweden (related to mafic rocks), in Finland on Precambrian Shield, all of Lithuania, Latvia and north-east tip of Poland on Precambrian Shield derived glacial deposits. In north-central and south Spain, a relation is found with alkaline pH and higher DOC, near Málaga in south Spain also with ultramafic rocks of the Ronda and Ojén massifs, whereas in east-central Spain high Cr is related to Triassic Keuper outcrops and associated ophiolite. High Cr concentrations also occur in north-western (Liguria), central (Roman-Tuscan province) and southern (Apulia) Italy, eastern Czech Republic and throughout Slovakia, and in eastern Croatia, in Albania and throughout most of Greece, all on Alpine terrains. The enhanced values of north-western Italy and on the Alpine

range, as well as those in Albania and Greece are related to the widespread occurrence of ophiolitic rocks. The isolated anomaly in the Po Valley of northern Italy is probably related to industrial pollution. In central Italy, anomalies are related to the occurrence of volcanic alkalic rocks, whereas the high values in the Apulia region may have an anthropogenic source. Isolated enhanced Cr in northern England is associated with heavy industrial pollution and/or underlying geology of the Durham Coalfield. The enhanced Cr values in Lithuania, Latvia and in part of northern Poland are not real, but are caused by contamination during acidification of the water samples. In western Finland, the enhanced Cr data are probably associated with clay-rich soil; in the east, they are possibly associated with black schist and sulphide deposits. In Finland and Sweden, elevated Cr content in stream water can also be linked to high organic carbon content of the water (see DOC map).

The isolated stream water Cr anomaly in Slovenia is related to industrial pollution. The point anomaly in eastern Croatia is probably related to Tertiary mafic volcanics or industrial pollution. An isolated highly anomalous value in southern Sweden is of anthropogenic origin. A Cr point anomaly in the south-east Czech Republic is geogenic, assigned to an ultramafic rock called durbachite, and to a smaller extent by gabbroamphibolitic inclusions in crystalline rocks; the anomalous Cr value is found in stream water, stream sediment and floodplain sediment.

Chromium is partly associated with Major-ions highly mineralised stream water (Spain, Italy, Slovakia) and partly with DOC-rich stream water that are responsible for its high values in Finland and Sweden. High alkalinity is typical for Albania, Greece and the Iberian Peninsula. In most regions with high chrome concentration in

stream water, the reason is clearly exogenic, as indicated by distribution patterns in solid sampling media. A geogenic explanation for high Cr in stream water can be found in Greece, Albania and northern Italy, related to ophiolite, and in central Italy, related to alkaline volcanism.

Cr in stream sediment

The median total Cr content (XRF analysis) in stream sediment is 64 mg kg^{-1} , with a range of values from <3 to 3324 mg kg^{-1} .

Low Cr values in stream sediment ($<40 \text{ mg kg}^{-1}$) occur over the Quaternary sediments of Denmark, north-eastern Germany and central Poland, in Estonia and Latvia, southern Norway, most of Sweden, part of southern Finland, central and eastern Spain, north and western Portugal, south-western France, central Austria and adjacent Italy, and northern Sardinia and southern Corsica.

The Cr stream sediment distribution map is dominated by a strong anomaly in Greece and Albania, over the ophiolite belt. High values ($>89 \text{ mg kg}^{-1}$) also occur in the northern Apennines of Italy (where ophiolite is also present), northern Fennoscandia (greenstone), northern Britain and northern Ireland (Antrim basalt), the Eifel in Germany, the border area between Spain and north-east Portugal (lower Palaeozoic schist and graywacke), the lower Palaeozoic mafic-

ultramafic intrusives of the Beja zone of southern Spain and Portugal. Some point anomalies also occur in Hungary, the Czech Republic, the central Alps, central and southern Norway (greenstone belts). In France, high Cr background ($90\text{-}150 \text{ mg kg}^{-1}$) occurs in areas with black shale, marly Jurassic rocks, and Quaternary basalt in the Massif Central.

The correlation between Cr and Ni in stream sediment is very strong (0.80). Chromium also has a weak correlation (0.3 to 0.4) with Co, Cu, Fe and V.

The median Cr content in stream sediment after *aqua regia* extraction (ICP-AES analysis) is 22 mg kg^{-1} , with a range from 2 to 1750 mg kg^{-1} . These values represent only about one third of the total extraction. The distribution pattern of extractable Cr is, however, roughly the same as for total Cr, but with high extractable values occurring in clay-rich sediments of southern Finland, and no high values in the Eifel area.

Cr in floodplain sediment

Total Cr values in floodplain sediments vary from 5 to 2731 mg kg^{-1} , with a median of 59 mg kg^{-1} , and *aqua regia* extractable concentrations range from 3 to 1596 mg kg^{-1} with a median of 23 mg kg^{-1} . The *aqua regia* extracts on average about 40% of the total Cr, therefore, some patterns are subdued.

Low total Cr values in floodplain sediment ($<35 \text{ mg kg}^{-1}$) occur over the granitic, granodioritic and gneissic areas of the southern and central Sweden, southern Norway, the glacial drift covered plain extending from north Germany, Poland, Lithuania to Latvia and

Estonia; the sandstone, metamorphic, and granitic rocks of north-east Scotland, the alluvial plain of the lower Garonne river basin in France; the clastic and carbonate rocks of central and eastern Spain, and southern Corsica with crystalline rocks.

High total Cr values in floodplain sediment ($>88 \text{ mg kg}^{-1}$) are found over the amphibolite of central and northern Norway; the greenstone belt of northern Finland; the shale and mafic volcanics of the Scottish Midland Valley; the high total Cr values in Wales extending into central and east England are possibly attributed to mafic volcanics

and the iron mineralisation; the Erzgebirge (mineralisation), and the extensive anomalous zone from the Czech Republic, Hungary, southern Austria, Slovenia and Croatia, and eastern Hungary is attributed to the occurrence of mafic rocks and mineralisation; in southern Portugal to schist, graywacke and mineralisation; the northern half of Italy with ophiolites, and Corsica with mafic and ultramafic rocks. Very high total Cr values ($>110 \text{ mg kg}^{-1}$) extend over the whole of Albania and Greece, and are ascribed to both the ophiolite rocks, and mineralisation.

There is a floodplain sediment Cr anomaly in Galicia related to ophiolites, and one in north-east Portugal associated with mafic-ultramafic rocks. A point Cr anomaly in south-east Spain (921 mg kg^{-1}) is of anthropogenic origin, related to leather tanning industry in the Guadalentín basin.

Outlying Cr values in floodplain sediment occur in Greece (2731 and 1233 mg kg^{-1}), and Albania (1526 mg kg^{-1}) in the ophiolite belt with Cr mineralisation. A highly anomalous Cr sample (1905 mg kg^{-1}) occurs in southern Hungary and may be related to the mafic volcanics in the Mecsek Mountains, or to industrial pollution, or both. A point Cr anomaly in south-west Sweden (963 mg kg^{-1}) may be caused by some industries upstream, but regional till geochemistry shows elevated Cr values, mainly related to Palaeozoic shale. An alternative explanation is that the sample also contains significant amounts of Mn, which may be responsible for absorption of Cr to Mn-oxides.

Cr comparison between sample media

Patterns in Cr distribution between all solid sample media are very similar; there is also little difference between total and *aqua regia* leachable Cr distributions. The highest Cr values occur over the ophiolite belt and mineralised areas of Greece and Albania and is observed in all sample media, including stream water. High Cr is also observed in all solid sample media in central Norway and northern Fennoscandia associated with greenstone belts. These anomalies are not observed, however, in stream water, because of dilution by rain water and absence of organic carbon. In central and

Chromium in floodplain sediment shows a strong correlation with Ni (0.74), a good correlation with Co, and a weak correlation with MgO.

The *aqua regia* extractable Cr floodplain sediment map is overall similar to the total XRF Cr map, with more pronounced high Cr patterns in south-west Finland, and Stockholm area in Sweden, and less pronounced in Wales, south-west Portugal, eastern Hungary and Slovakia.

Despite the fact that *aqua regia* extractable Cr in floodplain sediment is less than half the total XRF content, there are distinct similarities in their distribution patterns. This suggests that Cr may be present in similar proportion in at least two mineral phases, one of which would be more readily dissolved by *aqua regia*, being either in the form of clay minerals with adsorbed Cr or in strongly weathered material.

In conclusion, mafic and ultramafic lithologies, and ophiolite masses, together with their metamorphic equivalents (greenstone) and mineralisation, show the highest Cr concentrations in floodplain sediment. Greece and Albania appear to represent a geochemical province with respect to Cr, but also in association with Ni, Co, Mg, Cu and Mn. The distribution map of total Cr in floodplain sediment shows, therefore, the geochemical differences of the geological substratum and mineralised areas quite well, and no distinguishable influences from anthropogenic activities are recognised.

southern Finland, Cr is higher in stream water than other media as it is absorbed by high levels of organic matter. Similar effects are observed in Latvia and Lithuania (but it is influenced here by sampling contamination). High Cr in stream water throughout northern and central Spain is not observed in the solid sample media, reflecting the influence of alkaline pH and oxidising conditions on Cr solubility in water.

A boxplot comparing Cr variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 14.

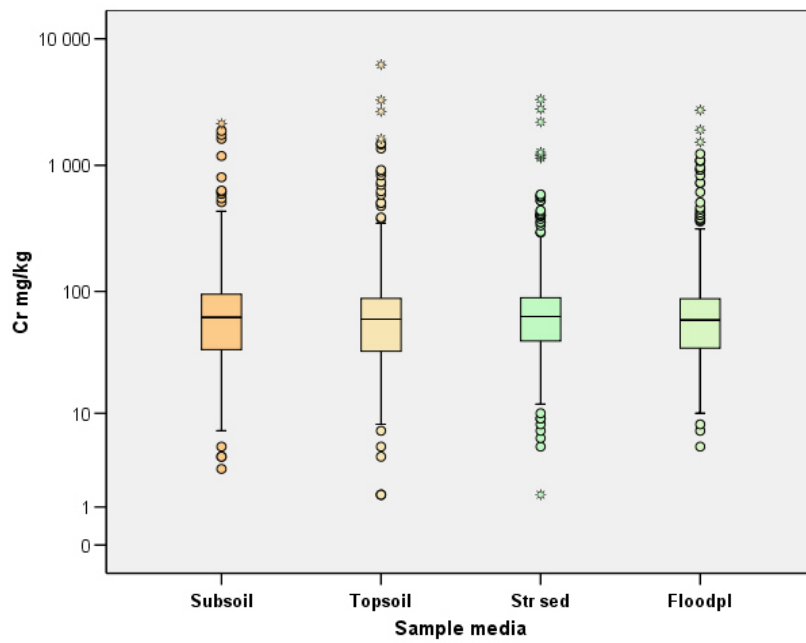


Figure 14. Boxplot comparison of Cr variation in subsoil, topsoil, stream sediment and floodplain sediment.