

Introduction

Strontium belongs to the group 2 elements of the periodic table, along with Be, Mg, Ca and Ba. It has an atomic number of 38, an atomic mass of 88, one oxidation state (+2) and four naturally occurring isotopes (^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr), of which ^{88}Sr is the most abundant at 82.6% of the total mass. Strontium is most similar chemically to the heavier alkali earth elements, Ca and Ba.

Strontium is a lithophile metallic element. The size of the Sr^{2+} ion (118 pm) is intermediate between those of Ca^{2+} (100 pm) and K^+ (138 pm), for which it may substitute in a variety of rock-forming minerals including K-feldspar, gypsum, plagioclase and, especially, calcite and dolomite, which are the main sources of Sr in stream water. Some substitution for Ba also takes place in barite BaSO_4 and witherite BaCO_3 . Minerals of Sr are relatively rare, but include strontianite SrCO_3 and celestite SrSO_4 , which are mainly associated with hydrothermal deposits or pegmatites.

During magmatic processes, Sr is partitioned into mid-stage fractionates and, thus, tends to be enriched in intermediate rocks (*ca.* 500 mg kg^{-1}) relative to evolved granite (<300 mg kg^{-1}) or mafic igneous rocks (<450 mg kg^{-1}). Particularly high concentrations (*ca.* 1000 mg kg^{-1}) have been recorded in anorthosite (Wedepohl 1978). Mielke (1979) cites levels of Sr in ultramafic, basaltic and granitic rocks as 1, 465 and 100–440 mg kg^{-1} respectively, and a crustal average of 384 mg kg^{-1} . The ratios of Rb:Sr, Sr:Ca and Ba:Sr are widely used to determine petrogenesis, the first two increasing and the last one decreasing with magmatic evolution. Strontium is relatively immobile at high metamorphic grades, often becoming concentrated in granulite in association with Ba and Zr (Drury 1973). However, pervasive redistribution may occur during hydrothermal alteration and contact metamorphism (Gale and Roberts 1974), and high Sr values in granulite have been attributed to the transfer of Sr to the lower crust during mantle degassing (Korringa and Noble 1971). Anomalous Sr concentrations have been reported in altered veins in granitoids (White 1966).

In sedimentary processes, the distribution of Sr is affected both by strong adsorption on clay minerals, extensive substitution of Sr^{2+} for Ca^{2+} in carbonate minerals (aragonite > calcite) and Sr^{2+}

for Ba^{2+} in sulphate minerals, as well as the amount of detrital feldspar (Simmons 1999b). Enrichment of Sr up to concentrations of *ca.* 1000 mg kg^{-1} is, therefore, common in limestone and evaporates, although the Sr:Ca ratio in most types of limestone is less than 1:1000 (Kulp *et al.* 1952). The minerals strontianite SrCO_3 and celestite SrSO_4 are present in sedimentary rocks. Discrete Sr minerals are relatively uncommon, although sulphate and carbonate phases may occur in evaporites and hydrothermal veins (Ure and Berrow 1982). High Sr levels can be associated with Ba minerals, *e.g.*, barite and witherite, due to preferential substitution for the larger (135 pm) Ba^{2+} ion. Otherwise feldspar is the principal Sr carrier, and pure quartzite (<40 mg kg^{-1}) and shale (<400 mg kg^{-1}) are generally poor in Sr relative to quartzo-feldspathic rocks (*ca.* 600 mg kg^{-1}). Mielke (1979) cites levels of Sr in shale, sandstone and carbonate rocks as 300, 20 and 610 mg kg^{-1} respectively.

Strontium is strongly associated with calcium and is indicative of calcareous rocks, especially in association with Sr, Mg and Ba. Where Ca and other elements indicate calcareous rocks, and other elements (*e.g.*, REEs) indicate felsic intrusives, bedrock geology may be favourable for skarn mineralisation.

Strontium is easily mobilised during weathering, especially in oxidising acid environments, and is incorporated in clay minerals and strongly fixed by organic matter. The Sr content in soil is highly controlled by parent rocks and climate and, therefore, its concentrations range from 50 to 1000 mg kg^{-1} (Taylor 1964). Soil derived from glacial till under humid climate is comparatively poor in Sr, and an average value for loess is given as 192 mg kg^{-1} (McLennan and Murray 1999). In acid soil, Sr is highly leached down the profile, and coastal areas have an apparent enrichment in surface soil; this may be explained as evidence of atmospheric input of sea salt (Kabata-Pendias 2001).

Most of the Sr in stream sediment is contained in lithic fragments and detrital feldspars, but it may also be present in mineralised areas in such minerals as barite and witherite. The release of Sr^{2+} from these minerals is relatively slow, but subsequent dispersal can be widespread under pH

conditions below 5.5 (Short 1961). At higher pH values or in the presence of high CO₂ concentrations, Sr tends to precipitate as an authigenic carbonate. The average content of Sr in river particulates is given as 150 mg kg⁻¹ (McLennan and Murray 1999).

Strontium as the aqueous cation Sr²⁺ is mobile under most environmental conditions, despite the relatively low solubility of the carbonate and sulphate at neutral to high pHs (Brookins 1988). At pH values below 4.5, the Sr²⁺ ion is dominant. Under more basic conditions (pH 5 to 7.5), SrSO₄ forms, and under alkaline conditions (pH>8), SrCO₃ is predominant. It has been estimated that approximately 80% of Sr entering the oceans from the world's rivers is derived from the weathering of carbonate and sulphate minerals (Brass 1976), with the remainder derived from silicates. As the Sr cycle is dominated by carbonate, attention has often focused on the Sr:Ca ratio in fresh water. The range of Sr:Ca ratios in rivers of the United States of America has been calculated to be 4.5–8.2 x 10⁻³ (Turekian 1964). Hem (1992) cites an

average Sr concentration for USA river waters of ca. 100 µg l⁻¹, and Simmons (1999b) gives the global average as ca. 70 µg l⁻¹; the concentration of Sr in sea water is ca. 8 mg l⁻¹.

Anthropogenic sources of Sr include industrial waste, especially from Zn refineries, disposal of coal ash and incinerator ash, and radiogenic Sr from nuclear tests (Reimann and de Caritat 1998). Strontium is also used in the production of ferrite magnets and glass for colour television picture tubes.

Biologically, Sr is considered to be a non-essential element. However, it can substitute for Ca²⁺ in living organisms, causing concern over radiogenic forms of Sr in the environment, such as the highly radiotoxic ⁹⁰Sr. Long-term toxicity causes “strontium rickets” where the skeleton fails to mineralise, even when there is adequate Ca and vitamin D (Mertz 1987).

Table 63 compares the median concentrations of Sr in the FOREGS samples and in some reference datasets.

Table 63. Median concentrations of Sr in the FOREGS samples and in some reference data sets.

Strontium (Sr)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	320
Subsoil	FOREGS	788	<2.0	Total (ICP-MS)	95.0
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	89.0
Soil ²⁾	World	n.a.	n.a.	Total	240
Humus	FOREGS	367	<2.0	Total (ICP-MS)	17.4
Humus ³⁾	Barents region	1357	<2	Total (HNO ₃ , ICP-MS)	23.9
Water	FOREGS	808	Filtered <0.45 µm		0.11 (mg l⁻¹)
Water ⁴⁾	World	n.a.	n.a.		0.50 (mg l ⁻¹)
Stream sediment	FOREGS	852	<0.15	Total (XRF)	126
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	131

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

Sr in soil

The median Sr content is 95 mg kg⁻¹ in subsoil and 89 mg kg⁻¹ in topsoil, with a range from 6 to 2010 mg kg⁻¹ in subsoil and from 8 to 3120 mg kg⁻¹ in topsoil. The average ratio topsoil/subsoil is 0.877.

The Sr subsoil and topsoil distribution maps show some similarities with the corresponding CaO maps. Low Sr values in subsoil (<63.0 mg kg⁻¹) occur in Ireland, parts of England, Portugal and western Spain, western France, the

glacial drift area from the Netherlands to Poland, and eastern Greece.

Calcareous areas in southern Europe, including southern and eastern Spain, southern France and central and southern Italy, have high Sr values in subsoil ($>180 \text{ mg kg}^{-1}$), as do crystalline areas in the Caledonides and Fennoscandian Shield throughout Finland, northern and south-western Sweden, southern Norway and north-west Scotland. Local anomalously high Sr in the Roman and Neapolitan igneous provinces is associated with alkaline volcanics, and in Sicily, with gypsum-sulphurous evaporites. In contrast to CaO, Ireland, south-east England and Greece show only a slight Sr enrichment in subsoil, despite the widespread calcareous lithology.

Sr in humus

The median Sr content in humus is 17.0 mg kg^{-1} , and the range varies from 1.10 to 205 mg kg^{-1} .

The Sr distribution map shows low values in humus ($<11 \text{ mg kg}^{-1}$) occurring mainly in central Britain, western France, Denmark and northern Germany, most of Poland, parts of south-central Sweden and southern Germany.

High Sr values in humus ($>27 \text{ mg kg}^{-1}$) are located mainly in northern Italy and adjacent southern Austria; central Finland; central Norway; part of southern Norway; a small area in south-east Sweden; Ireland; and isolated anomalies

Subsoil and topsoil Sr distribution maps show the same general patterns. There is however a slight depletion in topsoil: the average ratio topsoil/subsoil is 0.877, one of the lowest ratios (Map 14).

Strontium in soil has few positive correlations on the European continental scale: there is a weak positive correlation with CaO (0.36 in subsoil, 0.35 in topsoil), due to their association in limestone and marble, and also a weak to good correlation with Ba (0.37 in subsoil, 0.47 in topsoil) and Na_2O (0.38 subsoil and 0.47 topsoil), due to the crystalline association, especially in feldspar. Strontium has a weak negative correlation with SiO_2 (-0.38 in subsoil, -0.41 in topsoil).

related to lithological sources in the Black Forest (south-west Germany) and Thuringia (central Germany). The isolated anomaly in north-eastern Germany is related to anthropogenic sources (construction materials industry).

The Sr pattern in humus is not easy to explain. It is probably geogenic to some extent, because of large-scale similarities to the solid sample media; on close examination these similarities are less apparent.

Strontium in humus has a good correlation with Ba (0.42) and a weak correlation with Co (0.32).

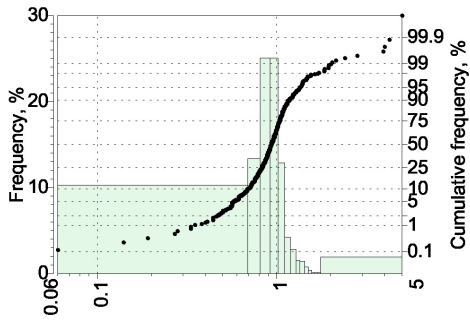
Sr in stream water

Strontium values in stream water range over four orders of magnitude, from 0.001 to 13.6 mg l^{-1} , with a median value of 0.11 mg l^{-1} . Strontium stream water data tend to correlate (especially in Fennoscandia, Britain, Spain, Italy and Hungary) with EC, Ca, Mg, Li and sulphate.

Lowest Sr values in stream water ($<0.05 \text{ mg l}^{-1}$) are found throughout Fennoscandia, northern Britain and Wales, north-west Iberian Peninsula, eastern Switzerland, over the Massif Central and Corsica. The low values are predominantly associated with granitic, metamorphic and felsic volcanic rocks, but there is also a close relation to acidic pH in northern Europe.

Enhanced Sr concentrations in stream water ($>1.0 \text{ mg l}^{-1}$) are found in south-east Britain, southern and eastern belt of the Iberian Peninsula (mostly on Mesozoic and Tertiary limestone and evaporite; some celestite mineralisation is known near Granada), western Hungary, south-east France and most of Italy. Relatively high Sr anomalies are also observed in eastern France and southern Germany. Celestite mineralisation is known in Thuringia, central Germany. These high concentrations are principally associated with limestone, evaporite and dolomite, and in Italy with alkaline volcanic rocks.

The described Sr distribution in stream water, applicable to the cation Sr^{2+} , follows closely the distribution pattern of the Major-ions

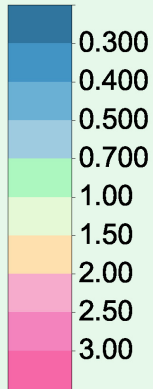


Sr (Ratio Topsoil / Subsoil)
 Number of samples 779
 Median 0.93

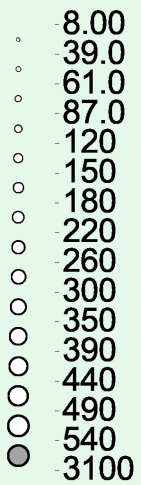
**Strontium
 Ratio
 Topsoil / Subsoil**



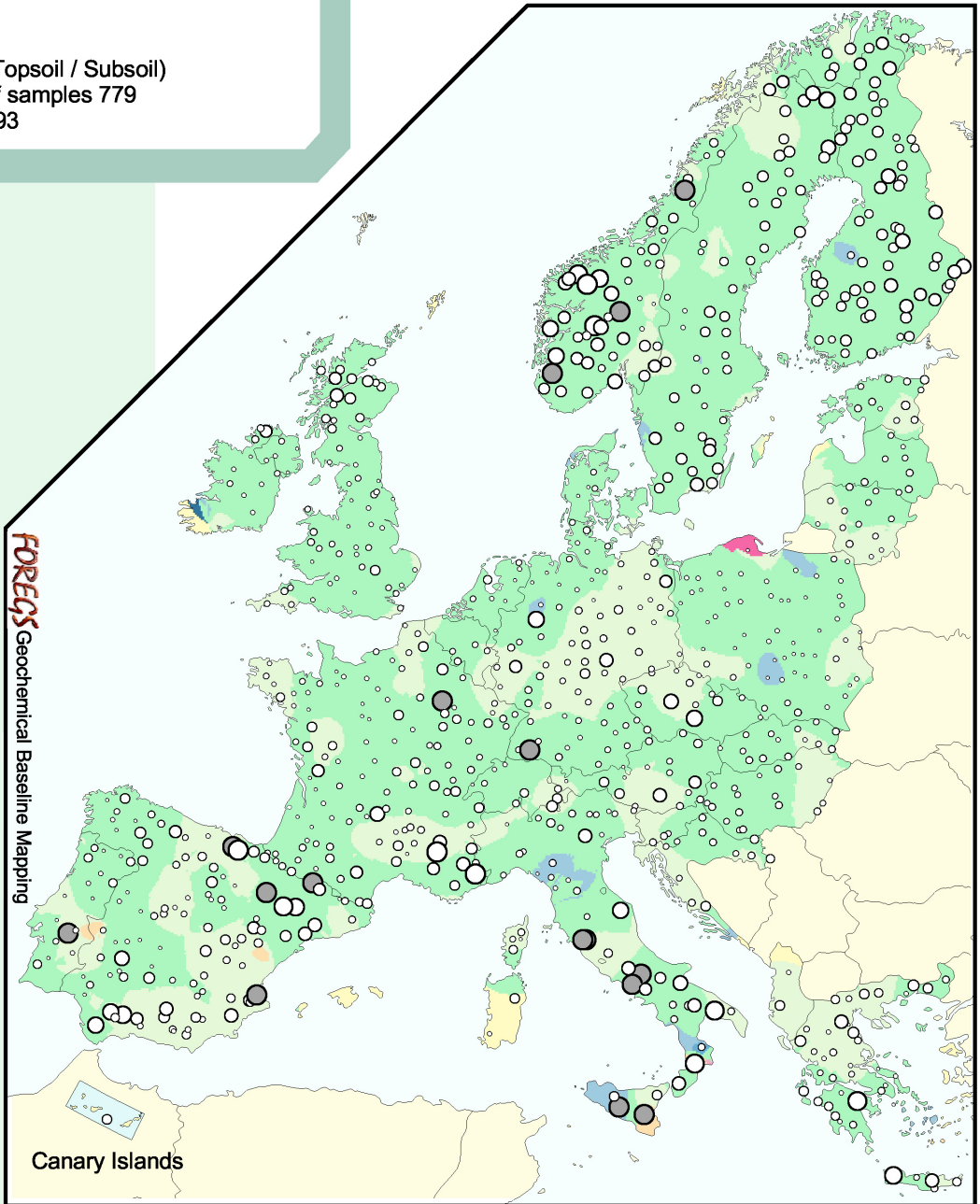
0 500 1000 Kilometers



Sr mg kg⁻¹
 (Topsoil)



FOREGS
 Geochemical Baseline Mapping



Sr

Map 14. Ratio of Sr in topsoil vs subsoil.

high-mineralisation stream water, especially Ca^{2+} and the bicarbonate and sulphate anions. It is distributed inversely to the REEs and associated elements. The pattern with a marked N-S zonation is climate-controlled. High Sr values in stream water reflect anomalous Sr in solid sample materials only in southern, but not in central Europe, with a small exception in western Ireland. However, very high Sr values in soil and sediments throughout Fennoscandia and in

northern Scotland are accompanied by very low Sr values in stream water. The reason seems to be incomplete weathering of feldspar minerals, which do not release Sr in the prevailing colder acid stream water of northern Europe. Higher Sr stream water values in the eastern part of France are related to the salt and dolomite dissolution from Triassic Keuper strata (see Br, Cl, Ca anomalies above).

Sr in stream sediment

The median Sr content in stream sediment is 126 mg kg^{-1} , with a range from 31 to 1352 mg kg^{-1} .

Areas with low Sr content in stream sediment ($<86 \text{ mg kg}^{-1}$) include central Sweden and adjacent Norway, crystalline areas of northern Portugal, north-west Spain, Brittany, and Bavaria; and Quaternary fluvio-glacial, fluvial and aeolian deposit areas extending from the Benelux through Germany, Denmark, Poland and the Baltic states.

High Sr values in stream sediment ($>205 \text{ mg kg}^{-1}$) occur throughout south-eastern Spain (Mesozoic and Tertiary limestone and evaporite, with occasional celestite mineralisation, e.g., Montevives and Escúzar), a small Mesozoic area in the Cantabrian Mountains, the western Alps, the Roman and Neapolitan recent alkaline volcanic provinces, and Mesozoic and Tertiary limestone of eastern and southern Italy including Sicily, and Crete.

High stream sediment Sr values in Scotland,

southern and northern Sweden and Norway and most of Finland probably reflect the underlying granitic basement of Precambrian to Caledonian age; however, the strontium contents are higher in Fennoscandia than in other areas with similar bedrock type such as northern Portugal, the Central Massif in France, etc.; this may be related to the unweathered state of feldspar minerals, an effect observed to a stronger degree for sodium and barium in Fennoscandia.

Strontium shows moderately high values over north-eastern Greece (mineralisation in felsic rocks), and western Ireland (Carboniferous limestone).

Strontium has a good positive correlation (0.43) with CaO (due to their association in carbonates and feldspar). This does not manifest itself in Fennoscandia and Scotland, where high Sr values are not accompanied by high CaO. Strontium also has a good negative correlation with SiO_2 (-0.40).

Sr in floodplain sediment

Total Sr values in floodplain sediment vary from 15 to 1660 mg kg^{-1} , with a median of 130 mg kg^{-1} .

Low Sr values in floodplain sediment ($<80 \text{ mg kg}^{-1}$) occur in the predominantly granitic areas of central Sweden; over the glacial drift plains in Germany, Poland and the Baltic countries; large parts of England (mainly shale, sandstone, igneous and metamorphic rocks); most of Ireland (calcareous and crystalline rocks), north-western France (granite, gneiss), the fluvial sediments of the Aquitaine basin, and most of the western Iberian Peninsula (Variscan sediments and crystalline rocks). The southern margin of the ice-

age glaciation area is well marked on the map.

The distribution of high Sr values in floodplain sediment ($>200 \text{ mg kg}^{-1}$) occurs in feldspar of the crystalline rocks of northern Europe (Precambrian Shield terrains of Finland and Caledonides of south-western Norway and Scotland), calcareous rocks of western Ireland, and on Alpine age, partly carbonate terrains in southern Europe (eastern Spain, south-east France, most of Italy, north-eastern Greece), and over basaltic rocks on Gran Canaria (Canary Islands). In the Murcia region in south-east Spain, there is widespread strontianite mineralisation.

It is noted that Sr minerals are known to occur

in gypsum beds of Messinian (Tertiary) age, which may explain many anomalies in southern Europe.

An outlier containing 1660 mg kg⁻¹ Sr in floodplain sediment occurs in the Neogene Tajo basin in central Spain, with marls, evaporitic limestone and gypsum layers, and Na and Mg sulphates that are mined. There are point Sr anomalies of 1063 mg kg⁻¹ on the Rance River near Dinan in Brittany (probably pollution by a phosphate fertiliser factory located nearby), and on the upper Rhine River in Switzerland with 892

mg kg⁻¹ near to Chur (Graubünden).

Strontium in floodplain sediment shows a good positive correlation with Ca (0.55), and a good negative correlation with SiO₂ (-0.51).

In conclusion, most of the high Sr values in floodplain sediment are due to its release from crystalline rocks, due to the weathering of feldspar, and from calcareous rocks. An interesting feature is the distinct division of the carbonate rocks of eastern Spain from the predominantly crystalline rocks of central and western Iberia peninsula.

Sr comparison between sample media

Patterns in Sr distribution between all solid sample media are very similar. The only marked difference is in the Canary Islands and the limestone areas of southern and eastern Spain, which have higher Sr in both stream and floodplain sediments compared to soil. The distribution of Sr in humus is generally similar to that of solid sample media for the large subdivisions: Fennoscandia is generally higher, whereas Britain, western France and the glacial drift area of northern mainland Europe are generally lower in Sr.

A boxplot comparing Sr variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 45.

Patterns in stream water Sr data are, in the main, different from distributions observed in solid sample media. Strontium in stream water is closely correlated with Ca and pH, with lowest concentrations in the most acid environments throughout Fennoscandia, and highest concentrations in some areas adjacent to the Mediterranean and in south-east England.

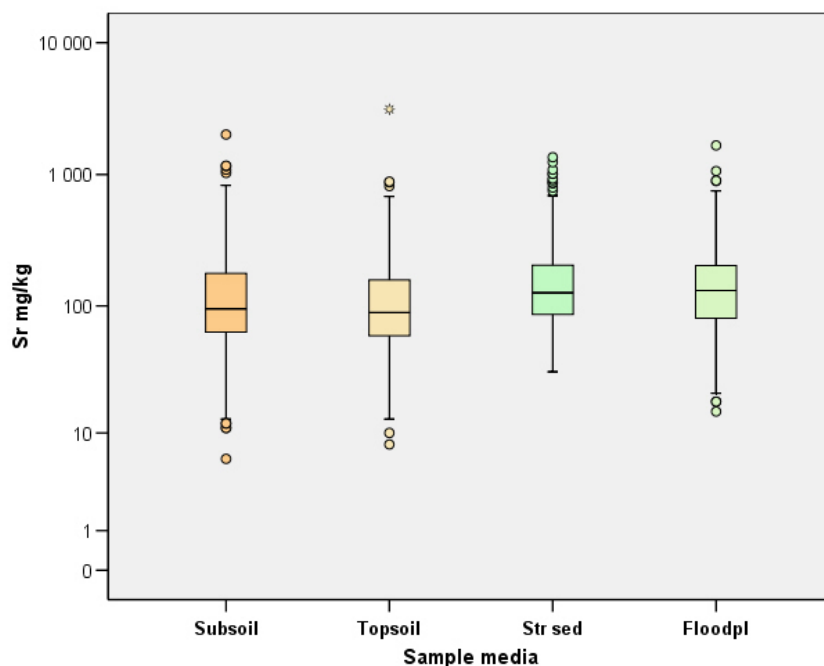


Figure 45. Boxplot comparison of Sr variation in subsoil, topsoil, stream sediment and floodplain sediment.