

Introduction

Sulphur belongs to group 16 of the periodic table, along with O, Se and Te. The element has an atomic number of 16, an atomic mass of 32, four oxidation states (-2, +2, +4 and +6) and four naturally occurring isotopes (^{32}S , ^{33}S , ^{34}S and ^{36}S), of which ^{32}S is most abundant at 95% of the mass.

Sulphur primarily occurs in four oxidation states in geological environments: S^{2-} (sulphides and sulphosalts), S^0 (elemental sulphur), S^{4+} (SO_2 in volcanic gas) and S^{6+} (SO_3 in volcanic gas). Its oxidation state determines how S is incorporated into mineral phases (Wedepohl 1978). The most important occurrence of S associated with igneous rocks is in metal sulphide mineralisation. Many metals exhibit chalcophilic tendencies, leading to the formation of many sulphide and sulphosalt ore minerals, such as chalcocite Cu_2S , pyrite FeS_2 , sphalerite ZnS , galena PbS , cinnabar HgS , stibnite Sb_2S_3 and oldhamite CaS (Wedepohl 1978). Evaporite minerals generally take the form of anhydrous or hydrated sulphates, e.g., barite BaSO_4 , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrite CaSO_4 and epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Pyrite present in sediments is another source of sulphate. Common rock-forming silicate minerals, including feldspar, mica and pyroxene, also contain significant amounts of sulphur, typically in the range 20 to 500 mg kg^{-1} . Sodalite commonly contains S up to percentage levels, and non-silicates, such as apatite, can contain up to 1100 mg kg^{-1} S (Wedepohl 1978).

Ultramafic and mafic rock types contain the highest concentrations of sulphur, typically between 300 and 23,000 mg kg^{-1} S. Intermediate and felsic rock types contain proportionally much less sulphur, with ranges of 60–3600 mg kg^{-1} and 45–3900 mg kg^{-1} respectively (Wedepohl 1978). Carbonate sediments generally contain more SO_4^{2-} (4550 mg kg^{-1}) than shale (1850 mg kg^{-1}) and sandstone (945 mg kg^{-1}) (Krauskopf 1982). Organic-rich sedimentary rock types, such as black shale (ca. 7%) and coal (up to 3%) tend to have the highest sulphur concentrations, although evaporite deposits, including gypsum and anhydrite, generally contain ca. 20% sulphur. Carbonate rocks and sandstone commonly contain less than 1% S (Wedepohl 1978).

The mobility of SO_4^{2-} in soil is constrained by processes of adsorption and reduction. In poorly

drained, peaty soil, SO_4^{2-} is reduced and immobilised as sulphide. Micro-organisms have a controlling influence on the oxidation state of sulphur, capable of either oxidation or reduction depending on microbial species and environment. Sulphates of metals, including Fe (jarosite), Al (alunite) and Ca (gypsum, anhydrite), are likely to occur under oxidising soil conditions; they are readily soluble and, therefore, are greatly involved in soil equilibrium processes (Kabata-Pendias 2001).

In stream water, S exists predominantly as the free SO_4^{2-} anion. However, the presence of protonated species and the influence of ion-pair interactions control the chemical behaviour of S, as does redox conditions. In acid water ($\text{pH} < 4$), sulphuric acid is not completely dissociated and some HSO_4^- may be present. In very reducing conditions, hydrogen sulphide, H_2S , can be significant. Systems controlled by gypsum rarely contain more than 1500 mg l^{-1} SO_4^{2-} and 650 mg l^{-1} Ca, but the tendency of SO_4^{2-} to form neutrally charged ion-pair associations can result in oversaturation with respect to gypsum. Magnesium sulphate has a very high solubility, so high SO_4^{2-} concentrations may occur in Mg-dominated systems in the absence of Ca. Sulphate concentrations in rainwater can exceed 10 mg l^{-1} in areas strongly affected by emissions of SO_2 . In contrast, unpolluted rainwater may have SO_4^{2-} concentrations as low as 1 mg l^{-1} . With an average concentration of 2700 mg l^{-1} , sulphate is the third most common species in sea water, after Na and Cl (Hem 1992).

Sulphates are discharged into the aquatic environment in wastes from industries that use sulphates and sulphuric acid, such as mining and smelting operations, kraft pulp and paper mills, textile mills and tanneries. Other potential anthropogenic sources include fertiliser and pesticide production and use, coal combustion, petrol refining, and vulcanisation of rubber.

Sulphur is essential to life; it is a major element in all plants, and a minor constituent of virtually all parts of the human body, including fats, body fluids and skeletal minerals. It is used in cell protection, liver function and digestive processes, and is an important part of vitamin B1 and insulin. Sulphate is one of the least toxic

anions, although relatively high levels (>1000 mg l⁻¹) may cause adverse effects in some aquatic species and catharsis and gastrointestinal irritation in humans (USEPA 1971). The presence of sulphate in drinking water can also result in a noticeable taste. Taste threshold concentrations for various sulphate salts are generally agreed to

be about 500 mg l⁻¹ (National Academy of Sciences 1977, Zoeteman 1980).

Table 56a compares the median concentrations of S in the FOREGS samples and in some reference datasets. Table 56b compares the median concentrations of SO₄²⁻ in the FOREGS samples and in some reference datasets.

Table 56 a. Median concentrations of S in the FOREGS samples and in some reference data sets.

Sulphur (S)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	62
Subsoil	FOREGS	784	<2.0	<i>Aqua regia</i> (ICP-AES)	105
Topsoil	FOREGS	837	<2.0	<i>Aqua regia</i> (ICP-AES)	227
Soil, C-horizon ²⁾	Barents region	1357	<2.0	<i>Aqua regia</i> (ICP-AES)	24.6
Stream sediment	FOREGS	845	<0.15	<i>Aqua regia</i> (ICP-AES)	510
Floodplain sediment	FOREGS	747	<2.0	<i>Aqua regia</i> (ICP-AES)	287

¹⁾Rudnick & Gao 2004, ²⁾Salminen *et al.* 2004.

Table 56 b. Median concentrations of SO₄²⁻ in the FOREGS samples and in some reference data sets.

Sulphate (SO₄²⁻)	Origin – Source	Number of samples	Size fraction	Extraction	Median mg kg⁻¹
Water	FOREGS	808	Filtered <0.45 µm		16.1 (mg l⁻¹)
Water ¹⁾	World	n.a.	n.a.		3.8 (mg l ⁻¹)
Water ²⁾	Barents region	1364	Filtered <0.45 µm		2.5 (mg l ⁻¹)

¹⁾Ivanov 1996, ²⁾Salminen *et al.* 2004.

S in soil

Sulphur was determined only by *aqua regia* dissolution (ICP-AES analysis). The extractable sulphur data have a median content of 110 mg kg⁻¹ in subsoil, with a range from <50 to 32800 mg kg⁻¹ (3.2%). In topsoil, the median S content is 230 mg kg⁻¹, and the range is from <50 to 112000 mg kg⁻¹ (11.2%). The average ratio topsoil/subsoil is 1.140.

Sulphur has a very particular distribution. Low values in subsoil (<58 mg kg⁻¹) occur in the south-west Iberian peninsula, central and northern Germany, Poland, Lithuania, Latvia and south Estonia, most of Sweden and the northern half of Finland.

In subsoil, there are high sulphur values (>190 mg kg⁻¹) in northern Scotland, the Netherlands,

north-east Germany, the calcareous areas of south-east Spain (limestone, marl, evaporite, gypsum, in Mesozoic and Tertiary sediments), the western Alps, Sicily and Calabria, and some isolated points in the Jura and Black Forest. The highest S value in subsoils is in the northern Netherlands (3.2% S); this sample also contains 23% total organic carbon, 0.1 mg kg⁻¹ Hg, and is very low in SiO₂ (only 26%). The second highest value (2.1% S) is in Switzerland; this sample contains 23% SiO₂, 18% CaO, 12% MgO and 2010 mg kg⁻¹ Sr.

The topsoil map shows more S anomalies in northern Britain and Ireland and the Netherlands, whereas in the Mediterranean area S anomalies appear much weaker. In France, a general

increase of the S background is observed in topsoil of evaporitic areas (Keuper in Lorraine, Eocene in Provence and Rhône valley).

The average ratio topsoil/subsoil is 1.140 for S, but the correlation between topsoil and subsoil is only 0.379 (Map 12). This means that there is a statistical sulphur enrichment in topsoil, which is not systematic, but rather a site-specific feature apparently strongly related to organic carbon. The site-specific sulphur enrichment also could be related to the increased use of fertilisers supplemented with sulphate.

Indeed, sulphur shows a good correlation of 0.57 with TOC in subsoil, whereas in topsoils the S-TOC correlation is strong with a value of 0.71. The scattergram of S-TOC in topsoil (Figure 37), and the strong positive correlation, suggest that sulphur is preferentially enriched as S^{2-} in soil with higher organic content, but this is not the only factor of enrichment. Sulphur also has a negative correlation with SiO_2 (-0.35 in subsoils, -0.39 in topsoil). In topsoil, sulphur has a good positive correlation with P_2O_5 (0.41) and a weak

correlation with mercury (0.37), iodine (0.35) and Pb (0.30).

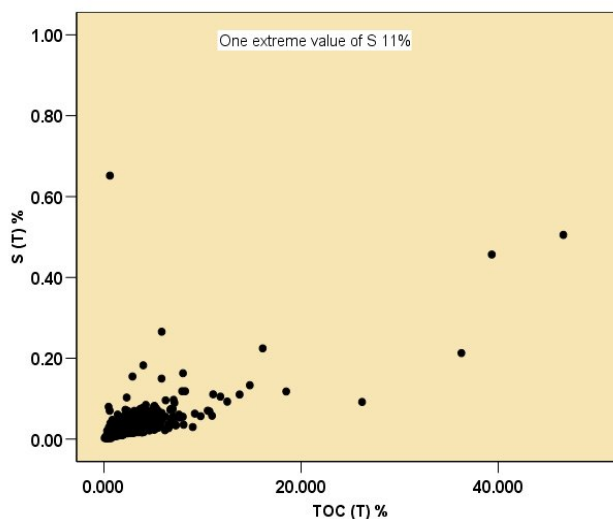


Figure 37. Scattergram of S and TOC values in topsoil.

Sulphate in stream water

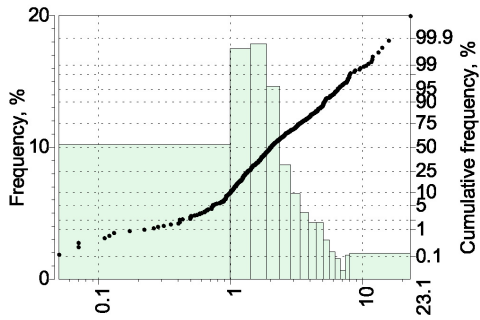
Note: in the printed Part 1 of the Geochemical Atlas of Europe, the SO_4 stream water map is placed on p.429 between Sn and Sr (Salminen *et al.* 2005).

Sulphate values in stream water show a wide range, over four orders of magnitude, from <0.3 to 1400 mg l^{-1} (excluding an outlier of 2420 mg l^{-1}), with a median of 16 mg l^{-1} . Sulphate data tend to correlate most closely with Ba and, to a lesser extent, Mg and Ca.

Lowest sulphate values in stream water ($<3 \text{ mg l}^{-1}$) are found throughout northern and western Fennoscandia, western Scotland, north-west Iberian Peninsula and over the Massif Central in France. The low values are predominantly associated with a range of granitic, metamorphic and acid volcanic rocks, *e.g.*, in the Caledonides, and with topographic and climatic effects such as high rainfall. Examining the SO_4 data expressed as a proportion of the sum of the concentration of the major anions might yield interesting results (*cf.* BGS, 1999).

Enhanced sulphate concentrations in stream water ($>76 \text{ mg l}^{-1}$) are found within a belt extending from central and eastern Britain through

Belgium, the Netherlands, northern Germany, Poland, eastern Czech Republic, western Slovakia and western Hungary, and are associated with complex inter-bedded loessic aeolian sand, soil, till and fluvial glacial sediments. In western Slovakia it is related to the Carpathian Keuper formation with variegated shales, sandstones, evaporite and dolomite, but also to anthropogenic activities. In central-western Poland, enhanced sulphate concentrations can be the result of fertilisers in agriculture and mine waters from coal mines (Silesia). High values are also observed in the southern and eastern part of the Iberian Peninsula and most parts of Italy, including Sicily and Sardinia. These values are associated with a range of lithologies, mostly sedimentary rocks, including limestones, evaporites and volcanics; they often correlate with high Ca values, pointing to gypsum occurrences. In central Spain, gypsum-bearing strata of the Neogene account for high sulphate levels. In the Baetic Cordillera there are Triassic shale and evaporite with gypsum layers. Two isolated highly anomalous sulphate values in south-western Germany also correlate with high calcium

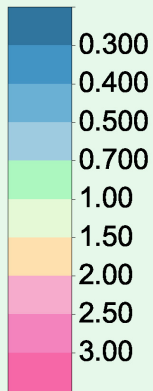


S (Ratio Topsoil / Subsoil)
 Number of samples 772
 Median 1.99

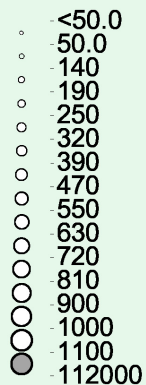
**Sulphur
 Ratio
 Topsoil / Subsoil**



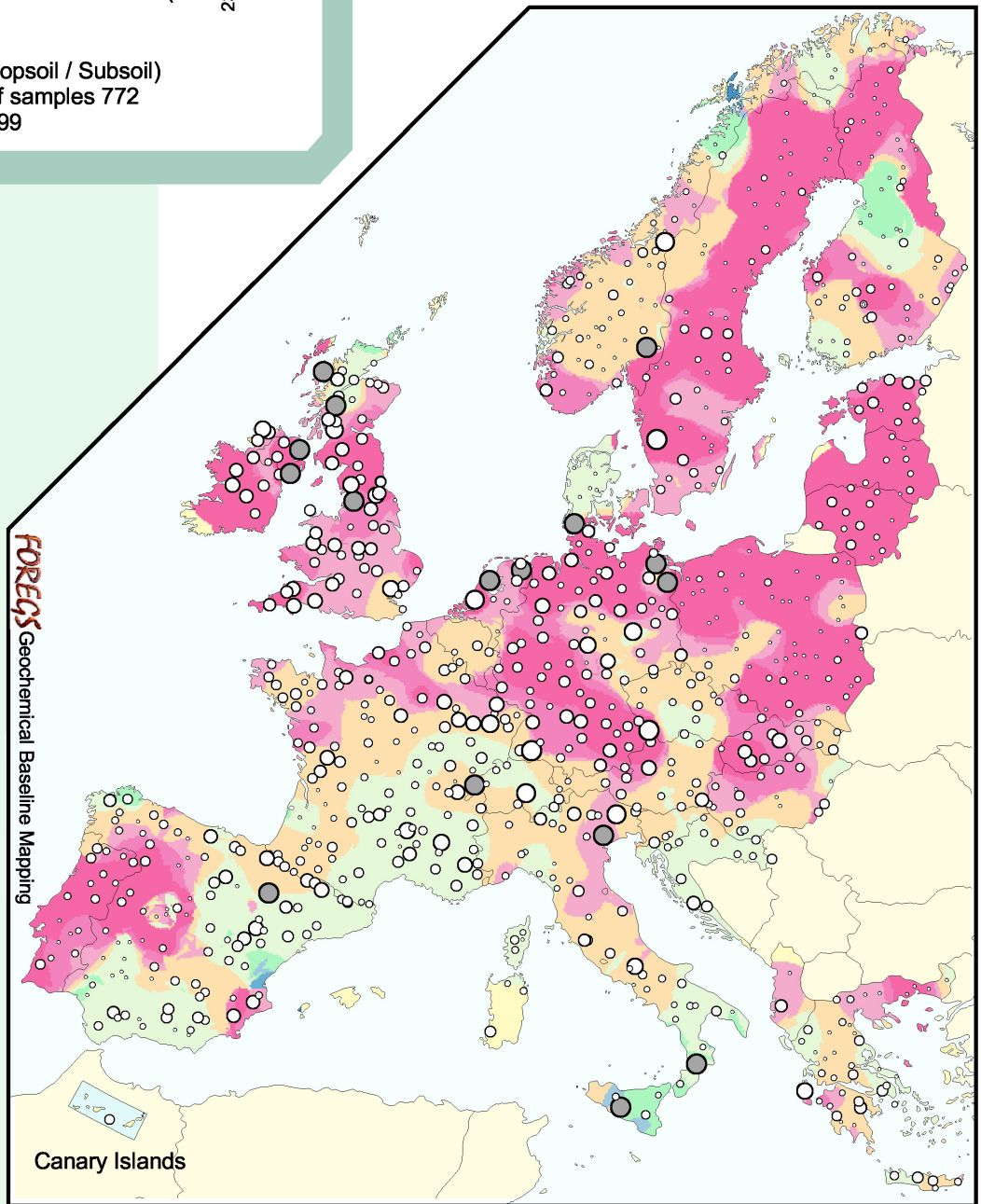
0 500 1000 Kilometers



S mg kg⁻¹
 (Topsoil)



FOREGS
 Geochemical Baseline Mapping



Map 12. Ratio of S in topsoil vs subsoil.

values. High stream water sulphate values in Lorraine, eastern France, have also high Br⁻ and Cl⁻, which is explained by contamination with exhaust water from salt mining operations in the Keuper evaporates. In Greece, high sulphate values are associated with lignite (Thrace), and sulphide mineralisation (Thrace, central Macedonia and Peloponnese). Highly anomalous values in eastern France are attributed to evaporites and coal mines.

The described distribution pattern of SO₄²⁻ in stream water follows the pattern of the Major-ions high-mineralisation stream water. Its pronounced N-S zonation is predominantly climate-dependent, but the high concentrations in southern countries are mainly geogenic, being derived from gypsum

and alkaline volcanism. There are similarities and even more dissimilarities between sulphate distribution in stream waters and sulphur distribution in solid sample media (and even more among the solid media). What they have in common, however, is the absence of a sharp 'ice boundary' between glacial drift regions in northern central Europe and territory south of it, which is typical for a large number of elements in soils and sediments.

A more detailed description on the chemistry of sulphate in stream water is given in Annex 1 of this volume by Ander *et al.* (2006), where the thematic interpretation of stream water chemistry is discussed (see sections on anion dominance, gypsum solubility and barite solubility).

S in stream sediment

The median sulphur content in stream sediment (ICP-AES analysis after *aqua regia* extraction) is 502 mg kg⁻¹, and the range of values is from <50 to 33500 mg kg⁻¹ (3.35%).

Low S values in stream sediment (<280 mg kg⁻¹) occur mainly in southern and western Spain, southern France, north-west Germany, central Austria, eastern Slovenia, northern Croatia, most of Norway, northern and central Finland, eastern Greece, and south-central Italy. The Iberian Pyrite Belt in southern Spain and Portugal does not show high S contents in stream sediment.

High values in stream sediment (>922 mg kg⁻¹) are observed in eastern England, the Netherlands, north-east Germany, southern Denmark, western and eastern Poland, Lithuania, small areas in Finland, central and southern Sweden, and northern Norway, southern Brittany in France (Sb-As mineralised shear zone with a redox

influence of the organic matter and nitrate-nitrite equilibrium in marshy water, also anomalous for As, Sb, Cu, Pb, Sn, W) and Lorraine in France (Br⁻, Cl⁻, SO₄²⁻ enriched stream water in the corresponding site shows contamination by exhaust water from salt brining operations in Keuper evaporite deposits), an area from the central Pyrenees to Aragón in Spain (Zn-Pb sulphide mineralisation, and evaporitic layers in the Ebro River Basin), the south-western Alps, Sardinia and Sicily, and coastal Croatia. Sulphide mineralisation accounts for some S anomalies, *e.g.*, in the central Pyrenees and in north-west Ireland. The highest S value in stream sediment occurs in coastal England (3.3% S).

There is a good correlation in stream sediment between S and total organic carbon (0.40), but the highest S values do not necessarily coincide with the highest TOC values. Sulphur also has a very weak correlation with P₂O₅ (0.28).

S in floodplain sediment

Aqua regia extractable S values in floodplain sediment vary from <50 to 5440 mg kg⁻¹, with a median of 290 mg kg⁻¹.

Low S values in floodplain sediment (<180 mg kg⁻¹) occur in the predominantly felsic metamorphic basement terrain of much of Finland and Sweden, south-west Norway, granitoids and Old Red Sandstone of north-east Scottish highlands, crystalline rocks of Massif Central in

France, and much of the western Iberian Peninsula with Variscan granite and clastic rocks; the crystalline rocks of Italian-Swiss Alps, the crystalline and volcanic rocks of Sardinia, the calcareous, clastic and alkaline igneous rocks of southern Italy, the Quaternary sediments of central Poland, and the ophiolite, calcareous, and metamorphic basement rocks of north-eastern Greece.

High S values in floodplain sediment ($>470 \text{ mg kg}^{-1}$) are related to either sulphide mineralisation and to soil rich in organic matter, or to both. When the two occur together, such as in Ireland, England, Fennoscandia and Germany, the distinction can be made by correlation with the TOC distribution map. Overall, the patterns of high S values throughout Europe are ascribed mostly to sediments rich in organic matter. The S anomaly in southern Norway is associated with both organic rich soil and sulphide mineralisation (e.g., Killingdal Cu-Zn, Røros Cu-Zn, Vassbo Pb-Zn); similarly in southern Finland (e.g., Orijärvi Cu-Zn-Pb, Kotalahti Ni-Cu); the point S anomaly on the Dalmatian coast of Croatia is due to industrial activities. High S values occur over most of Albania, and are possibly associated with sulphide mineralisation. In the western coast of Finland elevated S concentrations are found in areas of acid sulphate soil. Sulphur anomalies, which are most likely related to sulphide mineralisation are on the Rance River in Brittany (e.g., Porte-aux-moines Zn-Cu-Pb), Baetic Cordillera in Spain (e.g., La Unión-Cartagena district Pb-Zn-Fe stratabound and vein mineralisation, Mazarrón Pb-Zn-Fe), western Iberian Pyrite Belt in Spain (e.g., Tharsis Cu-Zn-Pb) and southern Portugal. The high S values in western Sicily are due to the Gessoso-Solfifera formation (gypsum and sulphur deposits). A rather elevated S value is found on the basaltic volcanics of Gran Canaria in the Canary Islands. It is worth noting that floodplain sediment, contrary to stream sediment, does show a few high S values in the Iberian Pyrite Belt of southern Spain and Portugal (De Vos *et al.* 2005).

A notable feature worth mentioning is the break shown in floodplain sediment from low to

high S values between the metamorphic basement rocks of the Iberian Meseta to the west and Cretaceous limestone and clastic rocks in the east of Spain. The same applies to the Massif Central in France with low S values over the predominantly crystalline and the surrounding sedimentary rocks.

Highly anomalous floodplain sediment S values in east-central and south-east Spain (5438, 4963 and 3291 mg kg^{-1}) are related to sulphide mineralisation and in the Almería region to gypsum deposits in Mesozoic and Tertiary evaporitic sediments; the highly anomalous S value near the German-Danish border is also high in sulphur in the stream sediment and high in phosphorus in topsoil and sediments. Three highly anomalous sulphur values in eastern Germany are associated with high or elevated sulphur values in soil, stream sediment and stream water. They are also high in phosphorus in subsoil, stream sediment and floodplain sediment; influences of both anthropogenic and geogenic sources cannot be separated. The highly anomalous S value in southernmost Sweden (3364 mg kg^{-1}) is probably related to acid sulphate soil. The high S value (3309 mg kg^{-1}) in central Hungary is possibly caused by volcano-sedimentary sulphide deposits. The point anomaly in central-east Poland (2361 mg kg^{-1}) is probably related to peat land.

Sulphur in floodplain sediment shows a good positive correlation with TOC (0.52), and a weak correlation with P_2O_5 (0.37). It also has a weak negative correlation with SiO_2 (-0.34).

In conclusion, patterns of high S values in floodplain sediment throughout Europe are mainly caused by sediments rich in organic matter, and sulphide, gypsum and evaporite mineralisation. Crystalline and calcareous rocks have generally low to intermediate S contents.

S comparison between sample media

There are significant differences in the distribution patterns of leachable (*aqua regia*) S data. In stream sediment, eastern England, the Netherlands, Denmark, north-eastern Germany, Lithuania, Poland and parts of Finland are richer in S than in soil. The south-eastern coast of Spain and the Massif Central and Scotland are depleted in S in stream sediments compared to soils. In floodplain sediment, Estonia, eastern Germany, Ireland, northern France, south-western Portugal

and central Hungary are much richer in S compared to subsoil.

A boxplot comparing S variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 38.

Stream water sulphate data show mostly similarities to S in stream sediment throughout Britain and central and northern mainland Europe, but totally opposite patterns in parts of the Iberian Peninsula and areas adjacent to the

Mediterranean. When compared to subsoil, however, there are similarities in sulphate distribution patterns throughout the Iberian

Peninsula and Mediterranean areas, as well as throughout Fennoscandia, but opposite patterns in Britain and central and northern mainland Europe.

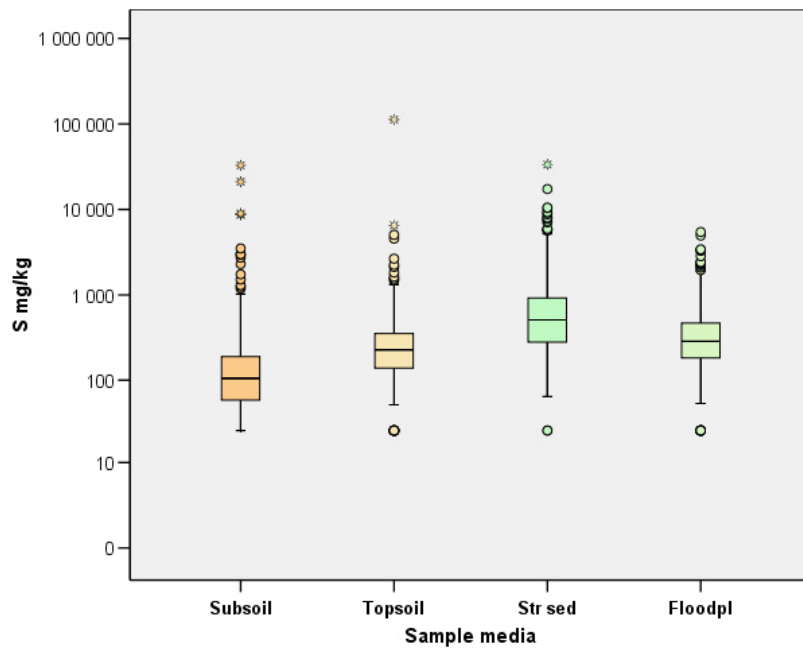


Figure 38. Boxplot comparison of S variation in subsoil, topsoil, stream sediment and floodplain sediment.