Sb – Antimony

Introduction

Antimony is a member of group 15 of the periodic table, along with N, P, As and Bi. The element has an atomic number of 51, an atomic mass of 122, three oxidation states (-3, +3 and +5) and two naturally occurring isotopes (^{121}Sb and ^{123}Sb) with abundances of 57.3% and 42.7% respectively. The chemistry and geochemistry of Sb is most similar to that of As.

Antimony is a low-abundance chalcophile element forming several rather rare minerals including stibnite Sb_2S_3, valentinite Sb_2O_3 and kermesite Sb_2S_2O, but is more usually present at trace levels in minerals such as ilmenite, Mg-olivine, galena, sphalerite and pyrite. The highest concentrations (>3 mg kg^{-1}) typically occur in the vicinity of hydrothermal deposits of galena and sphalerite. It is occasionally found in its native form. Antimony can be used as a pathfinder element for Au mineralisation, especially in combination with other pathfinders such as As and Bi (Boyle 1974, Plant *et al.* 1989, 1991).

During magmatic processes Sb can substitute for Fe in minerals such as olivine and ilmenite, but it tends not to be preferentially enriched at any stage of magmatic fractionation (Ure and Berrow, 1982). Boyle and Jonasson (1984) state that there appear to be some differences in the Sb content of igneous rocks; intermediate and felsic rocks being slightly enriched compared to other igneous rock types. Lueth (1999b) cites a crustal abundance of 0.5 mg kg^{-1}, and a systematic increase in its concentration in igneous rocks from mafic <1.0 mg kg^{-1} to felsic 7.8 mg kg^{-1}. Fine-grained argillaceous and organic-rich sediments are typically enriched in Sb (>1 mg kg^{-1}) relative to their parent igneous lithologies, reflecting the strong tendency for the element to become sorbed to hydrous oxides, organic residues and clay minerals in favourable environments (Ure and Berrow 1982). Pyritic black shale and mudstone may also contain relatively high levels of Sb in the authigenic sulphide phase. Coarse quartzo-feldspathic sediments, quartzite and carbonate rocks usually contain less than 0.5 mg kg^{-1} Sb. Mielke (1979) reports levels of Sb in shale, sandstone and carbonates as 1.5, <0.1 and 0.15 mg kg^{-1} respectively.

In stream sediment, Sb is present primarily in detrital sulphide minerals, *e.g.,* stibnite, sphalerite and galena, some of which may weather relatively rapidly under acid, oxidising conditions. Further remobilisation of Sb is rather limited due to the tendency of Sb^{3+} to hydrolyse to insoluble basic salts and be adsorbed by secondary hydrous oxides of Fe, Al and Mn at pH levels in the range 4.0–8.0. Antimony in the form of Sb_2O_3 is largely immobile. In studies of polluted stream sediment from North Carolina, USA, Shuman *et al.* (1978) found that in clean sediments most Sb was in crystalline minerals, whereas in the polluted sediment, containing higher levels of Sb, the element was largely held in oxide coatings, and with some in the organic fraction.

In soil, Sb is enriched in the surface horizon due chelation with organic matter, but there is also an enrichment in the B-horizon as a result of strong adsorption and absorption of Sb by hydrous Fe-oxides, clay minerals and wad (Boyle and Jonasson 1984). Average values for soil are given by Wedepohl (1978) as 1 mg kg^{-1} and by Kabata-Pendias (2001) as 0.9 mg kg^{-1}.

Data for Sb concentrations in natural water are quite sparse; Wedepohl (1978) quotes Sb concentrations of 0.07 µg l^{-1} to <0.5 µg l^{-1} in groundwater, with similar, but more variable levels in sea water and thermal springs. Reimann and de Caritat (1998) give average values of <0.1 µg l^{-1} in stream water and 0.24 µg l^{-1} in sea water.

With its low natural abundance, Sb is a useful indicator of industrial contamination. Anthropogenic Sb is associated with metalliferous mining (gold and sulphides) and metal smelting (Edwards *et al.* 1995). It is also associated with coal combustion, urban waste and car exhaust fumes, and is used in the manufacture of lead solder, batteries, arms and tracer bullets, composite car body panels and dashboards (Reimann and de Caritat 1998), as well as flame-proofing compounds, paints, ceramic enamels, glass and pottery.

Antimony has no known function in living organisms (Mertz 1987). High concentrations of Sb are highly toxic – more so than either arsenic or lead – and Sb is a known carcinogen. Sb^{3+}

compounds are more toxic than Sb^{5+} compounds. Most antimony compounds show little or no tendency to accumulate in aquatic life.

Table 57 compares the median concentrations of Sb in the FOREGS samples and in some reference datasets.

Table 57. Median concentrations of Sb in the FOREGS samples and in some reference data sets.

Antimony (Sb)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1)]	Upper continental	n.a.	n.a.	Total	0.4
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**0.47**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**0.60**
Soil[2)]	World	n.a.	n.a.	Total	0.5
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.07 (µg l^{-1})**
Water[3)]	World	n.a.	n.a.		0.1 (µg l^{-1})
Stream sediment	**FOREGS**	**848**	**<0.15**	**Total (XRF)**	**0.62**
Floodplain sediment	**FOREGS**	**743**	**<2.0**	**Total (XRF)**	**0.74**
Stream sediment[4)]	Canada	26 227	<0.18	Total (INAA)	0.9

[1)]Rudnick & Gao 2004, [2)]Koljonen 1992, [3)]Ivanov 1996, [4)]Garret 2006.

Sb in soil

The median Sb content is 0.47 mg kg^{-1} in subsoil and 0.60 mg kg^{-1} in topsoil, and the range varies from <0.02 to 30.3 mg kg^{-1} in subsoils and from 0.02 to 31.1 mg kg^{-1} in topsoils. The average ratio topsoil/subsoil is 1.184.

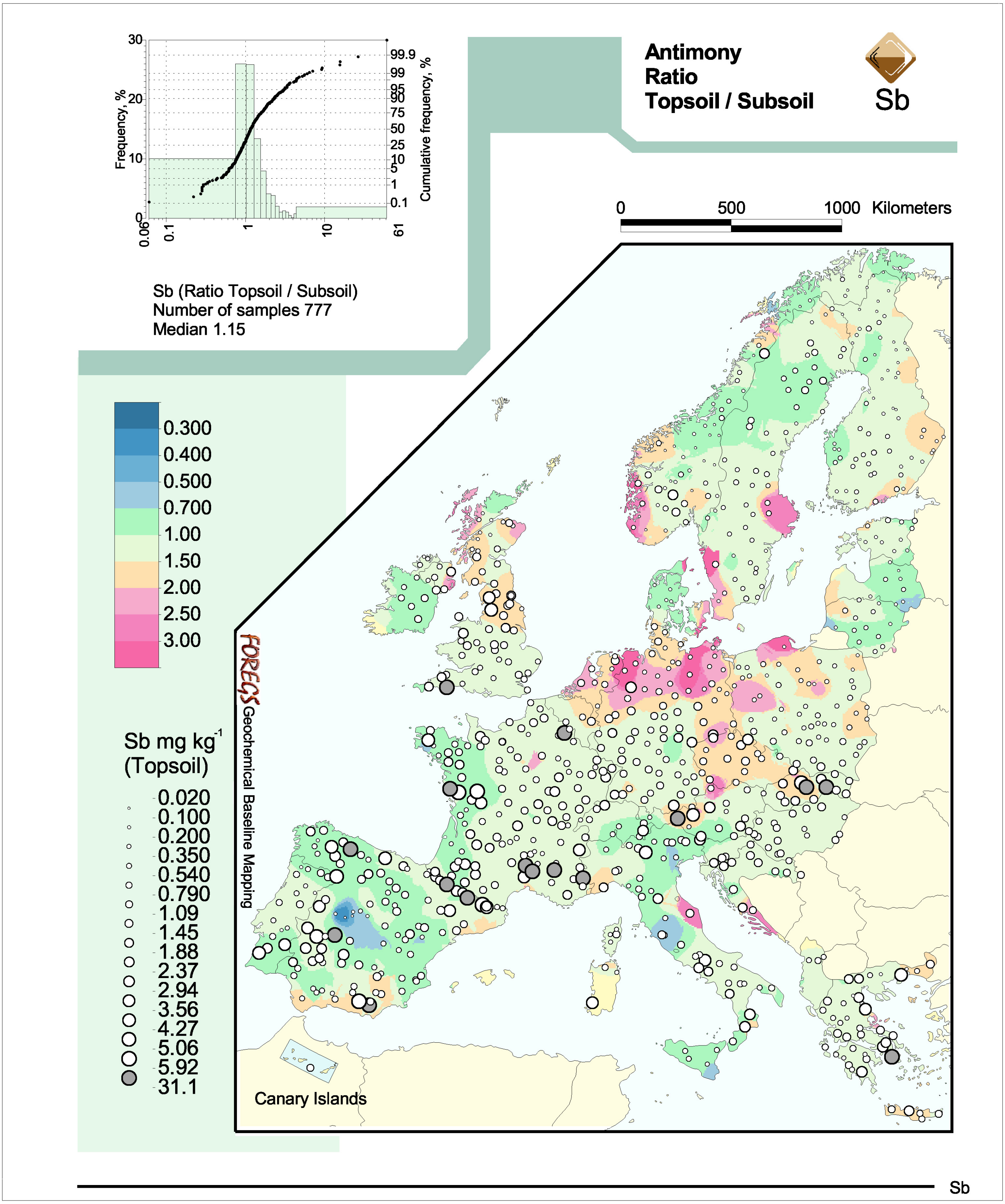
The subsoil Sb distribution map shows a strong similarity to the As map. Northern Europe (Scandinavia, northern Scotland, the Baltic states, Poland, northern Germany) generally has low values Sb in subsoil (<0.21 mg kg^{-1}). The southern limit of the ice-age glaciated area is well marked on the map, with low values to the north of it.

High values in subsoil (>0.90 mg kg^{-1}) occur in mineralised areas of Greece, including the Pb-Ag-mining district of Lavrion in Attica, the alkaline volcanic region of western Italy and Calabria, the Iberian Pyrite Belt from southern Portugal into Spain (Pb-Zn veins in Sierra Morena, and Sb-Au veins, *e.g.,* San Antonio), northern Spain (Sb mineralisation in Cambrian Vegadeo limestone, *e.g.,* Cervantes deposit) and the Pyrenees (Silurian black shale), the southern Central Massif (formerly Sb mining in Alès district), Brittany (strong impact of the ancient Sb-As mining district of Les Brouzils, especially in topsoil) and Poitou, Cornwall (ancient tin mines), northern England, karstic soil of Slovenia-Croatia and adjacent areas, eastern Slovakia (Spišsko-gemerské Rudohorie Mountains ore district) and the Carpathians (De Vos *et al.* 2005). The pattern of enrichment is related in the first place to ore deposits, and old mining and smelting areas.

The topsoil Sb distribution map is very similar to that of subsoil, with a more pronounced anomaly in the Pyrenees and central Slovakia (caused by Sb-ore processing smelters). There appears to be a systematic enrichment in topsoil, with a ratio topsoil/subsoil of 1.184 (Map 13).

In subsoil, Sb has a good correlation with As (0.55) and a weak correlation (between 0.4 and 0.3) with Pb, Hg, Cs, Tl, Te, Ti, Al, Ga, In, Fe, V, Nb, Y and most of the REEs.

In topsoil, Sb has a good correlation with Pb (0.41) and Hg (0.42), and a weak correlation with As, Cd, Cu, Zn, In, Y and some REEs. The enhanced correlation with Pb, Hg, Zn, Cu and Cd in topsoil points to mineralisation and contamination by heavy metals.



Map 13. Ratio of Sb in topsoil vs subsoil.

Sb in stream water

Antimony values in stream water range over three orders of magnitude from <0.002 to 1.21 µg l^{-1} (excluding two outliers up to 2.91 µg l^{-1}), with a median value of 0.07 µg l^{-1}. Antimony values tend to correlate with As, Mo, U, V and W in some areas.

Lowest Sb values in stream water (<0.04 µg l^{-1}) are found throughout central and northern Fennoscandia on the Precambrian Shield rocks, throughout most of Norway and Scotland (also in the Laurentian belt) and the north-western tip of Ireland on Caledonian terrains, in central western Germany, parts of the Massif Central in France, in northern Portugal and western and parts of south-eastern Spain and on Corsica in the Variscan region. Low antimony values are also found in Slovenia and western Croatia, northern Albania and southern Greece and Crete in the region of the Alpine Orogen.

Enhanced antimony values in stream water (>0.13 µg l^{-1}) occur in parts of Denmark and northern and western Poland on glacial drift originating from the Fennoscandian Shield; in the Netherlands on Quaternary deposits; in central and south-eastern England, central Czech Republic, southern Germany, the Lorraine and south Brittany areas of France, in south-western Spain (associated with Sb-Au and Pb-Zn mineralisation in Extremadura and Sierra Morena) and west Sardinia in the Variscan region. Isolated high Sb values in Belgium (Vesdre basin) are related to industrial pollution (mining, metallurgical, textile, paper industry). High Sb values are found in southernmost Poland, Slovakia and the north-eastern half of Hungary, in central and south-eastern Italy including Sicily, and in the eastern part of Baetics in Spain, all on the Alpine Orogen. The isolated anomalously high Sb in northern Estonia is probably related to pollution from oil shale tailings. The anomalous concentration of Sb (2.48 µg.l^{-1}) in eastern Slovakia reflects metamorphic-hydrothermal mineralisation (antimonite-gold veins and complex siderite-sulphide ores). High contents of Sb in central Slovakia are the remnants of mining and processing of Sb ore from the Nízke Tatry Mountains (quartz-antimony-gold deposit in crystalline granitoids and metamorphics). A point anomaly in the northern Czech Republic is atributed to atmospheric precipitation from coal burnt in power plants. Isolated highly anomalous Sb values in southern Sweden are probably of anthropogenic origin. The point Sb anomaly southwest of Cologne is related to geogenic and anthropogenic sources (Pb-Zn mineralisations and non-ferrous metallurgical industry).

The described antimony distribution in stream water follows two important elemental patterns in European stream water, mostly those of the Major-ions high-mineralisation stream water and partly also of the Base metal stream water. In stream water displaying the Major-ions pattern the Sb species consist of Sb anions and Sb anionic complexes with Cl, SO_4 and HCO_3. A large part of the high Sb concentrations in stream water correspond to high Sb areas in solid sample media. The exception is high Sb stream water north of the former glaciation line, where Sb is very low in soil and sediments on the glaciofluvial outwash material in Denmark, southern Sweden, Netherlands and Poland. This indicates the exogenic – probably climate-induced origin of these Sb anomalies. The Sb stream water anomalies of the Base metals pattern occur in the mineralised Slovakian Ore mountains, in neighbouring east Hungary and in the Czech Republic. All appear to be related to high Sb sources in solid sample media. On the other hand, many high Sb areas in soil and sediments are not accompanied by high Sb values in stream water.

Sb in stream sediment

The median Sb content in stream sediment is 0.64 mg kg^{-1}, and the range varies from <0.02 to 34.1 mg kg^{-1}.

On the Sb stream sediment distribution map northern Europe (most of Norway, Finland, northern Sweden, Denmark, north-eastern Scotland, the Baltic states and northern Poland) shows low values (<0.34 mg kg^{-1}). Northern Portugal, central and south-eastern Spain, and most of Greece are also low in antimony.

High Sb values in stream sediment (>1.15 mg kg^{-1}) occur in the extreme south of Sweden, related to known shear zones that are probably mineralised, throughout the Iberian Pyrite Belt extending from southern Portugal to the Sierra Morena in Spain, the Malaga area in southern Spain (polymetallic veins of the Baetic Cordillera, also anomalous for As), Asturias in north-western Spain (Au epithermal ore of El Valle, and Au mineralisation of Navelgas district), the eastern Pyrenees, the Central Massif (former Sb mining in Alès district), Brittany (ancient Sb-As mining district of Les Brouzils), parts of England (mineralised Pennines), north-west Ireland, Belgium, north-eastern France and adjacent Germany, north-eastern Italy, northern Bohemia, Slovakia, Slovenia, Pannonian Croatia and Albania (De Vos *et al*. 2005). The pattern of Sb enrichment is related mainly to ore deposits and old mining and smelting areas. Several of these show up as point anomalies. The richest sample occurs in Tullyhonwar near Ardara, Donegal, in north-western Ireland, and contains 34 mg kg^{-1} Sb, 14.8% Fe_2O_3, 694 mg kg^{-1} Pb, 1036 mg kg^{-1} S and 48 mg kg^{-1} As. The second richest sample is in the Sierra Nevada in south-eastern Spain, with 14.7 mg kg^{-1} Sb and 84 mg kg^{-1} As. Another sample at Rio Tinto in the Spanish part of the Iberian Pyrite Belt, contains 11 mg kg^{-1} Sb and 64 mg kg^{-1} As. Other point anomalies related to mineralisation occur in southern Sardinia, and in Greece at the Lavrion polymetallic sulphide mineralised area, a second point anomaly in Attica, which may be related to unknown mineralisation or industrial pollution, and in Thrace, north-eastern Greece, possibly associated with sulphide and Au mineralisation.

Antimony in stream sediment has a good correlation with As (0.51), which is not caused by high values but by the general tendency of the population (see scattergram, Figure 39). There is also a good correlation with Pb (0.41), a weak correlation with Zn (0.35) and Cu (0.33), and a very weak correlation with Hg (0.25) and Cd (0.25).

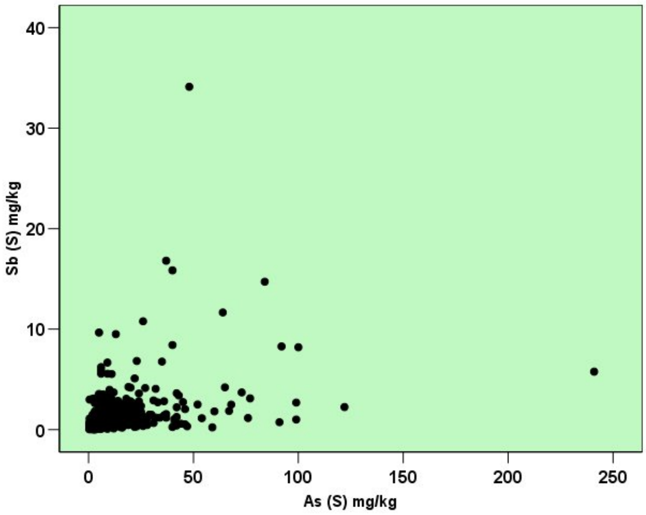


Figure 39. Scattergram of Sb and As values in stream sediment.

Sb in floodplain sediment

Total Sb values in floodplain sediment vary from <0.02 to 99 mg kg^{-1}, with a median of 0.74 mg kg^{-1}.

Low Sb values in floodplain sediment (<0.37 mg kg^{-1}) occur over most of the Precambrian Fennoscandian Shield and Caledonides of the Fennoscandian countries, and northern Scotland, made of mainly metamorphic and igneous rocks, and the glacial outwash covered Lithuania and Latvia. In southern Europe, low Sb values occur in central and eastern Spain and in the Gibraltar area, on mainly calcareous and clastic rocks, in southern Italy on clastic, volcanic and carbonate rocks, and most of Greece over carbonate, clastic rocks and ophiolites.

High Sb values in floodplain sediment (>1.53 mg kg^{-1}) occur over most of England and parts of Wales, with especially highly anomalous values in north-eastern England on the River Wear on Carboniferous coal bearing clastics and limestone, reported as probable pollution from heavy industry, but they may also reflect the sulphide mineralisation of the northern Pennines; in Cornwall and Devon in south-west England they are associated with the Variscan granitic intrusions and mineralisation; in the western Scottish Midland Valley they are possibly related to mafic volcanics and mineralisation. A belt of high Sb values extends from Belgium (26.8 mg kg^{-1} in the Vesdre basin with metallurgical pollution), across central Germany with clastic and partly crystalline rocks, over the Harz Mountains to Erzgebirge and Sudetes mining districts in Germany and south-west Poland, the western and eastern Czech Republic extending into most of Slovakia and eastern part of Hungary, probably related to the Banska Stiavnica – Vyhne – Medzibrod and Zlata Idka mining districts (Dubrava Sb-Au, Zlata Idka Sb-Au, Mariabana Sb in Slovakia). Anomalous Sb values are found in France on metamorphic and igneous rocks of Brittany, Poitou and parts of the Massif Central towards the Pyrenees, associated with mineralisation (*e.g.,* Bodennec Zn-Cu-Pb, Porte-Aux-Moines Zn-Cu-Pb, La Lucette Sb-Au, Le Brouzils Sb, Rochetrejoux Sb, La Bessade Sb), and in the Vosges on largely igneous and clastic rocks, and mineralisation (*e.g.,* Sainte-Marie-Aux-Mines Cu-Pb-Zn-Ag-Co-As). In northern Portugal, the high Sb values are possibly due to the precious metals vein deposits associated with granite (but anthropogenic influence is also possible), and in south Portugal and Spain with the volcanogenic-sedimentary Iberian Pyrite Belt, Pedroches, Valle de Alcudia, and Linares mining district (*e.g.,* Spain: Rio Tinto Zn-Cu-pyrite, Aznalcollar Zn-Pb-Cu-Ag-Au-pyrite, Tharsis Cu-pyrite, Linares Pb-Zn-Ag, La Carolina Pb-Zn, Horcajo Pb-Ag, and Almadén Hg deposits); in southern Sardinia (*e.g.,* Ballao Sb-W, Silius F-Ba-Sb); in Italy the Roman Alkaline Province (*e.g.,* Tafone Sb); and most of Croatia (De Vos *et al.* 2005).

The highest anomalous Sb value in floodplain sediment occurs in central-northern Slovakia (99.4 mg kg^{-1}), and is possibly due to the Dubrava Sb-Au deposit; another anomalous Sb value (54.48 mg kg^{-1}) is in eastern Slovakia and lies within a mineralised district. In Poland, the high Sb value is on the Oder river near Lubin (53.7 mg kg^{-1}), and is also anomalous in Zn, obviously a result of Kupferschiefer mining (De Vos *et al.* 2005). In Greece, the point Sb anomaly (52.5 mg kg^{-1}) is related to the Lavrion mining and smelting region. The high Sb anomaly in France (39.03 mg kg^{-1}) is near to a mineralised shear zone.

Antimony in floodplain sediment shows a weak positive correlation with As (0.33) only.

In conclusion, Sb distribution in floodplain sediment is related to both the bedrock geology (mineralisation) and to anthropogenic activities. Generally, northern Europe is characterised by low Sb contents in floodplain sediments, as well as parts of southern Europe, whereas high values are observed in much of western and central Europe.

Sb comparison between sample media

In general, there are broad similarities between all solid sample media; patterns in topsoil and subsoil are very closely related, but topsoil concentrations are enhanced by a factor of 1.19 on average. Stream and floodplain sediments are depleted in Sb compared to soil in Greece and central Italy. In floodplain sediment, Sb is low in central and eastern Spain. Floodplain sediment Sb concentrations in a belt from central Germany to western Poland are significantly higher than in soil; similarly both stream and floodplain sediments are enhanced in Sb in England compared to soil. Northern Portugal is enhanced in floodplain sediment compared to all other solid sample media; north-western Spain shows the opposite trend with lower values in floodplain sediment. A boxplot comparing Sb variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 40.

The distribution of Sb in stream water is quite complex and closely related to the distribution observed for As. Distribution patterns are similar to those in sediments in Britain and Ireland, northern Fennoscandia, Greece, Slovakia and parts of France and Germany, but are otherwise opposite to trends observed in soil and sediments. In southern Finland and Sweden, Denmark, the Baltic states and northern Poland, slightly elevated Sb concentrations in stream water compared to soil and sediments are associated with high DOC.

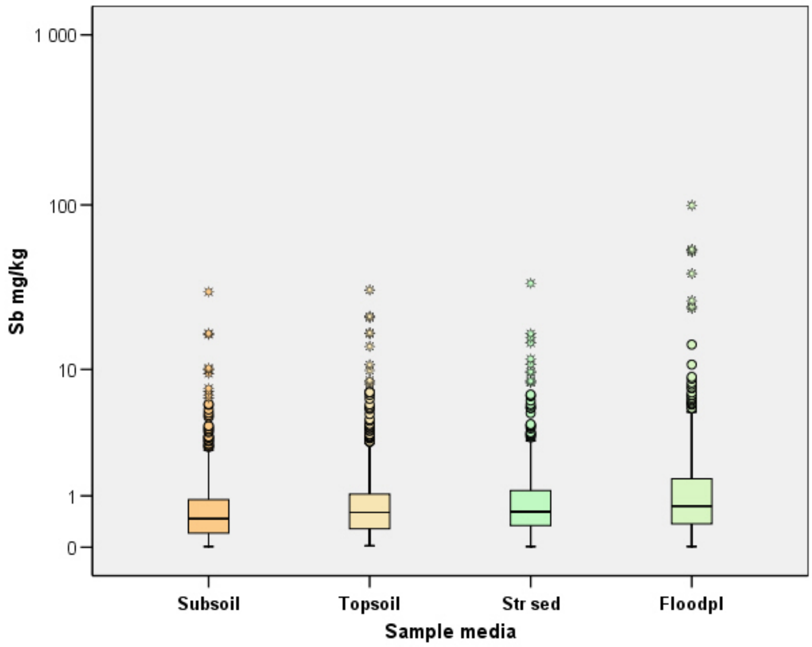


Figure 40. Boxplot comparison of Sb variation in subsoil, topsoil, stream sediment and floodplain sediment.