

Introduction

Barium is a member of group 2 elements of the periodic table, along with Be, Mg, Ca and Sr, which are all highly electropositive metals. The element has an atomic number of 56, an atomic mass of 137, one oxidation state (+2), and seven naturally occurring isotopes (^{130}Ba , ^{132}Ba and ^{134}Ba to ^{138}Ba), of which ^{138}Ba is the most abundant at 71.7% of the total mass. Barium is most similar chemically to the heavier alkali earth elements Ca and Sr.

Barium is a lithophile element and is the 14th commonest element in the Earth's crust. The Ba^{2+} ion is large and has a high charge ratio (radius/valence) resulting in its concentration in more felsic components of magmas in the later stages of crystallisation. It occurs mostly in K-feldspar and mica through the substitution of K^+ by Ba^{2+} , which have similar ionic radii (Ba^{2+} , 135 pm; K^+ , 138 pm). Barium concentrations tend to be higher in K-feldspars than in phyllosilicates. The Ba^{2+} ion also substitutes for Ca^{2+} in plagioclase, pyroxenes and amphibole, and in the non-silicate minerals apatite and calcite. The principal Ba mineral, barite BaSO_4 , is frequently associated with metalliferous mineral deposits. Secondary Ba minerals may include authigenic barite and witherite BaCO_3 .

The Ba content of igneous rocks generally increases with increasing Si content (Ure and Berrow 1982, Smith 1999a) from mafic to felsic, though some highly evolved granites contain very low levels, *e.g.*, $<200 \text{ mg kg}^{-1}$ (Plant *et al.* 1980). Mielke (1979) quotes values of Ba in igneous rocks as: ultramafic 0.4 mg kg^{-1} ; basaltic 330 mg kg^{-1} ; granitic $420\text{--}840 \text{ mg kg}^{-1}$; and syenite 1600 mg kg^{-1} . In sedimentary rocks the concentration of Ba is related to the abundance of K-feldspar, clay minerals and hydrous Fe and Mn oxides, on to which the element may be adsorbed (Wedepohl 1978). The highest Ba concentrations are found in shale (580 mg kg^{-1}), whilst carbonate rocks and sandstone contain only *ca.* 10 mg kg^{-1} (Mielke 1979). McLennan and Murray (1999) quote average values for river particulates and loess as 600 and 625 mg kg^{-1} Ba respectively. Elevated Ba values may indicate the presence of felsic rocks, especially kaolinised intrusives, in

association with K, or calcareous rocks, in association with Ca, Mg and Sr.

Barium released from weathered rocks is not very mobile since it is easily precipitated as sulphate and carbonate, strongly adsorbed by clays, concentrated in Mn and P concretions, and specifically sorbed onto oxides and hydroxides (Kabata-Pendias 2001). Barium easily displaces other sorbed alkaline earth metals from some oxides, *e.g.*, MnO_2 and TiO_2 , but is displaced from Al_2O_3 by alkaline earth metals such as Be and Sr. In soil of temperate humid climatic zones, Ba is likely to be fixed by Fe-oxides and becomes immobile. Barium in soil may be easily mobilised under different physico-chemical conditions. Its concentration in soil solutions shows considerable variation, from $43 \mu\text{g l}^{-1}$ in loamy soil to $307 \mu\text{g l}^{-1}$ in sandy soil. The reported range of Ba on a global scale varies from 19 to 2368 mg kg^{-1} , depending on parent lithology. Barium distribution among the different soil types shows much lower contents in histosols (mean 175 mg kg^{-1}) than in other soil types (range of mean values from 330 to 520 mg kg^{-1}) (Kabata-Pendias 2001).

The presence and concentration of Ba in surface water is strongly controlled by the abundance of Ba in the bedrock, as hydrogeochemical and biogeochemical processes show little variability from one environment to another. However, the behaviour of Ba in solution, particularly the insolubility of BaSO_4 , tends to result in a smaller level range of Ba concentrations in solution than for many other elements, *e.g.*, Sr. In natural water, Ba occurs as the Ba^{2+} ion. Its mobility is not controlled strongly by pH and Eh conditions, although oxic acidic conditions promote its release from biotite. Compared with the other alkaline earth metals, Ba carbonate and sulphate exhibit low solubilities. BaCl_2 and $\text{Ba}(\text{NO}_3)_2$ are more soluble, and the presence of high levels of Cl^- may enable sulphate-rich water to retain more Ba in solution. The dispersal of Ba in surface water is also controlled by the presence or absence of hydrous Mn and Fe oxides, which adsorb Ba^{2+} . Adsorption on the surfaces of clay minerals and

organic matter can also be significant at higher pH (Wedepohl 1978).

Concentrations of Ba are low in sea water, *ca.* 0.02 mg l⁻¹, and the levels in rain are too low to make a significant contribution to stream water composition. The average abundance of Ba in river water is given by Turekian (1969) as 10 µg l⁻¹.

Anthropogenic contamination is a potential, although relatively uncommon, source of Ba in stream water. The major use of barite is as a heavy mud slurry for drilling processes in the oil and gas industry. It is also used in the manufacture of rubber, paper, fabrics, glass, plastics and enamels. It is reported that in Britain coal and mineral extraction activities can have

considerable influence on the distribution of Ba in the surface environment (BGS 1996).

Barium is essential for some organisms at low concentrations but, at higher concentrations, soluble Ba compounds are toxic to humans, animals and plants, *e.g.*, BaCl₂ is used as a rat poison and insecticide. Barium is an undesirable impurity in drinking water, and high levels of Ba in potable water have been associated with gastroenteritis and muscular paralysis (International Programme on Chemical Safety 1990).

Table 11 compares the median concentrations of Ba in the FOREGS samples and in some reference datasets.

Table 11. Median concentrations of Ba in the FOREGS samples and in some reference data sets.

Barium (Ba)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	628
Subsoil	FOREGS	788	<2.0	Total (ICP-MS)	385
Subsoil	FOREGS	784	<2.0	<i>Aqua regia</i> (ICP-MS)	68.0
Topsoil	FOREGS	845	<2.0	Total (ICP-MS)	375
Topsoil	FOREGS	837	<2.0	<i>Aqua regia</i> (ICP-MS)	65.0
Soil ²⁾	World	n.a.	n.a.	Total	500
Soil, C-horizon ³⁾	Barents region	1357	<2	<i>Aqua regia</i> (ICP-AES)	33.1
Humus	FOREGS	367	<2.0	Total (ICP-MS)	60.6
Humus ³⁾	Barents region	1357	<2	Total (HNO ₃ , ICP-MS)	78.6
Water	FOREGS	807	Filtered <0.45 µm		24.9 (µg l⁻¹)
Water ⁴⁾	World	n.a.	n.a.		30 (µg l ⁻¹)
Stream sediment	FOREGS	852	<0.15	Total (XRF)	386
Stream sediment	FOREGS	845	<0.15	<i>Aqua regia</i> (ICP-AES)	86.0
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	379
Floodplain sediment	FOREGS	747	<2.0	<i>Aqua regia</i> (ICP-AES)	82.0
Stream sediment ⁵⁾	Canada	26 227	<0.18	Total (INAA)	720

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

Ba in soil

The median total Ba content (XRFS analysis) is 385 mg kg⁻¹ in subsoil and 375 mg kg⁻¹ in

topsoil; the range of Ba is from 13 to 2050 mg kg⁻¹ in subsoil and from 30 to 1870 mg kg⁻¹ in

topsoil. The average ratio topsoil/subsoil is 0.976.

Low Ba values ($<270 \text{ mg kg}^{-1}$) in subsoil occur in Ireland, a small area in central Norway, in the glacial drift area from the Netherlands to Poland, in central Hungary, in the Paris, Garonne and Rhône basins in France, in most of eastern Spain, and in southern Greece.

High Ba values in subsoil ($>520 \text{ mg kg}^{-1}$) occur in felsic crystalline and Palaeozoic schist areas in the Fennoscandian Shield and Scotland, where Ba substitutes for K in feldspar and mica; this enrichment is less pronounced than for Na_2O . In similar lithologies, the western Iberian Peninsula, parts of the French Massif Central and of Bohemia are also high in Ba. The Italian alkaline magmatic province shows some high values in both subsoil and topsoil.

High Ba values in Extremadura (south-west Spain) are related to the Llerena mining district (barite veins) and the Azagua Zn-Pb district. High Ba values near Cádiz (south Spain) and in the eastern Pyrenees are related to Permo-Triassic continental clastic sediments with barite disseminations and diacause fillings resulting from water mixing during the Triassic emersion; these late anomalies are enhanced in *aqua regia* extractable values. High Ba in the Canary Islands is related to volcanic rocks.

No major differences appear between the total Ba distribution in subsoil and topsoil. The distribution patterns on the maps are intermediate

between K_2O and Na_2O .

Total barium in subsoils shows a strong positive correlation with K (0.62), and a good correlation (>0.4) with Al, Ga, Na, Rb, Nb, Ag, Ce, La, Eu, Nd, Pr, Sm and Gd. In topsoil, there is also a strong correlation with K, and a good correlation with Al, Ga, Na, Rb and Sr.

Aqua regia extractable Ba (ICP-AES analysis) values in soil are much lower than total Ba values, with a median value of only 68 mg kg^{-1} in subsoil and 65 mg kg^{-1} in topsoil. The range of extractable Ba is from 6 to 1730 mg kg^{-1} in subsoil and from 10 to 1700 mg kg^{-1} in topsoil. Feldspar, which contains much of the Ba, does not dissolve in *aqua regia*. Consequently, crystalline areas are much lower in extractable Ba than in total Ba, as can be observed, *for example*, in the Fennoscandian Shield. On the *aqua regia* extractable Ba maps (both subsoil and topsoil) the highest Ba values appear in the alkaline magmatic province of Italy, extending into Sicily. High Ba values also occur in southern and north-western Spain, the Massif Central and Poitou area in France, the Rhenish Massif, central Europe from Germany over the Czech Republic, central Austria, Slovenia, Croatia, eastern Slovakia, eastern Hungary, and northern Greece. *Aqua regia* extractable point anomalies for Ba in Greece are related to soil over feldspathic sandstone (Thrace), gneiss (central Macedonia) and *terra rossa* soil (Epirus and Kefallinia).

Ba in humus

The median Ba content in humus is 60.6 mg kg^{-1} and the range varies from 3.1 to 435 mg kg^{-1} .

The Ba distribution map shows low values in humus ($<38 \text{ mg kg}^{-1}$) occurring over most of Britain, Ireland (except the far west), western France, the glacial drift covered area extending over Denmark, northern Germany, Poland (except the south-west) and Estonia, small coastal areas in south-western Norway (possibly explained by dilution due to high rainfall), and the border area of Germany and Austria with molasse deposits. The former southern limit of the glaciation is well marked through Germany and Poland, with low values to the north of it.

High Ba values in humus ($>95 \text{ mg kg}^{-1}$) occur in an area extending from southern Norway into central Sweden; most of central Finland; a small area in south-eastern Sweden (also high in Ga); east-central Germany; the Black Forest in south-west-Germany; north-eastern Italy; and south-eastern Austria and Slovenia. High Ba values are possibly related to fine-grained feldspar and other K-bearing minerals in the humus samples, pointing to a mostly geogenic origin of Ba, even in Fennoscandia. In contrast to Ga and Co, Fennoscandia shows larger continuous areas with high Ba values than central Europe.

Barium in humus has a good correlation with Sr (0.42) and a weak but significant correlation with Ga (0.37).

Ba in stream water

Barium values in stream water range over three orders of magnitude from 0.2 to 436 $\mu\text{g l}^{-1}$, with a median value of 24.9 $\mu\text{g l}^{-1}$. Barium data tend to correlate most closely with magnesium in most areas. Barium distribution in European stream water is similar to the pattern of Major-ions and associated elements, characterised by high Ba values in central and southern Europe, and low values in the north and west of the continent, in Fennoscandia, western Britain and Ireland, and western Iberian peninsula, in the Pyrenees and the Alps. These Ba patterns are opposite to those in solid sample media, with patterns of *aqua regia* extractable Ba in soil in between. This is an indication that barium concentrations in stream water are controlled by exogenic factors, such as kinetics of Ba mineral weathering, rainfall *etc.*, and only partly by geogenic factors.

Lowest Ba values in stream water (<14.9 $\mu\text{g l}^{-1}$) are found throughout northern and western Fennoscandia, western Scotland and Wales, north-west Iberian Peninsula (granite, Palaeozoic and Proterozoic schist of the Iberian Massif, with Ba in feldspar and other silicates), and eastern Switzerland, west Austria, Slovenia and Croatia, Corsica, northern Albania and Crete. The low values are predominantly associated with metamorphic and acid igneous rocks, and high rainfall regions of western Scandinavia, Britain, Ireland and the Iberian Peninsula.

Enhanced Ba concentrations in stream water (> 62.5 $\mu\text{g l}^{-1}$) are found in the Baltic states (Ba is quite mobile in reducing conditions in this humid cool climate, it is leached out of Devonian sulfate-bearing deposits underlying the glacial till at a depth of 15-20 meters), central-eastern Britain, southern and eastern rim of the Iberian Peninsula (associated with Permo-Triassic clastic lithologies, with barite as cement or as filling of joints and fractures, resulting from water mixing under an emersion surface in Triassic times), northern Spain (Cantabrian area, karstic barite at

top of Carboniferous limestone covered by Permo-Triassic sediments); medium to high values in the Miocene basins of Old Castilla and Ebro can be associated to evaporitic processes in lacustrine environment. High Ba also in central Europe, including most areas of Germany, western Poland, Slovakia, south-east France, Sardinia and northern Tuscany. All these areas are characterised by stream water of high alkalinity and high mineralisation. These values are associated with a range of lithologies. In central eastern Scotland, the isolated Ba anomaly is probably derived from barite in the Old Red Sandstone bedrock, while in north-east Ireland an isolated Ba anomaly is likely to be due to minor vein sulphide mineralisation (elevated Cu, Sb and Mn also observed). In the Essone valley of France, north of Orleans, high Ba is associated with continental Eocene sediments of slightly alkaline nature. In Tuscany, high Ba anomalies are associated with a range of sedimentary rocks; in Sardinia the anomalies are related to polymetallic ore deposits in the Iglesias-Sulcis area. In southern Poland, the origin of Ba concentrations (Silesia) may be connected with the occurrence of crystalline and sedimentary rocks, as well as with mine water from coal and metal ore mines. In the area between Wroclaw and Poznan, Ca-Mg fertilisers applied to sandy soil can be the source of Ba enrichment in stream water. This explanation could also be applicable to the high Ba content in stream water throughout most of Germany. The highest Ba value in Sweden is related to a Pb mining area. There is no explanation for isolated point anomalies in north-central France.

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

Ba in stream sediment

The median total Ba content (XRFS analysis) in stream sediment is 386 mg kg^{-1} , with a range from 8 to 5000 mg kg^{-1} .

Low total Ba values in stream sediment (<268 mg kg^{-1}) are found throughout the greenstone belt

of central Norway, the Netherlands, south-eastern Poland, north-western and eastern France (Jura), Aquitaine, central Austria, Slovenia and coastal Croatia, central Hungary, most of Greece, north-western Italy, and eastern calcareous Spain.

High total Ba values in stream sediment (>529 mg kg⁻¹) occur throughout Finland with the exception of the north-east, southern Norway, parts of southern and northern Sweden, Scotland, northern England, northern Ireland (Precambrian igneous complex), the Bohemian Massif, the Massif Central and Poitou in France, feldspar rich granitic rocks of northern Portugal and Galicia (over granitic rocks and schist), southern Portugal and Spain, point anomalies in eastern Pyrenees (Permo-Triassic clastic lithologies) and western Pyrenees (barite vein-type mineralisation at Peñas de Haya); high Ba values occur also near Córdoba and Ciudad Real (south Spain) where barite mining is widespread. In southern Sardinia, high Ba probably arises from barite in old Zn-Pb mining areas. Ba is also high in the Roman Alkaline Province and in point anomalies in Germany.

Total Ba in stream sediment shows a good correlation with Al, Ga, K, Rb and Eu.

Aqua regia extractable Ba (ICP-AES analysis)

in stream sediment has a median of 88 mg kg⁻¹, with a range from 4 to 3120 mg kg⁻¹. This would indicate that, on average, less than half of the Ba is extracted by *aqua regia*. The correlation coefficient for Ba analysed by both analytical methods is only 0.76. The distribution of extractable Ba shows some major differences compared to the total Ba map. Essentially, Ba contained in feldspar and other silicates of granitoid rocks is not easily dissolved; the opposite is true of Ba in carbonates, barite or sorbed to clay minerals. Fennoscandia and Scotland show no high Ba values except for southern coastal Finland (marine clay) and south-eastern coastal Sweden. The Variscan parts of the Iberian Peninsula (schist and granite) are low in extractable Ba. On the other hand, the Baetic Cordillera in southern Spain shows high extractable Ba values related to barite or sorbed Ba. The same is true for an area from central Germany to southern Poland and western Slovakia.

Ba in floodplain sediment

The total Ba distribution in floodplain sediment, determined by XRF, varies from 15 to 4837 mg kg⁻¹, with a median of 380 mg kg⁻¹, and the *aqua regia* extractable from 7 to 2210 mg kg⁻¹ Ba (median 82 mg kg⁻¹). As with stream sediment, approximately half of the Ba is extracted by *aqua regia*, suggesting that barium containing minerals, such as feldspar and silicates of felsic rocks, are not easily dissolved.

Low Ba values (<250 mg kg⁻¹) characterise the floodplain sediment of central Norway with crystalline rocks, the calcareous rocks of north-western Ireland, the glacial drift covered plain extending from parts of north and western Germany to much of Poland; the upper Paris basin with calcareous rocks and the alluvial plain of the lower Garonne river; the eastern half of Spain with mainly calcareous and clastic rocks and Gibraltar, the molasse basin of southern Germany and Austria, the Dalmatian coast of Croatia with calcareous and flysch rocks; southern Albania and most of western Greece and Crete with calcareous rocks, flysch and ophiolites.

High Ba values in floodplain sediment (>530 mg kg⁻¹) occur over most of Finland, northern and southern Sweden and southern Norway, northern Scotland, the Massif Central and Vosges in

France, all these are characterised by felsic igneous lithologies with abundant K-feldspar. A notable feature is the extensive north-west to south-east trending zone with high Ba values, beginning on the Belgian-German border and extending to western Slovakia, including granitic and mineralised areas, such as the Harz Mountains, the Erzgebirge (or Krušné Hory), and the Bohemian Massif (De Vos *et al.* 2005). High Ba values are also associated with crystalline rocks in south-eastern Sardinia, Sicily (calcareous, clastic and volcanic rocks), Calabria (granite and metamorphic rocks), the Roman Alkaline Province in Italy (Plant *et al.* 2005); central Macedonia and Thrace in Greece, where they are related to Pb-Zn-Ba mineralisation, and also to granitic and gneissic rocks.

In floodplain sediment, point Ba anomalies in England (4837 and 1869 mg kg⁻¹) are most likely associated with the mineralisation of the northern Pennines; in northern Germany (3820 and 2557 mg kg⁻¹) the point anomalous values (3820 and 2557 mg kg⁻¹) are located on rivers draining the mineralised Erzgebirge region; in northern Sweden (2803 mg kg⁻¹) it is situated in the Skellefte mineralised belt; the point anomalous Ba value in the floodplain sediment of the Loire-

Sarthe-Huisne basin to the north-east of Nantes (1936 mg kg⁻¹) is related to the Pb-Zn-Ba mineralisation of the Poitou ridge area. A point Ba anomaly of 1056 mg kg⁻¹ (as well as anomalies of Hg, Pb and Zn) in north-west Poland is related to anthropogenic pollution.

As for the *aqua regia* extractable Ba floodplain sediment distribution map, Fennoscandia, Scotland and northern Massif Central in France do not show the high values observed on the total Ba map, suggesting that the element is in silicate minerals and, hence, not easily dissolved. On the other hand, the Baetic Range (south Spain), the Catalanian Coastal range, and to a lower degree Cantabria (north Spain) show enhanced extractable Ba values related to Permo-Triassic clastic rocks. In Britain, there is an extensive area with high *aqua regia* extractable Ba from south

Scotland to the Thames-Bristol line, which may be associated with mineralisation, but also with phosphate fertilisers. This possibly explains the widespread distribution of *aqua regia* extractable Ba in the agricultural areas of Britain and Ireland, Nantes-Rennes in north-west France, the Po and Reno basin in Italy, and the plain north of Berlin in Germany.

Total barium in floodplain sediment shows a good positive correlation (>0.4) with K₂O, Ga and Pb, and a weak correlation (>0.3) with Al₂O₃, Rb, Fe, Ti, Nb, Th, Zn, Y, most of the REE, and Tl.

In conclusion, the marked variability in total and *aqua regia* extractable Ba concentrations in floodplain sediment are related to mainly bedrock lithology and mineralisation, and to a lesser extent to contamination by human activities.

Ba comparison between sample media

Patterns in total Ba distribution between all solid sample media are very similar, although data in floodplain sediment tend to be lower over the Pyrenees and in central and western Iberian Peninsula compared to the other solid sample

media. Floodplain sediment Ba values are higher in a belt extending over central Germany through the central Czech Republic to Slovakia. Stream sediment Ba is higher in central England compared to other solid sample media. A boxplot

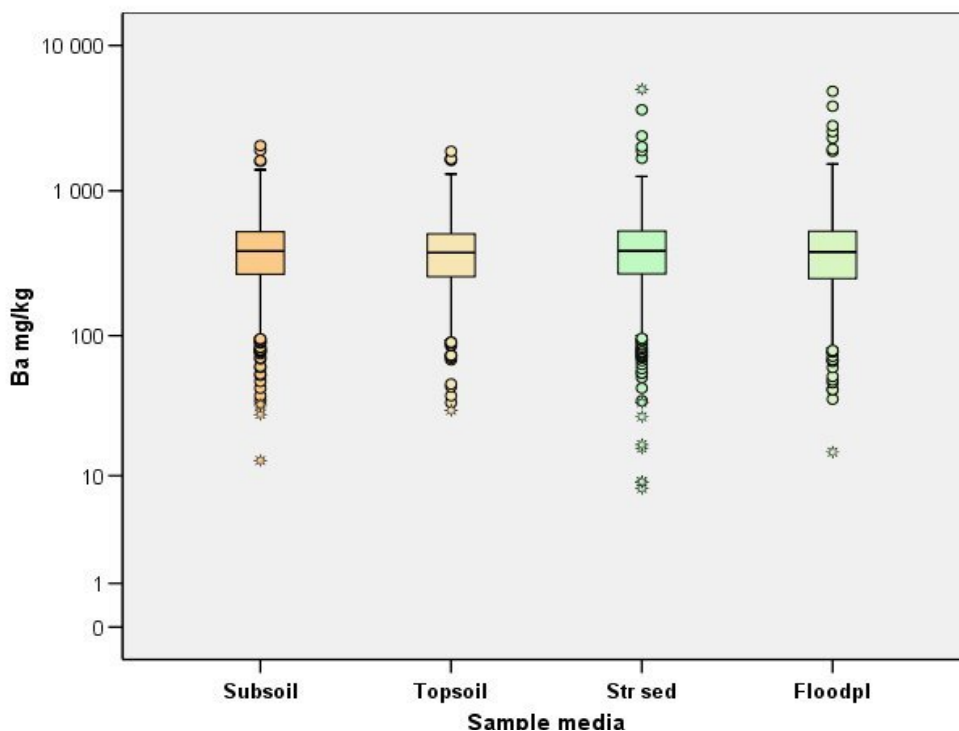


Figure 4. Boxplot comparison of Ba variation in subsoil, topsoil, stream sediment and floodplain sediment.

comparing Ba variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 4. Patterns in humus data are quite similar to those observed in all solid sample media, indicating geogenic mineral sources.

Patterns between total and leachable (*aqua regia*) Ba concentrations are quite dissimilar in many areas, especially throughout Fennoscandia, where Ba content is much lower because feldspar minerals are insoluble in *aqua regia*. In the Baetic areas of southern Spain and in Britain and Ireland, the distribution of leachable Ba is different from the total Ba due to mineralising influences. In coastal southern Finland, leachable Ba is much higher in sediments, since these contain more readily soluble phyllosilicates. In soil, Ba is much higher in northern Greece

(granite and gneiss) and in central and southern Italy, possibly related to alkaline volcanic hydrothermal activity. In Slovenia and Croatia, stream sediment values are lower compared to other solid sample media.

Stream water Ba data show almost exactly the opposite patterns to those observed in solid sample media, but quite similar to the trends in leachable (*aqua regia*) data. The main exception is throughout parts of the Baltic states, in which stream water Ba concentrations appear anomalously high. Barium concentrations are quite low in stream water and all solid sample media in Greece and Albania, throughout the Alpine region and through parts of central and northern Norway and Sweden.