As – Arsenic

Introduction

Arsenic, along with P, Sb and Bi, is a chemical element belonging to group 15 of the periodic table. The element has an atomic number of 33, an atomic mass of 75, three main oxidation states (-3, +3 and +5) and one naturally occurring isotope (^{75}As). The chemistry and geochemistry of As is most similar to that of Sb.

Arsenic is strongly chalcophile, and is partitioned into a variety of sulphide and sulpharsenide minerals, notably arsenopyrite FeAsS, but also realgar AsS and orpiment As_2S_3. It is also widely present as an accessory element in other sulphide minerals such as galena, pyrite and sphalerite. In primary rock-forming silicate minerals, As is incorporated to a limited extent through the replacement of Fe^{3+} or Al^{3+} by As^{3+}. Substitution of P^{5+} by As^{5+} may also give rise to elevated As concentrations in phosphate minerals such as apatite due to the similarity of the PO_4^{3-} and AsO_4^{3-} anionic groups (Tremearne and Jacob 1941). Arsenic's use as a pathfinder element for Au, Ag and other precious metals is well documented (Boyle and Jonasson 1973, Boyle 1974, Dunn 1989, Plant *et al.* 1989, 1991). High As anomalies are a common characteristic of epithermal and mesothermal gold deposits.

Arsenic is not preferentially enriched in felsic or mafic igneous rocks, though hydrothermal processes lead to its enrichment. McLennan and Taylor (1999) quote an average bulk crustal abundance of 1.0 mg kg^{-1} and a give a value of 1.5 mg kg^{-1} for the upper continental crust; Mielke (1979) reports the latter as 1.8 mg kg^{-1}. Mielke (1979) cites values for igneous rocks as ultramafic 1 mg kg^{-1}, basaltic 2 mg kg^{-1} and granitic 1.5–1.9 mg kg^{-1}. In sedimentary rocks, As is concentrated in clays, hydrous Fe and Mn oxides, sulphides and phosphates (Ure and Berrow 1982). The average As concentration in shale of 13 mg kg^{-1} is an order of magnitude greater than that in sandstone (<5 mg kg^{-1}; Davies 1980) and carbonates (Wedepohl 1978). The highest concentrations, *ca.* 20 mg kg^{-1}, are typically found in phosphatic sediments (Tremearne and Jacob 1941), although coal and ironstone, particularly phosphatic ones, can also contain appreciable amounts of As.

Arsenic in stream sediment occurs mainly as the oxides As_2O_3 and As_2O_5, which form soluble arsenites and arsenates in acidic water (Irgolic *et al.* 1995), and as sulphides, *e.g.*, FeAsS and As_2S_3, heavy-metal arsenates and co-precipitated complexes with iron oxides, which are much less soluble (Wedepohl 1978). The relatively small amount of As released into stream water during weathering will remain mobile only if pH and Eh are sufficiently low to favour its persistence in trivalent form. Otherwise, dissolved As is rapidly oxidised to relatively insoluble As^{5+} and, as arsenate (AsO_4^{3-}), becomes sorbed to hydrous oxides of Fe and Mn, clays and organic matter. Arsenic adsorption onto Fe oxides occurs more readily at acid pH, and consequently As can be preferentially removed from acid effluents (such as acidified mine drainage) by natural precipitates of Fe oxide under conditions that do not favour adsorption of other metals such as Cu, Pb and Zn (Webster 1999).

Overall, As minerals and compounds are readily soluble, but As migration is greatly limited, because of strong sorption by clays, hydroxides and organic matter; the latter may have a marked influence on the measured As concentration (Reimann *et al.* 2003). The most common mobile forms of As (AsO_2^-, AsO_4^{3-}, $HAsO_4^{2-}$, $HAsO_3^-$) are sorbed within the pH range from 7 to 9. In most environments, As^{5+} occurs as the $H_2AsO_4^-$ species, whilst As^{3+} as the $H_3AsO_3^0$ species is only dominant in low pH and Eh conditions. The reactions of As in soil are strongly governed by its oxidation state. However, arsenate ions are known to be readily fixed by clays, phosphatic gels, humus, and calcium; hydrated Fe (goethite) and Al oxides are the most active for As retention (Kabata-Pendias 2001, Reimann *et al.* 2003). Although adsorbed As in soil is unlikely to be desorbed again, it may be liberated when As is combined with Fe and Al oxides by hydrolysis caused by the reduction of soil potential. Arsenic enrichment in argillaceous sediments (13 mg kg^{-1}), as well as in surface soil, in comparison to concentrations in igneous rocks, possibly reflects some external As sources, such as volcanic exhalations and anthropogenic pollution (Kabata-Pendias 2001). Arsenic in soil is present in the heavy mineral fraction, but its contribution to the total As content is very small (commonly about 1%); a much higher proportion of total As is associated with the clay fraction (27-90%). Global As contents in soil vary from 4.4 mg kg^{-1} in podzols to 9.3 mg kg^{-1} in histosols; the lowest As levels are found in sandy soil and, in particular, those derived from granite, whereas higher As concentrations often occur in alluvial soil rich in organic matter; acid sulphate soil also accumulates a high proportion of native As, up to 30 to 50 mg kg^{-1} in lower horizons (Kabata-Pendias 2001).

In natural fresh water, concentrations of As rarely exceed a few µg l^{-1}, although concentrations can vary by more than four orders of magnitude depending on the source of the arsenic and the local geochemical conditions (Smedley and Kinniburgh 2002, O'Day 2006). However, acidic surface waters, such as those associated with mine drainage, and some strongly reducing groundwater, have been reported to contain significantly more than 100 mg l^{-1} As (Plant *et al.* 2004). The average As concentration in sea water is reported as ~1.5 by Plant *et al.* (2004). Fordyce *et al.* (1995) note that the retention of As in solution is constrained by co-precipitation with Fe along with other elements, such as Ba, Co, Ni, Pb and Zn.

Anthropogenic sources of arsenic include coal combustion, geothermal power plants, sulphidic ore roasting and smelting, and pig and poultry sewage (Reimann and de Caritat 1998). Arsenic contamination of the environment as a result of mining and smelting is relatively common (Breward *et al.* 1994, Thornton 1996, Chappell *et al.* 1999, Demetriades *et al.* 1996, Demetriades 1999, Charlet and Polya 2006, Hopenhayn 2006, Lloyd and Oremland 2006, Morin and Calas 2006). Pentavalent As^{5+} can substitute for P^{5+} in phosphates such as apatite, used in fertilisers, thus contaminating agricultural soil. Other sources of soil pollution include herbicides, insecticides and fungicides containing arsenic compounds (Kabata-Pendias 2001, Reimann *et al.* 2003).

Arsenic is essential for some organisms, *e.g.*, 12 to 25 µg per day is required by humans, but is toxic depending on its valency and speciation. Pentavalent arsenic (As^{5+}) compounds are less toxic than trivalent (As^{3+}). Chronic exposure increases the risk of cancer and skin pigmentation (WHO 1996, Chappell *et al.* 1999). Arsenic has great notoriety as a poison, though there are great differences in the toxicity of different arsenic compounds.

Table 9 compares the median concentrations of As in the FOREGS samples and in some reference datasets.

As in soil

The median total As content (ICP-MS) is 6.02 mg kg^{-1} in subsoil and 7.03 mg kg^{-1} in topsoil, with a range varying from 0.22 to 593 mg kg^{-1} in subsoil and 0.32 to 282 mg kg^{-1} in topsoil. The average ratio topsoil/subsoil is 1.017.

The subsoil total As distribution map shows that northern Europe (most of Fennoscandia, the Baltic states, Scotland, Poland, northern Germany and Denmark) is dominated by low As levels (< 2.48 mg kg^{-1}). There is a sharp break on the southern margin of the former glacial cover, with most areas to the north showing lower As concentrations in soil.

High total As values in subsoil (>12.1 mg kg^{-1}) occur in Portugal and western Spain, the Pyrenees, Brittany and Poitou in France, a belt from the Central Massif to the Jura and Switzerland, south-west England, karstic soil of Slovenia and Croatia, and eastern Greece, including the Attica peninsula (Lavrion). In Spain, high As distribution is controlled by geology and mineralisation: in Galicia by regional shear zones showing dissemination of arsenopyrite-pyrite in granitic and metamorphic rocks, and associated As-W-Sn or As-Au mineralisations; in neighbouring Asturias, several small granitic stocks are accompanied by epithermal Au-As-Cu mineralisation (El Valle gold mine, Boinas, Carlés Au mine); Sn-W and precious metals mineralisations explain high As values in the remaining Iberian Massif. In south Portugal, high As is linked to its presence in Palaeozoic basement rocks and to sorption by clay and iron oxide-hydroxide. In north-west France, high As in soil delineates the south-western Armorican shear zone from Brittany to the Massif Central, with Sb-As-Au mineralisation Arsenic-rich lithologies sometimes have an impact on soil, *e.g.*, the Cambrian black shale in the Pyrenees. The highest As value in subsoil (593 mg kg^{-1}) occurs

Table 9. Median concentrations of As in the FOREGS samples and in some reference data sets.

Arsenic (As)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median mg kg^{-1}*
Crust[1]	Upper continental	n.a.	n.a.	Total	4.8
Subsoil	**FOREGS**	**783**	**<2.0**	**Total (ICP-MS)**	**6.02**
Subsoil	**FOREGS**	**784**	**<2.0**	***Aqua regia* (ICP-MS)**	**5.00**
Topsoil	**FOREGS**	**840**	**<2.0**	**Total (ICP-MS)**	**7.03**
Topsoil	**FOREGS**	**837**	**<2.0**	***Aqua regia* (ICP-MS)**	**6.00**
Soil[2]	World	n.a.	n.a.	Total	5
Soil, C-horizon[3]	Barents region	1357	<2	*Aqua regia* (GFAAS)	1.71
Water	**FOREGS**	**807**	**Filtered <0.45 µm**		**0.63 (µg l^{-1})**
Water[4]	World	n.a.			2 (µg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**6.00**
Stream sediment	**FOREGS**	**845**	**<0.15**	***Aqua regia* (ICP-AES)**	**6.00**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**6.00**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	***Aqua regia* (ICP-AES)**	**6.00**
Stream sediment[5]	Canada	26 227	<0.18	INAA	8.2
Stream sediment[5]	Canada	56 555	<0.18	Colorimetry and Hydride	4

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

in northern Portugal and is ascribed to mining activities. The second highest value (203 mg kg^{-1}) occurs in the southern Massif Central and is associated with primary mineralisation (Alès Sb-As district), followed by 157 mg kg^{-1} in Lavrion, Greece, related to ancient and recent lead-silver mining and smelting activities (De Vos *et al.* 2005). The point anomaly in east-central Greece is attributed to mineralisation.

The topsoil total As map is very similar to that of the subsoil distribution, with some additional point anomalies, *e.g.*, in the Spišsko-gemerské Rudohorie Mountains ore district in eastern Slovakia. There is a good correspondence between subsoil and topsoil, with an average ratio topsoil/subsoil of 1.017, but a correlation of only 0.48, which means that some locations have contrasting values (see scattergram in figure 2).

Arsenic in subsoil shows a good correlation (>0.4) with Sb, Cs, In, Tl, Fe and Ta. In topsoil, only Cs has a good correlation with As.

For As determined after partial extraction with *aqua regia* (ICP-AES), about half the samples are below the detection limit of 5 mg kg^{-1}. Extractable As values range up to 562 mg kg^{-1} for subsoil and up to 220 mg kg^{-1} for topsoil, with a median of 5.0 mg kg^{-1} for subsoil and 6.0 for topsoil. Comparison of both analytical methods points to nearly total extraction with *aqua regia*; both methods lead to similar distribution maps for subsoil and topsoil.

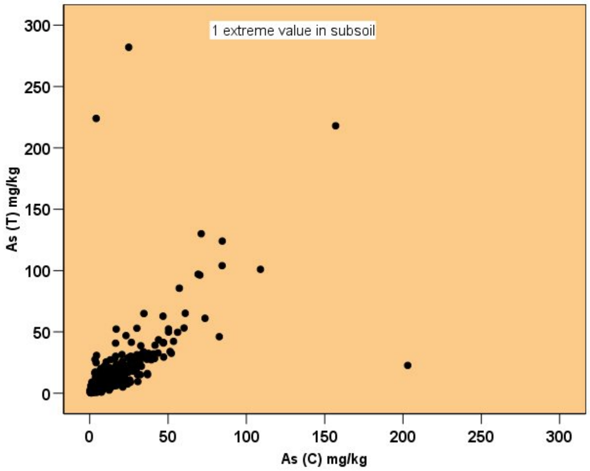

Figure 2. Scattergram of arsenic concentrations in topsoil and subsoil.

As in stream water

Arsenic values in stream water range from <0.01 to 27.3 µg l^{-1}, over three orders of magnitude, with a median value of 0.63 µg l^{-1}. The arsenic distribution in Europe resembles generally the distributions of Mo, Sb, Se, U and V, although concentrations in alkaline stream water in the Mediterranean region tend to be enhanced. The distribution of As in stream water is most similar to patterns of major ions and associated elements, controlled mostly by exogenic and less geogenic factors, but also to felsic element patterns explained by geogenic sources of As in central and southern Europe. Distribution patterns are similar to those in soil in the Britain and Ireland, northern Fennoscandia, southern Portugal and parts of France and Germany, but is otherwise opposite to patterns observed in soil and sediments, indicating a variety of As sources for stream water.

Lowest As values in stream water (<0.30 µg l^{-1}) are found on Precambrian Shield terrains in western and northern Sweden, northern Finland and Norway, over Caledonian rocks in most of Norway and in Scotland (here also on Laurentian terrains), and on Variscan terrains in small areas in Spain and France, and in Corsica. On the Alpine Orogen, low As occurs in a small area in northern Italy, in a belt from west Croatia and Slovenia across central Austria to south-eastern Germany and the Czech Republic, in north Albania, central and southern mainland Greece and Crete, and in the eastern Baetics of southern Spain.

Enhanced As concentrations in stream water (>1.31 µg l^{-1}) are found in Lithuania (possible agrogenic contamination), eastern and west-central Poland, in parts of Denmark and north Germany on glacial drift originating in Fennoscandia, and on other Quaternary deposits, as in the Netherlands. In Variscan terrains, enhanced levels are found in the Black Forest region in south-west Germany, in Vosges, Massif Central, southern parts of Brittany and in south-western France extending across the Alpidic eastern Pyrenees to north-east Spain, in south-east, central and south-west Spain extending to south Portugal (including the Iberian pyrite belt), and on north Sardinia, where high As is linked to base metal deposits. In France, the high As (and Hg) values are inherited from natural geogenic anomalies, following the late Hercynian distensive system developed in southern Brittany fault system and in the Argentat faults of Massif Central. Also, As anomalies are related to late Hercynian peraluminous leucogranite intrusive (along with Be, Li, Cs). In Lorraine, the high As values are correlated with As-contaminated mine water from iron mines due to pyrite oxidation. The anomalous As value in south-west France near the border with Spain is probably related to a previously mined Pb-Zn district (Moncoutan) enclosed in carbon rich Ordovician black shale. Enhanced arsenic concentrations in the Alpine Orogen are found in the Baetic Cordillera in southern Spain, in central and south-east Italy (as a result of recent volcanic activity), in eastern Switzerland and in a belt from Variscan Czech Republic across eastern Austria, west and east Carpathian Slovakia, most of Hungary to north-east Croatia, the latter two mostly on Quaternary deposits of the Pannonian basin. The highest anomalous content of As in western Slovakia is related to local geological phenomena; it represents a seepage flow of natural mineral water to stream water. Elevated content of As in part of the Slovak lowlands is probably caused by agricultural and/or industrial contamination. Moderately enhanced arsenic is also found in the stream water samples of northern Greece associated with base metal mineralisation and gold.

As in stream sediment

The median total As content (ICP-MS analysis) in stream sediment is 6 mg kg^{-1}, with a range varying from <1 to 241 mg kg^{-1}.

The distribution map shows low total As values (<4.00 mg kg^{-1}) in stream sediment throughout parts of northern Europe (most of Norway, Finland, southern Sweden, north-west Scotland, northern Poland and the Baltic States), south and south-east Spain.

High As values in stream sediment (>11.0 mg kg^{-1}) occur in the Skellefte mineralised belt in northern Sweden, Portugal and western Spain

(Variscan terrains, including crystalline basement rocks, and vein-type mineralisation in northern Portugal and Galicia; Iberian Pyrite Belt in southern Portugal and Spain), the eastern Pyrenees, a zone from the Massif Central to southern Brittany in France, most of England (known mineralisation in south-west England, Wales and the Pennines of central England), northern Ireland (mineralisation in the west, Mourne granite in the east), northern Bohemia (mineralisation in Erzgebirge), and point anomalies in southern Hungary, south-eastern Switzerland, and south-eastern Spain (also a point anomaly for Hg). In Attica, Greece, a point anomaly lies in the Lavrion former mining area, and another one to its north-west is ascribed to industrial pollution, although the existence of unknown mineralisation cannot be precluded.

The most enhanced stream sediment sample occurs in Brittany, with 241 mg kg^{-1} As and 1.7% S, and is associated with a major shear zone with known mineralisation (high Sn, Li, Sb and Cs), indicating a leucogranitic hydrothermal alteration. The second richest sample occurs in the eastern Pyrenees, with 122 mg kg^{-1} As. It is probably influenced by the As-rich lithology of the Cambrian black shale, although there is also evidence of mineralisation, with high values for As, Cu, Pb and S. Higher As values and anomalies thus seem mostly influenced by lithology, mineralisation or old mining and smelting activities, although point source As enhancement is doubtless also caused by industrial pollution in some areas.

Arsenic in stream sediment has a good correlation (>0.4) with Sb, Pb and Li, and a weak correlation (>0.3) with Cu, Zn, Tl, W, Al, Ga and Rb.

The median content for As in stream sediment,. determined after partial dissolution with *aqua regia* (ICP-AES analysis), is the same as for total As (6 mg kg^{-1}), with a range of values from <5 mg kg^{-1} to 231 mg kg^{-1}; however, close to 50% of determinations by ICP-AES are below the detection limit of 5 mg kg^{-1}. Comparison of both analytical methods points to a nearly total extraction; both methods lead to similar distribution maps, and correlation between them is 0.99.

As in floodplain sediment

The total As distribution in floodplain sediment, determined by XRF, varies from <1 to 390 mg kg^{-1} with a median of 6 mg kg^{-1}. The *aqua regia* extractable varies from <5 to 410 mg kg^{-1} As with a median of 6 mg kg^{-1}, and in the data set there are about 40% determinations below detection limit. Nevertheless, the total and extractable As geochemical maps of floodplain sediment show almost identical distribution patterns.

Low total As values (<3 mg kg^{-1}) characterise the floodplain sediment of the Caledonian and Fennoscandian and Baltic states, the glacial drift covered plain extending from north-east Germany to Poland; the Caledonian rocks of north Scotland. Small areas with low total As values occur in the molasse basin of Austria.

High total As values in floodplain sediment (>13 mg kg^{-1}) are found in Wales and the southern half of England, and are possibly due to mineralisation (*e.g.*, Cornwall in south-west England Cu-Sn-As-Zn), and industrial pollution; the Armorican Massif to Poitou, possibly associated with Au and Sb mineralisation (*e.g.*, La Lucette Sb-Au, La Belliere Au-arsenopyrite, Le Brouzils Sb, Rochetrejoux Sb), and an arcuate belt extending from the Cevennes, Massif Central to the Vosges, Black Forest in Germany and into central Switzerland and northern Italy (*e.g.*, France: Le Bessade Sb, La Chatelet Au-As, Sainte-Marie-Aux-Mines Cu-Pb-Zn-Ag-Co-As; Switzerland: Malcantone Au-Ag-As-Sb-Ba); the mineralised western part of the Iberian Peninsula, and its northern coastal area (*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 and Horcajo Pb-Ag deposits); the Roman Alkaline Province, the Taranto region in Italy (also possibly related to industrial pollution), and southern Sardinia; an extensive belt from southern Belgium to the Harz Mountains in Germany, the Erzgebirge and Bohemian Forest; western Slovakia and Hungary, possibly associated with mineralisation; northern Albania and central Macedonia Greece with base metal mineralisation (De Vos *et al*. 2005).

Point anomalous As values in floodplain sediment occur in the Lavrion mineralised district in Greece (390 mg kg^{-1}), north-west Portugal (197 mg kg^{-1}), associated with vein type mineralisation; the two point anomalies in southern Spain are in the Iberian Pyrite Belt near Rio Tinto (194 mg kg^{-1}), and Linares (168 mg kg^{-1}) mineralised areas (De Vos *et al*. 2005). In northern Sweden the point As anomaly is associated with mineral deposits of the Skellefte ore district (187 mg kg^{-1}). Another point anomaly is in eastern Slovakia (113 mg kg^{-1}).

Arsenic in floodplain sediment shows a good positive correlation (>0.4) with Sn, Cu and W, and a weak correlation (>0.3) with Sb, Fe, V, Ga, Rb, Nb, Th, Zn, Tl, Ta, Ce, La, Y, Ti and Li. This points to associations with mineralisation and mining contamination, but also adsorption on clay minerals. When the Lavrion (Greece) outlier is included, the correlation with Cd, Hg, Sb, Zn and Pb is enhanced.

In conclusion, the marked variability of As distribution in floodplain sediment is related to both the bedrock geology (mineralisation) and to anthropogenic activities.

As comparison between sample media

In general there are broad similarities between all solid sample media; patterns in top and subsoils are very closely related. Compared to soil lower As values are present in stream and floodplain sediments throughout the coastal region of Croatia and Slovenia and the adjacent areas of western Austria, explained by theremoval of fine-grained material from the residual soil and karst. Stream sediment As concentrations throughout the Britain and Ireland, in a belt from eastern Germany to western Poland, and in Sardinia are significantly higher than in soil. Floodplain sediment is enhanced in As in Slovakia and western Hungary compared to all other solid sample media. There is good agreement in distribution patterns between total and leachable (*aqua regia*) As concentrations in all solid sample media. Because the ratio of topsoil to subsoil As does not show any significant differences for both total and leachable As, except on the local scale, it can be implied that there is no large scale anthropogenic contamination in Europe. The same observation also leads to the conclusion that As is not related to soil organic matter. A boxplot comparing As variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 3.

The distribution pattern of As in stream water is similar to that of soil in Britain and Ireland, northern Fennoscandia, the south-west Iberian Peninsula and parts of France and Germany, but elsewhere it is opposite to patterns observed in

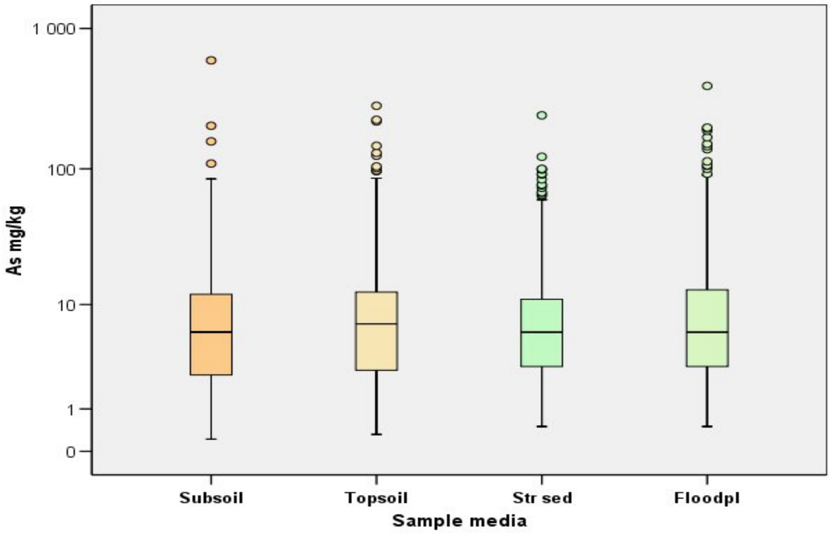

Figure. 3. Boxplotcomparison of As variation in subsoil, topsoil, stream sediment and floodplain sediment.

soil and sediments. In Portugal, the wide distribution of As is due to different sources. The concordance of patterns indicates predominance of geogenic As input into waters, and their discordance the influence of various exogenic, mostly climatic factors. High As in stream water in the Netherlands may be the result of human influences or of association with organic matter. In southern Finland and Sweden, the Baltic states and northern Poland, slightly elevated As concentrations in stream water compared to soil are associated with high DOC.

Although no large-scale anthropogenic contamination is observed for As, there are significant areas throughout Europe that have naturally occurring high As levels, many of which are above currently used national acceptable guideline values.