Introduction

Uranium is a member of the actinide series of elements, along with Th and human-made elements such as Pu. The element has an atomic number of 92, an atomic mass of 238, five main oxidation states (+2, +3, +4, +5 and +6), of which +4 and +6 are most common in nature, and three naturally occurring isotopes (\(^{234}\text{U}, ^{235}\text{U} \text{ and } ^{238}\text{U}\)), of which \(^{238}\text{U}\) is the most abundant at 99%. Like Th, it is a radioactive element, and its most stable isotope, \(^{238}\text{U}\), has a very long half-life of 4.46 x 10\(^9\) years.

Uranium is a lithophile metallic element present in several minerals, including uraninite \(\text{UO}_2\), brannerite \((\text{U},\text{Ca},\text{Ce})(\text{Ti},\text{Fe})_2\text{O}_8\) and carnottite \(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2\cdot3\text{H}_2\text{O}\). It is also present as an accessory element in zircon, apatite, allanite and monazite, and in complexes with organic matter and phosphatic ironstone.

In magmas, the highly charged \(\text{U}^{4+}\) ion (ionic radii 89 pm), behaves incompatibly, becoming concentrated in late-stage differentiates in accessory minerals such as zircon and allanite. Granite and pegmatites, especially those produced from evolved magmas, are therefore richer in U than mafic igneous rocks. Secondary concentration of U may occur as a result of deuteric and hydrothermal activity associated with the emplacement of felsic volcanics and intrusives. Mielke (1979) cites very low levels of U in ultramafic rocks (1 mg kg\(^{-1}\)) and other igneous rocks (1-3 mg kg\(^{-1}\)), and a crustal abundance of 2.3 mg kg\(^{-1}\). Uranium is used in geochemical prospecting as a pathfinder element for its mineralisation. High U values indicate the presence of felsic rocks, especially intrusives.

In sedimentary rocks, the levels of U are closely related to the redox conditions pertaining during their formation. Thus, the highest concentrations are found in organic-rich facies (6–1000 mg kg\(^{-1}\)) associated with anoxic environments and phosphatic sediments (50–300 mg kg\(^{-1}\)). Lower values are recorded in coarse-grained inorganic rocks (e.g., quartzite 0.5–1.5 mg kg\(^{-1}\) and arkose 1.5 mg kg\(^{-1}\)) with clay-rich sediments having generally higher levels. The average value cited for shale is 3.7 mg kg\(^{-1}\) and 2.2 mg kg\(^{-1}\) for carbonate rocks (Mielke 1979). Average values for loess and river particulates are given as 2.5 and 3 mg kg\(^{-1}\) U respectively (McLennan and Murray 1999).

Kabata-Pendias (2001) reports that there is very little information with respect to U in soil. The global average for soil is given as 0.79 to 11 mg kg\(^{-1}\) U. The mobility of U in soil, like Th, is governed by the formation of the hydrated cation \(\text{UO}_2^{2+}\), which is responsible for its solubility over a wide range of soil pH. Organic acids may increase the solubility of U in soil, but its mobility may be limited by the formation of slightly soluble precipitates (e.g., phosphates and oxides) and by adsorption on clay minerals and organic matter.

The aqueous geochemistry of U is unusual for a metal, in that it is generally more soluble in oxidising, alkaline and carbonate-rich water than under acidic, reducing conditions. However, U is readily soluble in the strongly acid, oxidising water often associated with acid mine drainage. Under such conditions the main species in solution is the uranyl cation \(\text{UO}_2^{2+}\), in which U is in its highest (hexavalent) oxidation state, although forms such as \(\text{UO}_2\text{F}^-\) may be present (Drever 1997). Under neutral to alkaline oxidising conditions, soluble uranyl-carbonate complexes, such as \(\text{UO}_2(\text{CO}_3)_2^{2-}\) predominate (Brookins 1988, Duff et al. 1997). Under reducing conditions, the insoluble \(\text{U}^{4+}\) oxide \(\text{UO}_2\) and mixed oxides, such as \(\text{U}_3\text{O}_8\) are formed. Sulphate- and iron-reducing bacteria are known to reduce \(\text{U}^{6+}\) to \(\text{U}^{4+}\) (Duff et al. 1997) and this mechanism almost certainly operates in anoxic sediments.

Dissolved U tends to form strong associations with organic matter such as humic and fulvic acids, iron oxides and with dissolved phosphates, the latter inducing co-precipitation with Ca or Pb, or with secondary Fe oxides (Drever 1988, 2002). Where dissolved silica is present, U may precipitate as coffinite, USiO\(_4\) (Brookins 1988). Uranium solubility is also reduced in the presence of dissolved V by complexation with vanadate to form the very low solubility mineral carnotite, which is often found as a cementing phase in uraniumiferous sandstone. In most natural water U is present at concentrations between 0.1 and 10 µg l\(^{-1}\) (Hem 1992), although concentrations exceeding 1 mg l\(^{-1}\) can occur in water associated with uranium ore deposits. The complex solution
chemistry of U ensures that high levels in water and stream sediment rarely occur together on regional geochemical maps.

The main anthropogenic sources of U include uranium mining and milling, nuclear effluents, phosphate fertilisers and coal combustion (Reimann and de Caritat 1998). Uranium is of great importance as a nuclear fuel. Depleted U is used in inertial guidance devices, gyro compasses, counterweights for aircraft control surfaces, as ballast for missile re-entry vehicles and as a shielding material. Uranium metal is also used for X-ray targets for the production of high-energy X-rays.

Uranium is a non-essential element. It is chemotoxic, radiotoxic and a carcinogen. Because U is a radioactive substance, its effects on human health have been widely researched. Long-term exposure to U radionuclides can result in medical conditions such as kidney disease and the development of cancer. The radioactive decay of U releases radon gas, which is itself radiotoxic, highly mobile and of more environmental concern than U itself.

Table 71 compares the median concentrations of U in the FOREGS samples and in some reference datasets.

Table 71. Median concentrations of U in the FOREGS samples and in some reference data sets.

<table>
<thead>
<tr>
<th>Uranium (U)</th>
<th>Origin – Source</th>
<th>Number of samples</th>
<th>Size fraction mm</th>
<th>Extraction</th>
<th>Median mg kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crust¹</td>
<td>Upper continental</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Total</td>
<td>2.7</td>
</tr>
<tr>
<td>Subsoil</td>
<td>FOREGS</td>
<td>790</td>
<td>&lt;2.0</td>
<td>Total (ICP-MS)</td>
<td>2.03</td>
</tr>
<tr>
<td>Topsoil</td>
<td>FOREGS</td>
<td>843</td>
<td>&lt;2.0</td>
<td>Total (ICP-MS)</td>
<td>2.00</td>
</tr>
<tr>
<td>Soil²</td>
<td>World</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Total</td>
<td>2.7</td>
</tr>
<tr>
<td>Water</td>
<td>FOREGS</td>
<td>807</td>
<td>Filtered &lt;0.45 µm</td>
<td>0.32 (µg l⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Water³</td>
<td>World</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.5 (µg l⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Stream sediment</td>
<td>FOREGS</td>
<td>852</td>
<td>&lt;0.15</td>
<td>Total (XRF)</td>
<td>2.00</td>
</tr>
<tr>
<td>Floodplain sediment</td>
<td>FOREGS</td>
<td>747</td>
<td>&lt;2.0</td>
<td>Total (XRF)</td>
<td>2.00</td>
</tr>
<tr>
<td>Stream sediment⁴</td>
<td>Canada</td>
<td>24 439</td>
<td>&lt;0.18</td>
<td>Total (INAA)</td>
<td>3</td>
</tr>
</tbody>
</table>


U in soil

The median U content is 2.03 mg kg⁻¹ in subsoil and 2.00 mg kg⁻¹ topsoil; the range varies from <0.1 to 30.3 mg kg⁻¹ in subsoils and from 0.21 to 53.2 mg kg⁻¹ in topsoil. The average ratio topsoil/subsoil is 0.952.

Low U values in subsoil (<1.35 mg kg⁻¹) occur in the glacial drift area from the Netherlands to Poland and Lithuania, in central and northern Finland, and in southern Spain.

The largest soil U anomalous area is the crystalline French Massif Central, where several U deposits were exploited, and are related either to granitic cupola hydrothermal secondary alteration, to vein type deposits, or to Autunian black shale in the south. Other anomalous uranium areas in subsoil (>5.21 mg kg⁻¹) are found in northern Portugal and the Italian alkaline magmatic province. High U values in subsoil (>2.88 mg kg⁻¹) also occur in relation with granitic rocks in Galicia and western Spain, Brittany (France) and the eastern Alps; on karst of Slovenia and Croatia; an area from the Black Forest of Germany to the Bohemian Massif; point anomalies in southern Norway; near the Mourne granite in northern Ireland, and in north-eastern Greece (related to granitic intrusions, U mineralisation and their weathering products).

In comparison, the topsoil U map shows that the Portuguese anomaly extends into western Spain, over the crystalline basement of the Iberian Massif in a known U province. North-eastern Greece has a point anomaly (U mineralised...
district), and in Austria two anomalies are stronger than in subsoil.

Uranium in subsoil shows a strong correlation (>0.6) with Th and Rb, and a good correlation (>0.4) with Be, Nb, Ta, Bi, Cs, Ti, Ce, La, Pr, Nd, Sm, Al, Ga and K. In topsoil, the correlation with Cs, Ta and the REEs is generally stronger, and also Pb has a good correlation.

**U in stream water**

Uranium values in stream water range over four orders of magnitude, from <0.002 to 11.1 µg l\(^{-1}\) (excluding two outliers of up to 21.4 µg l\(^{-1}\)), with a median value of 0.32 µg l\(^{-1}\).

Lowest U values in stream water (<0.04 µg l\(^{-1}\)) are found throughout Norway, northern Sweden and most of northern and central Finland on Precambrian Shield and partly Caledonides, to which also belong most of Scotland, Wales and south-west England, northern Ireland, Denmark on Precambrian Shield derived glacial drift, and on Variscan terrains north-west and central Iberian Peninsula, parts of Brittany and the Massif Central in France and in western Germany.

Enhanced U concentrations in stream water (>1.7 µg l\(^{-1}\)) are found within the Baltic states (U is easily extractable from calcareous clay, limestone and dolomite and is very mobile in alkaline water together with ions of Ca, Mg, HCO\(_3\); Sr and S; uranyl carbonate complexes are likely to exist), northern Poland mostly on glacial drift, on Variscan terrains of south and eastern Iberian Peninsula, and in the Alpidic Orogen in Hungary, Slovakia, northern Greece (associated with uraniferous granite), and in volcanic areas of Italy. These U values are associated with a range of lithologies. In France, the major U anomalies are not correlated with leucogranitic bodies enclosing U mineralisation. The isolated stream water U anomaly in the Essone River valley is located on continental Eocene sediments, which are known to host some U and Se mineralisation, in a slightly alkaline water (pH 8). In Italy, the anomalously high stream water U data in central and southern regions are associated with recent alkaline volcanics; in Apulia and Sicily regions agricultural influences (phosphate fertilisers) may also be important. In northern Estonia, oil shale mine tailings cause U pollution in stream water.

In Spain and Portugal, as in France, the stream water pattern of uranium is the opposite to those of the solid sample media; in stream water U is mainly controlled by pH and oxidising factors. In southern and eastern Spain, high U in stream water is associated with alkaline pH; a point U anomaly in stream water near Badajoz (south-west Spain) can be related to black shale and U veins in granitic rocks; and in the Ebro River basin (northeast Spain) to sandstone with high uranium content.

A highly anomalous U value in stream water (7.3 µg l\(^{-1}\)) in south Poland near the Czech border occurs in a catchment draining magmatic and metamorphic Palaeozoic rocks with possible uranium mineralisation. In northern Poland, and also in Pannonian Croatia and Hungary, high U concentrations, sometimes anomalous, are possibly derived from mineral fertilisers, that were produced from phosphorites rich in uranium. In central Sweden in the Stockholm area, a point anomaly is caused by U-rich granite and pegmatite in combination with alkaline soil conditions. In south-east Czech Republic, a point U anomaly in stream water is related to the occurrence of durbachite melasyenite rock. High concentrations are also observed in the DOC-rich environments of the Baltic states and parts of northern Poland.

The discussed U distribution pattern in stream water of Europe is similar to the Major-ions and associated elements model that is dependent on climate and only locally on geology, showing association with the elements typical for Felsic and Alkaline rocks, e.g., alkaline volcanism in Italy and northern Greece. Several anomalous areas might be anthropogenic, a result of U-containing phosphate fertilisers. Uranium patterns in stream water tend to be virtually opposite to those in stream sediments.
U in stream sediment

The median U content in stream sediment is 2.0 mg kg\(^{-1}\), and the range varies from <1 to 98 mg kg\(^{-1}\). Close to 30% of determinations are below the detection limit.

Low U values in stream sediment (<1 mg kg\(^{-1}\)) occur in eastern Finland, south-central Norway, most of Poland, northern Germany and western Denmark, most of eastern France, eastern and south-east Spain, south-east Italy, central Hungary and coastal Croatia, and most of Greece.

High U values in stream sediment are mostly associated with granitic intrusive rocks. The most anomalous stream sediment U area (up to 98 mg kg\(^{-1}\)) is found in central Sweden near well known U-rich granite; there are radon problems in drinking water in this district. The second highest U area (up to 59 mg kg\(^{-1}\)) in stream sediment is the crystalline French Massif Central, where several U deposits were exploited, related either to granitic cupola hydrothermal secondary alteration, to vein type deposits, or to Autunian black shales in the south. Other highly anomalous U areas (>13 mg kg\(^{-1}\)) are located in northern Portugal (known U province), Old Castilia and Galicia (Spain), Corsica and northern and southern Sweden. Some high U values in stream sediment (>4 mg kg\(^{-1}\)) also occur in the Roman Alkaline Province, the Bohemian Massif (especially its southern part), southern and central Norway, southern Finland, western Scotland, and the Mourn granite area in northern Ireland.

Uranium in stream sediment has a strong correlation (between 0.6 and 0.8) with Th, Y and the REEs except Eu (a very weak 0.29), a good correlation (0.4 to 0.6) with K, Rb, Cs, Tl, Ga, Nb, Ta, Sn and Be, and a weak correlation (>0.3) with Al, Na, W and Zr.

U in floodplain sediment

Uranium values in floodplain sediment vary from <1.00 to 89 mg kg\(^{-1}\), with a median of 2.00 mg kg\(^{-1}\). About 30% of determinations are below the detection limit of 1.00 mg kg\(^{-1}\). The variation in the lower U values is, therefore, somewhat constrained by the detection limit of the XRF analytical method.

Low U values in floodplain sediment (<1 mg kg\(^{-1}\)) characterise the glacial drift covered plain from north Germany across Poland, Lithuania and Latvia to western Estonia; eastern, central and northern Finland to northermost Norway on mainly gneiss, schist and greenstone of Archaean age on the Fennoscanian Shield; low U values in floodplain sediment occur in central and south-central Norway and eastern Scotland on mostly metamorphic rocks, and northern Ireland and England on mostly clastic and also carbonate rocks, and most of central and south-eastern England on clastic and carbonate rocks. Low U levels in floodplain sediment are found in southern Portugal and Spain on clastic and metamorphic rocks, and in eastern Spain on clastic and carbonate rocks; over large parts of the Paris, Aquitaine and Rhône basins in France on carbonate and clastic rocks; part of the river Po River basin in Italy on fluvial deposits; northern, central and southern Apennines in Italy on clastic, carbonate and ophiolitic rocks; in central Austria in the Alps and on the molasse foreland; in central Hungary on loose fluvial deposits; the Dalmatian coast of Croatia on limestone and flysch sediments; southern Albania and most of Greece over limestone, clastics and ophiolite.

High U values in floodplain sediment (>2 mg kg\(^{-1}\)) occur mainly on exposed late and postorogenic granite in Variscan terrains, and in the proximity of ore deposits and historical mining associated with granite, in France from the Armorican massif in Brittany to Poitou (Margmac-Peny U deposit) and the Massif Central (Les Bois Noirs and Lodève U deposits) towards the Pyrenees and Vosges; in the northern half of Portugal and adjacent Spain (Galicia and Central Meseta); south-west England granite intrusives; Erzgebirge and Bohemian massif, and Moravian Heights (durbachite) in the Czech Republic. In Hungary, high U values in floodplain sediment appear to be connected with the Mecsek uranium deposit. High and anomalous U values are also associated with granite of the Precambrian Fennoscandian Shield, as in all of southern Sweden (e.g., Ranstad U-Mo deposit), in northern Sweden (e.g., Pleutajokk U deposit), southern Norway including the Oslo rift, and southern Finland (associated with rapakivi granite and...
other granitic rocks). In the southern Alpine Europe, elevated U values in floodplain sediment are found in the Roman Alkaline Province, Corsica (on Hercynian granite) and north Sardinian granite. It is worth noting that in Spain the most important economic U deposits, hosted by black shale or present in veins near granitic intrusives in Salamanca and Extremadura, do not cause anomalous U values in floodplain sediment.

The floodplain sediment U anomaly in eastern Estonia is connected to the phosphorite deposits and mining of bituminous shale. The comparatively elevated U values in Slovenia and west Croatia are the result of U accumulation in karstic soil.

Outlying and anomalous U values in floodplain sediment occur in the mineralised district of Skellefte in northern Sweden (89 mg kg\(^{-1}\)), and Oslo Graben in southern Norway (18 mg kg\(^{-1}\)); southern Corsica (14 mg kg\(^{-1}\)) associated with Variscan granite.

Uranium in floodplain sediment has a strong positive correlation (>0.6) with Rb and Th, and a good correlation (0.4 to 0.6) with Al, Ga, K, Cs, Be, Ta, Tl, Y and some REEs (Ce, La, Pr, Nd, Sm, Gd).

It is concluded that the distribution map of U in floodplain sediment reflects patterns related to the geological substratum, and high values occur in areas with felsic intrusives, which are often host uranium mineralisation. It also maps areas with black shale and phosphorite mineralisation.

**U comparison between sample media**

In general, there are broad similarities between the U distribution in all solid sample media; patterns in topsoil and subsoil are almost identical. Corsica is richer in U in stream and floodplain sediments compared to soil. In the alkaline region of Campania, U is low in sediments compared to the anomaly in soil. Coastal Croatia and Slovenia, and western parts of Austria, are low in U in sediments compared to soil (explained by the possible removal of fine-grained material from the residual soil and karst). In floodplain and stream sediments, higher U concentrations are observed in southern Norway and Finland and eastern parts of Estonia and Latvia compared to soil. A boxplot comparing U variation in subsoil, topsoil, stream sediment and floodplain sediment is in Figure 50.

Patterns in stream water U tend to be virtually the opposite to those found in stream sediment.

![Figure 50. Boxplot comparison of U variation in subsoil, topsoil, stream sediment and floodplain sediment.](image)
Aqueous uranium chemistry is complex and U distribution is higher in the more alkaline carbonate-rich environments of the Mediterranean, especially in central and southern Italy, north-eastern Greece and south and western Spain. High U concentrations are also observed in the DOC-rich environments of the Baltic states and parts of northern Poland.

A more extensive discussion on some aspects of the distribution of uranium throughout Europe based on the FOREGS data is presented by Plant et al. (2003).