K – Potassium

Introduction

Potassium is an alkali metal belonging to group 1 of the periodic table, which also includes Li, Na, Rb and Cs. The element has an atomic number of 19, an atomic mass of 39, one oxidation state (+1) and three naturally occurring isotopes (^{39}K, ^{40}K and ^{41}K), of which ^{39}K forms 93.3% of the total mass.

Potassium is the eighth most abundant element in the Earth's crust with an estimated concentration in the Earth's crust of 1.84% (Fyfe 1999). It is a lithophile and biophile metallic element, and is a major constituent of many rock-forming minerals, including important silicate minerals such as alkali feldspar, leucite, biotite, muscovite, phlogopite and some amphiboles. It is also a component of many phosphate, halide and sulphate minerals. It forms several minerals in its own right, including sylvite KCl and carnallite $KMgCl_3.6H_2O$, which occur in evaporite deposits.

Potassium is a major constituent in many igneous rocks, and their petrographic classification is often based on K concentrations or abundances. It is progressively concentrated during magmatic fractionation, and is thus enriched in felsic relative to mafic igneous rocks. This is seen in the difference in K content of basalt, commonly <1%, and granite, which contains 2% to >6% (Wedepohl 1978). The K content of argillaceous sediments and shale is primarily a function of the clay mineral content, commonly illite in shale units. Impure carbonates tend to have high potassium concentrations, up to 6%, because of the occurrence of detrital silicate material (clays) in the non-carbonate fraction; pure carbonates normally contain <2% K. Sand, sandstone and non-detrital siliceous sediments commonly contain <1% K, and this is a function of the presence of three minerals, K-feldspar, K-mica and glauconite (Wedepohl 1978). Loess contains on average 1.9% K (McLennan and Murray 1999). Evaporite K-minerals, such as KCl, are extremely soluble and can lead to high K concentrations in brines. Elevated values of K indicate the presence of felsic rocks, especially kaolinised intrusives.

Once released through the weathering of feldspar minerals, K is very soluble and occurs as the simple cation K^+ over the entire stability field of natural water (Brookins 1988). Although K is an abundant element, its mobility is limited by three processes: (a) it is readily incorporated into clay-mineral lattices because of its large size; (b) it is adsorbed more strongly than Na^+ on the surfaces of clay minerals and organic matter; and (c) it is an important element in the biosphere and is readily taken up by growing plants. As a consequence, K concentrations exceeding a few tens of mg l^{-1} are unusual, except in water with a high dissolved solids content or water from hydrothermal systems (Hem 1992). Sea water contains 390 mg l^{-1} K on average (Hem 1992). McLennan and Murray (1999) quote an average value of 2% in river particulate matter.

Fertilisers are the main anthropogenic source of potassium. Many K salts have important chemical and medicinal applications, including the hydroxide, nitrate, carbonate, chloride, chlorate, bromide, iodide, cyanide, sulphate, chromate and dichromate. However, natural sources are considered to be far more important in the environment than anthropogenic ones (Reimann and de Caritat 1998).

Potassium is an essential element for all organisms. In humans, its main role is as an electrolyte in the regulation of blood pressure and muscle contraction; K is also essential to the functioning of the nerves, kidneys and a host of other body processes. Potassium toxicity, a condition called hyperkalemia, is very rare and most people can safely absorb up to about 18 g of K a day. Together with N and P, potassium is essential for the survival of plants. Its presence is of great importance for soil health, plant growth and animal nutrition. Its primary function in plants is in the maintenance of osmotic pressure and cell size, thereby influencing photosynthesis and energy production. Very high levels of K^+ in soil water can, however, cause damage to germinating seedlings, inhibit the uptake of other minerals and reduce the quality of crops.

Table 39 compares the median concentrations of K_2O in the FOREGS samples and in some reference datasets.

Table 39. Median concentrations of K_2O in the FOREGS samples and in some reference data sets.

Potassium (K_2O)	*Origin – Source*	*Number of samples*	*Size fraction mm*	*Extraction*	*Median %*
Crust[1)]	Upper continental	n.a.	n.a.	Total	2.8
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (XRF)**	**2.02**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (XRF)**	**1.92**
Soil[2)]	World	n.a.	n.a.	Total	1.97
Water *(K)*	**FOREGS**	**808**	**Filtered <0.45 µm**		**1.60 (mg l^{-1})**
Water *(K)*[3)]	World	n.a.	n.a.		2.3 (mg l^{-1})
Stream sediment	**FOREGS**	**852**	**<0.15**	**Total (XRF)**	**2.01**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**2.00**

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

K_2O in soil

The median K_2O content is 2.02% in subsoil and 1.92% in topsoil, with a range between <0.01 and 6.05% K_2O in subsoil and 0.026 and 6.13% K_2O in topsoil. The average ratio topsoil/subsoil is 0.940.

Low K_2O values in subsoil (<1.40%) occur in central Norway, in Ireland, in the glacial drift area from the Netherlands to Poland, central Hungary, northern France, the Garonne basin in south-west France, in calcareous southern Spain, Sicily, eastern Greece and Crete.

The subsoil distribution map shows high K_2O values (>2.78%) in the Fennoscandian shield, with concentrations increasing from Archaean rocks in the north-east towards Proterozoic rocks in the south-west. Archaean bedrock has higher Na and lower K content; as the crustal maturity increases with geological time, the ratio K/Na also increases. High K_2O values are also found in Estonia and Latvia (Devonian clay and basal Quaternary till rich in mica), northern Scotland, south-west England, central Germany, the French Massif Central (two-mica granite is known to be enriched in K, Rb and Cs) and to a lesser extent Brittany, the Alps near the Austrian-Italian border, the western Iberian Peninsula (Central System of the Iberian Massif with granitic and metamorphic lithologies), especially the crystalline areas of northern Portugal, the eastern Pyrenees granitic intrusives), Corsica, and a few points in the west-Italian alkaline province. A high K value near Santander in northern Spain is caused by the Polanco salt diapir within Triassic shale and sandstone.

The topsoil K_2O map is very similar to that of subsoil. The eastern Pyrenees have apparently a more extensive anomalous area, but this may be sampling bias due to the smaller number of subsoil samples collected.

The correlation K-Rb is very strong, 0.83 in subsoil and 0.82 in topsoil. The correlation of K_2O with Al_2O_3 is strong (0.62 in subsoils and topsoils), pointing to their association in feldspar and phyllosilicate minerals in shale and igneous rocks. Also, Ba and K_2O show a strong correlation (0.62 in subsoil, 0.63 in topsoil), which is due to the ionic substitution of Ba^{2+} for K^+ in K-containing silicates. In subsoils, potassium also has a strong correlation (>0.6) with Ga, and a good correlation (>0.4) with Be, Nb, Ta, Th, U, Ag, In, Tl and the lighter REEs. The pattern of correlations is very similar in topsoil.

K in stream water

Potassium values in stream water range over three orders of magnitude, from <0.01 to 36.6 mg l^{-1} (excluding an outlier of 182 mg l^{-1}), with a median value of 1.6 mg l^{-1}.

Lowest K values (<0.7 mg l^{-1}) are found throughout Fennoscandia, western Britain and Wales, north-west Iberian Peninsula, and in the Alpine area of eastern Switzerland, western Austria and northern Italy. Low K values are also found throughout parts of Albania and Greece and Corsica. The low values are associated with a variety of rock types.

Enhanced K concentrations (>5 mg l^{-1}) are found in southern and eastern Britain extending through a wide area that continues through Belgium, the Netherlands, northern Germany and western Poland towards Hungary. Anomalously high concentrations of K are also found in parts of Brittany, the southern tip of Spain (related to Triassic shale and sandstone in olisthostrome complex) and in central and southern Italy. In Italy, the high K values are associated with alkaline volcanics or, in the Apulia area in the south-east, sedimentary sequences, *e.g.,* evaporites, and agricultural influences. In general, high K data are associated with a variety of geogenic sources but, especially in the area that extends across south-east Britain, across northern mainland Europe and towards Hungary, are also strongly associated with agricultural input from fertilisers. This also applies to an isolated anomaly in south-west Hungary. In western Poland, enhanced K concentrations (associated with Na) may be the result of fertilisers and mine water from coal and metal ore mines (Silesia), as well as from salt mines (in Wroclaw and Krakow areas). In Slovakia, in addition to fertilisers and municipal sewage, weathering of Tertiary volcanic and alkaline crystalline rocks contributes to higher K values.

Stream water K data show almost exactly the opposite trends to those observed in the solid sample media. The distribution of K is, however, closely related to the Major-ions type, corresponding to high-mineralisation stream water, dominated primarily by climatic factors. It appears that only in the Italian magmatic province and in southern Portugal there may be stream water that is clearly dominated by geology. Potassium data tend to correlate closely with Na and, to a lesser extent, with Li and Sr.

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

K_2O in stream sediment

The median K_2O content in stream sediment is 2.01%, with a range between 0.05 and 5.79%.

The K_2O stream sediment distribution map shows that values are low (<1.47%) throughout northern Finland, part of central Norway, western calcareous Ireland, the glacial drift covered European plain, the Meso-Caenozoic basins of France, northern Italy, central Austria and central Hungary, the Dalmatian coast and the island of Crete.

High K_2O values in stream sediment (>2.59%) are found in central and southern Finland (Proterozoic granites, richer in K towards the south; coastal southern Finland has a substrate of clay-rich marine sediments high in K), southern Norway (granite, gneiss), parts of southern Sweden, Lithuania (due to micas from Fennoscandia which are abundant in glacial moraines throughout Lithuania), northern Scotland, south-west England, Wales, Alsace in north-east France, central and western Germany, the French Massif Central (two-mica granite is known to be enriched in K, Rb and Cs), the Variscan western Iberian Peninsula (especially the peralkaline granite intrusions of northern Portugal and Galicia), the eastern Pyrenees (granitic intrusions), Sardinia (Variscan granite), the central Alps across the Austrian-Italian border (felsic rocks), southern Italy, and isolated anomalies in the Roman Alkaline Province and in Campania. Granitoids and pelitic rocks are responsible for high K_2O values.

K_2O in stream sediment has a very strong correlation with Rb (0.86), because Rb substitutes for K in silicates, especially feldspar, and they are enriched in alkaline and felsic rocks in general.

K_2O has a strong correlation with Al_2O_3 (0.66) and Ga (0.65), pointing to their association in K-feldspar and phyllosilicate minerals, in igneous rocks and shale. There is also a strong correlation with Tl (0.60), and a good correlation with Be (0.53), Ba (0.58), Li (0.43), Ta (0.44), Cs (0.42), U (0.46) and Th (0.42). Weak positive correlations (<0.4 and >0.3) exist between K_2O and all the REEs, Y, Na and Nb. There is a good negative correlation with Ca (-0.44).

K_2O in floodplain sediment

K_2O values in floodplain sediment vary from 0.11 to 5.10%, with a median of 2.00%.

Low K_2O values in floodplain sediment (<1.43%) occur over the glacial drift covered region extending from north Germany to Poland; the amphibolite belt of central Norway; throughout calcareous Ireland, the eastern part of the Scottish Southern Uplands and north-east England; the calcareous and clastic Paris Basin, the lower alluvial basins of Garonne and Rhône rivers in France; western Sicily with Na-alkaline volcanics and Tertiary sediments; the molasse basin of central Austria; the karst limestone and flysch Dalmatian coast in Croatia; the ophiolite and calcareous rocks of Albania and Greece.

High K_2O values in floodplain sediment (>2.62%) occur over the granite, granodiorite and gneiss terrains of south Norway, Sweden and south Finland; schist, gneiss, granite and Old Red Sandstone of north-east Scotland; the felsic rocks of central and northern Portugal, Galicia and central Iberian Meseta in Spain; the easternmost Pyrenees (granitic intrusions), Massif Central in France, Vosges and Black Forest, Harz Mountains, Erzgebirge, Bohemian Massif, central Swiss Alps with felsic intrusives; Variscan alkaline igneous rocks in Sardinia, Corsica and Calabria, the Roman Alkaline Province, eastern Sicily (Na-alkaline volcanics), and the granite-granodiorite-gneiss of central Macedonia and Thrace in north-east Greece.

A point anomaly of 4.67% K_2O in floodplain sediment occurs in south-west England and is related to the Dartmoor granite.

K_2O in floodplain sediment shows a very strong correlation with Rb (0.89), a strong correlation with Al_2O_3, Ga, Th and Tl, and a good correlation with Na_2O, Be, Ba, Cs, Ta, Ti, U, Nb and the REEs; there is a good negative correlation with CaO (-0.41).

It is concluded that the distribution map of K_2O in floodplain sediment reflects the geochemical differences of the lithology quite well, and there are no distinguishable influences from anthropogenic activities by the application of K-fertilisers on agricultural land, because the stronger natural patterns mask any human inputs at this scale of geochemical mapping.

K comparison between sample media

Patterns in K distribution between all solid sample media are very similar, although data in the floodplain sediment tend to be lower over the eastern Pyrenees compared to the other solid sample media.

A boxplot comparing K variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 23.

Stream water K data show almost exactly the opposite trends to those observed in the solid sample media, although K concentrations are quite low in all sample media in Greece and Albania (no antagonism in this region).

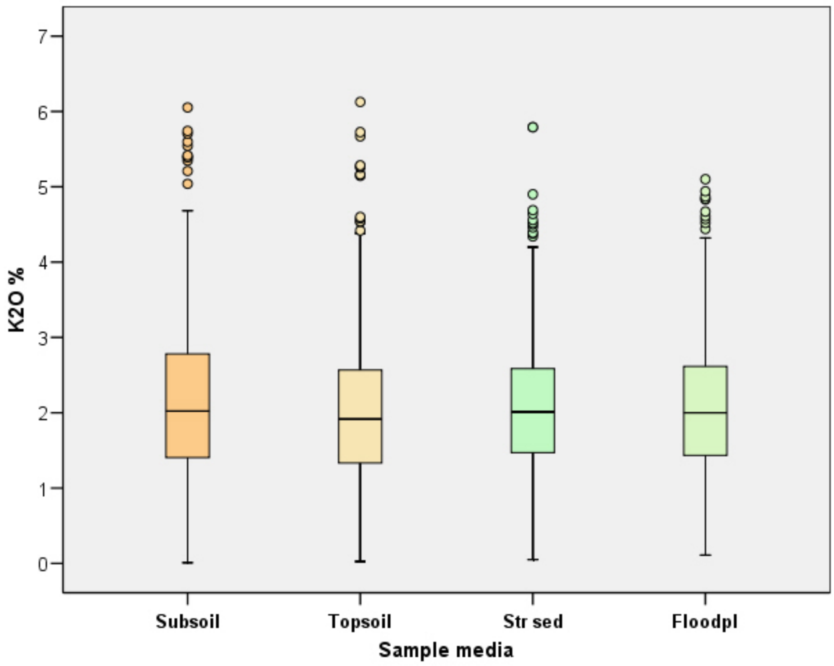

Figure 23. Boxplot variation of K_2O variation in subsoil, topsoil, stream sediment and floodplain sediment.