Na – Sodium

Introduction

Sodium is one of the alkali metals belonging to group 1 of the periodic table, along with Li, K, Rb and Cs. The element has an atomic number of 11, an atomic mass of 23, one oxidation state (+1) and one natural isotope (^{23}Na). It is the most abundant of the alkali metals, the fifth most abundant metal in the Earth's crust with an average value of 22,700 mg kg^{-1} (Fyfe 1999), and the principal cation in sea water, at a typical concentration 10,500 mg l^{-1} (Hem 1992).

Sodium is a lithophile element and has an affinity for forming compounds with oxygen and the halogens, and all Na compounds in nature contain chlorine, fluorine or oxygen. Minerals containing Na are numerous, the most common being the silicates, *i.e.,* feldspar and Na-mica. However, Na forms a major and/or minor component of many phosphate, halide, carbonate, nitrate, borate and sulphate minerals. Examples include the nitrate, soda-niter $NaNO_3$, halides, such as halite NaCl, and sulphates as mirabilite $Na_2SO_4.10H_2O$ and galeite $Na_{15}(SO_4)_5F_4Cl$.

Sodium is a major element in all igneous rock types except ultramafic rocks. Stueber and Goles (1967) report an average Na concentration of 105 mg kg^{-1}, although ultramafic inclusions were found to contain up to 1,490 mg kg^{-1} Na. Felsic and mafic plutonic rock types, such as granite and gabbro, contain percentage level concentrations of Na (around 2-3%); other felsic rocks, *e.g.,* nepheline syenite, have been reported to contain up to 6.6% Na (Wedepohl 1978). Basalt, andesite and other effusive rocks contain similar concentrations of Na to the plutonic series, with an average of 2–3%.

Limestone and dolomite contain the highest sodium concentrations, up to 5,400 mg kg^{-1} Na, of all sedimentary rocks; this is attributed to the influx of sea water during their formation and the presence of skeletal material (Billings and Ragland 1968). The major sources of sodium in almost all detrital sedimentary rock types are detrital feldspar and clay minerals. Shale displays a wide range of Na concentrations (0.1–9.2% Na) although the mean value is closer to 0.8% (Hill *et al.* 1967). Sandstone contains on average 1.4% Na. The average content of Na in loess is given as 1.4% (McLennan and Murray 1999). Very low values of sodium in relatively unweathered bedrock or saprock may indicate hydrothermal alteration.

There are no low-solubility salts of Na, so once the element is in solution it tends to remain in the dissolved form, although its mobility may be reduced by adsorption on clay minerals with high cation-exchange capacities. Sodium concentrations in natural water can cover a very wide range, from less than 1 mg l^{-1} in rainwater and low ionic-strength stream water, to very high levels (>100,000 mg l^{-1}) in brines and evaporite deposits. Sodium in dilute water (TDS <1000 mg l^{-1}) is present entirely as Na^+. In high TDS water, it also forms complexes and ion pairs, *e.g.,* $NaCO_3^-$, $NaHCO_3$ and $NaSO_4^-$. Because of its high concentration in sea water, Na may be enriched in marine-derived drift. The Na:Cl molar ratio in sea water, and thus also in precipitation, is 0.85. Areas where weathering of Na from minerals other than halite, in bedrock or overburden, makes a significant contribution to Na concentrations in stream water are marked by higher Na:Cl ratios. The average concentration of Na in river particulates is given as 0.71% (McLennan and Murray 1999).

Sodium compounds are important to the paper, glass, soap, textile, petroleum, chemical and metal industries. The concentration of Na in surface and groundwater is influenced by human activities, such as the disposal of waste in landfill sites, the pumping of fresh water from coastal aquifers, which leads to the intrusion of saline water, the application of NaCl for the de-icing of roads, and the use of soaps derived from saponified fats.

Sodium is essential to human life. It forms an important part of blood plasma, and is used in functioning of the nervous system, controlling muscle contraction and aiding digestive processes. Too much Na in the diet can, however, damage kidneys and increase the chances of high blood pressure.

Table 47 compares the median concentrations of Na_2O in the FOREGS samples and in some reference datasets.

Table 47. Median concentrations of Na_2O in the FOREGS samples and in some reference data sets.

Sodium (Na_2O)	***Origin – Source***	***Number of samples***	***Size fraction mm***	***Extraction***	***Median %***
Crust[1]	Upper continental	n.a.	n.a.	Total	**3.27**
Subsoil	**FOREGS**	**788**	**<2.0**	**Total (XRF)**	**0.86**
Topsoil	**FOREGS**	**845**	**<2.0**	**Total (XRF)**	**0.80**
Soil[2]	World	n.a.	n.a.	Total	1.3
Water *(Na)*	**FOREGS**	**807**	**Filtered <0.45 µm**		**6.58 (mg l^{-1})**
Water *(Na)*[3]	World	n.a.	n.a.		5.0 (mg l^{-1})
Stream sediment	**FOREGS**	**850**	**<0.15**	**Total (XRF)**	**0.90**
Floodplain sediment	**FOREGS**	**747**	**<2.0**	**Total (XRF)**	**0.80**
Stream sediment[4]	Canada	26 221	<0.18	Total (INAA)	1.6

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

Na_2O in soil

The median Na_2O content is 0.86% for subsoil and 0.80% for topsoil, and the range of values is from 0.03 to 4.76% Na_2O in subsoil and 0.04 to 4.45% in topsoil. On the Na_2O distribution maps, little difference can be seen between subsoil and topsoil; the ratio topsoil/subsoil is 0.951.

There is a very strong north-south contrast in the maps of Na_2O in topsoil and subsoil. Low Na values (<0.42%) occur predominantly in eastern and northern Spain, south-western and south-eastern France, south-eastern Greece, coastal Croatia, southern Poland, eastern Britain and central Ireland. In these areas, except Greece, the surficial deposits consist of old weathered material which, after leaching the mobile elements away, is enriched in silica and aluminium silicates.

The CIA weathering index (Map 2) shows that Fennoscandia has a much lower weathering index than the rest of Europe. The CIA index is defined as follows:

$$CIA = 100x[Al_2O_3/(Al_2O_3+CaO^*+Na_2O+K_2O)],$$

where CaO* = Ca in silicate fraction (McLennan *et al.* 1990). A high CIA value indicates a long weathering history of the soil. It is noted that the underlying bedrock also affects the CIA index value, *e.g.*, Al-rich sedimentary rocks tend to have higher values, whereas Al-poor limestone always has low values (usually <40).

Fennoscandia and Scotland show systematically higher Na_2O contents in subsoil (>1.95%) compared to the rest of Europe; northern Scandinavia especially is highly anomalous, although high Na_2O concentrations are typical for the whole of Fennoscandia, where the crystalline bedrock contains higher Na concentrations than most detrital sedimentary rocks and carbonates. The soil in Fennoscandia is much younger than in the rest of Europe, and shows less weathering. The high Na_2O values in soil are due to the presence of fine-grained unweathered plagioclase in glacial till in Fennoscandia and Scotland. This feature is emphasised on the Na_2O map, because plagioclase is practically the only source of sodium, and the leaching of Na from silicates is slow. South of Fennoscandia, at the regional scale, there is a pattern of relative Na-enrichment in felsic crystalline and shale areas, similar to the one observed for K_2O and Al_2O_3 at the European scale. *For example*, in Greece Na_2O is enriched in areas with felsic igneous rocks and shale. Other examples in similar litholgy are in the French Massif Central, in the eastern Pyrenees and parts of central Spain.

Na_2O has a good correlation with Ba (0.53 in subsoil and topsoil), and weaker correlations with Al_2O_3 (0.36 in subsoil, 0.47 in topsoil), Ga (0.30 in subsoil, 0.44 in topsoil), K_2O (0.34 in subsoil, 0.36 in subsoil) and Sr (0.38 in subsoil, 0.47 in topsoil). Sodium in soils has a good negative correlation with pH (<-0.4), and a weak negative correlation with clay- and silt-content.

Na in stream water

Sodium values in stream water range over four orders of magnitude, from 0.23 to 1284 mg l^{-1} (excluding an outlier of 4030 mg l^{-1}), with a median value of 6.58 mg l^{-1}. Sodium data tend to correlate closely with Li and Sr and, in some areas, to EC, Ca and Mg.

Lowest Na values in stream water (<1.6 mg l^{-1}) are found throughout Fennoscandia, eastern Switzerland, western parts of Austria, and adjacent parts of northern Italy and over a small area of the central Pyrenees. The low values are associated with a range of rock types.

Enhanced Na concentrations in stream water (>21 mg l^{-1}) are found in south-east Britain, the Netherlands, parts of Brittany, southern Portugal, south-west Spain (enhanced salinity of aquifers and surface water in hot dry region, with strong evapotranspiration), and most parts of central and southern Italy, including Sardinia and Sicily. Significantly higher than median values of Na (13 to 20 mg l^{-1}) are located in an area that trends through south and east Britain, Belgium, the Netherlands, northern Germany, western Poland and parts of the Czech Republic, Slovakia and Hungary. This low-lying area in continental northern Europe collects surface water from all other regions and also receives effluent seepage from groundwater, both processes leading to increased salt content. In western Poland, enhanced Na values (associated with K) 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). These medium to high concentrations of Na relate to a variety of rock types. There is evidence of sea spray influence causing some high anomalies along the coasts of western Portugal, southern Spain, Brittany, southern Britain, the Netherlands, Denmark and parts of Italy. In coastal areas, however, high Na content in stream water may be the result of discharge by saline aquifers, especially in areas, such as the Netherlands where pumping raises the level of deeper saline water. A point anomaly in the Ebro basin in north Spain is related to Triassic evaporitic lithology with salt layers.

The sodium distribution pattern in stream water in Europe is preponderantly associated with the Major-ions type, and to a smaller degree also with the Sea influence type pattern. The first pattern is an almost exact replica of the Na distribution, while in the second, much less pronounced pattern, the higher values are confined to western shores of European countries, as an effect of sea spray, and in the Mediterranean, chiefly of evaporitic deposits. The overall Na pattern is consequently the result of meteorology and topography, and only in the south, of geology. This is confirmed by comparison with the Na maps for solid sample media, in which the distribution pattern is opposite to that in the stream water map in most regions.

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

Na_2O in stream sediment

The median Na_2O content in stream sediment is 0.90%, with about 15% of the values below the detection limit of 0.20% Na_2O. The highest value is 4.1% Na_2O.

Low Na_2O values in stream sediment (<0.5%) are present in eastern and northern Spain, south-western and south-eastern France, most of the northern half of France, central Ireland, most of England, most of Poland and Lithuania, coastal Croatia and Slovenia.

Most stream sediment of Fennoscandia shows high Na_2O values (>1.7%), with highly anomalous values (>2.9%), in the northern part of Finland and adjacent Sweden, and south-west Norway. High values in stream sediment (>1.7%) also appear in smaller areas in Scotland, the central

Alps, the Massif Central, Corsica and Sardinia, the central and western parts of Iberia (Variscan evolved granite types of the Cordillera Central), the eastern Pyrenees (granite), southern Italy and north-eastern Greece (felsic rocks and shale). The high values in Fennoscandia and Scotland are related to a generally higher Na content in older Precambrian igneous rocks, which have a relatively low weathering index, defined as the ratio in silicates of Al_2O_3 over the sum of Al, Na, K and Ca oxides. Older igneous rocks contain more plagioclase and the plagioclase is richer in Na than is the case for similar, but geologically younger rocks, because the latter have been geochemically recycled more often in the crust, losing some Na in each cycle. Moreover, the degree of Holocene weathering, after the last Ice Age is very low in Fennoscandia, so Na is not yet leached from the silicate minerals. In France, a secondary Na enrichment of the Massif Central basement rocks has been described in relation with the Triassic palaeosurface.

Sodium in stream sediment shows a good correlation with Al and Ga, and a weak correlation with K, Ba and U. There is a weak negative correlation with CaO (-0.34).

Na_2O in floodplain sediment

Total Na_2O values in floodplain sediment range from <0.2 to 3.7%, with a median of 0.8%.

Like the maps for subsoil, topsoil and stream sediment, the floodplain sediment map shows a Fennoscandia-Scotland area rich in Na_2O, characterised by unweathered plagioclases in the Precambrian shield and Caledonides with glacial till cover. South of Fennoscandia, differences in bedrock are very clear, with some Variscan felsic rocks and crystalline massifs being highlighted.

Low Na_2O values in floodplain sediment (<0.4%) occur over parts of Europe with occurrences of glacial drift deposits stretching from north-east Germany to southern Poland, and part of Latvia; over calcareous and clastic rocks covering most of England and central Ireland, the central Paris Basin extending eastwards to Lorraine into the Variscan Rhenish Massif of Germany and Belgium; the calcareous and clastic rocks of northern and eastern Spain and Gibraltar; the volcanic and Tertiary sediments of Sicily.

High total Na_2O in floodplain sediment (>1.50%) occurs in areas with shale, feldspathic sandstone, felsic and intermediate rocks, such as granite and granodiorite, leuco-gneiss, and alkaline volcanic rocks, throughout Fennoscandia, northern Scotland, Massif Central in France, the Iberian Pyrite Belt in Spain and Portugal, the eastern part of the Pyrenees, Italian-Swiss Alps, Sardinia, Corsica, Tuscany, Calabria and north-east Sicily, central and eastern Macedonia and Thrace in Greece. Highly anomalous Na_2O values in floodplain sediment occur in northern and southern Sweden (3.7, 3.6 and 3.4%), in Finland (3.6 and 3.5%) and Norway (3.6, 3.5 and 3.4%), all associated with felsic rocks.

It is worth noting that the overall sodium pattern in floodplain sediment is similar to those in stream sediment and soil, and opposite to patterns in stream water.

Na_2O in floodplain sediment shows a good positive correlation (>0.4) with Al_2O_3, K_2O and Ga, a weaker correlation (>0.3) with Ti and some REE, and a weak negative correlation (-0.32) with CaO.

In conclusion, the distribution map of total Na_2O in floodplain sediment shows the geochemical differences of the bedrock geology well, highlighting especially the crystalline Precambrian and Caledonian, and some Variscan and Alpine felsic rocks, but also areas with shale and feldspathic sandstone.

Na comparison between sample media

Patterns in Na distribution between all solid sample media are very similar, with highest concentrations throughout Fennoscandia and Caledonian Scotland, and generally much lower Na concentrations throughout most of the rest of Europe. A boxplot comparing Na variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 30.

Stream water Na data generally show opposite trends to those observed in the solid sample media. The low Na concentrations in stream water throughout Fennoscandia are related to the short weathering history of soil and short residence time of shallow groundwater. In Spain, the Baltic states and most of Poland, the situation is more complex.

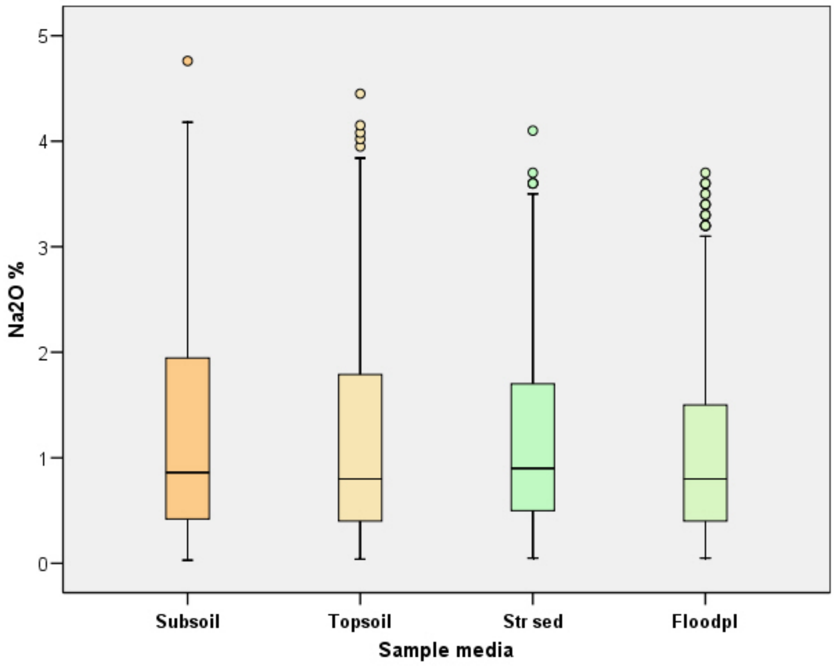

Figure 30. Boxplot comparison of Na_2O variation in subsoils, topsoils, stream sediments and floodplain sediments.