

Introduction

Caesium - or cesium in American English - is the heaviest of the stable alkali metal elements, Li, Na, K, Rb and Cs, which comprise group 1 of the periodic table. It has an atomic number of 55, an atomic mass of 133, one oxidation state (+1) and one naturally occurring isotope (^{133}Cs). Its chemical properties resemble those of the other members of this group.

Caesium is a relatively rare element, present at a crustal abundance of about 2.6 mg kg^{-1} . It has a large ionic radius of 174 pm in 8-fold coordination, which renders it incompatible with many rock-forming silicate minerals. It can, however, make a limited substitution for K in mica and K-feldspar, which contain most of the Cs in the Earth's crust. Typically for an incompatible element, Cs accumulates in the late-stage volatile phase of igneous activity. The highest Cs contents of ordinary rock-forming minerals are found in pegmatite micas. Heier and Adams (1964) report a range of $140\text{--}3400 \text{ mg kg}^{-1}$ for muscovite and Foster (1960) quotes Cs levels of more than 1% in Li-rich mica. Gordiyenko (1973) describes lepidolite from pegmatite containing several percent Cs. Beryl is another mineral enriched in Cs, with Sosedko (1957) recording a value of 3.9% Cs. Caesium levels in ultramafic and mafic rocks are $<0.1 \text{ mg kg}^{-1}$. In volcanic rocks, Cs values between 0.04 and 5.1 mg kg^{-1} are reported (Wedepohl 1978). The concentration of Cs in igneous rocks is related to the degree of differentiation; levels in gabbro are estimated to be 0.1 mg kg^{-1} , granodiorite $2\text{--}3 \text{ mg kg}^{-1}$ and granite $3\text{--}6 \text{ mg kg}^{-1}$ (Wedepohl 1978). Sand generally contains less Cs than finer sediments. Hirst (1962) reports values of $1\text{--}3.2 \text{ mg kg}^{-1}$ for modern marine sand and $7.9\text{--}3 \text{ mg kg}^{-1}$ in modern marine clay. Caesium has a strong tendency to bind with clay, because the finer grain size results in more ion exchange sites. There is very little data available for the Cs content of

sedimentary rocks, although Horstman (1957) reports average values of 5 mg kg^{-1} for marine shale and 1 mg kg^{-1} for sandstone and limestone. Evaporite deposits might be expected to be enriched in Cs, especially deposits of K salts, but data on these are sparse. McLennan and Murray (1999) quote average values for river particulates and loess as 6 and 4 mg kg^{-1} Cs respectively.

Caesium is used in geochemical prospecting as a pathfinder for Cs-rich pegmatite (Boyle 1974). It is also indicative of felsic intrusive rocks, especially in association with REE, U, Th, Bi, Mo, *etc.*

Caesium released by weathering of rocks and minerals is rapidly and strongly adsorbed by soil, especially clay (Davis 1963, Kabata-Pendias 2001), and therefore tends not to be present in the aqueous surface environment. Turekian (1969) estimates an average concentration of $0.02 \mu\text{g l}^{-1}$ Cs in river water, although concentrations may be slightly higher in geothermal water. The range of Cs in soil has been estimated to be between 0.3 to 26 mg kg^{-1} (Kabata-Pendias 2001).

Caesium has relatively few uses and applications, so it is not often encountered as an anthropogenic contaminant from industrial or manufacturing sources. The Chernobyl nuclear reactor explosion in 1986, however, liberated considerable quantities of radioactive ^{137}Cs to the atmosphere (Higgitt *et al.* 1993, Smith and Beresford 2005).

Caesium has no known biological role. Because of its chemical similarity to potassium, it is capable of replacing K in the body and is hence considered toxic. The radioisotopes ^{134}Cs and ^{137}Cs , present in the biosphere in small amounts as a result of radiation leaks, are particularly toxic for the same reason.

Table 22 compares the median concentrations of Cs in the FOREGS samples and in some reference datasets.

Cs in soil

The median Cs content is 3.69 mg kg^{-1} in subsoil and 3.71 mg kg^{-1} in topsoil, with a range varying from <0.5 to 74.6 mg kg^{-1} in subsoil and up to 69.1 mg kg^{-1} in topsoil. The average ratio

topsoil/subsoil is 0.909.

Caesium has low values in subsoil ($<1.62 \text{ mg kg}^{-1}$) throughout most of northern Europe, except for a slight enrichment in central Sweden.

Table 22. Median concentrations of Cs in the FOREGS samples and in some reference data sets.

Cesium (Cs)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	4.9
Subsoil	FOREGS	783	<2.0	Total (ICP-MS)	3.69
Topsoil	FOREGS	840	<2.0	Total (ICP-MS)	3.71
Soil ²⁾	World	n.a.	n.a.	Total	3
Water	FOREGS	808	Filtered <0.45 µm		0.006 (µg l⁻¹)
Water ³⁾	World	n.a.	n.a.		0.3 (µg l ⁻¹)
Water ⁴⁾	Barents region	1365	Filtered <0.45 µm		0.004 (µg l ⁻¹)
Stream sediment	FOREGS	838	<0.15	Total (XRF)	<4.0
Floodplain sediment	FOREGS	749	<2.0	Total (XRF)	4.00
Stream sediment ⁵⁾	Canada	26 227	<0.18	Total (INAA)	3.3

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

The only other low Cs values are found in small areas in southern Spain and central Hungary. The southern limit of the glacial drift area is clearly marked on the map with lower values to the north of it.

Higher Cs values in subsoil (>7.29 mg kg⁻¹) occur throughout Variscan Iberia (alumina-rich granitic and metamorphic rocks of the Iberian Massif, partly resedimented as clays and marls in the Duero basin), eastern Spain (detrital Mesozoic sediments), France, central Italy, the western and eastern Alps, coastal Croatia and Slovenia, south-central Germany and northern Switzerland, and south-west England. The topsoil and subsoil patterns are very similar. The impression is that geological substrate controls most of the Cs

distribution, with basement and Palaeozoic areas containing more Cs, but in northern Europe the whole pattern is depressed because of higher Cs mobility, whereas in dryer southern Europe it is likely to be retained in clay minerals in soils. Thus, the geochemical behaviour of Cs is similar to that of Rb in this respect, and this is shown by the ratio topsoil/subsoil, which is on average for the whole of Europe 0.956 for Cs, and 0.963 for Rb.

In subsoil, Cs shows a strong correlation (>0.6) with Tl, Rb and Th, and a good correlation (>0.4) with Al, Ga, In, Nb, Ta, Sn, Pb, Bi, Be, U and the light REEs. In topsoil, Cs has a strong correlation with Tl, Rb, Be and U, and a good correlation with Ga, In, Sn, Nb, Ta, Th and the light REEs.

Cs in stream water

Caesium values in stream water range over almost three orders of magnitude, from <0.002 µg l⁻¹ to 0.97 µg l⁻¹ (excluding three outliers up to 24.3 µg l⁻¹), with a median value of 0.006 µg l⁻¹. Caesium data correlate, to a limited extent, with Ga and Tl.

Lowest Cs in stream water (less than the analytical limit of quantification of 0.002 µg l⁻¹, which constitutes approximately 10% of the total data) are predominantly found in south-central Spain (Variscan terrains), north-eastern France (Variscan terrains), western Ireland (Irish

Caledonides), central Sweden (related to high pH values caused by Palaeozoic rocks), northern Finland (Precambrian Sveco Norwegian and Kola Karelian terrains), Denmark, western and eastern Latvia and Lithuania and northern and central Poland (Precambrian East European Platform terrains), southern Germany (Variscan terrains), and in the Alpine Orogen terrains of central Austria, eastern Croatia, southern Hungary, northern Italy, northern Albania and most of Greece including Crete.

Highest Cs values in stream water (>0.09

$\mu\text{g l}^{-1}$) are found in north-western Spain (leucogranitic intrusions in Iberian Massif), south-central Spain (small intrusive stocks in Toledo Mountains, and Los Pedroches batholith), and France (Brittany, the Massif Central and the border with Germany and Italy), lying in by Variscan terrains; in south-western England (Cornwall), south-western and eastern Germany, characterised by Variscan terrains, and around the southern border between Norway and Sweden (Precambrian Sveco Norwegian terrains). The high anomalies in France (correlated with Pb and Tl) are mainly located on Hercynian leucogranite intrusives (northern Vosges, western Massif Central and south-western Brittany). Isolated enhanced Cs in northern England is associated with heavy industrial pollution and/or underlying geology of the Durham Coalfield; the isolated anomaly in south-west England is associated with the Dartmoor granite intrusion. The high values occurring throughout parts of Italy are certainly controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces. The highly anomalous Cs value in western

Slovakia ($0.80 \mu\text{g l}^{-1}$) represents the impact of natural mineral water seepage to stream water.

Caesium in stream water is distributed according to three distribution pattern types. In Fennoscandia, in low-mineralisation high-DOC stream water it is similar to REEs and associated elements, not supported by high Cs contents in the solid sample media. The distribution pattern in stream water characteristic of Felsic rocks is typically geology-dominated, showing high values in alkaline volcanic areas of Italy, on granite of the north-west Iberian peninsula and in Cornwall, and in the Armorican and Central Massifs of France, in the Black Forest and Erzgebirge of Germany. The highly anomalous values in the eastern Erzgebirge and the Black Forest are related to Sn-W-Mo-As- and U-mineralisations and ore deposits, with possible input by the non-ferrous metallurgical industry.

Similarity of distribution patterns in stream water with the Base metal elements type might explain anomalies in southern Norway.

Cs in stream sediment

More than half the values for caesium in stream sediment are below the detection limit of 4 mg kg^{-1} . The highest value recorded is 68 mg kg^{-1} .

The Cs stream sediment distribution map shows highly anomalous values ($>15 \text{ mg kg}^{-1}$) in Variscan areas in Cornwall, the Black Forest and Vosges, the French Massif Central including Morvan in the north-east, Brittany, the Erzgebirge, the western Iberian Peninsula (felsic rocks especially the peraluminous granite of northern Portugal, but also the crystalline basement of the Cordillera Ibérica in adjacent

Spain, and Triassic detrital rocks in the Mesozoic cover), Sardinia and Corsica. High Cs values ($>6 \text{ mg kg}^{-1}$) are also present in the Roman and Neapolitan volcanic provinces. Mesozoic sediments show high values in central Portugal and the Levante in eastern Spain. In western Hungary, Cs is also high. Low Cs values ($<4 \text{ mg kg}^{-1}$) are prevalent elsewhere in Europe.

Caesium in stream sediment has a strong correlation (>0.6) with Rb and Tl, a good correlation with Be, Ta, K and U, and a weak correlation with Sn, Li, Th, Al and La.

Cs in floodplain sediment

Caesium values in floodplain sediment vary from <4 to 40 mg kg^{-1} , with a median of 4 mg kg^{-1} . Over 50% of Cs analytical data are below detection limit. Nevertheless, patterns are still discernible for the higher values.

Low Cs values in floodplain sediment ($<4 \text{ mg kg}^{-1}$) cover much of Europe with different lithologies. They occur over most of

Fennoscandia on Precambrian metamorphic and igneous rocks of the Baltic Shield and Caledonian rocks with the lowest values in most of Sweden, central and northern Norway, northern Finland, eastern Latvia and Lithuania, most of Germany, and central Austria; the Paris Basin and western Belgium; the clastic and crystalline rocks of Cantabria, southern and south-eastern Iberian

Peninsula, Catalonia and the eastern Pyrenees, the Western Alps and north-west Italy, parts of central Italy, Calabria, Sicily, Sardinia, central Croatia and Slovenia, southern Albania and Greece

High Cs values in floodplain sediment (>8 mg kg⁻¹) are found in extensive zones (a) from northern to south-west England with the highest value (40 mg kg⁻¹) in Cornwall, (b) from Brittany to Poitou, Massif Central, Jura and the Vosges in France and adjacent parts of Germany, (c) western, north-western and central parts of the Iberian Peninsula (crystalline basement of the Iberian Massif and its detrital Mesozoic cover), and (d) from the Bohemian Forest in the Czech Republic to central Hungary, and are ascribed to felsic rocks, shale and their metamorphic equivalents and/or mineralisation. Caesium anomalies occur in the Roman Alkaline Province and Salentina Peninsula in Italy, and the mineralised area of south-central Austria, the

granitic-mineralised south-western part of Norway, and eastern Estonia. The elevated concentrations in central Finland appear to be in areas where pegmatite with rare elements occur.

Highly anomalous Cs values in floodplain sediment occur in south-west England (Saint Austell and Dartmoor granites, 40 and 35 mg kg⁻¹ respectively), and one in a river draining the granitic rocks of the Vosges (32 mg kg⁻¹).

Caesium in floodplain sediment shows a strong correlation with Rb, a good correlation with K₂O, Rb, Ta, Tl, Th and U, and a weak, but significant correlation with Be, Li, Al₂O₃, Ga, Nb, Sn, W, Ce and La.

In conclusion, the Cs distribution in floodplain sediment maps geochemistry of materials derived from felsic rocks (granite, pegmatite), and shale. From the available data it is difficult to distinguish influences from human activities.

Cs comparison between sample media

Patterns in Cs distribution between all solid sample media are very similar, although it is difficult to compare at lower concentrations since the detection limit for stream and floodplain sediment data by XRFS is not as good as that for soils by ICP-MS. A boxplot comparing Cs variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 15.

General trends in stream water data are similar in most cases to those occurring in solid sample media. The main differences are throughout large parts of the northern, eastern and southern Iberian Peninsula and Greece, where Cs tends to have lower concentrations in stream water, and in Brittany and most of Fennoscandia stream water data tend to higher concentrations.

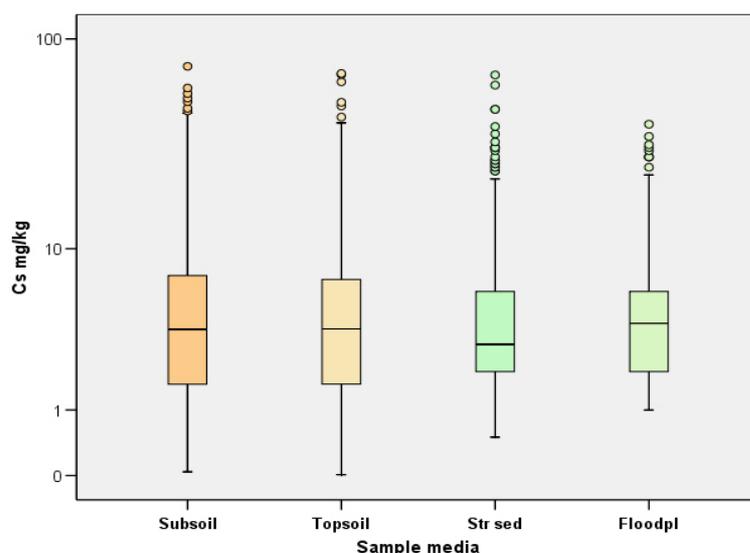


Figure 15. Boxplot comparison of Cs variation in subsoil, topsoil, stream sediment and floodplain sediment.