

Introduction

Calcium belongs to group 2 of the periodic table, along with Be, Mg, Sr and Ba. It has an atomic number of 20, an atomic mass of 40, one oxidation state (+2) and six naturally occurring isotopes (^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca and ^{48}Ca), with ^{40}Ca accounting for 96.9% and ^{44}Ca for 2.1% of the total mass (Mittlefehldt 1999a). Calcium is most similar chemically to the heavier alkali earth elements Sr and Ba.

Calcium is the fifth most abundant of all the elements, constituting approximately 3% by weight (equivalent to 4.2% CaO) of the upper continental crust and 5.29% (7.41% CaO) for the bulk continental crust (McLennan and Taylor 1999). It is a widespread refractory lithophile element forming several common minerals including calcite CaCO_3 , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, dolomite $\text{CaMg}(\text{CO}_3)_2$, anhydrite CaSO_4 and fluorite CaF_2 . Calcium is also widely distributed in other minerals such as feldspar, amphibole and pyroxene, and is often associated with clay minerals such as illite, chlorite and Ca-montmorillonite (Zupancic and Pirc 1999). In igneous rocks, calcium is enriched in anorthosite, which is composed predominantly of calcium-rich plagioclase feldspar, and in mafic rocks. However, rocks such as granite and sandstone, and their metamorphic equivalents, have relatively low total CaO contents.

Limestone and dolomite are carbonate sediments that are an important sink for Ca in its geochemical cycle. Levels of Ca in most sedimentary rocks reflect the abundance of carbonate minerals (calcite and dolomite), though sulphate minerals, such as gypsum and anhydrite can also be important, particularly in sandstone and evaporites. Plagioclase is the principal host for Ca in some detrital sediments. Calcium levels in pelite vary widely, some Lower Palaeozoic deep-water shale having less than 0.05% CaO, while some types of calcareous mudstone may have several per cent CaO and grade into impure limestone. Where Ca carbonates or sulphates are important constituents of sedimentary rocks, they supply most of the Ca in stream water; levels are lower in areas where Ca is derived from the slower weathering of minerals, such as plagioclase feldspar. McLennan and Murray

(1999) quote average values for river particulates and loess as 2.2 and 0.79% Ca respectively.

Estimates for the Ca contents of igneous rocks are very variable, but Mielke (1979) quotes: ultramafic 25,000 mg kg^{-1} ; basaltic 76,000 mg kg^{-1} ; high-Ca granite 25,300 mg kg^{-1} , low-Ca granite 5100 mg kg^{-1} , and syenite 18,000 mg kg^{-1} . Calcium is indicative of calcareous rocks, especially in association with Sr, Mg and Ba. Where Ca and other elements indicate calcareous rocks, and other elements (*e.g.*, REEs) indicate felsic intrusives, bedrock geology may be favourable for skarn type mineralisation.

Calcium generally has a high mobility and, except under strongly alkaline conditions, occurs in solution as dissociated Ca^{2+} ions. Concentrations generally increase with stream order as a result of increasing contact time between water and soil or rock. The most common Ca-bearing minerals in sedimentary rocks, calcite and dolomite, weather on contact with acid solutions, typically carbonic acid (H_2CO_3) derived from the dissolution of atmospheric CO_2 in rain, releasing Ca^{2+} or Ca^{2+} and Mg^{2+} , respectively. Soil air has higher CO_2 concentrations than the atmosphere, due to the respiration of soil organisms and the decay of organic matter. Soil solutions thus contain higher levels of H_2CO_3 than rain, and have a greater capacity to dissolve carbonate minerals. Soluble major ions, such as Ca^{2+} , influence the quantities of soluble trace elements. Solutions of most soil types contain an excess of Ca, which constitutes more than 90% of the total cation concentration; Ca, is, therefore, the most important cation in governing the solubility of trace elements in soil (Kabata-Pendias 2001). Divalent calcium (Ca^{2+}) ions are held more strongly than monovalent ions on the negatively-charged surfaces of clay minerals and organic matter. As soil acidity increases, Al^{3+} replaces Ca^{2+} as the dominant exchangeable cation, so high Al^{3+} concentrations in stream water tend to correlate with low Ca^{2+} levels. Calcium concentrations in surface water are highly variable; in a study of United Kingdom rivers, Neal and Robson (2000) reported Ca concentrations in the range 10 to 150 mg l^{-1} .

The main anthropogenic activity that would lead to an increase of Ca in the drainage system is

the long-established agricultural practice of liming land to correct for soil acidity. Other anthropogenic sources of calcium include cement factories, fertilisers and dust, although geogenic sources are much more important than anthropogenic ones in the environment (Reimann and de Caritat 1998).

Calcium is an essential nutrient element for plants and animals for the development of bone,

nervous system and cells. It is practically non-toxic. In upland areas with base-poor rocks and low stream water pH, added Ca has been shown to reduce the toxic effects of high concentrations of Al on aquatic biota such as brown trout (Brown 1983).

Table 16 compares the median concentrations of Ca in the FOREGS samples and in some reference datasets.

Table 16. Median concentrations of Ca in the FOREGS samples and in some reference data sets.

Calcium (CaO)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median %
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	3.59
Subsoil	FOREGS	788	<2.0	Total (XRF)	1.13
Topsoil	FOREGS	845	<2.0	Total (XRF)	0.92
Soil ²⁾	World	n.a.	n.a.	Total	1.96
Water (Ca)	FOREGS	808	Filtered <0.45 μm		40.2 (mg l⁻¹)
Water (Ca) ³⁾	World	n.a.	n.a.		12 (mg l ⁻¹)
Stream sediment	FOREGS	852	<0.15	Total (XRF)	2.33
Floodplain sediment	FOREGS	747	<2.0	Total (XRF)	2.07

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

CaO in soil

The median CaO content in subsoil is 1.13% and in topsoil 0.92%, with a range varying from 0.02 to 51.6% in subsoils and 0.03 to 47.7% in topsoils. The histograms show multimodal populations, with the highest frequency between 0.6 and 1% CaO (low-Ca samples). For subsoil a second low-CaO mode is present at about 2% CaO. High CaO modes occur at around 15% and 30% in subsoil, and near to 9% and 30% in topsoil. The average ratio topsoil/subsoil is 0.702.

Low CaO values in subsoil (<0.38%) occur in the eastern Iberian peninsula, the Armorican Massif and the Central Massif in France (all Variscan areas), over most of England, Wales and Ireland, and in the glacial drift area of Denmark, northern Germany and Poland. The topsoil pattern is very similar.

On the subsoil CaO distribution map, the following calcareous regions show high CaO values (>2.97%): eastern Spain (Triassic limestone in the Baetic Cordillera in southern Spain, Jurassic and Cretaceous limestone in the Cordillera Ibérica in eastern Spain, Cretaceous

and Palaeogene limestone and marl in the Pyrenees, Carboniferous and Cretaceous limestone in Cantabria in northern Spain); southern Italy, Greece, the Dalmatian coast, southern France and the western Alps, the eastern part of the Paris Basin and the Charente, western Ireland, and the Baltic states (Estonia, Latvia, Lithuania). In addition, high CaO occurs in western Slovakia (calcareous loess), parts of the Norwegian Caledonides, northern Fennoscandia, and Albania, where greenstone belts and other mafic and ultramafic crystalline rocks with Ca-rich plagioclase account for the higher values.

The topsoil CaO distribution map generally shows the same pattern as the subsoil map, with only minor differences. In Latvia and Lithuania, the topsoils are depleted in Ca, reflecting natural leaching in the loose freely drained calcareous soil in a cold climate with abundant precipitation; soils are made up from a mixture of Quaternary (Weichsel) glacial till with Devonian dolomite, Jurassic limestone, Cretaceous chalk, etc. Similar leaching can be observed in Poland, but Polish

soil types are developed mainly on non-calcareous older deposits of the penultimate glaciation, which were deeply leached after the glaciation. Similar depletion also occurs in the arable soil of northern Germany, but Ca is added there by liming, a practice stopped in the Baltic states after 1990 (Reimann *et al.* 2003). Some Ca depletion also occurs in topsoil in Slovakia, and Ca enrichment of topsoil occurs in Austria.

Topsoil in calcareous areas contains on average less CaO than subsoil: the ratio of topsoil/subsoil is 0.70 for the whole dataset (Map 3). This is mostly due to leaching of carbonates from topsoil by acid rain, with simultaneous enrichment of the clay fraction. From map 3 it can be deduced that the intensity of Ca leaching is independent of the Ca content of the soil, and occurs both in calcareous and non-calcareous areas. This relative uniformity is mathematically expressed in the correlation of 0.819 between topsoils and subsoils (table 4)"

CaO in soil has a strong negative correlation with SiO₂ (-0.78 in subsoil and -0.72 in topsoil). Because Si and Ca are two major elements in a closed number system, this is an autocorrelation (see introduction). CaO also has a weak negative correlation with Zr, Hf, Al, K, Ba. CaO in soil

shows a good positive correlation with pH, and a weak one with Sr. In topsoil, Ca also has a weak positive correlation with Mg. The positive correlation of pH with CaO (0.52 in subsoil and 0.49 in topsoil) does not correspond to a gradual increase in both values, but to a sharp boundary at around pH 6.6 between acidic low-Ca soil and neutral to slightly alkaline Ca-bearing soil, as is seen in the scattergram (Figure 9).

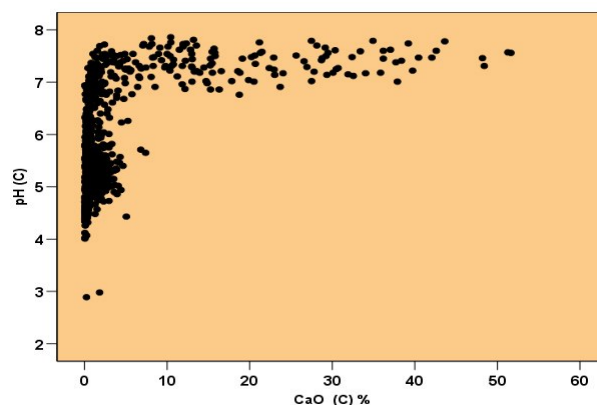


Figure 9. Scattergram of CaO and pH values in subsoils.

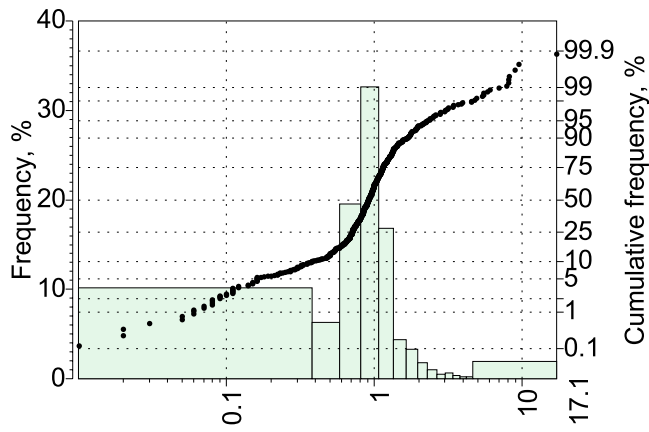
Ca in stream water

Calcium values in stream water range over three orders of magnitude, from 0.02 to 592 mg l⁻¹, with a median value of 40 mg l⁻¹. Calcium data tend to correlate with pH, conductivity and bicarbonate. The Ca distribution pattern is closely associated with the Major ions high mineralization waters, while it is negatively correlated with the REEs water patterns. Patterns in stream water Ca data are generally markedly different from distributions in the solid sample media and strongly related to pH, with lowest concentrations in the most acid environments throughout most of southern and central Fennoscandia, and highest concentrations in some areas adjacent to the Mediterranean, in calcareous environments of northern France and south-east England, and in Germany, Poland and the Baltic states, possibly associated with intensive agricultural activity.

Lowest Ca in stream water (<14 mg l⁻¹) are found throughout Fennoscandia, northern Britain and Wales on Precambrian Shield, Laurentian and Caledonian terrains, in north-west Iberian Peninsula, Brittany, Massif Central and Corsica

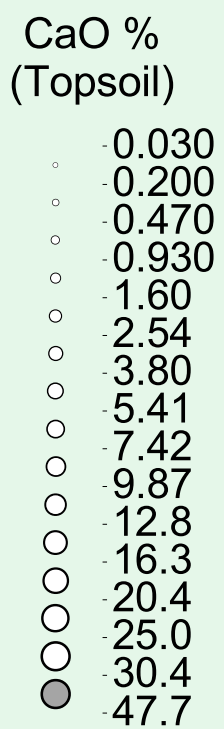
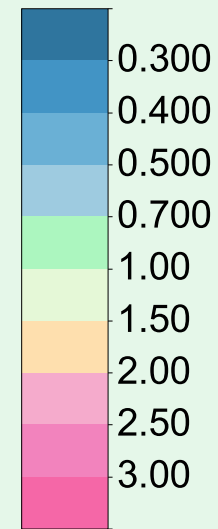
on Variscan and in eastern Switzerland in the Alpidic Orogen. The low Ca values are predominantly associated with acid igneous and metamorphic (schist) rocks.

Enhanced Ca concentrations in stream water (>90 mg l⁻¹) are found in Baltic countries on Palaeozoic limestone, Poland and parts of north Germany on Precambrian Shield derived glacial drift, in central and south-east England on Mesozoic carbonate rocks, western Ireland on Carboniferous limestone, northern and south-western France, western Germany, southern and eastern Iberian Peninsula and Sardinia on Variscan with Mesozoic cover rocks, in the Pannonian basin of Hungary and parts of Italy with Sicily on Alpine Orogen. These high Ca values represent water generally derived from calcareous rocks (mainly calcitic clastics, mudstone and chalk). In Spain, high Ca values are associated with Triassic limestone in the Baetic Cordillera, Jurassic and Cretaceous limestone in the Cordillera Ibérica, Cretaceous and Palaeogene limestone and marl in the

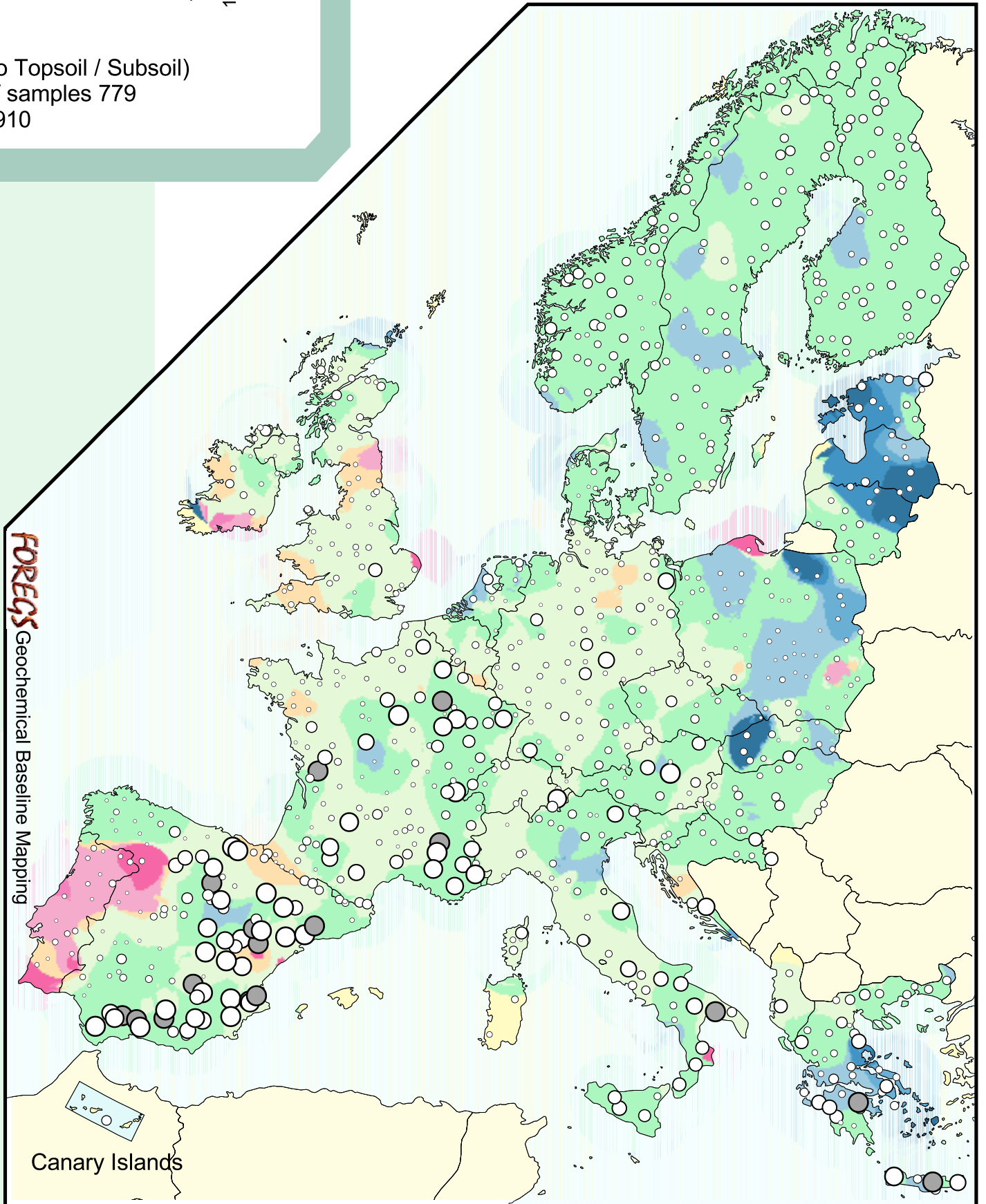


CaO (Ratio Topsoil / Subsoil)
 Number of samples 779
 Median 0.910

Calcium
 Ratio
 Topsoil / Subsoil



FOREGS
 Geochemical Baseline Mapping



Canary Islands

Map 3. Ratio of CaO in topsoil vs subsoil.

Pyrenees, Carboniferous and Cretaceous limestone in Cantabria; Cambrian limestone in Extremadura and in Galicia-Asturias. In Poland, in addition to the occurrence of carbonate rocks (e.g., Silesia-Krakow and Lublin Uplands), the origin of higher concentrations of Ca (and Sr and Mg) is attributed to Ca-Mg fertilisers used to lime soils. A similar explanation is valid for highly anomalous values in Germany, with Jurassic

limestone, loess and fertilisers.

A more detailed description on the chemistry of Ca 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, calcite solubility, gypsum solubility and fluorite solubility).

CaO in stream sediment

The median CaO content in stream sediment is 2.44%, with a range varying from 0.08 to 55.7%.

The western Iberian Peninsula stream sediment is low in CaO (<1.18%), as is the French Massif Central, Brittany, the Garonne area, most of Germany, Denmark, central Poland, western and northern Britain, central Sweden and adjacent Norway.

High CaO contents in stream sediment (>5.91%) appear over Mesozoic and Cenozoic calcareous rocks in an area extending from southern France and the western Alps through the upper Rhône valley, to the Paris Basin. High values also characterise eastern Spain over Mesozoic limestones, and southern Spain over Palaeozoic calcareous parts of the Baetic Cordillera. The high CaO values over central Ireland reflect the underlying Carboniferous limestone. Mesozoic and Tertiary limestone gives rise to high values in parts of south-western France, most of Italy including Sicily, Greece, Albania, the Dalmatian coast of Croatia, Slovenia, and the eastern Alps. High CaO values are also present over the Italian alkaline volcanic province.

Areas above the median value for Ca in stream

sediment also occur over Mesozoic limestone in north-eastern Germany, over glacial drift in Lithuania, western Latvia and western Estonia (over calcareous Devonian clay, dolomite and limestone), in western Norway (Proterozoic amphibolite and anorthosite) and northern Norway (greenstone belts with Ca-rich plagioclase). In the eastern part of France, and in the Rhône-Provence Tertiary graben, anthropogenic contribution of Ca by salt brining factories is suspected (CaCl₂ release); this salt possibly has a measurable impact when used as a de-icing medium for road maintenance in winter.

CaO in stream sediment has a strong negative correlation with SiO₂ (-0.78), a good negative correlation with Al₂O₃, Ga, Nb, Ti, K₂O and Ba, and a weak negative correlation with Na₂O, Rb, Ta, Tm, Yb, Lu, Hf and Zr. As all these elements are related to normal silicate substrates, the contrast with Ca-bearing limestone is apparent. Calcium has a good positive correlation with Sr (substitution in carbonates and feldspars), and a weak positive correlation with Mg (e.g., dolomite).

CaO in floodplain sediment

Total CaO values in floodplain sediment vary from <0.05 to 54.4%, with a median of 2.07%.

Low CaO values in floodplain sediment (<0.83%) occur in the predominantly granitic areas of central Sweden, a few areas within the glacial drift plains in Germany and Poland; the Bohemian Massif (Czech-German border), southern Scotland (gneiss and sandstone parts), western part of England and Wales (mainly shale, igneous and metamorphic rocks), north-eastern Ireland (granite), Brittany (granite, gneiss),

northern Massif Central (granite), and most of the western Iberian Peninsula (Variscan sediments and crystalline rocks).

High total CaO values in floodplain sediment (>6.83%) occur over calcareous rocks in Ireland, the Paris and the coastal Charente basins, the French Mediterranean coastal region, the Rhône-Saône River basin draining the limestone of the Jura Mountains and the calcareous rocks of the Western Alps; the mainly calcareous rocks of the eastern half of Spain from the Pyrenees to the

Baetic Cordillera; the Alpine calcareous rocks covering Switzerland, south Germany and Austria; the calcareous rich sediments of the Po river basin and the Apennine carbonate rocks of Italy, including Sicily; the Dalmatian coast of Croatia with limestone; and the calcareous and ophiolitic rocks of Albania and Greece.

Calcium in floodplain sediment shows a good positive correlation with Sr (0.55), a weak correlation with MgO (0.32); a very strong negative correlation with SiO₂ (-0.81), and a good negative correlation with Zr (-0.49) and K (-0.41).

In conclusion, most of the CaO patterns in floodplain sediment are due to the calcareous

lithology, and there are no discernible influences from anthropogenic activities concerned with addition of phosphate fertilisers or liming of non-calcareous agricultural soil in humid climates. However, in the eastern part of France, and in the Rhône-Provence Tertiary graben, an anthropogenic contribution has been reported that may have influenced the natural patterns, *i.e.*, introduction of Ca by salt brining factories is suspected (CaCl₂ release); this salt possibly has a measurable impact when used as a de-icing medium for road maintenance in winter.

Ca comparison between sample media

Patterns in Ca distribution between all solid sample media are broadly similar, although higher Ca is present in stream sediment throughout the coastal region of Croatia (presence of limestone particles) - this is the opposite to trends observed in Al, Fe and related elements. Floodplain and topsoil distributions in the Baltic states are similar, with less Ca than observed in subsoil and stream sediments (agricultural soils used for soil sampling). In Ireland, Ca is higher in stream and floodplain sediments compared to soil. A boxplot comparing CaO variation in subsoil, topsoil, stream sediment and floodplain sediment is

presented in Figure 10.

Patterns in stream water Ca data are, in the main, markedly different from distributions in the solid sample media and strongly related to pH, with lowest concentrations in the most acid environments throughout most of southern and central Fennoscandia, and highest concentrations in some areas adjacent to the Mediterranean, in calcareous environments of northern France and south-east England, and in Germany, Poland and the Baltic states, possibly associated with intensive agricultural activity.

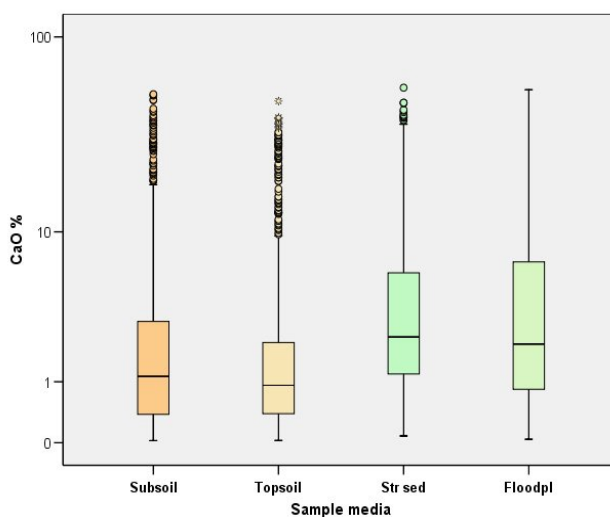


Figure 10. Boxplot comparison of CaO variation in subsoil, topsoil, stream sediment and floodplain sediment.