

**Introduction**

Phosphorus is a group 15 element in the periodic table, along with N, As, Sb and Bi. It has an atomic number of 15, an atomic mass of 31, three main oxidation states (-3, +3 and +5) and one naturally occurring isotope ( $^{31}\text{P}$ ).

Phosphorus is the eleventh most abundant element in the Earth's crust, constituting approximately 0.1% by weight. It is an abundant non-metallic element and exhibits lithophile, siderophile and biophile properties depending on the circumstances. It occurs almost exclusively in nature as orthophosphate ( $\text{PO}_4^{3-}$ ), principally in the mineral apatite  $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ , but also in monazite  $(\text{Ce},\text{La},\text{Nd},\text{Th},\text{Sm})(\text{PO}_4,\text{SiO}_4)$  and xenotime  $\text{YPO}_4$ . It is widely dispersed at trace levels in minerals such as olivine, pyroxene, amphibole and mica, and is also present in biological materials such as bone. Phosphorus is a major element in all plants.

Phosphorus belongs to the volatile components of magmas, although great variation of P levels are found in magmatic rocks, even with rocks of a similar type (Wedepohl 1978). Mielke (1979) reports average concentrations of P in various rock types as: ultramafic  $220 \text{ mg kg}^{-1}$ ; basaltic  $1100 \text{ mg kg}^{-1}$ ; granitic  $600\text{--}920 \text{ mg kg}^{-1}$ , with a crustal average of  $1120 \text{ mg kg}^{-1}$ . Data on abundances for P in metamorphic rocks are rare, but there is a trend of increasing P content with increasing metamorphic grade (Wedepohl 1978). The amount of P in clastic rocks depends on their origin and grain size, with the P content generally increasing with decreasing grain size. Levels in shale are reported as  $700 \text{ mg kg}^{-1}$ ; sandstone  $170 \text{ mg kg}^{-1}$ , and carbonate rocks  $400 \text{ mg kg}^{-1}$  (Mielke 1979). Although they are rare, sedimentary bone beds contain abundant fossil phosphate, and high levels are also found in organic-rich black shale where Fe phosphate and U often occur together.

The solubility of apatite and Fe-Al phosphate and the adsorption of phosphate on clay minerals are the two most important factors in the weathering of minerals containing P. In acid environments, apatite is remarkably soluble, as  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  ions formed by the equilibrium reaction of  $\text{H}^+$  with  $\text{PO}_4^{3-}$  are soluble in the presence of  $\text{Ca}^{2+}$ . In neutral and alkaline conditions, calcium orthophosphate is largely

insoluble. Except in very acid conditions ( $\text{pH} < 3.0$ ), Al and Fe phosphates are highly insoluble, and their formation limits the mobility of P in soil and stream sediment. In soil, P also forms low solubility minerals with Pb and Ca, such as plumbogummite and pyromorphite, which are even less soluble than common Ca-phosphates. The sorption of phosphate to alumino-silicate clays and hydrous oxides of Fe and Al depends on soil pH. In carbonate-rich alkaline soil, phosphate is sorbed by calcite, but at higher concentrations Ca phosphate may precipitate. Phosphorus adsorption on organic matter occurs in association with the metal cations  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$ .

Elevated P values often indicate mafic rocks, though signature is rather ambiguous and should be verified by other elements, such as Cr, Ni and Cu.

The aqueous geochemistry of P is complex. The fully oxidised  $\text{P}^{5+}$  form, occurring as  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$  depending on the pH, is the main oxidation state of significance in natural water systems. Between pH 4 and 6,  $\text{H}_2\text{PO}_4^-$  is the dominant form;  $\text{HPO}_4^{2-}$  dominates the circum-neutral pH range; and  $\text{PO}_4^{3-}$  is most stable under alkaline conditions. Other forms of dissolved phosphate include inorganic polyphosphate and organic P compounds, mainly as complexes with organic acids, although a large proportion of total P exported from drainage basins is in particulate form from eroding soil and stream sediment (Holtan *et al.* 1988). River particulates have on average  $1150 \text{ mg kg}^{-1}$  P (McLennan and Murray 1999). Natural phosphate levels in fresh water are low, typically between 10 and  $25 \mu\text{g l}^{-1}$  (Meybeck 1982), because of the affinity of  $\text{PO}_4^{3-}$  for Al, Fe, Mn and Ca, with which it forms complexes that are poorly soluble.

Anthropogenic sources of phosphorous include fertilisers, waste water and detergents (Reimann and de Caritat 1998). Domestic and industrial waste water contain complex and condensed phosphates, such as those used in detergents. These are unstable in water and are slowly hydrolysed to orthophosphate. High concentrations of P have been reported in areas where fertilisers are applied, but the widespread

increase in P concentrations in large rivers in England and Wales, for example, is considered to be largely due to point source pollution, principally from sewage treatment works (Muscutt and Withers 1996).

Phosphorous is a key biological element and is essential for all organisms, although it is toxic as the element or oxide at high doses. Phosphorus as phosphate is an important plant nutrient, and is

added as a fertiliser to increase the production of agricultural crops. Excessive or improper use can, however, lead to eutrophication and algal blooms in rivers and lakes, due to surface run off from fields. The reduced forms, PH<sub>3</sub> and elemental P<sub>4</sub>, are very toxic to fish.

Table 51 compares the median concentrations of P<sub>2</sub>O<sub>5</sub> in the FOREGS samples and in some reference datasets.

Table 51. Median concentrations of P<sub>2</sub>O<sub>5</sub> in the FOREGS samples and in some reference data sets.

<b>Phosphorus (P<sub>2</sub>O<sub>5</sub>)</b>	<b>Origin – Source</b>	<b>Number of samples</b>	<b>Size fraction mm</b>	<b>Extraction</b>	<b>Median %</b>
Crust <sup>1)</sup>	Upper continental	n.a.	n.a.	Total	0.15
<b>Subsoil</b>	<b>FOREGS</b>	<b>788</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>0.096</b>
<b>Topsoil</b>	<b>FOREGS</b>	<b>845</b>	<b>&lt;2.0</b>	<b>Total (ICP-MS)</b>	<b>0.128</b>
Soil <sup>2)</sup>	World	n.a.	n.a.	Total	0.17
<b>Stream sediment</b>	<b>FOREGS</b>	<b>852</b>	<b>&lt;0.15</b>	<b>Total (XRF)</b>	<b>0.140</b>
<b>Floodplain sediment</b>	<b>FOREGS</b>	<b>747</b>	<b>&lt;2.0</b>	<b>Total (XRF)</b>	<b>0.110</b>

<sup>1)</sup>Rudnick & Gao 2004, <sup>2)</sup>Koljonen 1992.

### P<sub>2</sub>O<sub>5</sub> in soil

The median P<sub>2</sub>O<sub>5</sub> content is 0.100% in subsoil and 0.130% in topsoil, with a range of values from 0.010 to 1.66% in subsoil and from 0.010 to 1.32% in topsoil. The average ratio topsoil/subsoil is 1.261.

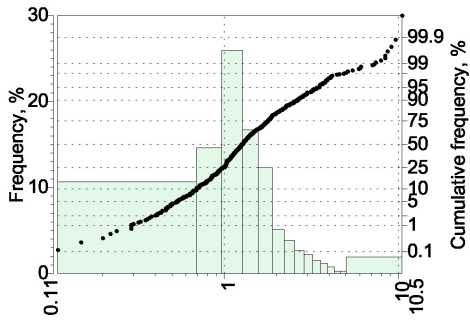
Low P<sub>2</sub>O<sub>5</sub> values in subsoil (<0.07%) occur in eastern Finland, central Sweden, the glacial drift area from Denmark to Poland, eastern Hungary, parts of Greece, north-central and south-west France, central Portugal, and most of eastern Spain.

The highest P<sub>2</sub>O<sub>5</sub> values in subsoil are scattered over Europe, apparently without direct correlation to regional geology; the individual meaning of these point anomalies should be investigated locally. In north-west France, phosphorus is partly inherited from Cretaceous stratabound phosphorite mineralisation, but an influx by fertiliser cannot be excluded (Cd correlation) in that area of intensive farming; the latter explanation can be proposed for P<sub>2</sub>O<sub>5</sub> enrichment in topsoil of Brittany. Other high P<sub>2</sub>O<sub>5</sub> areas (>0.14%) include southern Italy, the Massif Central, north-west Spain (crystalline basement of the Iberian Massif), south-central Spain

(perphosphoric granite in Sierra Morena and Extremadura), Croatia and adjacent areas, western Hungary, Austria, south-western Norway, northern Sweden and the lower-Palaeozoic phosphorite basin of northern Estonia. In Greece, two subsoil P<sub>2</sub>O<sub>5</sub> point anomalies are in terra rossa soil, and in the region there is known low grade phosphate mineralisation.

The ratio topsoil/subsoil is 1.261 for P<sub>2</sub>O<sub>5</sub>, one of the highest ratios of the soil dataset. This points to both natural enrichment in the organic matter (more abundant in topsoil, and anthropogenic (agricultural) influence (Map 10). Many of the topsoil P<sub>2</sub>O<sub>5</sub> anomalies in seemingly agricultural areas may be ascribed to phosphate fertilisers, and stronger than average enrichment in the topsoils is observed on the maps in Ireland, Britain (especially in south-west England, the Lake District and south-western Scotland), northern France, Belgium and Germany, where agriculture is more intense.

Phosphorus in both subsoil and topsoil has a weak to good correlation with the REEs, especially Eu (0.43 in subsoil and topsoil). In subsoil, it has also a good correlation with Fe, and

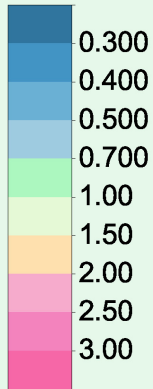


$P_2O_5$  (Ratio Topsoil / Subsoil)  
 Number of samples 779  
 Median 1.25

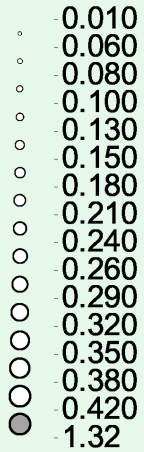
**Phosphorus  
 Ratio  
 Topsoil / Subsoil**



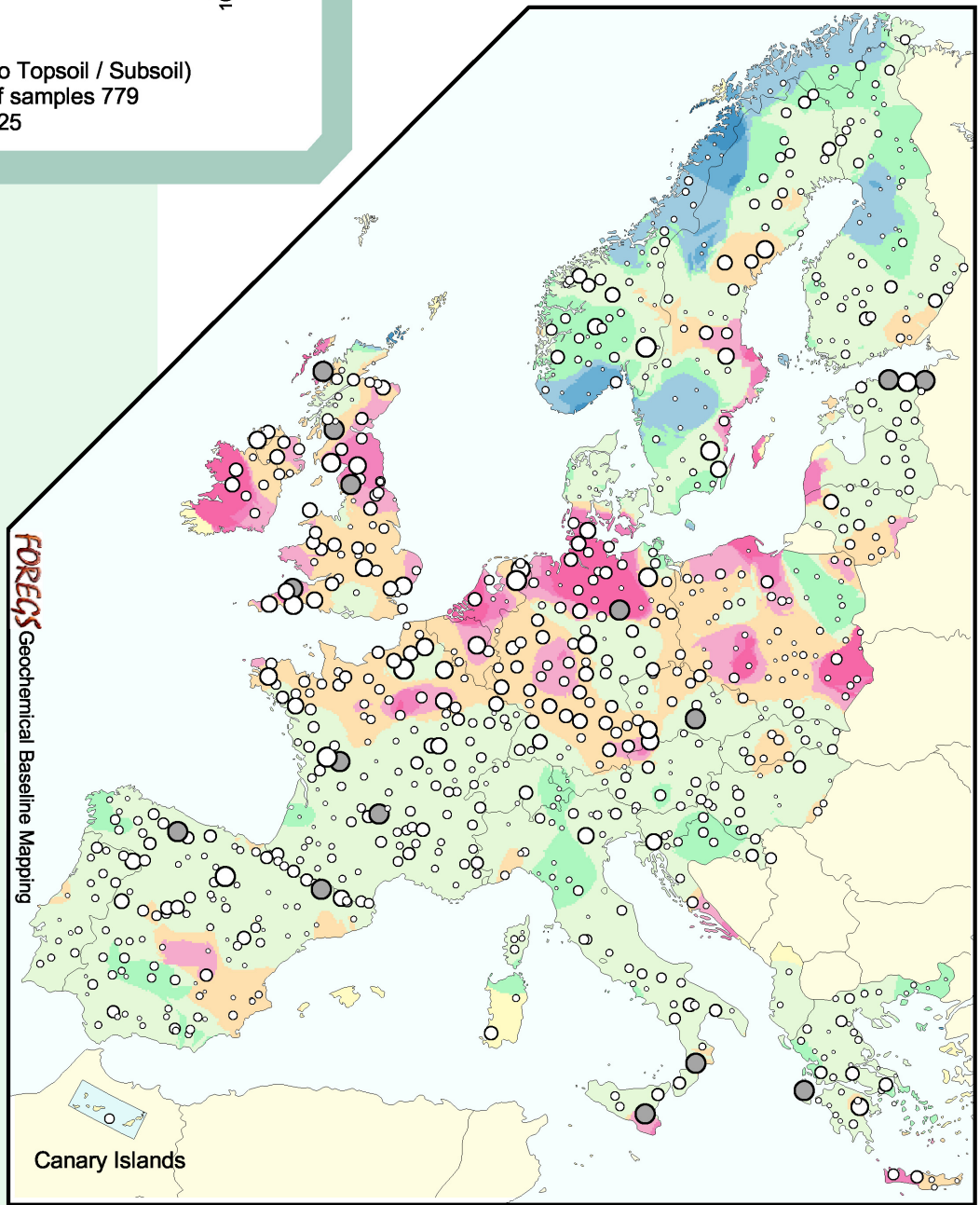
0 500 1000 Kilometers



$P_2O_5$  mg  $kg^{-1}$   
 (Topsoil)



FOREGS  
 Geochemical Baseline Mapping



$P_2O_5$

Map 10. Ratio of  $P_2O_5$  in topsoil vs subsoil.

a weak correlation with Mn, Y, Ga, In, Sc, Ti, Nb and Zn. In topsoils, there is a good correlation with Mn and Zn, and a weak correlation with Fe and Y only. The contrast between subsoils and topsoils points to different mineral phases

carrying the phosphate (notably a weaker association with phyllosilicate minerals in topsoil), and could generally be related to fertiliser use (anthropogenic contamination in topsoil).

### **P<sub>2</sub>O<sub>5</sub> in stream sediment**

The median P<sub>2</sub>O<sub>5</sub> content in stream sediment is 0.13%, with a range of values from <0.01 to 2.47%.

Low P<sub>2</sub>O<sub>5</sub> areas in stream sediment (<0.09%) include eastern Finland, central and eastern Norway, Estonia, parts of Poland, northern Denmark, Aquitaine, Normandy and the Rhône valley in France, northern Italy (a belt from Tuscany to central Austria) and Albania.

High values of total P<sub>2</sub>O<sub>5</sub> in stream sediment (>0.21%) are confined to some well-defined areas, the largest extending from Denmark over eastern Germany and adjacent parts of south-west Poland to the Czech Republic, mostly attributed to agricultural activities (although in the southern Czech Republic a local durbachite ultramafic rock is enriched in phosphorus). Phosphate is also high in central and eastern England; small areas in eastern Poland and southern Lithuania (caused by agricultural pollution, *i.e.*, use of fertiliser and pig or cow manure in flat sandy glaciofluvial terrain with high groundwater level); and Apulia in southern Italy. Fertiliser use is probably responsible for most of the high values listed above. Elsewhere the link with fertilisers is not clear, and natural causes could account for the

high values: the Massif Central in France, northern Portugal (igneous rocks), the Sierra de Gredos in central Spain (granitic rocks), northern Ireland and northern Scotland, northern Greece (intrusive rocks), a point anomaly near Verona (Italy) possibly related to basaltic rocks, a point anomaly in southern Hungary, a larger area in south-western Norway (igneous rocks) and a few more scattered points in Norway; a large area in southern Sweden and more areas throughout central and northern Sweden. In France, some similarity exists between the distribution of P, Mn and Fe, an association known to be related to the palaeoshoreline of the upper Cretaceous sea (Cenomanian).

Phosphate in stream sediment has a good correlation (0.46) with TOC (total organic carbon), and a weak correlation (>0.3) with Fe and Zn. There is also a very weak correlation (>0.2) with S, As, Nb, Cu and Cd, and some similarity with the Cd distribution in Britain and central Europe. This pattern reinforces the impression that the distribution of high values is dominated by human influence, mainly through the agricultural use of phosphates.

### **P<sub>2</sub>O<sub>5</sub> in floodplain sediment**

Total P<sub>2</sub>O<sub>5</sub> values in floodplain sediment vary from <0.01 to 2.61%, with a median of 0.11%.

Low P<sub>2</sub>O<sub>5</sub> values in floodplain sediment (<0.07%) occur over the crystalline shield of eastern and northern Finland, northern and southern Norway, most of glacial drift covered Poland; most of Scotland and northern England, and northern Ireland with crystalline, igneous and clastic rocks; parts of France and Corsica with variable lithology.

High P<sub>2</sub>O<sub>5</sub> values in floodplain sediment (>0.17%), which may be due to agricultural practices are mainly found in Germany (the whole country shows a striking enrichment), west

Hungary and north-eastern Croatia. Further, high P<sub>2</sub>O<sub>5</sub> values occur in eastern Latvia, Estonia, the Buskerud area in southern Norway, and English Midlands, although in the latter two areas they may also be related to mineralisation (*e.g.*, Northampton Fe-ore deposits). The anomalous P<sub>2</sub>O<sub>5</sub> contents in northern Sweden may be due to phosphorus mineralisation (*e.g.*, Kirunavaara, Mertainen, Pattok, Ekströmsberg and Malmberget Fe-P deposits), in northern Estonia are ascribed to the lower Palaeozoic phosphorite basin (*e.g.*, Azeri and Toolse deposits). Other P<sub>2</sub>O<sub>5</sub> floodplain sediment anomalous areas that may be related to base metal mineralisation are in Brittany

(Segre Fe-deposit) in France and the upper Paris Basin with phosphate rich layers in Cretaceous sediments. There is a high  $P_2O_5$  value associated with the basalt of Gran Canaria in the Canary Islands. High  $P_2O_5$  in northern coastal Portugal is caused by weathering of felsic rocks and some agricultural influence.

The highest anomalous  $P_2O_5$  values in floodplain sediment, including two outliers, occur in northern Germany (2.61, 1.63 and 1.06%). A point anomaly in northern Spain is caused by chemical industries near Miranda de Ebro.

The peculiar pattern of very low floodplain sediment  $P_2O_5$  values in Poland was considered to be dubious, since there appears to be a border effect. However, the topsoil and subsoil patterns

are approximately similar. Stream sediment patterns are slightly different, especially in the western and north-eastern parts of Poland.

$P_2O_5$  in floodplain sediment has a good correlation with TOC (0.41) and a weak correlation ( $>0.3$ ) with Cd, Cu, Zn, Hg, S and MnO. This pattern is very different from the one in soil, and points very strongly to an overall anthropogenic influence.

In conclusion, the  $P_2O_5$  distribution in floodplain sediment shows both the geological substratum, and especially mineralised areas with phosphorus included in the paragenesis, but also agricultural practices by the use of phosphate fertilisers, and industrial pollution.

### P comparison between sample media

There is a clear enrichment in  $P_2O_5$  from subsoil to the topsoil to the sediments. Especially in central Europe, Britain and Ireland, topsoil are higher than subsoil probably because of agricultural practices. In stream sediment, there are particularly high  $P_2O_5$  values in western Poland, the Czech Republic, eastern and northern Germany and Denmark compared to other solid sample media. In floodplain sediment, the whole of Germany, Estonia, eastern Latvia, western

Hungary and Pannonian Croatia are particularly high in  $P_2O_5$  compared to subsoil. In northern Estonia, the  $P_2O_5$  anomaly occurring in the phosphorite basin is not expressed in the stream sediment compared to other solid sample media. In floodplain sediment, northern Britain and northern Ireland, Brittany and western France and Poland are lower in  $P_2O_5$  relative to other solid sample media.

A boxplot comparing  $P_2O_5$  variation in subsoil,

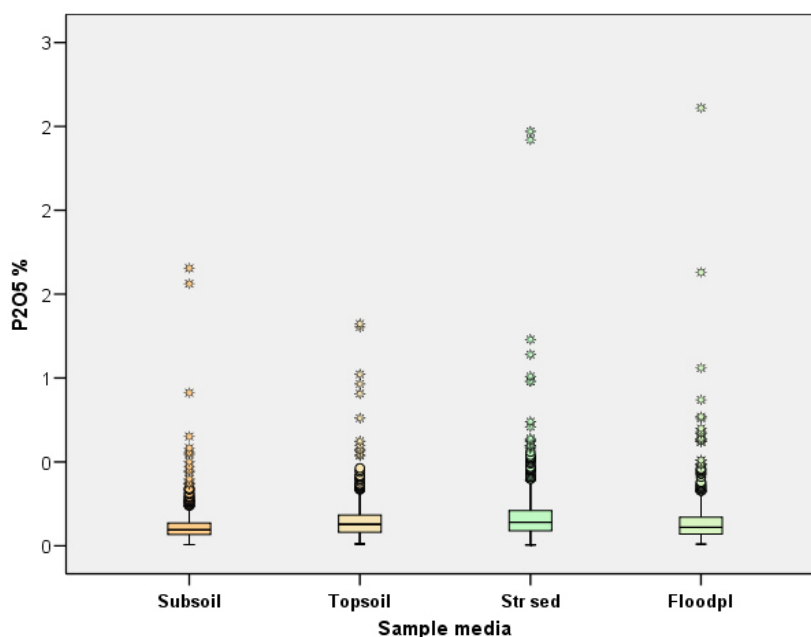


Figure 33. Boxplot comparison of  $P_2O_5$  variation in subsoil, topsoil, stream sediment and floodplain sediment.

topsoil, stream sediment and floodplain sediment is presented in Figure 33.

Orthophosphate in stream water is not worthy of consideration since the species is relatively unstable in solution and was probably lost in the time between sample collection and analysis.

From the distribution patterns of the topsoil, stream and floodplain sediment maps, and given

the absence of pollution in subsoil, it can be concluded that major agricultural contamination is present in certain parts of central Europe. This has significant implications for the protection of surface and groundwater quality in these areas, and should be considered in conjunction with the distribution of nitrate pollution in stream water.