

## **CHARACTERISTICS OF THE CHEMICAL ELEMENTS MAPPED by Sabrina SAVE**

### **1 Arsenic - As**

Arsenic is a metalloid element existing in organic and inorganic forms, with the inorganic form predominant in sediments. Arsenic bonds to iron, aluminium and manganese oxides, and its stability in sediments is influenced by redox conditions, pH, and microbial activity (Conseil canadien des ministres de l'environnement 1999a; Fournier 2004). Arsenic is often present in iron minerals (pyrites, magnetites, ilmenites, etc) (Michel 1987), but also in copper (<http://weppi.gtk.fi/publ/foregsatlas/text/As.pdf>), lead, tin, zinc and gold minerals (Fournier 2004; Smith *et al.* 1998, 153-154). Its natural concentration in sediment depends on the local geological and parent material. Arsenic concentration in sediments usually do not exceed 15ppm (Smith *et al.* 1998, citing National Research Council of Canada 1978), with concentrations between 0.2 to 40ppm registered in polluted and non polluted contexts (Smith *et al.* 1998). The use of fossil energies (coal and bituminous coal) can engender environmental arsenic enrichment (Fournier 2004; Smith *et al.* 1998, 157). Other modern industries are responsible for arsenic pollution: the manufacture of ceramics and glass, electronic components, pigments, cosmetics, fireworks; the anti-corrosion treatment of copper alloys; arsenic wood treatment (in addition to copper and chrome treatments); and agriculture (pesticides, fertilisers, draining treatments) (Smith *et al.* 1998). Arsenic has been used as a pesticide in the leather tanning process (Smith *et al.* 1998, 158). Pork and poultry husbandry may also be a source of arsenic pollution (<http://weppi.gtk.fi/publ/foregsatlas/text/As.pdf>).

The behaviour of arsenic in soil depends on the nature and properties of the sediment. Arsenic will be more stable in clayey sediments when compared to sandy sediments, as it will be less exposed to weathering and percolation (Fournier 2004). Arsenic is also heavily adsorbed by clays, hydroxides and organic matter (<http://weppi.gtk.fi/publ/foregsatlas/text/As.pdf>).

### **2 Bismuth - Bi**

Bismuth is a component of rare minerals like bismuthinite and bismite. It is a chalcophile element, and is found in chalcopyrite and sphalerite. Sometimes it can show lithophile properties and can replace calcium in apatite. The mean concentration of bismuth in soils is low, usually under 0.5ppm. Bismuth is rarely mobile in sediments; it bonds to iron and manganese oxides, and also to organic matter. Modern anthropogenic sources of bismuth are silver, gold, copper and lead ore exploitation, and in general waste waters. Bismuth is also used in cosmetics, pigments, ceramic glazing, magnets, fire retardant materials, and electronic components (<http://weppi.gtk.fi/publ/foregsatlas/text/Bi.pdf>).

### **3 Calcium - Ca**

Calcium is an alkaline earth metal, never present in a pure form in nature, is the fifth most abundant element in the Earth's crust (<http://weppi.gtk.fi/publ/foregsatlas/text/Ca.pdf>), and is essential to the formation of organic matter (bone, teeth, shell). Calcium carbonate is the main component of calcareous rocks, while calcium sulphate is the main component of gypsum. In rocks, calcium is often associated with sodium and potassium (Gis Sol 2011, 64).

Calcium has an important flocculant power in soils, and is often associated with magnesium (Massenet 2010). It is very mobile in sediments, except in very alkaline conditions (<http://weppi.gtk.fi/publ/foregsatlas/text/Ca.pdf>). Calcium also enhances the mobility of potassium and helps fix phosphates (UNIFA 2013a).

### **4 Cobalt - Co**

Cobalt is a metal, usually present in copper, nickel, lead and silver ore (Pichard *et al.* 2006). Most rocks, sediments, plants, animals and surface water contain some cobalt (Ministère de l'Environnement 2001). In european soils, the mean concentration of cobalt is between 1 and 20ppm

but can reach 2500ppm in areas geologically rich in cobalt (<https://www.cobaltinstitute.org/cobalt-in-soil.html>). Quartz, feldspath and calcium carbonate contain little cobalt; sandstones and limestones are thus poor in cobalt (<http://weppi.gtk.fi/publ/foregsatlas/text/Co.pdf>). Soils become enriched in cobalt from the decomposition of organic matter, or the weathering of minerals (<https://www.cobaltinstitute.org/cobalt-in-soil.html>). Today, cobalt is used in numerous alloys, but also in the production of inks and pigments for glass and porcelain manufacture (Pichard *et al.* 2006), as well as in agriculture (<https://www.cobaltinstitute.org/cobalt-in-soil.html>). Cobalt is not easily transported by water but the pH of sediment can influence its adsorption: the higher the pH, the more that cobalt is adsorbed. It is also easily adsorbed by iron and manganese oxides, as well as by clays and organic matter (Pichard *et al.* 2006; <http://weppi.gtk.fi/publ/foregsatlas/text/Co.pdf>).

## 5 Chromium - Cr

Chromium is a metal and a trace metal. Chromium concentrations in sediments depends mainly on the parent material. Some basaltic rocks, moraines and alpine flyschs, as well as some Liassic rocks (clayey limestone, marl and lower Jurassic clays) produce chromium-rich soils (Gis Sol 2017a). The mean concentration of chromium in soils is around 60ppm (<http://weppi.gtk.fi/publ/foregsatlas/text/Cr.pdf>).

Today, chromium used in industries (steel, chroming) is extracted from chromite, an iron and chromium ore. Chromium is also present in crocoïte, a lead chromate with a red colour, used during the XIXth century in pigments, then as a refractory on furnaces walls. Modern anthropogenic chromium pollution comes mainly from coal and oil combustion, as well as metallurgical activities. Chromium is soluble in water and present in living organisms (Chiffolleau 1994), but relatively immobile in soils, in particular in moderate redox and neutral pH conditions (<http://weppi.gtk.fi/publ/foregsatlas/text/Cr.pdf>).

## 6 Copper - Cu

Copper is a metal and a trace metal. It tends to accumulate in sediments, bonding to iron and manganese oxides as well as to organic matter (Conseil canadien des ministres de l'environnement 1999c; <http://weppi.gtk.fi/publ/foregsatlas/text/Cu.pdf>). Copper is present in nature as native copper, oxidised, or as sulphured ore. Soils rich in copper are located in volcanic and Hercynian massives (Gis Sol 2017b). The mean concentration of copper in soils is between 13 and 24ppm (<http://weppi.gtk.fi/publ/foregsatlas/text/Cu.pdf>). Anthropogenic sources of copper are diverse: metal working, carbon combustion, manure, fertilisers, etc. Copper oxides, carbonates and hydroxides are not or little soluble in water, while copper chlorides, nitrates and sulphates are very soluble. Copper is mobile in oxidised, low pH conditions.

Recent archaeological studies demonstrate copper enrichment in domestic hearths (Cook *et al.* 2014; Jones *et al.* 2010, 44-45; Wilson 2009), in bone fragments (Wilson 2008,) and in butchery areas (Cook *et al.* 2014; Coronel *et al.* 2014, 268).

## 7 Iron - Fe

Iron is present in nature as an ore, the most common being magnetite and hematite. Iron is the fourth most common element in the Earth's crust, and the second metal after aluminium (<http://weppi.gtk.fi/publ/foregsatlas/text/Fe.pdf>). Each kilogram of terrestrial crust contain a mean of 45g of iron. Iron is thus abundant in soils; it represents between 0,05 and 19% of sediment's composition (Gil 2011, 4), with a mean around 2,1% (<http://weppi.gtk.fi/publ/foregsatlas/text/Fe.pdf>). Iron does not exist in Nature in a pure state as it oxidises quickly in contact with air. Some consider iron to be un-mobile in soils (Boust *et al.* 1999), while others consider it very mobile (Gis Sol 2011, 64).

Recent archaeological studies demonstrate iron enrichment relating to butchery (Coronel *et al.* 2014, 267) and kitchen (Fernandez *et al.* 2002, 508) areas.

## 8 Potassium - K

Potassium is a soft metal. It is the eighth most common element in the Earth's crust, with a mean concentration in soils of about 1.84% (<http://weppi.gtk.fi/publ/foregsatlas/text/K.pdf>). Potassium is present in soils in four different forms: potassium derived from silicate minerals, adsorbed potassium, retrograded potassium, and organic potassium ([www.ecosociosystemes.fr/potassium.html](http://www.ecosociosystemes.fr/potassium.html)). Potassium from silicate minerals comes from micas, feldspaths and some types of clays, such as illite. Soils from crystalline and volcanic parent materials are richer in potassium than calcareous soils. Adsorbed potassium is present in soil as solution or at the surface of clay-humus contexts. Retrograded potassium corresponds to  $K^+$  ions fixed inside clay beds. The rate of fixation of retrograded potassium increases with pH. Organic potassium is linked to microbial activity in organic matter. The weathering of feldspath delivers a very soluble potassium but its mobility is usually affected by its rapid fixation to clayey minerals and organic matter, and its adsorption by plants for their growth needs (<http://weppi.gtk.fi/publ/foregsatlas/text/K.pdf>). Fertilisers are the main modern anthropogenic source of potassium., with potassium salts also used in many chemical and medicinal processes (<http://weppi.gtk.fi/publ/foregsatlas/text/K.pdf>).

Recent archaeological studies demonstrate potassium enrichment in combustion areas (Dirix *et al.* 2013, 2966; Holliday et Gartner 2007, 307; Middleton et Price 1996, 678; Misarti *et al.* 2011, 1442; Vos *et al.* 2018, 685; Vyncke *et al.* 2011, 2287; Wilson 2009), fish drying areas (Holliday et Gartner 2007, 307), the processing and combustion of some species of nuts (Homsey et Capo 2006, 248), in middens (Misarti *et al.* 2011, 1448), and in manure, plant debris and ash (Oonk *et al.* 2009a, 41; Vos *et al.* 2018, 685).

## 9 Manganese - Mn

Manganese is relatively abundant in the Earth's crust, with a mean concentration around 600ppm. It is a common component of minerals like pyrolusite, rhodochrosite and manganite. Manganese's behaviour in soil is complex and depends on several environmental factors including pH. While  $Mn^{2+}$  ions are very soluble, manganese is not very mobile, especially in oxidised conditions, as  $Mn^{3+}$  and  $Mn^{4+}$  ions are insoluble oxides. Manganese is thus heavily impacted by redox conditions and easily mobile only in anoxic conditions under its  $Mn^{2+}$  form. Modern anthropogenic sources of manganese are mining and metal working activities, agriculture, and from more recent periods, the manufacture of batteries, steel, glass and chemicals (permanganate) (<http://weppi.gtk.fi/publ/foregsatlas/text/Mn.pdf>).

Recent archaeological studies demonstrate manganese enrichment in middens (Misarti *et al.* 2011, 1448), fish processing areas (Misarti *et al.* 2011, 1442), burials (Misarti *et al.* 2011, 1452), and domestic hearths (Vos *et al.* 2018, 685).

## 10 Phosphorus - P

Phosphorus is the 11th most abundant element in Earth's crust, representing about 0.1% of its weight. It is a non metallic element, lithophile, siderophile and biophile (<http://weppi.gtk.fi/publ/foregsatlas/text/P.pdf>). Phosphorus, as well as nitrogen and potassium, is essential to plant growth and is used as a fertiliser. Phosphorus is present in urine and excrement (Arte future 2013; Audoin 1991), bone, plant, and other organic matter (<http://weppi.gtk.fi/publ/foregsatlas/text/P.pdf>).

Phosphorus geochemistry is complex. In an acid environment, with a pH between 4 and 6,  $H_2PO_4^-$  is the dominant form.  $HPO_4^{2-}$  is the most abundant form at a neutral pH, while  $PO_4^{3-}$  is more stable in basic conditions (<http://weppi.gtk.fi/publ/foregsatlas/text/P.pdf>). The Phosphate anion  $PO_4H^{2-}$  is fixed in clay by  $Ca^{2+}$  ions on iron and aluminium hydroxides.  $PO_1H^{2-}$  ions show little mobility

(Audouin 1991; UNIFA 2013b). Except in very acidic conditions, phosphorus mobility in soil is limited by the formation of aluminium and iron phosphates. Phosphorus can also bond to lead and calcium to form poorly soluble minerals. In basic, calcareous soils, phosphates are adsorbed by calcite, and in high concentrations calcium phosphate can precipitate (<http://weppi.gtk.fi/publ/foregsatlas/text/P.pdf>). Modern anthropogenic sources of phosphorus are usually fertilisers, waste water and detergents (<http://weppi.gtk.fi/publ/foregsatlas/text/P.pdf>).

Recent archaeological studies show phosphorus enrichment in combustion areas (Cook *et al.* 2014; Dirix *et al.* 2013, 2966; Holliday et Gartner 2007, 302; Jones *et al.* 2010, 44-45; Middleton et Price 1996, 678; Vos *et al.* 2018, 685; Vyncke *et al.* 2011, 2287; Wilson 2008), in the presence of bones and excrement (Cook *et al.* 2014; Coronel *et al.* 2014, 266-267; Entwistle *et al.* 2007, 409; Holliday et Gartner 2007, 302; Misarti *et al.* 2011, 1442; Oonk *et al.* 2009b, 164; Vos *et al.* 2018, 685; Vyncke *et al.* 2011, 2288; Wilson 2008, 2009), in plant remains (Holliday et Gartner 2007, 302), in middens (Fernandez *et al.* 2002, 502-503; Misarti *et al.* 2011, 1448; Wilson 2008), and in burials (Misarti *et al.* 2011, 1452).

### 11 Lead - Pb

Lead is a metal present in nature as carbonates (cerusite), phosphates (pyrophosphate), and primarily, sulphurs (galena). It can also be extracted from zinc, silver and copper ore. Lead concentration in soil is influenced by the parent material and some mineralisation processes in some sedimentary rocks in contact with Hercynian massives (Gis Sol 2017d). Lead is associated to clay minerals, manganese oxides, iron and aluminium hydroxides, and organic matter (<http://weppi.gtk.fi/publ/foregsatlas/text/Pb.pdf>). In some soils, lead can be concentrated in calcium carbonates particles and phosphates (<http://weppi.gtk.fi/publ/foregsatlas/text/Pb.pdf>).

Lead was exploited early in human history to produce pigments and metal artefacts, in particular thanks to its low fusion point. Lead has little mobility in soils as it is easily fixed to organic matter, iron and manganese oxides, clays and some secondary minerals (Baize 2010; <http://weppi.gtk.fi/publ/foregsatlas/text/Pb.pdf>). Recent archaeological studies show lead enrichment in combustion areas (Cook *et al.* 2014; Wilson 2008, 2009), stables (Wilson 2008, 2009), and middens (Wilson 2008).

### 12 Rubidium - Rb

Rubidium is not found as a pure ore but is present in numerous ores where it frequently replaces potassium. Rubidium is not very abundant in the Earth's crust, with a mean concentration around 78ppm. In sedimentary rocks, rubidium is present in feldspaths, micas and clays. Despite its stability and its important solubility, rubidium shows little mobility in soils because of its strong bonding to clays like illites. A high pH enhances rubidium's bond to clay. Before the 1920s there was no significant use of rubidium in industry. Today it is used in the manufacture of electronic tubes, photo-resistances and for some medical purposes (<http://weppi.gtk.fi/publ/foregsatlas/text/Rb.pdf>).

### 13 Antimony - Sb

Antimony is a low-abundance chalcophile element forming several rather rare minerals including stibnite, valentinite and kermesite. Antimony is also present as a trace element in minerals as ilmenite, Mg-olivine, galena, sphalerite and pyrite. The chemistry and geochemistry of Sb is most similar to that of As. Fine-grained argillaceous and organic-rich sediments are typically enriched in Sb (>1 mg.kg<sup>-1</sup>) relative to their parent igneous lithologies. Pyritic black shale and mudstone may also contain relatively high levels of Sb. Coarse quartzo-feldspathic sediments, quartzite and carbonate rocks usually contain less than 0.5mg.kg<sup>-1</sup> Sb. Remobilisation of antimony is rather limited due to the tendency of Sb<sup>3+</sup> to hydrolyse to insoluble basic salts and be adsorbed by secondary hydrous oxides of Fe, Al and Mn at pH levels in the range 4.0-8.0. In soil, Sb is enriched

in the surface horizon due chelation with organic matter, but there is also an enrichment in the B-horizon as a result of strong absorption of Sb by hydrous Fe-oxides, and clay minerals. Average values for soil are between 0.9 and 1mg.kg<sup>-1</sup>.

With its low natural abundance, Sb is a useful indicator of industrial contamination. Anthropogenic Sb is associated with metalliferous mining and metal smelting. It is also associated with coal combustion, urban waste and car exhaust fumes, and is used in the manufacture of lead solder, batteries, arms and tracer bullets, composite car body panels, flame-proofing compounds, paints, ceramic enamels, glass and pottery (<http://weppi.gtk.fi/publ/foregsatlas/text/Sb.pdf>).

#### 14 Strontium - Sr

Strontium is a lithophile metal, chemically very similar to calcium and barium (<http://weppi.gtk.fi/publ/foregsatlas/text/Sr.pdf>). Strontium is present in Earth's crust in minerals like celestite (strontium sulphate) and strontianite (strontium carbonate), in hydrothermal deposits and pegmatites. Most of the strontium present in water (streams and rivers) comes from the weathering of gypsum, anhydrite, limestone, marl, sandstone and dolomite. The mean concentration of strontium in soils is around 95ppm. Anthropogenic sources of strontium are milling, coal combustion, fertilisers, and fireworks. Today strontium is also used by the glass, ceramic and pigment industries. Strontium is easily mobile in soils, especially in acidic and oxidised conditions, but it can bond strongly to metal oxides, clays and organic matter (Watts et Howe 2010; <http://weppi.gtk.fi/publ/foregsatlas/text/Sr.pdf>).

Recent archaeological studies show strontium enrichment in areas rich in mollusc shells (Entwistle *et al.* 2007, 411; Misarti *et al.* 2011, 1448), in processing and combustion areas associated with some types of nuts (Homsey et Capo 2006, 248), in domestic hearths (Jones *et al.* 2010, 44-45; Vos *et al.* 2018, 685; Wilson 2008, 2009), in production and use areas of lime chalk (Middleton et Price 1996, 678), in enclosed and roofed spaces (Middleton et Price 1996, 679), in middens (Misarti *et al.* 2011, 1448), in burials (Misarti *et al.* 2011, p. 1452), and in excrement (Vyncke *et al.* 2011, 2288).

#### 15 Thorium - Th

Thorium is a metal present in granites, basalts, schists, sedimentary rocks, and more precisely in carbonates, phosphates, silicates and oxides. It is the most abundant of the heavy metals (<http://weppi.gtk.fi/publ/foregsatlas/text/Th.pdf>). The mean concentration of thorium in soils ranges between 3.4 and 10.5ppm. In soils, thorium concentrates in the fine fraction of sediments, bonding to organic matter and oxides, especially when the pH is high. Thorium shows little mobility in soils, except in acidic conditions. Anthropogenic sources of thorium come from uranium exploitation and processing, coal combustion, and phosphate fertilisers (IRSN 2002; <http://weppi.gtk.fi/publ/foregsatlas/text/Th.pdf>).

#### 16 Titanium - Ti

Titanium is a light metal, very common, with a mean concentration in soils around 5700ppm. It is a component of several minerals like ilmenite, rutile, brookite, anatase and sphene. Some traces of titanium are present in pyroxene, amphibole, mica and garnet. Titanium minerals are very resistant to weathering, with titanium showing little mobility in soils. Today, titanium is used in pigments manufacture, and in specific alloys, generally for planes and weapons ([http://weppi.gtk.fi/publ/foregsatlas/text/Ti\\_TiO2.pdf](http://weppi.gtk.fi/publ/foregsatlas/text/Ti_TiO2.pdf)).

Recent archaeological studies demonstrated titanium enrichment in domestic hearths and lithic working areas (Misarti *et al.* 2011, 1442).

#### 17 Vanadium - V

Vanadium is a metal present in numerous minerals (magnetite, vanadinite, carnotite, mica, pyroxene, apatite and amphibole). In soils, vanadinite bonds to organic matter, iron and manganese oxides, and clays. The mean concentration of vanadium in soils is around 63ppm (<http://weppi.gtk.fi/publ/foregsatlas/text/V.pdf>). Vanadium's mobility increases with pH (Bisson *et al.* 2012); redox conditions also influence vanadium's mobility which increases in oxidised conditions (<http://weppi.gtk.fi/publ/foregsatlas/text/V.pdf>). Modern anthropogenic sources of vanadium are oil and coal combustion, steel production and road traffic pollution (<http://weppi.gtk.fi/publ/foregsatlas/text/V.pdf>).

#### 18 Yttrium - Y

Yttrium is a lithophile metal present in several minerals like xenotime and yttrialite, but also in smaller quantities in biotite, feldspath, pyroxene, garnet and apatite. Yttrium is chemically similar to the Rare Earth Elements, and has a mean concentration in soils around 23ppm. Yttrium shows little mobility in soils, regardless of the environmental conditions. Modern anthropogenic yttrium pollution sources are rare earth element mines and exploitations, as well as ceramic dust. Yttrium is also used in the manufacture of televisions, fluorescent lamps, energy saving lamps, and glass (<http://weppi.gtk.fi/publ/foregsatlas/text/Y.pdf>).

#### 19 Zinc - Zn

Zinc is chalcophile metal, very abundant in Earth's crust, with a mean concentration in soils of around 47ppm. It is an important part of several minerals like sphalerite and smithsonite, and, in smaller quantities, in pyroxene, amphibole, mica, garnet and magnetite (<http://weppi.gtk.fi/publ/foregsatlas/text/Zn.pdf>). Zinc is present in soils forming over crystalline and Jurassic rocks, including Liassic rocks (clayey limestones, marls and clays from the inferior Jurassic) (Gis Sol 2017e). Zinc is usually linked to cadmium and iron. In soil, it bonds to iron, aluminium and manganese oxides, silicates and clay minerals. Zinc's mobility increases when pH decreases and oxidising conditions increase. Modern anthropogenic sources of zinc are numerous and include mining activities, coal combustion, and steel production. Zinc is also used as an anticorrosion treatment, and in the production of brass alloys, in white paint, and in the manufacture of batteries (<http://weppi.gtk.fi/publ/foregsatlas/text/Zn.pdf>).

Recent archaeological studies show zinc enrichment in combustion areas (Cook *et al.* 2014; Dirix *et al.* 2013, 2966; Jones *et al.* 2010, 44-45; Vos *et al.* 2018, 685; Vyncke *et al.* 2011, 2287; Wilson 2008, 2009), in cooking and butchery spaces (Cook *et al.* 2014; Coronel *et al.* 2014, 268; Vos *et al.* 2018, 685), in bones (Wilson 2008), in domestic sewage (Jones *et al.* 2010, 44), in middens (Fernandez *et al.* 2002, 510; Misarti *et al.* 2011, 1448; Wilson 2018), and in manure (Vos *et al.* 2018, 685; Wilson 2018).

#### 20 Zirconium - Zr

Zirconium is a lithophile metal. It is the 20th most common element on Earth (Shahid *et al.* 2013). Zirconium is present in several minerals like zircon and baddeleyite, and in smaller quantities in clinopyroxene, amphibole, mica, and garnet. Zirconium is little mobile in soils in most environmental conditions as it is little soluble (Shahid *et al.* 2013; <http://weppi.gtk.fi/publ/foregsatlas/text/Zr.pdf>). The mean concentration of zirconium in soils is around 220ppm. Modern anthropogenic sources of zirconium are nuclear activities and ceramic dust. Zirconium is also used in some alloys dedicated to the manufacture of catalytic converters, high-temperature furnace bricks, laboratory crucibles, and surgical tools (<http://weppi.gtk.fi/publ/foregsatlas/text/Zr.pdf>).

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