

## Introduction

Iodine is a halogen belonging to group 17 of the periodic table, along with F, Cl and Br. The element has an atomic number of 53, an atomic mass of 127, five main oxidation states (-1, +1, +3, +5 and +7), and one naturally occurring stable isotope ( $^{127}\text{I}$ ).

Although iodine is the least abundant of the halogen elements,  $^{127}\text{I}$  is ubiquitous at approximately  $0.5 \text{ mg kg}^{-1}$  on average of the Earth's crust. Iodine minerals are sub-divided into two distinct groups: insoluble iodides, *e.g.*, iodembolite  $\text{Ag}(\text{Cl}, \text{Br}, \text{I})$ , and soluble iodates, *e.g.*, schwartzembergite  $\text{Pb}_5\text{IO}_3\text{Cl}_3\text{O}_3$  (Fleischer 1966). It has been suggested that fluid inclusions within minerals may be a primary source of iodine (Wedepohl 1978). Substitution of chloride ions by iodide ions in some mineral groups is thought to occur (Kogarko and Gulyayeva 1965). It is also considered that the large ionic radius of iodine, its chalcophilic character (Fuge and Johnson 1984) and its possible occurrence in non-ionic form in melts are all factors controlling the distribution of iodine in igneous rocks (Wedepohl 1978).

Iodine concentrations in common rock-forming minerals range from  $<0.02 \text{ mg kg}^{-1}$  to  $1.2 \text{ mg kg}^{-1}$ ; similar concentrations are recorded for igneous and magmatic rocks, ranging from  $<0.02 \text{ mg kg}^{-1}$  to  $1.9 \text{ mg kg}^{-1}$  (Fuge and Johnson 1986). Iodine concentrations in clastic rock types are thought to be relatively low, but with a higher range than for igneous rocks (Butler 1999). Cosgrove (1970) reported high levels in samples of Kimmeridge shale (mean  $17 \text{ mg kg}^{-1}$ ), which he attributed to the high percentage of organic material in the shale - organic rich rocks do have the highest concentrations of iodine. Elevated levels of iodine have also been described in sandstone containing argillaceous material; probably resulting from adsorption of iodine onto clay surfaces (Becker *et al.* 1972). High levels of iodine occur in phosphate rock ( $0.8\text{-}130 \text{ mg kg}^{-1}$ ) and caliche (nitrate) deposits (about  $400 \text{ mg kg}^{-1}$ ) (Butler 1999).

The weathering of rocks releases up to about half the original iodine content as water-soluble compounds, mainly iodide (Fuge and Johnson 1986). Soil contains much more iodine than the rocks from which it is derived (global mean

content  $5 \text{ mg kg}^{-1}$ ), and the amount correlates closely with the organic matter content in soil; some iodine is also associated with Fe and Al oxides and illitic clay (Butler 1999, Kabata-Pendias 2001). This excess amount of iodine is unresolved whether it comes directly from the atmosphere or indirectly through uptake by plants that release it when they decay; iodine may also continue to be adsorbed from the atmosphere by decaying organic matter (Whitehead 1984). In non-calcareous soil iodine is positively correlated with the clay content, whereas in calcareous soil a positive relationship is observed with clay, exchangeable calcium and organic carbon. Soil developed in recently glaciated areas is usually iodine poor, because this element has not yet been highly accumulated from atmospheric precipitation (Kabata-Pendias 2001).

Marine water forms an important reservoir of iodine in the iodine cycle with high concentrations of  $60 \mu\text{g l}^{-1}$  (Hem 1992). Surface environments in coastal regions have a higher iodine status than areas more distant from the sea because of greater wet and dry deposition of iodine. Away from coastal areas, and into central continental regions, levels of iodine in surface water are much lower and highly variable, typically in the range  $0.1$  to  $18 \mu\text{g l}^{-1}$ . Mountainous areas can act as a barrier to atmospheric iodine migration, particularly due to iodine being washed-out by heavier rainfall. Iodine is easily oxidised, but about 90% of all iodine found in natural freshwater occurs as the anion  $\text{I}^-$ . In groundwater, the average  $\text{I}^-$  concentration is approximately  $1 \mu\text{g l}^{-1}$  (ATSDR 2006). Iodine is a volatile element and atmospheric migration is a peculiar feature of iodine geochemistry, volatilisation of iodine being influenced by biochemical activity. Thus, iodine can undergo microbial alkylation to methyl iodide, and substantial amounts of iodine ( $10\text{-}20 \text{ ng m}^{-3}$ ) are circulated in the atmosphere where is depleted photochemically or lost to the stratosphere.

Iodine compounds are important in organic chemistry and are an ingredient in many medicines, including preparations used to clean skin wounds. Potassium iodide is used in photography and is also an ingredient of water

purification tablets for sterilising drinking water. Many disinfectants contain iodine. Although most radioactive isotopes of iodine have very short half-lives,  $^{129}\text{I}$  has a half-life of 15.7 million years, and can be very harmful to the environment.  $^{131}\text{I}$  has a half-life of only 8.1 days, but it is very radioactive and hazardous in the immediate aftermath of nuclear events as it concentrates in the human thyroid gland. Nuclear power plants can be significant sources of both isotopes, particularly when accidents, such as the one that occurred at Chernobyl, result in the release of large amounts of radioactive iodine into air.

Iodine is an essential trace element in the diet of humans and animals and has, therefore, received considerable attention. It was the first recognised association between human health and a trace element in the environment. Iodine provides a substrate for the synthesis of thyroxide

hormones and is essential to normal human growth and development. Lack of iodine in the human diet causes a number of medical conditions collectively known as iodine deficiency disorders (IDDs). The most obvious manifestation is an enlarged neck caused by a swollen thyroid gland, referred to as goitre. A more widespread and significant effect is the mental impairment and cretinism that can afflict populations over large regions of the world, especially in central Asia (China, India, Nepal and Laos). IDDs affect over 740 million people worldwide (WHO 2002). In areas of the world where IDDs occur, iodine is added to table salt to help reduce the health risks to the local population. Sea foods are the richest source of iodine in the human diet.

Table 37 compares the median concentrations of I<sup>-</sup> in the FOREGS samples and in some reference datasets.

Table 37. Median concentrations of I in the FOREGS samples and in some reference data sets.

| <b>Iodine (I)</b>   | <b>Origin – Source</b> | <b>Number of samples</b> | <b>Size fraction mm</b>     | <b>Extraction</b>     | <b>Median mg kg<sup>-1</sup></b> |
|---------------------|------------------------|--------------------------|-----------------------------|-----------------------|----------------------------------|
| Crust <sup>1)</sup> | Upper continental      | n.a.                     | n.a.                        | Total                 | 1.4                              |
| <b>Subsoil</b>      | <b>FOREGS</b>          | <b>783</b>               | <b>&lt;2.0</b>              | <b>Total (ICP-MS)</b> | <b>3.40</b>                      |
| <b>Topsoil</b>      | <b>FOREGS</b>          | <b>840</b>               | <b>&lt;2.0</b>              | <b>Total (ICP-MS)</b> | <b>3.94</b>                      |
| Soil <sup>2)</sup>  | World                  | n.a.                     | n.a.                        | Total                 | 2                                |
| <b>Water</b>        | <b>FOREGS</b>          | <b>807</b>               | <b>Filtered &lt;0.45 µm</b> |                       | <b>0.33 (µg l<sup>-1</sup>)</b>  |
| Water <sup>3)</sup> | World                  | n.a.                     | n.a.                        |                       | 2 (µg l <sup>-1</sup> )          |

<sup>1)</sup>Rudnick & Gao 2004, <sup>2)</sup>Koljonen 1992, <sup>3)</sup>Ivanov 1996.

### Iodine in soil

The median iodine content is 3.40 mg kg<sup>-1</sup> in subsoil and 3.94 mg kg<sup>-1</sup> in topsoil; values range from <2 to 92.5 mg kg<sup>-1</sup> in subsoils and up to 70.8 mg kg<sup>-1</sup> in topsoils. About 30% of the samples are below the detection limit of 2 mg kg<sup>-1</sup>. It is to be noted that the median found in FOREGS geochemical baseline survey is much higher than the average of 1.4 mg kg<sup>-1</sup> for the upper crust (Rudnick and Gao 2005). The average ratio topsoil/subsoil is 1.013.

Low I values (<2.11 mg kg<sup>-1</sup>) in subsoil occur in most of central Europe (northern and southern Germany, Poland, Czech Republic, Austria, Hungary, eastern Croatia, Lithuania, Latvia), in

parts of central and northern Sweden and southern Norway, and parts of the Netherlands, southern Italy, Portugal and south-west Spain. Except for Portugal, Netherlands and Italy, these areas are relatively removed from marine influence.

The iodine distribution in subsoil shows high values (>6.05 mg kg<sup>-1</sup>) along the western side of Great Britain (possible sea salt influence) and in northern Ireland; in irregular patches through the Iberian Peninsula seemingly unrelated to geology (marine influence through sea spray in the Atlantic coastal rim, but a probable link with evaporites in south-east Spain, also saline diapirs in Murcia and the Ebro basin), in western and

southern France, Corsica, coastal Croatia and Greece (phosphate and sulphide mineralisation, saline soil, marine influence). At first sight, the pattern does not seem to be connected to geological features.

The distribution of iodine in topsoil is rather similar to the one in subsoil for most European countries. The main difference in the topsoil distribution is a stronger positive anomaly in south-western Norway, possibly related to sea spray influence because of high rainfall, up to 400 mm per year, and enriched iodine in southern Sweden, possibly related to fertilisers. Still in topsoil, Greece shows fewer high values, and central and northern Italy have higher values than for subsoil. The Kefallinia point anomaly in Greece is in *terra rossa* soil in a formation hosting low grade phosphate deposits. The ratio

topsoil/subsoil for I is 1.013.

As iodine is seldom analysed, interpretation of the observations is not straightforward. Nevertheless, the pattern of weak positive correlations ( $>0.3$ ) with TOC, Hg and Te in subsoil, and with TOC, S, Fe and V in topsoils; and a negative correlation with  $\text{SiO}_2$  ( $-0.38$  in subsoils,  $-0.36$  in topsoil) seems to indicate an affinity with organic matter, but also anthropogenic enrichment in some regions is possible. In Brittany for example, a common practice is to use sea algal manure for fertiliser. This may explain the strong iodine enrichment in topsoil in this area, which is correlated with TOC. Near coastal areas, there is an input from sea spray or heavy rainfall, as was mentioned for Britain and Norway.

### I in stream water

Iodide values in stream water range over four orders of magnitude, from  $<0.01$  to  $104 \mu\text{g l}^{-1}$ , with a median value of  $0.33 \mu\text{g l}^{-1}$ .

Lowest I values in stream water ( $<0.10 \mu\text{g l}^{-1}$ ) are found in northern Portugal and Spain on Variscan terrains, in northern Scotland on Scottish Caledonides, in a continuous belt stretching from south-eastern France to northern Italy, Switzerland and western Germany, on both Variscan and Alpine Orogen terrains, in eastern Lithuania and Latvia (Devonian sediments) and at the border between Poland and Slovakia on Precambrian terrains, and throughout most of Greece on Alpine terrain.

Enhanced I concentrations in stream water ( $>1.71 \mu\text{g l}^{-1}$ ) are found all over the southern Iberian Peninsula on both Variscan and Alpine Orogen (Baetics) terrains (mirroring the EC pattern, and caused by intense evapotranspiration in this Mediterranean climate, with concentration of major ions in stream water, enhanced by some evaporitic layers in sediments), in the Netherlands on Quaternary sediments, in an extensive north-south belt stretching from central Sweden to Austria, in southern Italy (mostly Apulia, south-western Sicily and Sardinia) on Alpine Orogen terrains. The high I values in southern Italy are related to evaporitic layers occurring in the area. High iodine in southern Sweden, eastern Germany

and the Czech Republic are probably related to the use of fertilisers, which are phosphates of marine origin rich in iodine, a feature shown by the high phosphate content in stream sediments in the same area. The use of different fertilisers in western and eastern Germany is also seen in selenium concentrations in agricultural soil (Reimann *et al.* 2003). High I near Bilbao in north Spain is due to industrial activities.

Iodine in stream water shows similarity with a number of distribution pattern types: the Sea influenced stream water and Felsic-ultramafic types, but also the REEs, Major-ions and Felsic rocks stream water types. This variety suggests its complex geochemistry in the supergene zone. The high concentrations in the Mediterranean countries, occurring mostly in stream water of the Major-ions type, are evidently related to weathering of evaporitic deposits, and those in the south of Fennoscandia of REEs stream water type are related to I anomalies in soil. Anomalies in the belt from Austria across Czechia to eastern Germany, in Lithuania, and very high concentrations in north Germany and the Netherlands, do not seem to be geogenic, since they do not correspond to any anomalous areas in soil. The sea spraying effects are not readily recognisable in the I distribution patterns.

### **Iodine comparison between sample media**

Of the solid sample media, iodine analyses are available only in soil, and distributions between topsoil and subsoil are generally quite similar, with some exceptions. The coastal areas of south-western Norway and Sweden have higher concentrations in topsoil than subsoil, because of high rainfall with marine salts, and fertiliser use, respectively. Greece and Corsica have lower I

content in topsoil compared to subsoil.

The distribution of I in stream water is rather complex and generally opposes the patterns observed in soil, although patterns between stream water and topsoil distributions are somewhat similar in northern Sweden and Norway, in Finland, Estonia, Latvia, Poland and Spain.