

SOILS AND IODINE DEFICIENCY

RON FUGE
University of Wales

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I. INTRODUCTION

Iodine has long been known as an essential element for humans, and mammals in general, where it is concentrated in the thyroid gland. It is a component of the thyroid hormone thyroxine. Deprivation of iodine results in a series of iodine deficiency disorders (IDD), the most common of which is endemic goiter, a condition where the thyroid gland becomes enlarged in an attempt to be more efficient. Iodine deficiency during fetal development and in the first year of life can result in endemic cretinism, a disease which causes stunted growth and general development along with

brain damage. However, while these two diseases are easily recognizable, perhaps the more insidious problem is that iodine deficiency impairs brain development in children even when there is no obvious physical effect. Indeed it has been suggested that iodine deficiency is the most common preventable cause of mental retardation (see *Geological Impacts on Nutrition, and Biological Responses of Elements*, this volume).

Endemic goiter and cretinism along with related IDD have long been recognized as serious health problems and consequently much work has been carried out on the etiology and geographical distribution of these diseases. Many authors have suggested the involvement of several other elements in the etiology of these diseases, whereas a group of sulfur-containing compounds, thiocyanates and thiouracils, identified collectively as goitrogens, have been strongly implicated in some endemics. These compounds have been found to either inhibit iodine uptake by the thyroid gland or inhibit the formation of the thyroid hormones. However, it is generally agreed that the primary cause of IDD is a lack of iodine in the diet.

Iodine was the first element recognized as being essential to humans and the disease of endemic goiter was the first to be related to environmental geochemistry. Indeed, this disease appears to have been identified by the ancient Chinese. One Chinese medical writer from the 4th century AD noted the use of the seaweeds *Sargassum* and *Laminaria* (which are known to

be very iodine rich) for treatment of goiter (Langer, 1960). However, there are many earlier records in ancient literature of seaweeds and burnt sea sponges used in the treatment of endemic goiter possibly from as early as 2700 BC (Langer, 1960). Iodine was discovered by the French chemist Bernard Courtois in 1811 when he accidentally added concentrated sulfuric acid to the seaweed *Fucus vesiculosus*, one of the seaweeds used in goiter treatment. It was soon realized that iodine was the active ingredient in the treatment. Iodine was later identified as an essential element in human nutrition. Despite this early recognition of the role of iodine in endemic goiter and related disorders, it is apparent that IDD is still affecting large numbers of people worldwide, with some estimates suggesting that around 30% of the world's population are at risk. Prior to the middle of the 20th century iodine-deficiency problems affected virtually every country (Kelly & Snedden, 1960). Although the problem has been eradicated in many countries, it is still a major concern in the developing world. In addition it has been shown recently that some more affluent countries in western Europe are also affected with IDD. Delange (1994) suggested that 50–100 million people in Europe are at risk.

The areas where IDD are concentrated tend to be geographically defined. Thus many of the most severe occurrences of endemic goiter and cretinism have been found to occur in high mountain ranges, rain shadow areas, and central continental regions (Kelly & Snedden, 1960). This distribution of IDD results from the unique geochemistry of iodine. Geochemists generally agree that little iodine in the secondary environment is derived from weathering of the lithosphere. Most iodine is derived from volatilization from the oceans with subsequent transport onto land (Goldschmidt, 1954). Therefore, to understand the role of soil iodine geochemistry in IDD it is essential to consider some aspects of the general geochemistry of iodine and its cyclicity in the environment.

II. IODINE GEOCHEMISTRY

Iodine has been shown to be concentrated in seawater, in the biosphere, and in the atmosphere. Because of this, it is classified as a hydrophile, biophile, and atmophile element (Goldschmidt, 1954). In addition iodine has been found to be concentrated in sulfur-containing minerals causing it to be classified as a chalcophile element.

A. The Lithosphere

In the lithosphere iodine is an ultra-trace element; its crustal abundance is estimated to be 0.25 mg kg^{-1} by Fuge (1988) and more recently 0.3 mg kg^{-1} by Muramatsu and Wedepohl (1998). Due to the large ionic radius of the iodide ion (220 pm), it is thought unlikely that iodine enters the crystal lattices of most rock-forming minerals. In fact the iodine content of the various rock-forming minerals has been shown to be fairly uniform and low, with some enrichment found in only the chlorine-containing minerals sodalite and eudialyte. Its distribution in the different igneous rocks is fairly uniform (Table I) with only volcanic glasses showing comparative enrichment. Some data suggest that carbonatites are also somewhat richer in iodine than average igneous rocks.

Sedimentary rocks show a greater range of iodine content with clay-rich or argillaceous rocks more enriched than the sand-rich, arenaceous rocks (Table I). The highest concentrations of iodine have been found in organic-rich shales, with concentrations as high as 44 mg kg^{-1} recorded in some bituminous shales. The iodine content of carbonate rocks (limestones) and shales is highly variable but generally correlates with the amount of organic matter.

Recent sediments of marine origin can be extremely enriched in iodine with concentrations of up to $20,000 \text{ mg kg}^{-1}$ recorded in some surficial sediments (Wong, 1991).

It seems likely that the iodine content of metamorphic rocks is similar to that of igneous rocks. Recent

TABLE I. Iodine in Igneous and Sedimentary Rocks

Rock type	Mean iodine content (mg kg^{-1})
Igneous rocks	
Granite	0.25
All other intrusives	0.22
Basalts	0.22
All other volcanics	0.24
Volcanic glasses	0.52
Sedimentary rocks	
Shales	2.3
Sandstones	0.80
Limestones	2.3
Organic-rich shales	16.7

analytical data produced by Muramatsu and Wedepohl (1998) suggest that metamorphic rocks have uniformly low iodine contents of $<0.025 \text{ mg kg}^{-1}$. The same authors suggest that felsic igneous rocks are also very low in iodine with $<0.009 \text{ mg kg}^{-1}$. It is suggested that the low concentrations are due to volatilization of iodine during the formation of these rocks.

B. The Marine Environment

Seawater is by far the biggest reservoir of iodine; its average concentration is about $60 \mu\text{g L}^{-1}$ (Wong, 1991). Iodine is thought to have fairly uniform concentrations with depth, but it is slightly depleted in surface ocean waters because it is concentrated by organisms. Iodine can exist in several forms in seawater and the transformations between the various forms and their mechanisms are vital for understanding the cycling of iodine in the general environment.

Inorganic iodine is essentially present in two forms, the iodide anion, I^- , and the iodate anion, IO_3^- . Iodate is the thermodynamically stable form of inorganic iodine in oxygenated, alkaline seawater, whereas iodide, the reduced species, is in a metastable state. There is considerable variation of the I^-/IO_3^- ratio with depth with I^- enriched in surface waters and depleted in deeper waters. There is also considerable geographic variation of the I^-/IO_3^- ratio with waters from the shallower inner shelf areas containing more iodide than the deeper mid-shelf waters. The conversion of IO_3^- to I^- is thought to be due to biological activity, with the enzyme nitrate reductase implicated in the reaction. The increased iodide in surface and shallow shelf waters is thus thought to be due to the high biological activity in these zones. However, it is possible that some abiological mechanisms might also be involved in the conversion of iodate to iodide. Once formed, iodide is only slowly re-oxidized to iodate (Wong, 1991).

It has long been suggested that some iodine in seawater is present as an organic phase, and recently it has been found that in some coastal waters dissolved organic iodine can constitute up to 40% of the total iodine content (Wong & Cheng, 1998). Although Wong (1991) has indicated that few specific organo-iodine compounds have been identified in seawater, one of the substances identified, methyl iodide (CH_3I), is of interest due to its volatility and possible role in the transfer of iodine from the oceans to the atmosphere. Lovelock et al. (1973) were the first researchers to detect methyl iodide in seawater. This compound can

be formed both biologically, by seaweeds and phytoplankton, and by photochemical reactions, with the likelihood that chemical formation of methyl iodide is more important in the open ocean. Recently it has been found that methyl iodide is oversaturated in surface ocean waters (Moore & Grosko, 1999).

The strong enrichment of iodine in marine organisms has long been recognized with Courtois discovering the element in the brown alga *F. vesiculosus*. Since that time brown algae have been shown to strongly concentrate iodine with an enrichment factor of alga/seawater having been estimated as being over 32,000 (Fuge & Johnson, 1986). Although concentration factors for red and green algae are lower, they are still enriched in iodine. Phytoplankton also concentrates iodine.

It is generally held that the iodide ion is preferentially incorporated into the organisms; however, it has been demonstrated that phytoplankton can take in iodate (Moisan et al., 1994). Whatever the mechanism of uptake, these marine organisms play an important role in transformation of iodine species and ultimately in its transfer from the oceanic environment to the atmosphere. It has been demonstrated that organo-iodine compounds are released from brown seaweeds and this could represent a source of atmospheric iodine.

C. Transfer of Iodine From the Marine to Terrestrial Environment Via the Atmosphere

Iodine has been shown to be concentrated in the atmosphere. This atmophile behavior is the most important part of its geochemical cycle, with the transfer of iodine from the oceans to the atmosphere ultimately governing its distribution in the terrestrial environment.

The mechanism of transfer of iodine from the oceans to the atmosphere has been a subject of some debate. Undoubtedly some iodine is transferred to the atmosphere as seawater spray. However, it has been shown that the amount of iodine relative to chlorine in the atmosphere is several hundred times that in seawater. Although some of the iodine is likely to be in aerosols, it has also been shown that a large percentage of atmospheric iodine is in a gaseous form (Duce et al., 1973). Therefore, the major mechanism of iodine transfer must reflect preferential volatilization of seawater iodine into the atmosphere.

The iodide ion can be converted to elemental iodine (I_2) by photochemical oxidation, and this has been proposed as a mechanism for volatilization of iodine from the oceans. More recently it has been proposed that I_2

(and possibly HOI) could be produced at the sea surface from oxidation of iodide by such species as ozone and nitrogen dioxide (Garland & Curtis, 1981; Heumann et al., 1987). However, some workers have suggested that volatilization of elemental iodine is not likely to be a major source of transfer of iodine from the oceans to the atmosphere.

As methyl iodide has been found to occur in the surface waters of the sea and as this compound is volatile, it could represent a significant source of atmospheric iodine. Yoshida and Muramatsu (1995) found that on the Japanese coast 90% of atmospheric iodine is gaseous with organically bound iodine as the dominant species. In addition, Gabler and Heumann (1993) found that organically bound iodine is the most abundant species of iodine in European air. In the atmosphere methyl iodide is broken down and has an estimated lifetime of about five days (Zafirou, 1974).

Whereas several authors have suggested that methyl iodide is the dominant form of iodine released from the oceans, it seems likely that there are several mechanisms of transfer of iodine from the oceans to the atmosphere and ultimately to the landmasses. From studies in Antarctica, Heumann et al. (1990) suggested that during short distance transport into coastal areas iodine is carried as I_2 , HI, and sea spray; for long distance transport CH_3I is responsible. The residence time of inorganic iodine in the atmosphere has been estimated to be 10 days (Rahn et al., 1976; Chameides & Davis, 1980) and the total residence time of iodine has been estimated to be 15 days (Kocher, 1981).

Iodine is transferred from the atmosphere to the terrestrial environment by wet and dry deposition. On the basis of the marine origin of atmospheric iodine it might be expected that deposition should be highest at the coast and decrease inland. However, literature data are limited on the iodine content of rain from coastal and inland locations. Several workers have quoted data for the iodine content of rainfall in the UK, the whole of which has a strong maritime influence. Generally the samples were found to contain around $2 \mu\text{g L}^{-1}$ iodine with some higher values (up to $5 \mu\text{g L}^{-1}$) recorded in coastal rainfall. It has been shown that rain collected from an upland area 12 km inland from the mid-Wales coast contained over three times as much iodine as rainfall from 84 km inland. Although some studies of iodine contents of rainfall have failed to demonstrate significantly higher values in coastal rain, analyses of rainfall from the continental United States (Missouri) showed iodine contents of $<1.0 \mu\text{g L}^{-1}$, and it does seem likely from the limited data that the iodine content of rain is influenced by its proximity to the oceans.

The form of iodine in rainfall has been the subject of much discussion. In general it has been shown that iodide is the most common form of iodine in rain making up over 50% of rainfall iodine, and the iodate ion is the second major component. It has also been demonstrated that the iodate content of rainfall decreases inland with iodide content showing a parallel increase. In view of the likely importance of organically bound forms in atmospheric transport of iodine, it would seem likely that some iodine in rain should be present as organo-iodine, with an early study suggesting as much as 40% is organically bound (Dean, 1963). However, more recently, only small amounts of "non-ionic" dissolved iodine have been found to occur in Japanese rain; iodide and iodate are the dominant forms (Takagi et al., 1994). It seems likely that any atmospheric methyl iodide is converted to inorganic forms before deposition.

Dry deposition of iodine could be an important transfer mechanism for iodine from the atmosphere to the land surface. Few studies have attempted to quantify the amount of iodine deposited on land surfaces by dry deposition. Those studies suggest that dry deposition in marine influenced areas is a significant source of terrestrial iodine. However, there is no agreement on the relative importance of wet and dry deposition, and little is known with regard to the quantities of iodine in dry deposition in areas remote from the sea.

III. IODINE GEOCHEMISTRY OF SOILS

There is a considerable body of data for iodine in soils and this shows a very broad range of concentrations from <0.1 – 150 mg kg^{-1} . The iodine content of soils is generally considerably higher than the rocks from which they derive. Most geochemists agree that the majority of the iodine in soils is derived from the atmosphere and ultimately the marine environment. The proximity of an area to the sea therefore is likely to exert a strong influence on the iodine content of soils in that area. This also results in considerable geographic variation of soil iodine content. The other important feature of soil iodine geochemistry is the fact that the element can become strongly adsorbed by various soil components, and thus its concentration and behavior in soils is going to depend on soil composition. In this respect the nature of the composition of the soil parent material indirectly exerts a strong influence on the iodine chemistry of the soil. The iodine geochemistry

of soils then can be summarized as dependent on the quantity of iodine supplied coupled with the soil's ability to retain this iodine.

A. Factors Influencing the Supply of Iodine to Soils

It has generally been suggested that soils in close proximity to the coast are likely to be enriched in iodine with those far removed from the coast depleted of iodine (Goldschmidt, 1954) (see also Table II). However, in some cases such a relationship is not obvious and some workers have found no correlation between iodine and distance from the sea. This has led some workers to suggest that marine influence extends a considerable distance inland. Whitehead (1984), for instance, suggested that all soils from the UK are affected by the strong maritime influence over the whole country and that low iodine soils would only be found in the middle of continental areas. To some extent this is true, but it is perhaps pertinent to point out that in a soil traverse from the Welsh coast 120 km inland (Figure 1), it was found that samples from beyond 100 km (8 samples) contained between 2 and 3 mg kg⁻¹ of iodine. Similarly, a traverse from the Irish coast showed that soil samples collected beyond 80 km inland contained between 1.7

and 2.8 mg kg⁻¹. These values are not much higher than concentrations in soils from continental United States (Table II). On this basis it is quite likely that the strong influence of the marine environment on soil iodine contents does not extend very far inland.

TABLE II. Iodine in Coastal and Inland Soils

Sample origin	Iodine Range Units	Content Mean Units	Ref.
Coastal areas			
Northwest Norway	5.4–16.6	9.0	Låg & Steinnes (1976)
Wales	1.5–14.9	14.7	Fuge (1996)
Ireland	4.2–5.4	14.7	Fuge (unpublished)
Inland areas			
East Norway	2.8–7.6	4.4	Låg & Steinnes (1976)
Wales/England	1.8–10.5	4.2	Fuge (1996)
Missouri, U. S.	0.12–5.6	1.3	Fuge (1987)
Whole of U. S. ^a	<0.5–9.6	1.2	Shacklette & Boerngen (1984)

^aIncludes some from coastal localities.

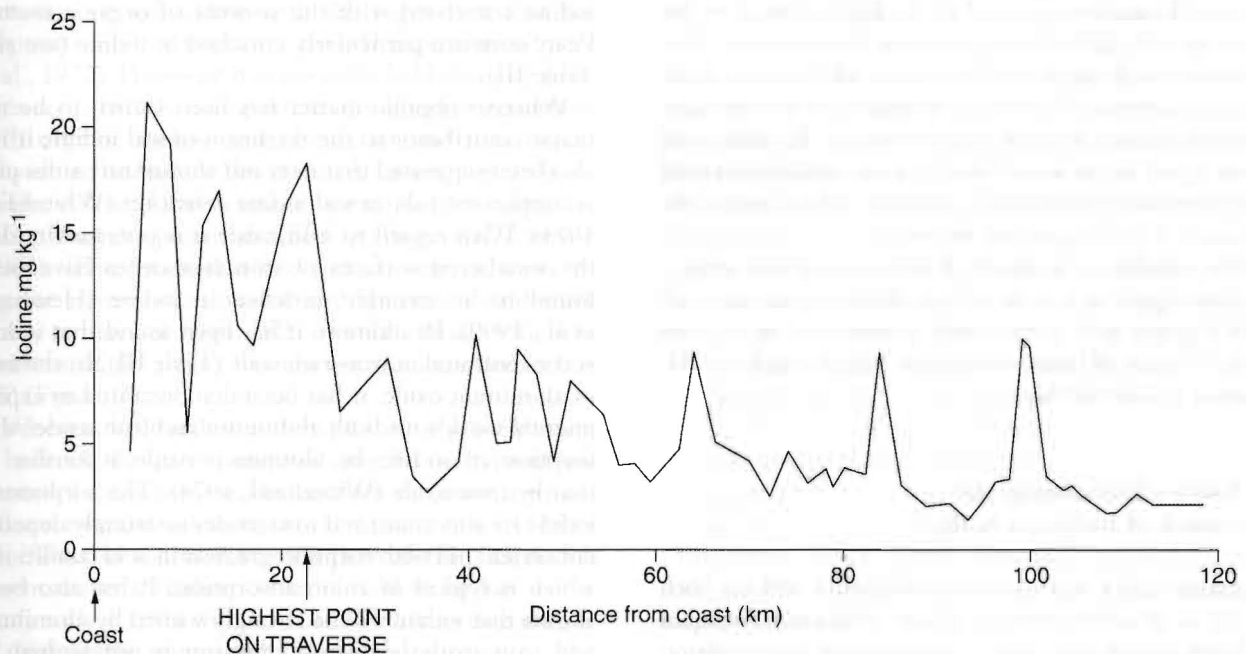


FIGURE 1 Iodine in topsoils on a traverse from the west Wales coast to the English Midlands. (After Fuge, 1996.)

TABLE III. Iodine Content of Various Soil Types

Soil type	Iodine Range Units	mg kg ⁻¹ Mean	Ref.
Peats (70% organic matter), UK	28-98	56	Johnson (1980); Fuge & Johnson (1986)
Peats, UK	18.7-98.2	46.8	Whitehead (1984)
Peaty tundra soils, Russian Plain	0.2-42	12.0	Vinogradov (1959)
Non-peaty soils, Russian Plain	0.3-9.8	2.8	Vinogradov (1959)
Iron-rich soils, UK	7.5-32.5	16.0	Fuge & Ander (1998) and unpublished information
Chalk and limestone parent material, UK	7.9-21.8	13.0	Whitehead (1984)
Over limestone, Derbyshire, UK	2.58-26.0	8.2	Fuge (1996)
Over shale, sandstone, and dolomite, Derbyshire, UK	1.88-8.53	3.44	Fuge (1996)
Carbonate-rich soils, Austria	1.64-5.63	3.75	Gerzabek et al. (1999)
Carbonate-free soils, Austria	1.08-4.80	2.58	Gerzabek et al. (1999)
Clay parent material, UK	2.1-8.9	5.2	Whitehead (1984)
Sand and sandstone parent material, UK	1.7-5.4	3.7	Whitehead (1984)
River and terrace alluvium parent material, UK	0.5-7.1	3.8	Whitehead (1984)
Marine estuarine alluvium parent material, UK	8.8-36.9	19.6	Whitehead (1984)

The influence of topography on the iodine concentration of soils is well illustrated in Figure 1. The highest values in the traverse occur in soils over the Welsh Mountains, which range up to 350 m (Ordnance Datum). In addition, several of the higher values in the latter half of the traverse occur on high ground. The greater precipitation that occurs in the upland areas causes a greater degree of washout of atmospheric iodine and hence a higher input of iodine. An additional factor is that in the area of the traverse, upland soils tend to be organic rich and thus are more able to retain the increased iodine input (see below).

The corollary of washout of iodine in upland areas is the low supply of iodine to rain shadow areas beyond. This is going to be particularly pronounced in the rain shadow areas of high mountain ranges such as the Himalayas and the Alps.

B. Factors Influencing the Retention of Iodine in Soils

As stated earlier soil iodine geochemistry reflects both the input of iodine and the ability of the soil to retain it. Many factors have been implicated in the retention of iodine in soil. Iodine is strongly enriched in organic-

rich sediments and it seems likely that one of the most influential soil components with regard to retention of iodine is organic matter. Soils rich in organic matter are frequently enriched in iodine with the concentration of iodine correlated with the content of organic matter. Peaty soils are particularly enriched in iodine (see also Table III).

Whereas organic matter has been shown to be the major contributor to the retention of soil iodine, it has also been suggested that iron and aluminum oxides play an important role in soil iodine retention (Whitehead, 1974). With regard to iron oxide it is noteworthy that the weathered surfaces of iron meteorites have been found to be strongly enriched in iodine (Heumann et al., 1990). In addition, it has been found that iodine is concentrated in iron-rich soils (Table III). In the case of aluminum oxide, it has been demonstrated in experimental work with both aluminum and iron oxides that sorption of iodide by aluminum oxide is similar to that by iron oxide (Whitehead, 1974). The sorption of iodide by aluminum and iron oxides is strongly dependent on soil pH with sorption greatest in acid conditions, which is typical of anion adsorption. It has also been shown that iodate will be strongly sorbed by aluminum and iron oxides; however, this ion is not sorbed by organic matter.

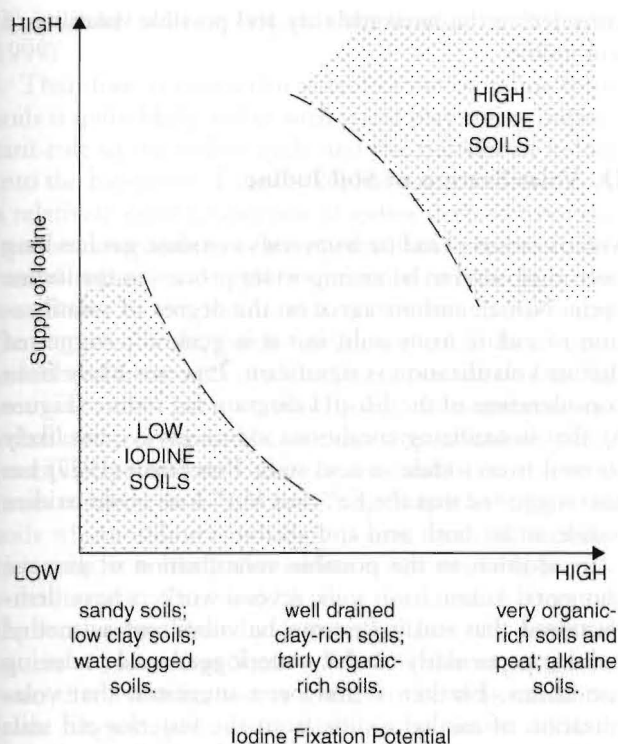


FIGURE 2 A simplified model for iodine content of soils based on supply and fixation potential. (Modified from Fuge & Johnson, 1986.)

Clay minerals have been thought to be involved in retention of soil iodine with the suggestion that the sorption of iodine to clays is also pH dependent (Prister et al., 1977). However, it is generally held that clay minerals are relatively unimportant in soil iodine retention, with organic matter and aluminum and iron oxides providing the bulk of the retentive capacity of soils.

The ability of soil to retain iodine has been called the iodine fixation potential (IFP) by Fuge and Johnson (1986). Thus soils that are rich in one or more of organic matter, iron oxides, and aluminum oxides are likely to have a high IFP, whereas those with low amounts of the major fixation components have a low IFP (Figure 2).

Whereas little iodine is derived from the weathering of bedrock, the parent material governs the type of soil formed. In this context, the bedrock can exert a strong influence on the iodine retention capacity of soils (Table III). Thus in the case of soils derived from sand-rich parent material, iodine contents tend to be low as the sandy soils derived will have little ability to trap iodine. A particularly interesting lithological control on the iodine content of soils occurs in areas underlain by

carbonate rocks. In such soils, which generally have alkaline or circum-neutral pH values, iodine contents are generally elevated. This association of iodine with carbonate bedrocks is particularly well illustrated when comparing the iodine content of soils overlying limestone with neighboring soils overlying non-limestone lithologies as illustrated for the Derbyshire area of the U.K. (Table III). A similar relationship has been demonstrated for carbonate-rich versus non-carbonate soils from Austria (Gerzabek et al., 1999) (see Table III). It has been shown that the soils overlying limestone have distinctly higher iodine contents and hence have a high fixation potential.

Whereas soils do not normally derive much iodine from their parent materials, where the parent material is sediment of fairly recent marine origin and likely to be iodine-rich, the soils derived could inherit some of their iodine from the parental source (Table III). In addition, it is likely that soils recently inundated by marine incursions or those that occur over reclaimed marine areas will be high in iodine.

As iodine is generally strongly sorbed within soils, very little is in a water-soluble form. Various researchers have found that up to 25% is in a soluble form with the water-soluble content of the majority of soils being less than 10% (Johnson, 1980). In most high-iodine, organic-rich soils water-soluble iodine accounts for much less than 10% of the total. More recently, a study of German soils revealed that 2.5–9.7% of the iodine was water soluble; however, in the same soils ^{129}I , recently added from a nuclear reprocessing plant, was considerably more soluble (21.7–48.7%). This suggests that natural iodine had become strongly bound through time (Schmitz & Aumann, 1994). For most soils it can be confidently predicted that water-soluble iodine will account for only a small percentage of the total, but in arid areas alkaline soils are likely to contain more elevated amounts of water-soluble iodine.

Whereas iodine sorbed in soils is generally strongly held and is not easily desorbed, it has been suggested that iodine is strongly desorbed in waterlogged soils. Thus Yuita et al. (1991) demonstrated that under flooding, and the resultant reducing conditions, 2–3 times as much iodine is solubilized from soils as in dry, oxidizing conditions. Such waterlogged, reducing conditions are typical of rice paddies and strong desorption of iodine has been found to occur in these soils (Muramatsu et al., 1996). Similarly lowland Japanese soils are low in iodine. It is suggested that this is due, in part, to flooding and desorption from the reducing conditions occasioned by microbial activity (Muramatsu & Yoshida, 1999).

C. Chemical Form of Iodine in Soils

As outlined in the previous section of this chapter, in most soils iodine is strongly bound to organic matter and iron and aluminum oxides. However, it is of interest to establish the form of the soluble or easily leached iodine in soils as this is the fraction which should be plant available. Several authors have found that the iodide ion is the dominant form of soluble soil iodine in acidic soils, particularly in waterlogged soils. However, in dry, oxidizing conditions iodate was found to be the dominant form of soluble iodine. The dominance of iodide in acidic soils, with iodate dominating in alkaline soils, demonstrates the importance of pH in governing the form of soluble iodine. However, Eh will also exert an important control on the form of soil iodine. It has also been demonstrated that Fe^{3+} and SO_4^{2-} reducing bacteria found in soils are capable of reducing iodate to iodide (Councell et al., 1997).

Despite some conflicting evidence in the literature, from the Eh-pH diagram for iodine (Figure 3), it seems likely that in acid soils soluble iodine will predominate as iodide, whereas in alkaline soils iodate will be dominant. As will be discussed later, this is important when

considering the bioavailability and possible volatility of soil iodine.

D. Volatilization of Soil Iodine

Volatilization of iodine from soils as iodine gas has long been suggested to be an important process in the iodine cycle. Not all authors agree on the degree of volatilization of iodine from soils, but it is generally suggested that its volatilization is significant. It seems likely from consideration of the Eh-pH diagram for iodine (Figure 3), that in oxidizing conditions iodine gas is quite likely formed from iodide in acid soils. Perel'man (1977) has also suggested that the Fe^{3+} and Mn^{++} ions could oxidize iodide under both acid and alkaline conditions.

In addition to the possible volatilization of gaseous elemental iodine from soils, several workers have demonstrated that soil iodine can be volatilized as methyl iodide, particularly under waterlogged and reducing conditions. Further, it has been suggested that volatilization of methyl iodide from the waterlogged soils may be a contributory cause of the low iodine contents

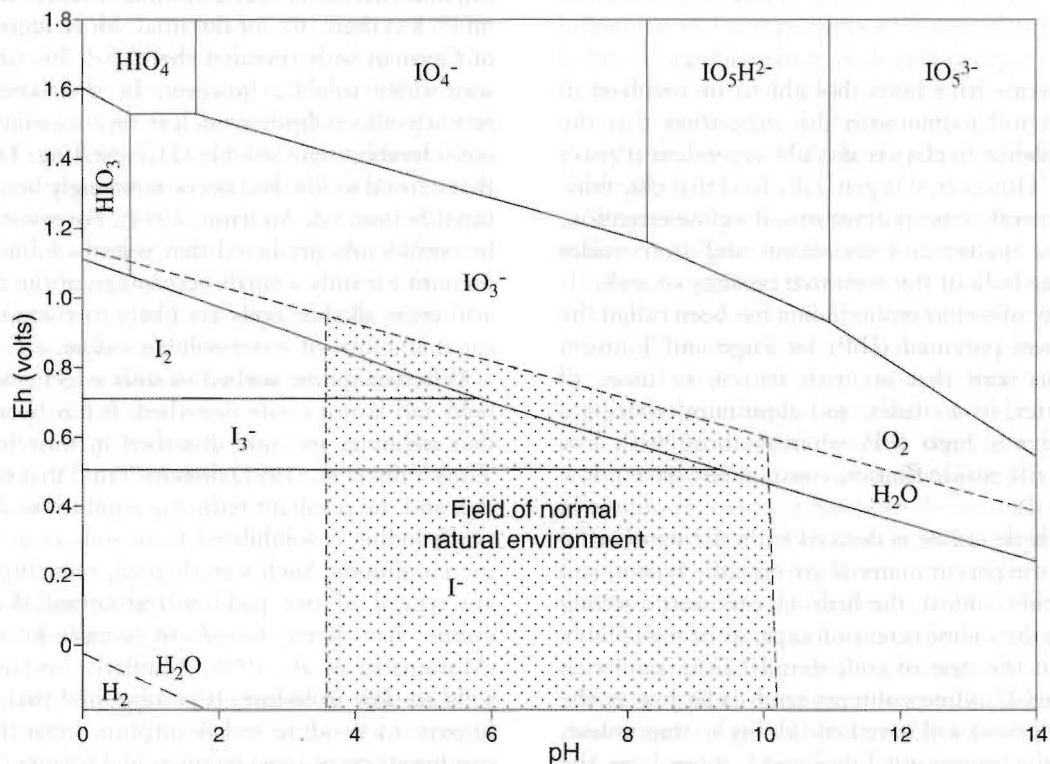


FIGURE 3 Eh-pH diagram for iodine. (Modified from Vinogradov & Lapp, 1971 and Bowen, 1979.)

of lowland soils in Japan (Muramatsu & Yoshida, 1999).

Therefore, it seems that volatilization of iodine from soils is quite likely and as such could play a very important role in the iodine cycle and the transfer of iodine into the biosphere. Fuge (1996) has suggested that only a relatively small proportion of iodine derived from the marine environment is transported into central continental regions and regions generally remote from the sea. Some of the iodine that occurs in environments far removed from marine influence could have been volatilized from soils, with iodine deposited on land by wet and dry precipitation being subsequently re-volatilized enriching the atmosphere in iodine. Such precipitation and re-volatilization could occur several times resulting in iodine migrating "stepwise" inland. In soils where iodine is strongly bound, such as organic-rich soils, it is likely that iodine is not available for re-volatilization. This could have a detrimental effect on the local iodine cycle by depriving plants of a potential source of iodine (see Section IV). It is also important to note that volatilization is going to be dependent on both Eh and pH, with volatilization under alkaline oxidizing conditions very unlikely, which is a possible explanation for the elevated iodine contents of the circum-neutral to alkaline soils occurring over limestone (Table III).

IV. TRANSFER OF IODINE FROM SOIL TO PLANTS

When iodine is strongly sorbed in most soils it will not be readily bioavailable. Therefore, the presence of high iodine concentrations in soil does not necessarily mean that plants growing in the soil will incorporate large concentrations of iodine; indeed, it has been shown that there is no correlation between the iodine content of soils and the plants growing on them (Al-Ajely, 1985). This is particularly important when considering the distribution of IDD. An additional consideration is that iodine in high concentrations has been shown to be toxic to most plants (Sheppard & Evenden, 1995), with high iodine uptake in rice plants thought to be responsible for Akagare disease (Yuita, 1994b).

In most circumstances the major pathway of elements into plants is through the root system followed by translocation to the upper parts of the plant. For iodine it has been shown experimentally that it can be taken in through the root system of plants with the iodide ion

more readily incorporated than iodate. However, it has also been demonstrated that there is little translocation from the roots to the aerial parts of the plant. In some circumstances high concentrations of iodine have been shown to occur in rice grown on flooded soil, which leads to Akagare disease. This has been suggested to be due to high soluble iodide in soils, which results in greater uptake by the roots; however, it has been demonstrated that there is only a relatively small increase in the iodine content of rice grown in flooded soil when compared with rice grown on drained soil, but submerged leaves when compared to other leaves showed dramatically increased iodine content.

From these considerations it seems likely that root uptake of iodine is relatively unimportant for the overall iodine content of plants. It is probable that the most important pathway into plants is from the atmosphere by direct absorption. Experiments utilizing radioactive isotopes of iodine have demonstrated that plant leaves can absorb this iodine, and it has been found that the absorption of gaseous iodine by leaves increases with increasing humidity. This is probably due to increased opening of the leaf stomata. Iodine absorbed through the leaf can be translocated through the rest of the plant, albeit slowly.

While the uptake of gaseous iodine has been demonstrated to be significant, doubt has been expressed that significant amounts of methyl iodide could be taken in through the stomata. However, even if little is absorbed, atmospheric iodine, whatever the form, could be deposited on plant surfaces and as such could represent a significant source of iodine to grazing animals, etc. The source of the atmospheric iodine in near-coastal areas will be mainly marine. However, the source in inland areas could be derived in part from iodine volatilized from soil, in some circumstances this being very significant.

The uptake of iodine into plants is, therefore, accomplished in two ways: through the roots and through leaf stomata. The latter is probably the most important. However, it must be stressed that the bioavailability of iodine in soils is low, whatever the preferred uptake route. Thus, strongly bound iodine will not be bioavailable for either root uptake or for volatilization from the soils. Several workers have quoted soil-to-plant concentration factors for iodine (iodine in plant/iodine in soil); these are generally very low and are in the range of 0.01–1.5 with most falling between 0.01 and 0.1 (Ng, 1982), while IAEA (1994) quoted a value of 0.0034 for grass. Variation of the plant concentration factor for different soil types has been demonstrated, and Muramatsu et al. (1993) quoted factors for brown rice

grown on an andosol and gray lowland soil in Japan of 0.007 and 0.002, respectively.

Not surprisingly then, the iodine content of plants is generally low. Grass and herbage analyses from many different countries have shown iodine contents to be about 0.2 mg kg^{-1} ; a typical example being for the UK with an estimated mean of $0.22 \pm 0.16 \text{ mg kg}^{-1}$ (Whitehead, 1984). In a study of Japanese plants Yuita (1994a) found the mean iodine content of different plant parts to be green leaves 0.46 mg kg^{-1} , fruit 0.14, edible roots 0.055, and seeds 0.0039.

V. IODINE SOURCES FOR HUMANS

The daily recommended dietary intake of iodine is variously quoted but is estimated to be 110–130 $\mu\text{g/day}$ for children under the age of 1, 90–120 $\mu\text{g/day}$ for children aged 1–10, and 150 $\mu\text{g/day}$ for adults and adolescents, with higher concentrations required during pregnancy and lactation (see *Geological Impacts on Nutrition*, this volume). The traditional view is that humans derive their iodine from consumption of crops and vegetables, etc. In near-coastal areas such a source may provide sufficient iodine. However, in inland areas this will provide only relatively low quantities of iodine. In this context it has been demonstrated that vegetarian diets result in low iodine intake, which could lead to iodine deficiency (Davidsson, 1999; Remer et al., 1999) (see also Chapter 7, this volume).

Seafood is a potentially rich source of dietary iodine and, where such food is a major part of the diet as in Japan and Iceland, some problems of excess iodine in the diet have been described. A high iodine intake causes a decrease of thyroid hormone production resulting in formation of "high iodine goiter." However, at the present time the major source of dietary iodine in many developed countries is dairy produce such as milk, butter, and cheese, which are rich sources due to the addition of iodine to cattle feed and the use of iodine-containing disinfectants in the dairy industry. On this point, it is likely that the recent re-emergence of IDD in some affluent countries is due to the consumption of lower quantities of dairy produce in the move to "healthy eating."

It is also likely that even without iodine added to animal diets, animal products are probably enriched in iodine as grazing animals will take in iodine that has been deposited on the surfaces of grass and leaves; human preparation of food is likely to remove much of

this surface-deposited iodine. In addition animals are known to inadvertently consume soil and this could add iodine that is not bioavailable to plants. This source of iodine has been shown to prevent iodine deficiency in grazing animals in some areas where pasture is iodine deficient as in New Zealand and Tasmania (see *Geophagy and the Involuntary Ingestion of Soil*, this volume), even though the soil contains only 1–2 mg kg^{-1} . In this context it is also of note that Lidiard (1995) found that farm animals in Exmoor, Somerset, UK, developed iodine deficiency symptoms when grazing areas of reclaimed land. These areas, which are about 40 km from the sea, were originally covered in peat and previous to reclamation no iodine-deficiency problems had occurred. Thus it seems likely that the animals had previously obtained iodine from inadvertent intake of peat.

It is possible that humans may obtain some iodine by inhalation, particularly in near-coastal environments. While it is indeed possible that some atmospheric iodine might be inhaled even in areas remote from the sea, this is unlikely to be a major component of iodine intake. It is of note that the Nordic Project Group (1995) suggested that an individual acquires only 0.5 μg per day from inhalation.

Although it has been suggested that some dietary iodine derives from drinking water, generally this source is unlikely to provide more than 10% of the daily adult iodine requirement. However, very high iodine drinking waters derived from groundwater have been recorded in some areas of China. In these areas it has been found that goiter incidence is negatively correlated with the iodine content of the drinking water. In some areas of China, such as around Bohai Bay in Hebei and Shandong Provinces and in some areas of Xinjiang and Shanxi Provinces, drinking waters contain between 100 and 200 $\mu\text{g L}^{-1}$ and the incidence of goiter was found to be positively correlated with the iodine content of the water. The high iodine causes populations in the areas to suffer from high iodine goiter (Tan, 1989).

VI. THE GLOBAL DISTRIBUTION OF IODINE DEFICIENCY DISORDERS AND THE IODINE CYCLE

The most important parts of the iodine cycle, in terms of the environmental distribution of iodine and its impact on human health, are summarized in Figure 4.

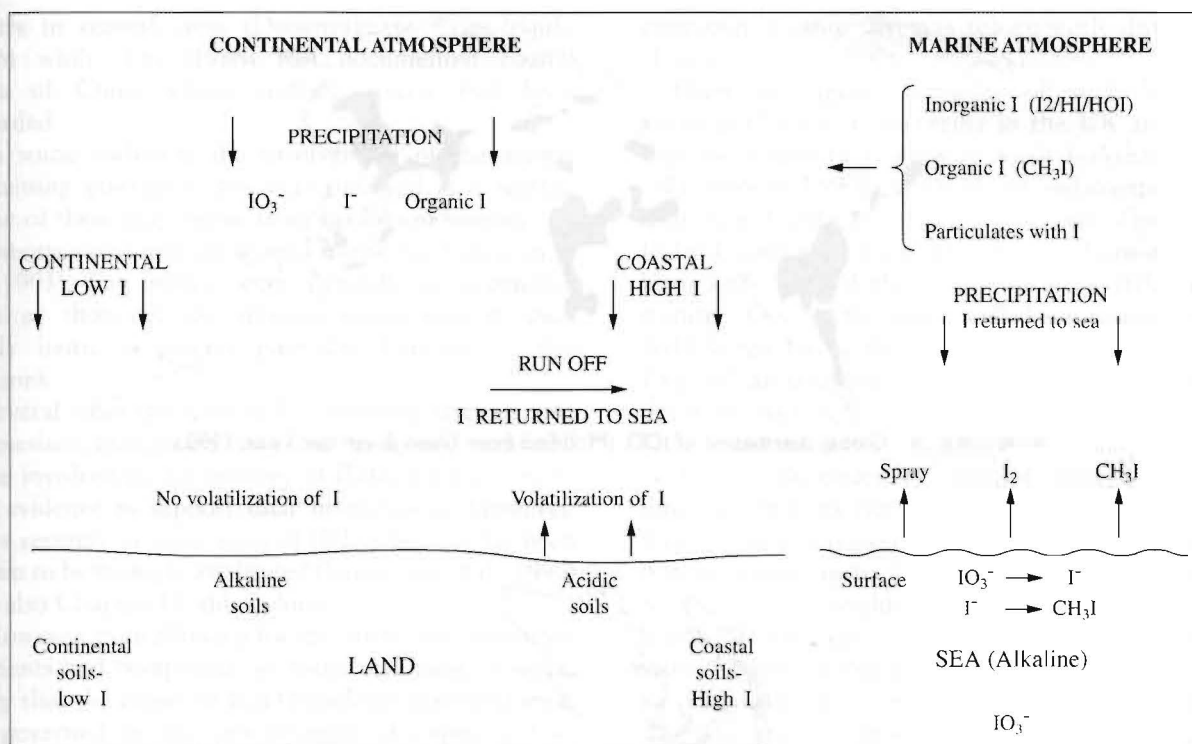


FIGURE 4 A simplified model of part of the iodine cycle.

Prior to about 1950 IDD had affected virtually every country in the world. Because the problem is known to be essentially due to the lack of iodine in the diet, it has been possible to introduce schemes for the mass treatment of affected populations such as the addition of iodine to the diet through the use of iodized salt and bread, etc., injections of iodized oil, or the addition of iodine to irrigation waters (see Cherian and Nordberg, this volume), which results in the alleviation of the symptoms in many countries. It was noted in the 1970s that IDD had been effectively eradicated in the developed world and endemic goiter was described as a disease of the poor that was largely confined to third world countries. However, it is important to point out that in the 1990s iodine deficiency has been reported to occur in several affluent countries in western Europe, probably as a result of dietary changes. This suggests that such changes could cause the reintroduction of IDD in many countries.

The global distribution of iodine-deficiency problems is shown in Figure 5. This figure is based on the data in Dunn and van der Haar (1990) and is limited as data are lacking for some areas such as parts of Africa and the Middle East.

As outlined by Kelly and Sneddon (1960) many of the areas affected by iodine deficiency are remote from marine influence. Many of the areas highlighted are the mountainous regions and their rain shadow areas such as the Himalayan region, the European Alps region, and the Andean Chain. Tan (1986) has indicated that many of the extremely seriously affected IDD areas of China are the mountainous and hilly regions over the whole country. Central continental regions, such as those of Africa and China, are also well-documented areas of iodine deficiency. In all of these situations IDD can be explained according to the classic explanations of low iodine supply and hence low iodine availability. Thus in continental areas such as the central United States, where iodine-deficiency problems were described prior to the 1950s (Kelly & Sneddon, 1960), soil iodine is relatively low with concentrations typically 1.3 mg kg^{-1} (Table II).

However, many endemias are not explicable in these simplistic terms and several countries and regions that are close to the coast have been known to suffer from IDD problems. For example, large regions of the UK have histories of IDD, despite the strong maritime influence on the country (see Figure 6). IDD in Sri Lanka

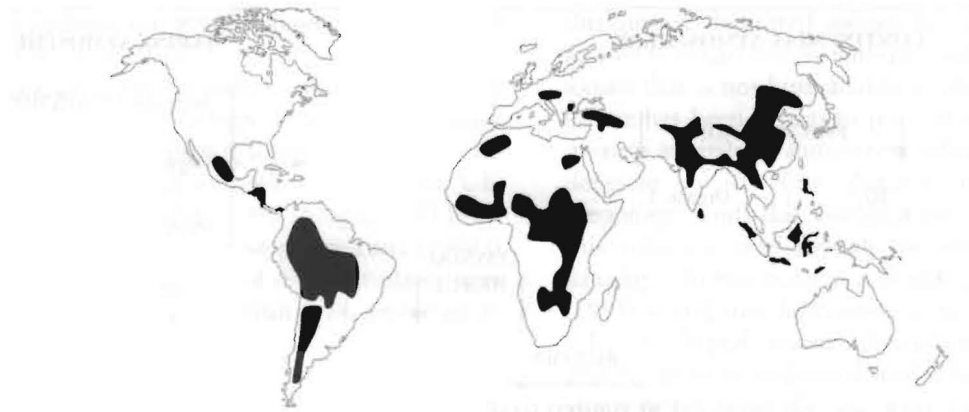


FIGURE 5 Global distribution of IDD. (Modified from Dunn & van der Haar, 1990.)



FIGURE 6 Distribution of IDD in the UK and Ireland. (Modified from Kelly & Snedden, 1960.)

occurs in coastal areas (Dissanyake & Chandrajith, 1996) while Tan (1986) had documented coastal areas of China where endemic goiter had been recorded.

In some endemias the involvement of the sulfur-containing goitrogens has been invoked as a reason. Some of these may derive from geological sources and be incorporated into drinking water or food (Gaitan et al., 1993), but others occur naturally in vegetables such as those of the *Brassica* genus and in such staple items as cassava (see also Chapter 8, this volume).

Several other elements such as fluorine, arsenic, zinc, magnesium, manganese and cobalt have been suggested to be involved in the etiology of IDD, but there is no real evidence to support their involvement. However, more recently in some areas of IDD selenium has been shown to be strongly implicated (Vanderpas et al., 1990) (see also Chapter 15, this volume).

However, even allowing for the involvement of other elements and compounds in some endemias, it seems likely that the causes of IDD problems in several areas are governed by the geochemistry of iodine and its bioavailability. In some cases sandy soils have been found to occur in goitrous areas such as the coastal regions of China. Here any iodine added to the soil from atmospheric sources is going to be leached from the soil rapidly, which results in low-iodine soils. This means little iodine is available for any plants or crops growing in the region, thus depriving humans and livestock of a source of iodine.

In sandy soils iodine is not retained, as outlined in Section III of this chapter. The iodine retention capacity of soils is related to composition with organic matter, and iron and aluminum oxides are the most important retentive components. So that in general, high-iodine soils are rich in one or more of these components. The iodine sorbed by these soil components is strongly held and little has been found to be easily leachable, so that in general terms this strongly held soil iodine is non-bioavailable. Thus Tan (1986) noted that some peaty areas of China were goitrous. Similarly, several peaty areas of the UK, even though some are in coastal regions, are listed as goitrous by Kelly and Sneddon (1960).

Another example of environmental control on IDD would seem to be the strong association of some goitrous regions with limestone bedrock as first mentioned by Boussingault (1831) for a region of Columbia, and subsequently by several other researchers such as Perel'man (1977). This association of limestone with goitrous areas led to the suggestion that calcium was a

goitrogen, a claim that was subsequently disproved in clinical tests.

There are many examples of such limestone-associated endemias occurring in the UK and Ireland with the limestone regions of north Yorkshire historically renowned for its severe goiter and cretinism problems (see Figure 6). Similarly County Tipperary in Ireland, underlain by Carboniferous Limestone, was historically one of the major areas of IDD in that country. One of the most well-documented areas of IDD in the UK is the Derbyshire region of northern England, an area that is between 150 and 180 km from the west coast in the direction of the prevailing wind. Here endemic goiter was rife, known as "Derbyshire neck," with the endemia confined to areas underlain by limestone bedrock (see Figure 6). Analyses of soil in the former goitrous region have shown that iodine concentrations range up to 26 mg kg^{-1} with a mean value of 8.2 mg kg^{-1} . In neighboring areas underlain by non-limestone lithologies and with no history of IDD, soil iodine concentrations are lower with a mean of 3.44 mg kg^{-1} . Similarly, there is an area of north Oxfordshire, England, where endemic goiter was prevalent (Kelly & Sneddon, 1960) and where iodine-deficiency problems in school children were recorded as recently as the 1950s. This area is underlain by limestone and soil iodine ranges between 5 and 10 mg kg^{-1} .

IDD occurs in these limestone areas despite relatively high iodine in soils. This would imply that iodine is not bioavailable. Soils over the limestones would generally be well drained and circum-neutral to alkaline in nature. In these conditions any soluble soil iodine is likely to be present as the iodate anion (Figure 3). It has been shown that iodate uptake through plant roots is more limited than the uptake of iodide, thus in neutral to alkaline soils root uptake of iodine may be low.

In addition, as stated earlier, it is likely that plants derive much of their iodine from the atmosphere, through the upper parts of the plant. In the neutral to alkaline soils generally found overlying limestones where iodate is going to be the dominant soluble species of iodine, there is no possibility of conversion of this species to gaseous elemental iodine (see Figure 3). An additional factor is that in the well-drained soils there is going to be no conversion of iodine to methyl iodide. Thus in the limestone areas, plants will be deprived of a local source of atmospheric iodine.

The distribution of IDD reflects the geochemistry of iodine and, as stated above, with large areas of iodine deficiency occurring in central continental regions and mountainous and rain shadow areas, this distribution fits in with the classical explanation of IDD governed

by the external supply of iodine from the marine environment via the atmosphere. However, the geochemistry of iodine is more complex than this simplistic approach, and from a closer scrutiny of the distribution of IDD it is apparent that, in many cases, iodine-deficiency problems are related to the bioavailability of iodine in soils and are not related directly to the external supply of iodine.

VII. RADIOACTIVE IODINE IN THE ENVIRONMENT

A relatively recent problem regarding iodine and human health is that of anthropogenically produced radioactive iodine, a topic that has received considerable attention during the last two decades. Although the problem of radioactive iodine that is of anthropogenic origin is perhaps out of place in this chapter, it is included because the distribution of natural iodine is likely to have a marked influence on the health effects of the radioactive iodine.

Whereas natural iodine is essentially mono isotopic and the one stable isotope is ^{127}I , over 20 radioactive isotopes have been identified ranging from ^{117}I to ^{139}I . Of these radioactive isotopes only ^{129}I has a significantly long half-life of 1.6×10^7 years. Extremely small amounts of ^{129}I are produced naturally by spontaneous fission of uranium and also by spallation of xenon in the upper atmosphere. However, comparatively large quantities of ^{129}I are produced from nuclear fission fallout and reactors. The pre-nuclear age $^{129}\text{I}/^{127}\text{I}$ ratio has been estimated as 10^{-12} while present day "background values" have been estimated to be about 10^{-10} .

Relatively high concentrations of ^{129}I have been found in the biosphere around nuclear plants, and elevated concentrations of this isotope have been shown to occur in the thyroid glands of animals in the vicinity of nuclear installations. The release of fairly large quantities of ^{129}I from nuclear sources is of concern, but it is the allied release of the shorter lived isotopes ^{125}I (half-life 60 days), ^{131}I (half-life 8.04 days), and ^{133}I (half-life 20.9 hours) that represents the greater threat to human health. Of these it is ^{131}I that has been suggested to pose the greatest risk because it is produced in fairly large quantities from fission of enriched uranium (the yield is about 3%). It has a particularly high specific activity, and hence is highly radioactive. It has been estimated that in the Chernobyl accident, in April 1986, 35 million curies of ^{131}I was released.

The problem of the short-lived radioactive isotopes of iodine was first encountered in the early years of the nuclear industry after an accident at Windscale, UK, in 1957. Radioactive iodine was found to enter the biosphere rapidly and was found in plants and in cow's milk shortly after the accident. Presumably as the radioactive iodine would have been released as a gas, it could be absorbed through plant stomata and deposited on foliage. Thus the contaminant iodine passes fairly rapidly through the food chain and into humans where it can be taken into the thyroid gland. Once there, radioactive breakdown would result in an increased risk of thyroid cancer.

In areas where natural iodine is deficient, the problem of large releases of ^{131}I would be potentially very serious, as a sudden increase of iodine would result in a high percentage of bioavailable iodine that is radioactive. Thus much of the iodine entering the human body would be radioactive. The area around Chernobyl is situated in a central continental region and as such has a history of iodine deficiency (Kelly & Sneddon, 1960) with goiter found to occur in schoolchildren in the area. Since the Chernobyl accident there has been an increased incidence of childhood thyroid cancers, and this has been shown to be causally linked to the release of radioactive iodine.

VIII. SUMMARY

The lithosphere is generally depleted in iodine and although it contributes to iodine in soils through weathering of bedrock, this is not the most important part of the iodine geochemical cycle. The oceans represent the largest reservoir of iodine on the Earth, and virtually all iodine in the terrestrial environment derives from the oceans by way of the atmosphere. Iodine is volatilized from the sea as methyl iodide (CH_3I), elemental iodine (I_2), and possibly as some other inorganic iodine compounds such as HI or HOI, with CH_3I probably the most important of these. This volatilized iodine is deposited on land by wet and dry precipitation and consequently soils from near-coastal environments are enriched in iodine and soils remote from the sea are depleted.

The iodine content of soils reflects not only the amount of iodine input from the atmosphere but is markedly dependent on soil composition. Thus organic matter, and iron and aluminum oxides in soils are able

to strongly sorb iodine, and soils enriched in these components are frequently enriched in iodine.

It has generally been assumed that iodine in soils is transferred to plants and these, in turn, represent a major pathway of iodine into animals and humans. However, the soil-to-plant concentration factor for iodine has been shown to be low due to the strong sorption of iodine by soil components such as organic matter and iron and aluminum oxides. Little iodine in soils has been found to be easily leachable and no correlation of soil and plant iodine has been demonstrated. In addition, it has been shown that although iodine is taken into plant roots with the iodide ion more readily incorporated than iodate, little of this iodine is translocated from the roots of plants to the aerial parts. It is likely that most iodine in plants is taken in from the atmosphere through the stomata. Whereas in coastal areas such an atmospheric source of iodine is likely to be abundant, in inland areas such an atmospheric source would, to a large extent, be dependent on iodine volatilized from soils. Volatilization of soil iodine is likely to be of major importance in the iodine cycle, but in many areas such volatilization may be limited due to iodine being strongly bound in soil. This is likely to be particularly important in areas underlain by limestone where soils would be expected to be circum-neutral to alkaline, which results in any labile iodine being present as the iodate ion and hence unable to be converted to gaseous elemental iodine.

Traditionally, crops and vegetables have been suggested to be important sources of dietary iodine for humans. However, this is unlikely to be true in all but coastal regions as little iodine in soils is generally bioavailable. Seafood is generally a rich source of dietary iodine, whereas in some areas drinking waters are important sources. In developed countries, dairy products are a major source of dietary iodine due to the addition of iodine to cattle feed and use of iodine-containing sterilants in the dairy industry. However, even without the addition of iodine to dairy products animal products are likely to be richer sources of dietary iodine as grazing animals will take in iodine that has been deposited on the surfaces of grass and leaves. In addition, many grazing animals are known to inadvertently take in soil, which has been shown to provide more iodine.

The global distribution of IDD reflects the geochemistry of iodine with large areas of iodine deficiency occurring in central continental regions and mountainous and rain shadow areas, which reflect the supply of iodine from the marine environment via the atmosphere. However, the geochemistry of iodine is more

complex than this simplistic approach, and from a closer scrutiny of the distribution of IDD it is apparent that, in many cases, iodine-deficiency problems are related to the bioavailability of iodine in soils and are not related directly to the external supply of iodine.

A relatively modern problem concerning iodine is the release of radioactive iodine from anthropogenic sources. Of the radioactive isotopes of iodine it is ^{131}I , with a half-life of 8.04 days, which has been suggested to pose the greatest risk as it is produced in fairly large quantities from fission of enriched uranium and is highly radioactive. In areas where natural iodine is deficient the problem of large releases of ^{131}I would be potentially very serious, as a sudden increase of iodine would result in a high percentage of bioavailable iodine being radioactive. This problem was highlighted in the Chernobyl accident which occurred in a central continental area where iodine-deficiency problems have been described. A high incidence of childhood thyroid cancer since the accident has been shown to be causally linked to the release of the radioactive iodine.

SEE ALSO THE FOLLOWING CHAPTERS

Chapter 6 (Biological Functions of the Elements) · Chapter 7 (Geological Impacts on Nutrition) · Chapter 8 (Biological Responses of Elements) · Chapter 14 (Bioavailability of Elements in Soil) · Chapter 15 (Selenium Deficiency and Toxicity in the Environment) · Chapter 17 (Geophagy and the Involuntary Ingestion of Soil)

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