



Review

Iodine and human health, the role of environmental geochemistry and diet, a review

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ARTICLE INFO

Article history:

Received 2 June 2015

Received in revised form

17 September 2015

Accepted 20 September 2015

Available online 25 September 2015

Keywords:

Iodine

Organo-iodine

Iodine deficiency disorders (IDD)

Global cycling

Volatilisation

Dietary iodine

ABSTRACT

Iodine is an essential element in the human diet and a deficiency can lead to a number of health outcomes collectively termed iodine deficiency disorders (IDD). The geochemistry of iodine is dominated by its volatility with volatilisation of organo-iodine compounds and elemental iodine from biological and non-biological sources in the oceans being a major component of its global cycle. As a result of the dominant oceanic source, iodine is strongly enriched in near-coastal soils, however, the major zone of marine influence generally stretches to only 50–80 km inland and terrestrial sources of volatilised iodine, from wetlands, soils and plants are also an important aspect of its global geochemical cycle. Iodine in soils is strongly bound with transfer factors from soil to plants being generally small and as a consequence there is only limited uptake of iodine through the plant root system. It is likely that uptake of atmospheric iodine by the aerial parts of plants is an essential process and, along with iodine deposited on plant surfaces, is a major source for grazing animals. Human intake of iodine is mainly from food with some populations also obtaining appreciable quantities of iodine from drinking water. Plant-derived dietary iodine is generally insufficient as evidenced from the low dietary iodine of strict vegan diets. Seafood provides major iodine-rich dietary items but other inputs are mainly from adventitious sources, such as the use of iodised salt and from dairy produce, which is a rich source mainly due to cattle-feed being fortified with iodine, and to the use of iodine-containing sterilants in the dairy industry. While the distribution and geochemistry of iodine are reflected in the global distribution of IDD, the recent upsurge of IDD in developed countries would seem to reflect changes in diet.

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1. Introduction

Iodine has been known to be an essential element for humans since the middle of the 19th century, it being a constituent of the thyroid hormones triiodothyronine (molecular formula – $C_{15}H_{11}I_4NO_4$) and thyroxine (molecular formula – $C_{15}H_{12}I_3NO_4$). Historically, dietary iodine deficiency was synonymous with the disease of endemic goitre which according to Kelly and Sneddon (1960) affected almost every country prior to 1950. However, following the wide use of dietary iodine supplementation, in particular the use of iodised salt (e.g. Brush and Altland, 1952) and iodine supplementation of cattle-feeds, by the 1970s endemic goitre was virtually eradicated from the developed world, the disease subsequently being described by Gillie (1971) as “a disease of the poor”.

Further research highlighted the importance of iodine in foetal brain development with deficiency during foetal development resulting in irreversible brain impairment (Delange, 2000; Morreale de Escobar et al., 2004; Zimmermann, 2009), while it has been shown very recently that in the mildly iodine deficient UK, offspring of mothers who were iodine deficient in early pregnancy had lower than average IQ scores (Bath et al., 2013; Bath and Rayman, 2015). As a result it became apparent that iodine deficiency was manifested in health problems other than goitre and to this end Hetzel (1983) introduced the term iodine deficiency disorders (IDD) to cover all aspects of health outcomes resulting from dietary iodine deficiency. It is now generally accepted that damage to the brain resulting in mental retardation is the most significant effect of iodine deficiency (Li and Eastman, 2012) and, it has been suggested that iodine deficiency is one of the world's most common causes of preventable mental development problems ranging from sub-clinical minor IQ reduction to, in its worst form, cretinism (WHO, 2006).

Hetzel (1983) suggested that iodine deficiency could be eradicated within five years, however, while considerable strides have been made, Pearce et al. (2013) list thirty countries that are currently iodine deficient. Furthermore, while iodine deficiency had been presumed to be eradicated from the developed world, problems have re-emerged in many developed countries such as Australia, New Zealand and in several Western Europe countries. According to Andersson et al. (2012), globally almost 30% of schoolchildren have a suboptimum dietary iodine intake, while recent studies have highlighted mild iodine deficiency in pregnant females in the USA (Caldwell et al., 2013) and European countries (Trumpff et al., 2013), such as in Italy (Mian et al., 2009), Norway (Brantsæter et al., 2013), Portugal (Limbirt et al., 2010) and the UK (Bath et al., 2013, 2014).

In view of its importance in human and animal health there has

been considerable interest in the environmental geochemistry of iodine and its cycling through the biosphere. However, due to analytical constraints much of the early data on iodine geochemistry is somewhat suspect (Fuge, 1974). With the advent of new sensitive analytical methodologies for iodine, such as the use of ICP-MS (e.g. Tagami et al., 2006), more reliable data have been generated and as a result a great deal has been published on the various aspects of the geochemistry of iodine and its sources in human and animal diets.

In this paper the authors update a previous review of iodine geochemistry (Fuge and Johnson, 1986) and focus on the parts of the iodine geochemical cycle that are most important in the environmental controls on IDD. The behaviour and distribution of iodine in the environment is of significant interest in a range of scientific disciplines though the results of such studies are generally considered only within the specific area of interest. Here the results are applied to the wider context of the complete iodine cycle in the total environment.

In recent years, climate scientists have studied the generation and speciation of iodine in the atmosphere particularly with respect to its destruction of atmospheric ozone (Chameides and Davis, 1980; Solomon et al., 1994; Saiz-Lopez et al., 2012). In addition iodine oxides in the atmosphere have been linked with the formation of ultrafine particles which are important in cloud condensation (O'Dowd et al., 2002). It has also been suggested that in Arctic regions, the reactive species iodine oxide (IO) and atomic I are involved in atmospheric mercury depletion events where gaseous elemental mercury is converted to reactive mercury (Hg^{II}) which subsequently precipitates (Calvert and Lindberg, 2004; Saiz-Lopez et al., 2007b; Raofie et al., 2008; Auzmendi-Murua et al., 2014).

The harmful health effects of the radioactive isotopes of iodine, ^{131}I (half-life 8.07 days) and the long lived ^{129}I (half-life 1.7×10^7

Table 1
Iodine in some common rock types.

Rock type	Mean iodine content (mg kg ⁻¹)
<i>Igneous rocks</i>	
Granite	0.25
Other intrusives	0.22
Basalts	0.22
Other volcanics	0.24
Volcanic glasses	0.52
<i>Sedimentary rocks</i>	
Shale	2.3
Sandstone	0.8
Limestone	2.7
Organic-rich shales	16.7

From Fuge and Ander (1998).

years), generated during nuclear fission, particularly with respect to nuclear installation accidents, has for six decades driven the search for a better understanding of iodine's migration in the environment, e.g. Windscale in 1957 (Chamberlain and Dunster, 1958), Chernobyl in 1986 (Cardis et al., 2005; Michel et al., 2005) and Fukushima Daiichi in 2011 (Chino et al., 2011; Miyake et al., 2012). Radioactive isotopes and human health are not discussed further in this review though it is worth noting that iodine deficient environments will have a significant impact on the migration of radioactive isotopes through the local food chain following nuclear accidents (Korobova et al., 2010).

Other reasons for studying and applying iodine geochemistry include, the use of ^{129}I as a geochemical tracer (e.g. Santschi and Schwehr, 2004; Landis et al., 2012), and the use of iodine as a pathfinder element in mineral exploration for deeply buried mineralisation (Fuge et al., 1986).

However, the major and longstanding interest in iodine geochemistry has been because of iodine's important function in humans and other animals as a constituent of thyroid hormones. Historically, the environmental distribution and availability of iodine was fundamental in the aetiology of IDD such as goitre and mental impairment and many substantial areas of the Earth's surface were affected and are still considered to be at risk (Andersson et al., 2012). The re-emergence of IDD in developed countries is a cause for concern, particularly with regard to sub-clinical mental impairment (Zimmermann, 2009; Li and Eastman, 2012).

2. The environmental chemistry of iodine

Iodine (atomic number 53) with an atomic weight of 126.9 is the heaviest stable member of group 17 of the periodic table, the halogens. In common with the other stable halogens, fluorine, chlorine and bromine, iodine forms a diatomic molecule, I_2 , however, in contrast to the other halogens, elemental iodine exists as a solid which is volatile at room temperature. By gaining an electron to become I^- , iodine acquires an inert element structure, however, the first electron affinity of iodine being relatively low, -295 kJ mol^{-1} , I^- loses the acquired electron fairly easily being converted to I_2 .

The ionic radius of the I^- ion is 220 pm and in view of its large size is unlikely to be admitted into the crystal lattice of rock-forming minerals. As a result, iodine is an ultra-trace element in the Earth's crust, its mean concentration having been estimated to be between 0.25 mg kg^{-1} (Fuge, 1988) and 0.3 mg kg^{-1} (Muramatsu and Wedepohl, 1998), with sedimentary rocks generally containing more than igneous and metamorphic rocks (Table 1). Muramatsu et al. (2004) have suggested that the major reservoirs of terrestrial iodine are oceanic sediment and continental sedimentary rocks.

In terms of its distribution in the environment iodine is unique. Most elements are derived from weathering of crustal rocks and surficial sediments with the released elements and compounds being incorporated into soils and waters, subsequently to be taken up by the biosphere. In view of the low iodine contents of crustal rocks, soils and waters would generally derive only very small quantities of iodine from weathering of most rocks. In contrast, seawater is relatively rich in iodine, containing on average about $60 \mu\text{g L}^{-1}$ (Wong, 1991) and, as such, represents a vital reservoir of iodine on the Earth and the major source in its environmental cycle.

A key part of the iodine geochemical cycle has been recognised as volatilisation from the marine environment to the atmosphere, involving both biological, with micro and macroalgae playing a key role (Carpenter, 2003; Saiz-Lopez et al., 2012), and non-biological, photochemical (Yokouchi et al., 2012; Stemmler et al., 2013), pathways. There is also increasing evidence of terrestrial volatilisation from soils, micro-organisms and plants (Redeker et al., 2004;

Amachi, 2008; Weng et al., 2013). This volatilisation of iodine is the most important aspect of iodine geochemistry with elemental iodine and various organo-iodine compounds being released to the atmosphere from both the marine and terrestrial environments. While both chlorine and, in particular, bromine compounds are also known to be volatilised, the degree of volatilisation of iodine is considerably greater and it is this aspect of its geochemistry which makes it unique.

2.1. Iodine in the marine environment

As stated earlier, the oceans represent the major reservoir in the global iodine cycle. Iodine in seawater exists mainly as the anions, iodide (I^-) and iodate (IO_3^-) with variable amounts of organically bound forms (Wong, 1991). The thermodynamically stable state of inorganic iodine in seawater is IO_3^- (Sillén, 1961) and it is the most abundant species. However, variable concentrations of I^- generally occur in surface waters with greater amounts occurring in coastal and shallow shelf waters (Tsunogai and Henmi, 1971; Wong, 1991). Bluhm et al. (2011) found that I^- concentrations were lower in surface waters of the southern Atlantic than in those from lower latitudes, due, they suggested, to higher temperatures, solar radiation and greater biomass. In a recent review of the distribution of I^- in marine surface waters, Chance et al. (2014) state that I^- is generally highest in low latitudes with pronounced increases between 50° and 20° . The reduction of the stable iodate ion to the metastable iodide ion in the oceans is important for the global cycling of iodine.

Spokes and Liss (1996) suggested that the reduction of IO_3^- to I^- can be occasioned by photolysis in the presence of organic matter, however, it is generally thought that the most important reduction process is biologically mediated with Tsunogai and Sase (1969) suggesting that it is accomplished using nitrate reductase. Tsunogai and Sase (1969) found that nitrate-reducing bacteria could reduce iodate, while Farrenkopf et al. (1997) also demonstrated the iodate-reducing ability of a marine bacterium. Bluhm et al. (2011) found that high I^- values in surface waters of the southern Atlantic were linked to phytoplankton blooms. The ability of phytoplankton to reduce IO_3^- to I^- has been demonstrated experimentally by Wong et al. (2002), Hung et al. (2005) and Chance et al. (2007); while Bluhm et al. (2010) showed that several plankton taxa have the ability to reduce IO_3^- to I^- , these authors suggest that the reduction is not dependent on nitrate reductase. Some macroalgae have also been shown to reduce IO_3^- to I^- (Truesdale, 2008; Chance et al., 2009).

It has long been established that iodine is strongly concentrated by several marine algae (Vinogradov, 1953; Shaw, 1962), indeed the element was discovered by the French chemist Bernard Courtois in 1811 when he added concentrated sulfuric acid to the ash remaining from burned brown seaweeds (Courtois, 1813). While most of the marine macroalgae (seaweeds) show strong enrichment in iodine, the brown algae (Phaeophyta) show the greatest enrichment followed by the red algae (Rhodophyta) with the green algae (Chlorophyta) showing the least enrichment (Saenko et al., 1978; Hou and Yan, 1998). The brown algae show a general enrichment factor of over 30,000 relative to seawater (Fuge and Johnson, 1986). Ar Gall et al. (2005) demonstrated that the iodine content of the brown alga *Laminaria digitata* shows seasonal variations with highest values in late autumn and winter, in addition, younger plants show greater enrichments of iodine.

Microalgae are also strong concentrators of iodine with Manley (1984) suggesting that iodine accumulation by phytoplankton is considerably greater than that of macroalgae. Of the phytoplankton, diatoms show the greatest ability to concentrate iodine (Vinogradov, 1953). It has been suggested that diatoms and other

phytoplankton can accumulate both I^- and IO_3^- but generally show a strong preference for I^- (Moisan et al., 1994; de la Cuesta and Manley, 2009).

2.2. Iodine transfer from the marine environment to the atmosphere

The volatilisation of iodine from the marine environment and its movement through the atmosphere onto the terrestrial environment is the most important aspect of its global cycle. Both Goldschmidt (1954) and Rankama and Sahama (1950) commented on the atmophile behaviour of iodine and several early researchers in eastern Europe showed that coastal atmosphere is strongly enriched in this element compared to inland areas (e.g. Zyrin and Imadi, 1967; Paslawska and Ostrowski, 1968; Perel'man, 1977).

Several iodine-containing species have been shown to be released from the marine environment, of these methyl iodide (CH_3I), diiodomethane (CH_2I_2), chloriodomethane (CH_2ICl), bromiodomethane (CH_2IBr) and I_2 are suggested to be the major sources of marine atmospheric iodine (Jones et al., 2010; Saiz-Lopez et al., 2012). The organo-iodine compounds and elemental iodine generally photodissociate in the atmosphere producing iodine species such as IO and OIO. The formation of hydroscopic iodine oxides leads to particles which are precursors to cloud condensation nuclei (Küpper et al., 2008).

Much of the iodine in the marine atmosphere derives from biological sources. In near coastal environments the macroalgae are major sources with several volatile organo-iodine compounds having been shown to be released (Gschwend et al., 1985; Nightingale et al., 1995; Carpenter et al., 2000). In addition the brown algae have been demonstrated to produce significant quantities of I_2 , which is suggested to be a considerably richer source of atmospheric iodine than the organo-iodine compounds released (e.g. McFiggans et al., 2004; Saiz-Lopez and Plane, 2004; Palmer et al., 2005; Küpper et al., 2011). While many workers have suggested that the major I_2 producers are Laminaria species, Sellegri et al. (2005), Ball et al. (2010) and Huang et al. (2013) have shown that other species of brown algae also produce significant amounts. Elemental iodine, thought to be derived from the brown algae, has been detected spectroscopically in coastal air in several different countries (e.g. Saiz-Lopez and Plane, 2004; Finley and Saltzman, 2008; Leigh et al., 2010; McFiggans et al., 2010; Mahajan et al., 2011).

Küpper et al. (2008) demonstrated that iodine in the Laminaria species is present as iodide and suggested that this is released in response to oxidative stress. As a result of de-toxicification of the oxidants elemental iodine would be released and Dixneuf et al. (2009) observed such releases of molecular iodine from Laminaria digitata under stress conditions. Chance et al. (2009) have shown that red algae also release iodide in response to oxidative stress.

In the open ocean microalgae are suggested to produce significant quantities of volatile organo-iodine compounds (Tokarczyk and Moore, 1994; Carpenter, 2003; Hughes et al., 2008; Saiz-Lopez et al., 2012), with diatoms, which are strong concentrators of iodine (Vinogradov, 1953), in particular having been shown to be major sources (Moore et al., 1996; Manley and de la Cuesta, 1997). Diatoms can also release HOI (Hill and Manley, 2009). Several studies have shown that marine cyanobacteria can produce CH_3I (e.g. Brownell et al., 2010; Hughes et al., 2011), while Amachi (2008) has claimed that the annual production of CH_3I from marine bacteria is at least an order of magnitude greater than that of macroalgae and is comparable with that produced by phytoplankton.

While biological sources of iodine have generally been held to be the prime source of organo-iodine compounds, it is apparent that direct production from the oceans is also a major source.

Moore and Zafriou (1994) and Happell and Wallace (1996) suggested that CH_3I can be produced directly from seawater due to photolytic production of methyl radicals which then react with atomic iodine. More recently, Richter and Wallace (2004), Yokouchi et al. (2008, 2012) and Stemmler et al. (2013) have concluded that the photochemical pathway is indeed the major producer of CH_3I in the marine environment. In addition, Martino et al. (2009) demonstrated that the reaction of ozone with iodide in surface seawater releases HOI and I_2 and these can then react with dissolved organic matter to produce organo-iodine compounds.

Until relatively recently, it was generally believed that the major source of marine-generated atmospheric iodine was organo-iodine compounds (Carpenter, 2003), however, it has become apparent that inorganic sources are also of major significance (Jones et al., 2010). Indeed Mahajan et al. (2012) and Großmann et al. (2013) suggest that the major iodine source in the open ocean is inorganic, probably I_2 , resulting from the reaction of ozone with iodide (Garland and Curtis, 1981; Carpenter et al., 2013). It has also been demonstrated experimentally that iodide in aerosols can be oxidised by ozone very rapidly to produce HIO, IO_3^- , I_3^- and I_2 , and it has been suggested that this could be an important source of iodine for the marine atmosphere (Pillar et al., 2013). A further potential mechanism for the production of inorganic iodine species outlined by Jammoul et al. (2009) involves photolytic oxidation of I^- by aromatic ketones.

It is perhaps pertinent to draw particular attention to the iodine geochemistry of the polar atmospheres as this has received much attention in recent years due mainly to its role in destruction of tropospheric ozone and its possible role in oxidation of atmospheric mercury and resultant mercury depletion events. The Antarctic atmosphere has been found to be strongly enriched in IO (Saiz-Lopez et al., 2007a, b), while Mahajan et al. (2010) have also recorded elevated IO in the Arctic atmosphere. The source of the iodine is suggested to be photolysis of that trapped in the ice pack, which is likely to be of biological origin (Saiz-Lopez et al., 2015).

2.3. Transfer of iodine to the terrestrial environment

In localities proximal to coastal areas (see section 2.5.1) sea spray will be a major contributor of iodine to the terrestrial environment. In addition, on coasts with extensive beds of brown algae gaseous elemental iodine is likely to be transferred to the atmosphere (Saiz-Lopez and Plane, 2004; Finley and Saltzman, 2008; Leigh et al., 2010; McFiggans et al., 2010; Mahajan et al., 2011) and so be transported into the immediate terrestrial environment (Smyth et al., 2011), possibly along with organically bound iodine. However, other mechanisms are responsible for more long range transport of iodine to the terrestrial environment.

Marine-derived iodine is transported through the atmosphere within both gaseous and aerosol phases with Moyers and Duce (1972) and Duce et al. (1973) suggesting that gaseous phase transport is more important. The atmospherically transported iodine is subsequently transferred to the land surface in wet and dry precipitation with rainfall being considered by many workers to be the most important transfer mechanism (e.g. Whitehead, 1984; Fuge et al., 1987; Truesdale and Jones, 1996; Englund et al., 2010), however, other workers have suggested that dry deposition is equally important (e.g. Chamberlain and Chadwick, 1996; Sugawara, 1967; Baker et al., 2001).

Recently published data (Baker, 2004, 2005; Pechtl et al., 2007; Gilfedder et al., 2007, 2008; Lai et al., 2008) indicates that organically-bound iodine accounts for over half, and sometimes considerably more, of that in rainfall and the soluble component of aerosols, together with a variable proportion of inorganic iodine. Surprisingly, while the oxidised forms of iodine would be expected

Table 2
Iodine in waters.

Sample and source	Range and mean ($\mu\text{g L}^{-1}$)		References
<i>Brines, thermal and mineral waters</i>			
Brine, Oklahoma, U.S.A.	133–519	320	Collins and Egleson (1967)
Brine, Canadian Shield	10–18,000	–	Bottomley et al. (2002)
Oilfield brine, Oklahoma, U.S.A.	23–1400	380	Collins (1969)
Thermal and mineral springs, Japan	30–329	126	Kikkawa and Shiga (1966)
Thermal waters, El Tatio, Chile	31–783	384	Cortecci et al. (2005)
Mineral waters, mid-Wales, U.K.	173–595	350	Fuge and Johnson (1986)
<i>Groundwaters</i>			
Spring and well waters, Wales, U.K.	1.18–7.30	4.17	Fuge (1989)
Spring and well waters, England, U.K.	1.66–14.0	4.10	Fuge (1989)
Central Russian Plain	0.30–21.0	3.72	Korobova (2010)
La Pampa, Argentina	63–316	184	Watts et al. (2010)
Denmark	0.4–1220	13.8	Vouchkova et al. (2014b)
Taiyuan Basin, Shanxi Province, China	0.02–4117	963	Tang et al. (2013)
North China Plain, shallow	<1–1901	159	Zhang et al. (2013)
North China Plain, deep	<1–1360	137	Zhang et al. (2013)
<i>Surface waters</i>			
Lakes, Argentina	1.12–10.4	2.82	Negri et al. (2013)
Lakes, Central Russian Plain	0.40–11.4	5.88	Korobova (2010)
Lakes, U.K.	1.47–12.6	4.77	Fuge (1989)
Rivers, Kabul, Afghanistan	7.90–22.7	15.4	Watts and Mitchell (2009)
Rivers, Nangarhar, Afghanistan	5.40–9.4	7.60	Watts and Mitchell (2009)
Rivers, San Juan Province, Argentina	16–95	48	Watts et al. (2010)
Rivers, Argentina	3.49–28	11.9	Negri et al. (2013)
Rivers, Central Russian Plain	0.40–11.4	3.18	Korobova (2010)
Streams and rivers, UK	0.40–15.6	2.78	Fuge (1989)
European	0.90–4.20	2.17	Moran et al. (2002)
British Columbia and Alberta, Canada	0.47–2.48	0.94	Fuge (1989)
Alaska and Canada	0.60–2.90	1.80	Moran et al. (2002)
U.S.A., West Coast Rivers	0.50–66	14.1	Moran et al. (2002)
U.S.A., South Coast Rivers	5.5–212	26.9	Moran et al. (2002)
U.S.A., East Coast Rivers	2.12–16.3	7.72	Moran et al. (2002)

to dominate the inorganic fraction, from thermodynamic considerations (Gilfedder et al., 2008), several authors point to the major occurrence of I^- in both the soluble component of aerosols and in rain. While Campos et al. (1996) and Truesdale and Jones (1996) found that the inorganic component of rain was composed of roughly equal quantities of I^- and IO_3^- , Gilfedder et al. (2007) recorded considerably more I^- than IO_3^- . Baker (2005) and Lai et al. (2008) found that I^- was considerable elevated over IO_3^- in the soluble fraction of aerosols. However, Baker (2004) and Gilfedder et al. (2008) point to IO_3^- being the dominant inorganic iodine species in large aerosol particles. Baker (2005) and Gilfedder et al. (2008) maintain that the soluble organic iodine component of aerosols forms from the reaction of HOI with organic matter and that this soluble organic iodine is the precursor of I^- .

It is generally accepted that the many species of iodine released to the atmosphere photodissociate to oxidised species and that these have limited residence times. Gilfedder et al. (2008) believe that the soluble iodine component of aerosols could be a major factor in increased residence times in the atmosphere so being vital in the transport and cycling of the element.

Yokouchi et al. (2008) maintain that CH_3I is the major iodine-containing component of the troposphere and as such is of major importance in the geochemical cycling of iodine.

2.3.1. Iodine in rainwater

From literature data it seems that the iodine content of rainwater is mostly within the range 0.5–2.5 $\mu\text{g L}^{-1}$ (Campos et al., 1996; Truesdale and Jones, 1996; Neal et al., 2007; Gilfedder et al., 2007, 2008; Aldehan et al., 2009; Bowley, 2013). However, it has been demonstrated that iodine in rainwater varies through a rainfall event, peaking during the early stages and declining through the event indicating progressive washout (Duce et al., 1963; Fuge et al., 1987; Truesdale and Jones, 1996). It has been postulated by Gilfedder et al. (2008) that the fairly uniform

concentrations of iodine in rain reflects that to a large extent it occurs in the atmosphere in a gaseous phase and interaction of this phase with water droplets controls its concentration in rainfall.

While some authors have suggested that there is little obvious difference in the iodine content of coastal rainfall with that occurring well inland (e.g. Zhu and Tan, 1988; Gilfedder et al., 2008) others have indicated that the iodine content of rainwater is higher near the coast (e.g. Krupp and Aumann, 1999; Aldehan et al., 2009). Moran et al. (1999) states that the iodine content of rainwater is higher near the coast but that the higher concentrations are limited to a narrow zone in close proximity to the coast. Fuge et al. (1987) collected rainwater samples from a single rainfall event on a traverse from the mid Wales coast, UK, to 84 km inland and found that the iodine content was relatively low in the low-lying coastal area (1.98 $\mu\text{g m}^{-2} \text{day}^{-1}$) and peaked from 12 to 35 km inland (2.5–5.5 $\mu\text{g m}^{-2} \text{day}^{-1}$) in the upland area (230–330 m), declining further inland to fairly constant values (1.5–2.2 $\mu\text{g m}^{-2} \text{day}^{-1}$). It is apparent with regard to its overall input to soils through rainfall, that there is a general correlation between total annual rainfall and the iodine content of soils (e.g. Krupp and Aumann, 1999; Aldehan et al., 2009; Bowley, 2013).

There is little literature data on potential anthropogenic influences on iodine in rainwater but Zhu and Tan (1988) found higher iodine in rainwater samples from urban Beijing than in those from surrounding areas (see section 2.6).

2.4. Iodine in terrestrial waters

Table 2 gives some literature values for iodine in various types of water.

2.4.1. Surface waters

Earlier literature compilations of data for surface waters suggest that they generally contain <20 $\mu\text{g L}^{-1}$ with many values falling

within the range of 0.5–5 $\mu\text{g L}^{-1}$ (Whitehead, 1984; Fuge and Johnson, 1986). More recent data, however, reveal a much broader range of values. Moran et al. (2002) in a survey of North American river waters found that while most contain $<20 \mu\text{g L}^{-1}$ and the mode was 5.5 $\mu\text{g L}^{-1}$, the values range up to 212 $\mu\text{g L}^{-1}$. Watts and Mitchell (2009) recorded 5.4–22.7 $\mu\text{g L}^{-1}$ in surface waters from Afghanistan, while Watts et al. (2010) quote values of 16–95 $\mu\text{g L}^{-1}$ for those of San Juan Province, Argentina. In a recent study, Negri et al. (2013) recorded iodine concentrations of 1.12–27.8 $\mu\text{g L}^{-1}$ in lake and river waters in Patagonia, Argentina, with values decreasing from north to south.

It is apparent that the iodine content of surface waters is influenced by several factors. Proximity to the marine environment has been shown to influence the iodine content of stream waters with those occurring in near coastal localities being somewhat richer than those from further inland (Fuge, 1989). Negri et al. (2013) suggest that decreasing iodine concentrations in surface waters from north to south in Patagonia reflect decreasing precipitation rates. Moran et al. (2002) point to the strong influence of geology with rivers draining areas of igneous rocks having low iodine contents while those from sedimentary rock areas are considerably higher. Iodine has been found to be more enriched in streams draining areas of carbonate lithologies than those draining non-carbonate areas (Fuge, 1989; Korobova, 2010). Streams draining peaty areas also show iodine enrichment (Whitehead, 1979; Johnson, 1980; Korobova, 2010). Moran et al. (2002) also point to the strong correlation of iodine and total dissolved solids in river waters, while there is a similar correlation with suspended particulate matter probably reflecting iodine adsorption on particles.

The iodine content of surface waters can also reflect anthropogenic influences such as agricultural practices (Whitehead, 1979; Fuge, 1989) and biomass burning (Negri et al. (2013), while Moran et al. (2002) found high iodine contents in rivers intercepting irrigation runoff and return waters. In addition, thermal waters, many of which are iodine-rich, can impact on surface waters as at El Tatio, Chile, where geyser waters containing up to 783 $\mu\text{g/L}$ iodine influence surface runoff (Cortecchi et al., 2005).

2.4.2. Groundwaters

In general, literature data indicate that groundwaters are more enriched in iodine than surface waters (e.g. Whitehead, 1984; Johnson, 2003b), with some showing very strong enrichments. Iodine-rich groundwaters have been reported from several Provinces of China (e.g. Tan, 1989; Zhao et al., 1998; Andersen, S. et al., 2009; Shen et al., 2011; Zhang et al., 2013) with iodine contents ranging up to 2800 $\mu\text{g L}^{-1}$ being recorded in Jiangsu Province (Zhao et al., 2000) and up to 4100 $\mu\text{g L}^{-1}$ in Shanxi Province (Tang et al., 2013).

The sources of iodine in the various aquifers have been generally ascribed to breakdown of iodine-containing organic matter, leaching from marine sediments in the aquifers and evapoconcentration in arid areas. In two very recent studies Li, J. et al. (2013, 2014) report iodine-rich groundwaters in the arid-semiarid area of the Datong Basin, China, a Cainozoic Basin where the sand and gravels composing the aquifer sediments were deposited during the Pleistocene and Holocene. Groundwaters extending down to 120 m are generally alkaline and contain high iodine contents (highest value recorded by Li et al. (2013) is 1890 $\mu\text{g L}^{-1}$ while that recorded by Li, J. et al. (2014) is 1380 $\mu\text{g L}^{-1}$). The aquifer sediments contain from 0.18 to 1.46 mg kg^{-1} iodine and are relatively enriched in organic matter (Li et al., 2013). Li, J. et al. (2013, 2014) suggest that the sediment iodine is mainly adsorbed on Fe oxyhydroxides while some is organically-bound and that it is mobilised into the very slow-moving groundwaters as a result of reductive dissolution of the Fe oxyhydroxides and breakdown of

iodine-containing organic matter.

Iodine-enriched groundwaters have also been reported in several other countries. Iodine contents of up to 430 $\mu\text{g L}^{-1}$ have been found to occur in the La Pampa Aquifer, Argentina (Smedley et al., 2002; Watts et al., 2010), the high iodine being thought to result, at least in part, from evapoconcentration in this arid area (Watts et al., 2010). Barikmo et al. (2011) report iodine concentrations of up to 545 $\mu\text{g L}^{-1}$ in groundwater from the Tindouf Basin in the Sahara, again possibly due to evapoconcentration. Iodine concentrations of up to 1220 $\mu\text{g L}^{-1}$ have been recorded in water from aquifers hosted by marine sediments in eastern Denmark (Voutchkova et al., 2014b), with some of the iodine being organically-bound (Voutchkova et al., 2014a). Iodine-enriched groundwater is also known to occur in Somalia and possibly Kenya (Kassim et al., 2014).

Many of the iodine-rich groundwaters listed above are used as sources of potable water. It is, therefore, worth noting that it has recently been shown that disinfection of potable water, with ozone, chlorine or chloramines etc., can result in the formation of iodine-containing disinfection bi-products such as iodo-trihalomethanes (e.g. Krasner et al., 2006; Plewa et al., 2004; Richardson et al., 2007). Some of these bi-products have been shown to be strongly genotoxic and cytotoxic (Richardson et al., 2007, 2008). The amounts of these iodine-containing compounds formed are likely to be elevated in iodine-rich waters.

2.4.3. Brines and formation waters

While not directly relevant to this review, it should be mentioned that some brines and formation waters are strongly enriched in iodine (Table 2). In some cases such brines can influence the composition of normal groundwaters, while it has recently been suggested that iodine content may be a useful tracer of the effects of hydrofracking on drinking water (Lu et al., 2015).

2.5. Iodine in soils

2.5.1. Sources

The iodine content of soils has been shown to vary widely, with Johnson (2003a), in a review of world literature data, quoting a range of <0.1 –150 ppm, the mean of all values being 5.1 ppm and the geometric mean 3.0 ppm. More recently, Smyth and Johnson (2011) have recorded values of up to 600 ppm in soils from Northern Ireland. Most soils contain considerably more iodine than the rocks and sediments from which they derive, a fact first noted by Goldschmidt (1954), and it was the same author who first proposed that much of the iodine in soils derives from the oceans by way of the atmosphere, being deposited by both wet and dry precipitation (see section 2.3). Subsequently, studies have shown that soils from near-coastal environments are enriched in iodine while those far removed from marine influence are relatively depleted in this element (Låg and Steinnes, 1976; Fuge, 1987, 1996; Johnson, 2003a, b; Steinnes et al., 1994), while soil geochemical maps of iodine distribution in Europe (DeVos et al., 2006), Great Britain (Rawlins et al., 2012) and Northern Ireland (Smyth and Johnson, 2011) show general enrichment in coastal areas, and, in particular, on south and west-facing coasts reflecting the predominant south westerly winds. Fuge (1996), Johnson et al. (2002) and Steinnes and Frontasyeva (2002) have demonstrated distance decline of soil iodine contents on transects from the coast in the direction of the prevailing wind.

However, it is apparent that the distribution of iodine in soils also reflects topography with upland areas, which experience orographic rainfall generally influencing the pattern of this distribution. Several authors have pointed out that the iodine content of soils reflects the amount of rainfall (e.g. Fuge, 1996; Schnell and

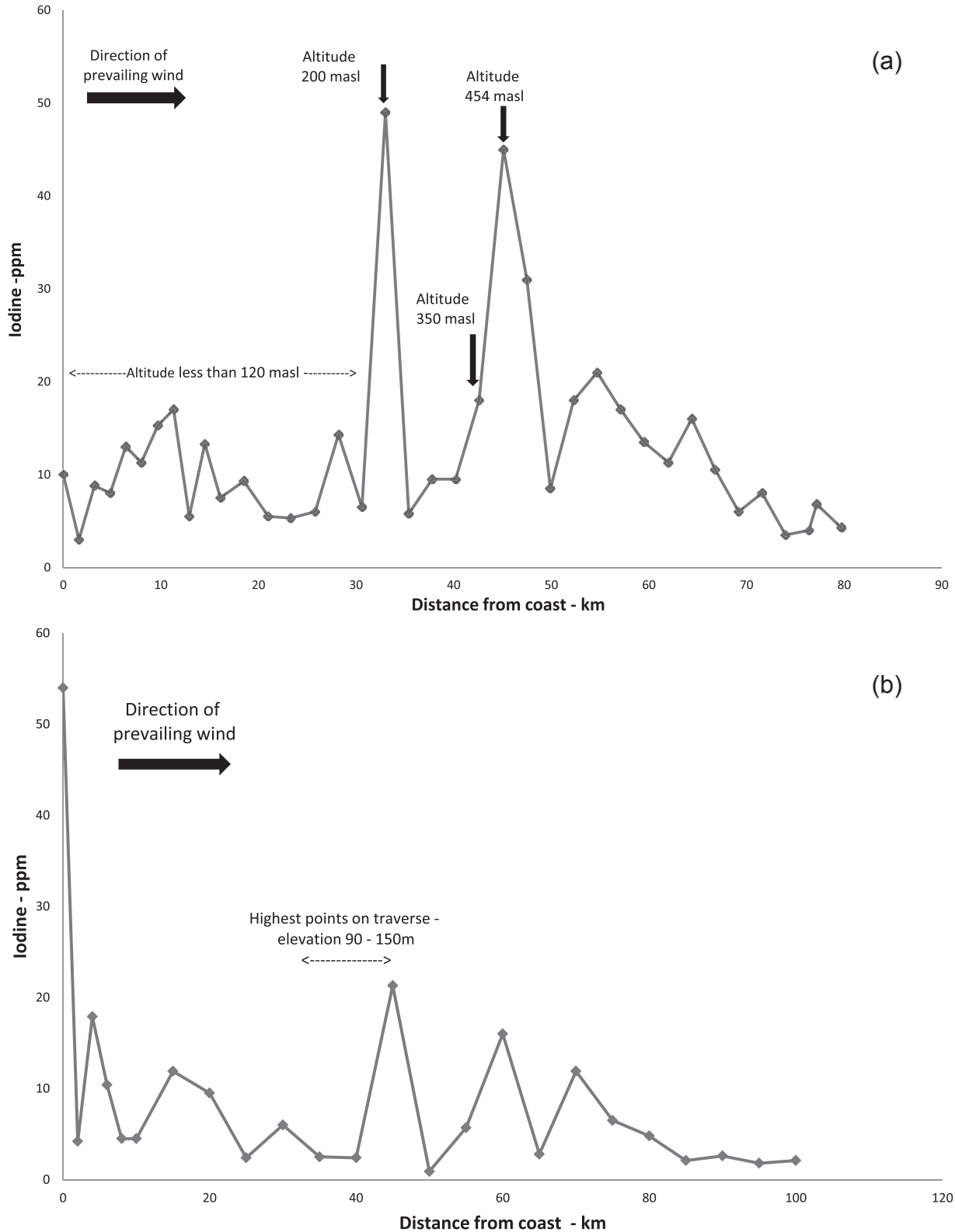


Fig. 1. a) Iodine in topsoils on a traverse from the coast of NW England across the Lake District along the direction of the prevailing wind. b) Iodine in topsoils on a traverse from Galway on the west coast of Ireland along the direction of the prevailing wind (modified from Fuge, 2007).

Aumann, 1999; Aldehan et al., 2009; Bowley, 2013), which in turn is influenced by topography. This influence of topography is illustrated in Fig. 1 which charts soil iodine along two traverses from the coast inland in the general direction of the prevailing wind. Fig. 1a

shows a traverse from the west coast of northern England along a north westerly direction across the English Lake District and demonstrates elevated soil iodine occurring in areas of higher altitude. Fig. 1b shows a traverse from Galway Bay on the west coast

Table 3
Iodine in various soil types.

Soil type (Topsoils)	Iodine range and mean (mg kg ⁻¹)		References
Peats (>70% organic matter), UK	28–98	56	Johnson (1980); Fuge and Johnson (1986); Fuge, unpublished data
Peat, from literature compilation	0.2–28	8.83	Johnson (2003a)
Iron-rich soils, UK	7.5–33	16.0	Fuge, unpublished data; Fuge and Ander (1998)
Silt, from literature compilation	0.1–135	8.15	Fuge and Ander (1998)
Clay, from literature compilation	0.1–69	7.27	Fuge and Ander (1998)
Sand, from literature compilation	0.08–58	4.11	Fuge and Ander (1998)
Over limestone, N. Wales, UK	1.0–76	11.0	Fuge, unpublished data
Over other lithologies, N. Wales, UK	3.4–9.0	6.5	Fuge, unpublished data
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)
Marine/estuarine alluvium parent	8.8–36.9	19.6	Whitehead (1984)

of Ireland in a general easterly direction over an area which has muted topography with limited variation and iodine contents that do not vary so dramatically but are generally elevated up to a distance of about 80 km from the coast.

The zone of direct marine-derived iodine input to soils appears to be fairly limited. Data in Fuge (1996) suggests that soils from the English Midlands area of the UK, >70 km from the sea, generally contain <5 ppm iodine, while Johnson (2003a) quotes a mean value of 2.6 ppm iodine from literature data for samples collected over 50 km from the coast. These values are not markedly different from values for central continental areas such as those for Missouri, USA, up to 5.6 ppm (mean 1.26) (Fuge, 1987) or those from Xinjiang Province, China, up to 3.9 ppm (mean values for various study areas 0.89–1.16) (Fordyce et al., 2003). It is suggested on the basis of the values quoted and those illustrated in Fig. 1 that the zone of major direct marine influence probably extends to 50–80 km inland. However, Steinnes and Frontasyeva (2002) found that the marine influence on soil iodine content extended to over 300 km in northern Norway, with iodine concentrations falling from 15.7 ppm at the coast to 2.2 ppm 305 km inland, the value at 100 km being about 5 ppm. The same authors (Frontasyeva and Steinnes, 2004) found that the iodine content of the feather moss (*Hylocomium splendens*) along two transects away from the coast in the same area of Norway showed a decline over 300 km. Therefore, it is possible that in some areas local conditions can result in the marine influence on the iodine content of soils being extended greater distances inland. While this is possible in some areas, it is likely that much of the iodine transferred further inland would require volatilisation from the terrestrial environment (see section 2.5.3, below).

It should be noted that the iodine content of coastal soils may also reflect agricultural activity, as seaweeds, rich in iodine, (see section 2.1) have been used as a source of fertiliser (Metting et al., 1990). This has been suggested by DeVos et al. (2006) and Smyth and Johnson (2011) to be reflected in the iodine content of some coastal soils in Brittany, France and in Northern Ireland, respectively. Other agricultural practices such as the application of manure or sewage sludge could also add iodine to cultivated fields (Whitehead, 1984). Soil iodine could also be enhanced in the vicinity of power plants and industrial areas from smoke and particulates released during fossil fuel combustion, as coal, in particular, can be somewhat enriched in iodine (Wu et al., 2014). Another potential anthropogenic source of soil iodine is mineral extraction as Fuge et al. (1988) found high iodine in soils affected by tailings waste and smelter fumes in Missouri.

As indicated in Table 3, while most soils derive little iodine from parental rocks, where soils are derived from sediments of fairly recent marine origin, or in areas where there has been recent marine inundation, they will be enriched in iodine from this source, e.g. in the East Anglian region of England, UK (Breward and

Johnson, 2007; Ander et al., 2008). In addition soils occurring over sulfide mineralisation are generally enriched in iodine (Andrews et al., 1984).

2.5.2. Retention of soil iodine

It is apparent that there is considerable variation in the iodine content of soils even when they are within the zone of marine influence (Johnson, 2003b). This variation reflects the ability of a soil to retain any added iodine. For example soils which are organic-rich, particularly peats and peaty soils, are generally strongly enriched in iodine (Table 3). This reflects the strong sorption of iodine by soil organic matter, which has been suggested to be the major host of soil iodine (e.g. Dai et al., 2009; Shimamoto et al., 2011; Hu et al., 2012). Other soil components implicated in the retention of iodine are Fe and Al oxides (Whitehead, 1978, 1979, 1984), while clay minerals are thought to play a lesser role in iodine retention (Fuge, 2013). The composition of soils generally reflects the composition of the parent material and as such the nature of the parent material indirectly influences the iodine chemistry of soils (see Table 3). It is of note that soils occurring over limestone are generally enriched in iodine (Table 3) as demonstrated by soils in the Peak District of Derbyshire, England, UK where the iodine content of soils occurring over limestone are strongly enriched in comparison to those over neighbouring non-limestone lithologies (Fuge and Long, 1989). This has also been demonstrated for carbonate-rich and non-carbonate-rich soils in Austria (Gerzabek et al., 1999) and in the central Russian Plain (Korobova, 2010). Its enrichment over limestone and chalk terrains is also well illustrated in the soil geochemical map of iodine for England and Wales, UK (Rawlins et al., 2012).

The ability of a soil to retain iodine has been termed the iodine fixation potential (Johnson, 1980, 2003b; Fuge and Johnson, 1986). Hence, soils which have a high organic content or are rich in aluminium and/or iron oxides and/or, to a lesser extent, clay minerals tend to have a high iodine fixation potential while those lacking in any of these materials will have a low iodine fixation potential. Therefore, the iodine content of any soil will reflect both the supply of iodine and its iodine fixation potential.

In view of the strong retention of iodine in peats and that such deposits cover in the region of 3% of the terrestrial surface, Keppler et al. (2003) and Biester et al. (2004) have suggested that peats represent a major reservoir of terrestrial iodine.

2.5.3. The form of iodine in soils

The chemical form of iodine in soils is of interest as this will govern its mobility, bioavailability and possible re-volatilisation. It has been shown that soil iodine is mainly in an organic form with variable amounts of IO₃⁻ and I⁻ (Hu et al., 2009, 2012; Shimamoto et al., 2011). Many researchers have pointed to the differing degrees of sorption of I⁻ and IO₃⁻ with the latter being more strongly

sorbed than I^- in most soils (e.g. Kodama et al., 2006; Dai et al., 2009; Hu et al., 2012) with the sorption of iodide in soils being suggested by some to be promoted by microorganisms (Muramatsu and Yoshida, 1999; Muramatsu et al., 2004). However, several studies have demonstrated that inorganic iodine added to soils is converted to organo-iodine (Yamaguchi et al., 2010; Shimamoto et al., 2011; Seki et al., 2013). Yamaguchi et al. (2010) found that while both IO_3^- and I^- were transformed to organo-iodine, the transformation was considerably faster for I^- . In addition the same authors found that while the conversion of I^- was dependent on microbial action, this was not the case for IO_3^- . The apparent dependence of iodide sorption on soil microbes together with the inhibition of sorption in anaerobic conditions has led to the suggestion that it is facilitated by an oxidase enzyme (Seki et al., 2013). As a result I^- is oxidised to the very reactive species I_2 and HOI, which in turn react with organic matter to produce organo-iodines (Seki et al., 2013). Shimamoto et al. (2011) and Seki et al. (2013) have proposed that the enzyme in question could be laccase, which is produced by soil fungi and bacteria.

Another possible mechanism for the transformation of iodide to organo-iodine compounds has been suggested by Li, H.-P. et al. (2012) to involve the reaction of H_2O_2 with organic acids produced by soil bacteria, so producing peroxycarboxylic acids which can subsequently oxidise I^- to I_2 and HOI.

While soil iodine is generally strongly held, several studies have indicated that small amounts of it are water soluble. In most cases the soluble iodine content of soils is <10% (e.g. Johnson, 1980; Schmitz and Aumann, 1994; Johnson et al., 2002; Hu et al., 2009). However, it has been demonstrated (Muramatsu et al., 1996b; Muramatsu and Yoshida, 1999; Yuita et al., 2005) that in water-logged soils, under reducing conditions, such as rice paddies, much iodine is released from the soils into the water. In such reducing conditions the iodine in the water is bioavailable which explains its enhanced uptake by rice plants (Watanabe and Tensho, 1970; Yuita, 1994; Sheppard and Motycka, 1997). This highlights the importance of Eh on the retention of soil iodine as in low Eh conditions iodine is less likely to be strongly bound than in oxidising conditions. In the low Eh conditions of paddy soils the iodine in soil water is likely to be predominantly I^- (Yuita, 1992; Yamaguchi et al., 2006), with Yamaguchi et al. (2006) finding that IO_3^- added to anoxic soils was converted to I^- . In contrast Yuita (1992) found IO_3^- to be the major iodine species in oxic soil waters. However, it has been reported that while IO_3^- and I^- tend to be the more dominant forms in oxidising and reducing conditions, respectively, varying proportions of both occur in soil waters under both conditions (e.g. Yuita et al., 2005).

Varying proportions of organically-bound iodine have also been recorded in soil waters (e.g. Sheppard et al., 1995; Shimamoto et al., 2011).

2.6. Volatilisation of iodine from the terrestrial environment

While volatilisation of iodine from the oceans represents a major source in the global cycle, it is likely that the direct influence of the marine environment on the terrestrial environment is limited to 50–80 km (see section 2.5.1.). Therefore, iodine occurring in soils and waters in areas remote from the marine environment would need alternative sources, which are likely to include terrestrial volatilisation (Fuge, 1990).

Volatilisation of iodine from soils has been demonstrated by several workers (e.g. Whitehead, 1981; Sheppard and Thibault, 1991; Sheppard et al., 1994; Weng et al., 2013); there have also been several reports of volatilisation of iodine from plants (e.g. Wildung et al., 1985; Amiro and Johnston, 1989; Weng et al., 2013), with Saini et al. (1995) demonstrating experimentally that several

higher plants are capable of producing CH_3I . Iodine has been shown to be phytotoxic (e.g. Yuita, 1994) and according to Saini et al. (1995) and Redeker et al. (2004) the volatilisation of CH_3I from plants probably represents a detoxification mechanism. Amachi et al. (2003) have shown that CH_3I is produced in soils under aerobic conditions as a result of microbial action, particularly bacteria, and that a wide range of soil bacteria have the ability to methylate iodine. Amachi (2008) has further suggested that soil bacteria could play an important role in the global cycling of iodine. In addition Ban-nai et al. (2006) using laboratory cultures found that filamentous fungi occurring in soils are capable of accumulating iodine and volatilising it as CH_3I . It is also apparent that iodine can be released during burning of vegetation with Andreae et al. (1996) finding that CH_3I is emitted during grassland fires.

Muramatsu and Yoshida (1995) found that CH_3I was volatilised from flooded soils with rice plants, or dry soils with oat plants, with volatilisation being much enhanced in the flooded soils. These authors suggested that most of the emissions derived from the roots of the plants. Redecker et al. (2000) found strong emissions of CH_3I from rice paddies and estimated that this source provided 5% of worldwide CH_3I emissions, while Redeker and Cicerone (2004) and Redeker et al. (2004) showed that these emissions were derived almost entirely from the rice plants. Coastal wetlands in California have been shown to release CH_3I , with almost 60% of the releases deriving from unvegetated areas, (Manley et al., 2006), with the authors estimating that coastal wetlands globally could produce 0.8% of total CH_3I emissions. Muramatsu and Yoshida (1999) have suggested that CH_3I emissions produced from water-logged soils are a contributory cause of the low iodine contents of lowland soils in Japan. Peatbogs (Dimmer et al., 2001; Keppler et al., 2003) have also been shown to be sources of significant CH_3I emissions, while Manley et al. (2007) demonstrated release of CH_3I from mangroves in pot experiments. It is clear that wetland areas in general are important sources of iodine emissions and that globally such releases are a significant source of terrestrially-derived atmospheric iodine.

It is apparent that much of the CH_3I volatilisation from the terrestrial environment is due to biological action. However, Keppler et al. (2000) have suggested the potential for a non-biological source. These authors found that in organic-rich surface waters, oxidation of organic matter by Fe(III) resulted in the formation of CH_3I along with C_2H_5I , C_3H_7I and C_4H_9I and suggest that this is also likely to occur in soils.

While most iodine-rich emissions from terrestrial sources are likely to be in the form of organo-iodine compounds, it is possible that there could be some emissions of molecular iodine gas from soils. From the Eh/pH diagram for iodine (Fig. 2) it is apparent that under oxidising acidic conditions, the I^- ion in near surface soils can be oxidised to I_2 (Fuge, 1990) while Perel'man (1977) suggested that Fe (III) and Mn(IV) in soils could also oxidise I^- to I_2 . More recently, Shimamoto et al. (2011) and Seki et al. (2013) have proposed that the oxidase enzyme laccase, which is produced by soil fungi and bacteria, is capable of oxidising I^- to I_2 in the surface layers of soil. While these authors further suggest that the I_2 reacts with organic matter to produce organo-iodine compounds which are retained in the soil, it seems likely that while some will be converted to CH_3I and volatilised, some molecular iodine will also escape to the atmosphere.

While several studies have demonstrated volatilisation of iodine from soils, Bostock et al. (2003) found minimal volatile loss of iodine (as ^{125}I) from grassland and coniferous forest soils, which the authors suggested was due to strong retention of iodine by organic matter. These authors also found no volatilisation of iodine from frozen soils.

Volcanic emissions can add some iodine to the atmosphere; the

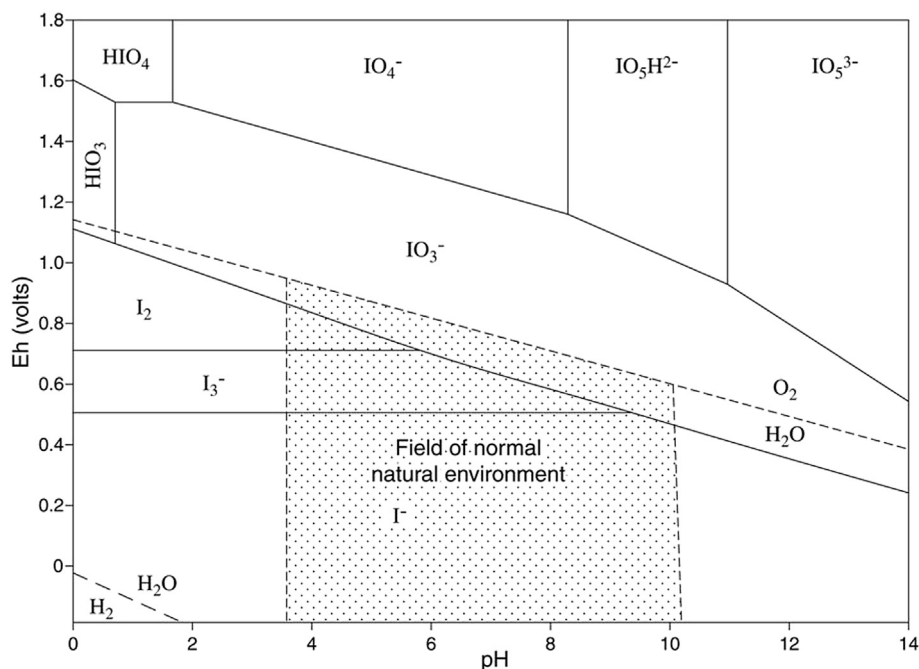


Fig. 2. Eh/pH diagram for iodine (from Fuge, 2013).

Table 4
Iodine in vegetation samples.

Material	Iodine content (mg kg ⁻¹)	References
Herbage/grass (literature review)	0.05–0.5	Whitehead (1984)
Plants/pasture (near coastal environment)	0.185–3.62	Bowley (2013)
Selected plant samples (central Russian Plain)	0.121–0.221	Korobova (2010)
Twigs from trees (near coastal environment)	0.11–3.39	Al-Ajely (1985)
Tree samples (central Russian Plain)	0.072–0.186	Korobova (2010)
Mixed herbage – aerial parts (central Russian Plain)	0.162	Korobova (2010)
Mixed herbage – roots (central Russian Plain)	0.701	Korobova (2010)
Lichens (central Russian Plain)	1.089	Korobova (2010)
Mosses (central Russian Plain)	0.743	Korobova (2010)

global contribution from this source has been estimated by Aiuppa et al. (2005) to be 0.11 kt a⁻¹, which is insignificant when compared to the other natural sources. In addition there are some anthropogenic sources which add iodine to the atmosphere the most important being combustion of fossil fuels (Miyake and Tsunogai, 1963). While such sources are generally minor contributors to atmospheric iodine, it has been shown recently (Wu et al., 2014) that Chinese coals contain significant amounts of iodine (range 0.04–39.5, mean 2.6 ppm). While Wu et al. (2014) estimate that combustion of these coals accounts for only 0.49% of global atmospheric iodine they suggest that it contributes significant quantities to the atmosphere in and around industrial centres. In this context it is significant that Zhu and Tan (1988) recorded higher iodine in rainwater samples from urban Beijing than in those from suburban areas. In addition it has been demonstrated (Wang et al., 2004; Finkelman, 2007) that atmospheric iodine derived from coal combustion is sufficient to mitigate iodine deficiency in human populations in parts of Guizhou Province. However, this could, in part, also be due to the use of domestic coal fires to dry vegetables for later consumption, with volatilised iodine being incorporated into the dried vegetables.

Relatively high concentrations of atmospheric iodine have been detected in inland sites which suggests that terrestrial sources of iodine volatilisation are extremely important (Yokouchi et al., 2008). Indeed, Sive et al. (2007) calculated that the terrestrial

CH₃I flux from the various sources is at least comparable to that released from the oceans; as such this would constitute a very significant part of the global iodine cycle.

2.7. Iodine transfer to plants

The iodine content of plants is generally low with most quoted values for samples deriving from soils with no added iodine being less than 1 ppm (see Table 4). In this context studies in New Zealand have shown that ingested soil is a better source of iodine in lambs than herbage growing on the soil (Healy et al., 1972).

Iodine has been described as a non-essential element for higher plants (Whitehead, 1984) and has been shown to be toxic to plants (e.g. Watanabe and Tensho, 1970; Yuita, 1994; Sheppard and Evenden, 1995) with the I⁻ ion suggested to be more toxic than the IO₃⁻ ion (Zhu et al., 2003). However, Küpper et al. (2008) has demonstrated that iodide is an antioxidant in kelp and Crockford (2009) has suggested that iodine is essential to unicellular organisms including cyanobacteria, which may also, in part, be due to its activity as an antioxidant.

2.7.1. Root uptake

In most high iodine soils, the iodine is strongly retained and its transfer factor for soils to most plants has been shown to be low (Ashworth, 2009; Uchida and Tagami, 2011). However, it is likely

that differing soil types and conditions result in varying degrees of plant uptake (e.g. Kashparov et al., 2005; Sheppard et al., 2010; Uchida and Tagami, 2011), presumably reflecting the soil's iodine fixation potential, with Korobova (2010) recording highest iodine values for herbaceous plants across the central Russian Plain in marshy floodplain soils. While there is some variation of iodine uptake between different species of plants (e.g. Korobova, 2010), it seems likely that this variation has less impact than the soil type and conditions.

Despite the general low transfer ratios quoted, it has been shown in some studies that plants grown in iodine-enriched soils generally contain elevated iodine (e.g. Yuita, 1994; Sheppard and Motycka, 1997). However, it seems likely that the iodine taken up reflects higher soil water iodine. Recently, Bowley (2013) found a weak correlation between the iodine content of vegetation and soil in northern Ireland, an area which is strongly influenced by marine iodine inputs, while some literature data also suggests that iodine is relatively enriched in plants in near-coastal sites (Table 4). In addition it has been demonstrated that iodine fortification of soils with iodides or iodates, or in the form of iodine-rich fertilisers such as brown algae results in enhanced uptake of iodine (e.g. Dai et al., 2006; Weng et al., 2013, 2014).

It has been shown that both I^- and IO_3^- are taken up by plant roots but there is conflicting evidence regarding their relative degree of uptake. A summary of the available literature lead Whitehead (1984) to suggest that in uptake from nutrient solutions the I^- ion is more readily incorporated than IO_3^- , this has been confirmed more recently by other workers (e.g. Zhu et al., 2003). However, Dai et al. (2006) found that in soil pot experiments with additions of I^- and IO_3^- the situation is reversed with IO_3^- being preferentially incorporated. An additional confounding factor is the suggestion that plant roots can reduce IO_3^- to I^- (Kato et al., 2013).

There is also some conflicting evidence regarding translocation of iodine from the roots to the upper parts of plants with Whitehead (1984) suggesting that much of the iodine taken into roots remains there. More recently, Tsukada et al. (2008) found that in rice plants grown in iodine-rich soil, the iodine content of roots was three times that in the above ground part of the plants, while the content of the edible rice grain was very low. In addition, Korobova (2010) found that the roots of mixed herbage samples from the central Russian plain contained over four times as much iodine as the aerial parts of the plants. However, other workers such as Dai et al. (2006) and Weng et al. (2013) have demonstrated that in spinach and Chinese cabbage, respectively, iodine is translocated easily from the roots to stem and leaf, indeed, Weng et al. (2009)

using the radioactive isotope ^{125}I found that over 80% of the iodine taken up by Chinese cabbage is transferred to the aerial part of the plant. Overall it seems likely that while translocation of iodine from the roots in most plants is limited there is significant translocation in some.

In summary, it is probable, due to the general strong retention of iodine in soils, that under natural conditions, most plants derive little iodine from root absorption. However, it seems likely that more labile iodine added to soils results in its greater incorporation into plants.

2.7.2. Uptake from the atmosphere

It has been suggested that iodine uptake from the atmosphere through the aerial parts of plants represents a more important pathway than that from soil through the roots (Whitehead, 1984). In this context it has been found that mosses and lichens, which have no root systems and derive nutrients from the atmosphere, contain similar amounts of iodine to plants which have root systems (Shacklette and Cuthbert, 1967; Whitehead, 1979). More recently, Korobova (2010) found that mosses and lichens had the highest iodine contents for a variety of plants from the central Russian plain (Table 4).

Whitehead (1984) suggests that atmospheric iodine uptake in plants is due to both stomatal and leaf surface absorption. Shaw et al. (2007) found that adaxial leaves of the broad bean (*Vicia faba* L.) exposed to potassium iodide solution labelled with ^{125}I strongly adsorbed I^- . The authors suggested that the adsorption was due to reaction of the I^- with the cuticular waxes. In laboratory experiments utilising iodine vapour labelled with ^{131}I Tschiersch et al. (2009) found that leafy vegetables such as spinach, leaf lettuce and curly kale rapidly sorbed iodine, only about 10% of which was removed during subsequent washing. The authors suggest that some of the iodine was taken up through stomata but that a significant quantity was fixed into the leaf structure.

It is likely that much of the iodine transported in the atmosphere or volatilised from soils will be in the form of CH_3I (e.g. Sive et al., 2007; Yokouchi et al., 2008). Doubt has been expressed regarding the plant uptake of volatilised CH_3I (e.g. Muramatsu et al., 1996a), however, Collins et al. (2004), using radioactively labelled CH_3I , demonstrated its uptake by leaves of a variety of crops, including cabbage, and subsequent translocation to other parts of the plant.

In addition to the adsorption or incorporation of iodine by plants, it is likely that significant quantities of atmospherically derived iodine, particularly that contained in or on solid particles,

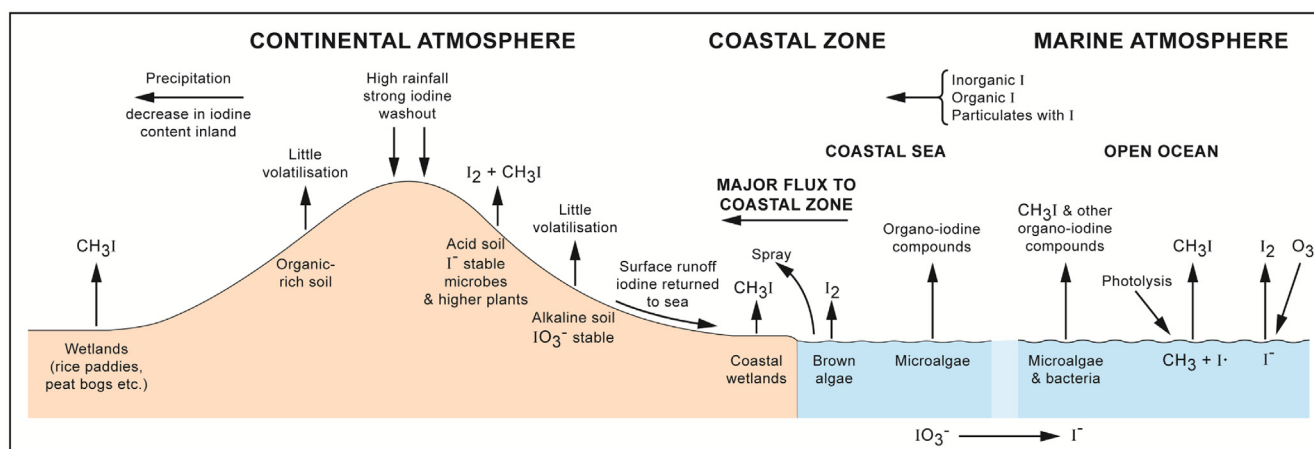


Fig. 3. The iodine cycle.

would be deposited on the surfaces of plants and thus become a potential source for grazing animals. This has been highlighted as a pathway into grazing cattle and subsequently milk for ^{131}I released from nuclear accidents etc. (e.g. Burch, 1959; Dreicer and Klusek, 1988; Zvonova et al., 2009).

2.8. Summary of the most important aspects of the iodine geochemical cycle

The global geochemical cycle of iodine is illustrated in Fig. 3.

The most important aspect of iodine geochemistry is its volatility and its consequent transport in the atmosphere. The oceans represent the major reservoir in the global iodine cycle with both biological and non-biological contributions to atmospheric iodine. Iodine volatilised from the marine environment is carried onto the terrestrial environment and this has generally been regarded as the major source for terrestrial iodine. While the major source of atmospheric iodine is the oceans, its transport onto the terrestrial environment is limited to a fairly narrow zone in the immediate coastal area. Therefore, the volatilisation of iodine from terrestrial sources is also an important aspect of its geochemical cycle. Iodine is volatilised in a variety of chemical forms, both organic and inorganic but the most important forms appear to be CH_3I and elemental iodine.

Iodine in soils is generally enriched in coastal zones with significant declines in concentration inland. Soil iodine is mainly strongly bound and the quoted transfer factors for iodine from soil to plants are small. Hence only limited amounts of iodine are taken up through the roots of plants. It seems likely that iodine uptake through the aerial parts of plants is a vital source and in areas where there is limited volatilisation there will be little iodine uptake in plants. It has been demonstrated that there is limited iodine volatilisation from organic-rich soils (Bostock et al., 2003). Similarly, in circumneutral and alkaline soils, such as those derived from limestone there is little likelihood of any volatilisation of iodine as most of the soil iodine will be present as IO_3^- (see Eh-pH diagram in Fig. 2), and in the absence of I^- no elemental iodine or CH_3I will be formed.

The traditional view of the distribution of IDD is coloured by the generalised perception of the transport of iodine from the marine to the terrestrial environment. Certainly the historical maps (Kelly and Sneddon, 1960) and the more recent map (Dunn and van der Haar, 1990) of the distribution of endemic goitre would seem to reflect this generalised model, with areas remote from the sea, such as central continental areas and rain shadow areas of large mountain ranges being seriously affected. However, it is apparent that this is an over simplification as areas which are subject to strong maritime influence, such as the UK, are also found to be affected by IDD (Andersson et al., 2012), with even oceanic islands such as the Azores also affected (Limbert et al., 2010).

3. Sources of iodine for human populations

General pathways into the human body for the various elements and compounds are via the food and water consumed and the air which is breathed. In the case of iodine, it is generally held that the major source for humans is food (Risher and Keith, 2009), with Weng et al. (2014) suggesting that in normal diets, plant materials provide the major source of iodine. While food is the major source of iodine for human intake there are some examples of non-food sources which are of interest.

According to Risher and Keith (2009) water is generally an insignificant source of dietary iodine, however, in some circumstances it can be a very major source. As outlined in section 2.4.2., some groundwaters which are used as potable sources are strongly

enriched in iodine. In many cases the iodine-enriched waters provide a large proportion of the iodine requirement for populations consuming them (e.g. Argentina, Watts et al., 2010; Denmark, Vouchkova et al., 2014b). However, in parts of China where the waters are extremely iodine-rich there are records of harmful effects of excessive iodine intake with iodine-induced goitre and hypothyroidism (Andersen, S. et al., 2009; Shen et al., 2011; Li, W. et al., 2012) resulting from their consumption. Tan (1989) recorded a correlation of endemic goitre in China with the iodine content of water, in most cases this was a negative correlation but when the iodine content of water exceeded $100\text{--}200\ \mu\text{g L}^{-1}$ endemic goitre occurrence correlated with the iodine content of the water.

It has been suggested that inhalation represents a very minor source of iodine intake for humans and that even in coastal areas where atmospheric iodine is likely to be elevated, inhalation would provide only an estimated $5\ \mu\text{g/day}$ (Risher and Keith, 2009). Several studies have indicated that molecular iodine is emitted from coastal areas where there are large areal occurrences of beds of brown seaweeds (e.g. Finley and Saltzman, 2008; Leigh et al., 2010; McFiggans et al., 2010; Mahajan et al., 2011), one of these being in the vicinity of Mace Head, County Galway, on the Atlantic coast of western Ireland (Saiz-Lopez and Plane, 2004). In this area there are considerable occurrences of brown seaweed beds (kelp beds) on the rocky foreshore and in a study of female schoolchildren resident in the immediate vicinity of the kelp beds, Smyth et al. (2011) found that concentrations of urinary iodine (a measure of iodine intake) were appreciably higher than in neighbouring coastal areas where there were minimal occurrences of kelp beds, and in inland areas. This led Smyth et al. (2011) to postulate that inhalation of iodine in this seaweed-rich coastal environment provides a significant source of human iodine intake.

The possible importance of iodine derived from inhalation has also been highlighted by Wang et al. (2004) and Finkelman (2007) who have suggested that atmospheric iodine derived from coal combustion contributes to mitigate iodine deficiency in human populations in parts of Guizhou Province, China.

3.1. Dietary iodine

3.1.1. From the marine environment

In the iodine-rich marine environment, iodine becomes concentrated in the biota with seaweeds being particularly enriched (see section 2.1). Marine fish and shellfish have long been known to be rich sources of dietary iodine (e.g. Lee et al., 1994) and according to Risher and Keith (2009), marine-sourced fish and shellfish are the richest sources of human dietary iodine. In a recent compilation of analytical data for human dietary items, Haldimann et al. (2005) quote values of $0.39\text{--}6.9\ \text{mg kg}^{-1}$ (median $1.44\ \text{mg kg}^{-1}$) for a selection of marine fish. Edible seaweeds are consumed in several countries and these have been found to contain up to $4920\ \text{mg kg}^{-1}$ iodine (Yeh et al., 2014). In view of the extremely elevated levels of iodine in some edible seaweeds consumption of seaweed-based foods can lead to excessive iodine intake and the consequent problems of hypothyroidism etc. (Teas et al., 2004). It seems likely, therefore, that in populations where seafood is a major dietary component there will be adequate iodine intake.

3.1.2. From the terrestrial environment

3.1.2.1. Plants and vegetables.

While the marine environment is likely to produce iodine-rich foods, this is not generally the case for the terrestrial environment. There is in most cases only very limited uptake of iodine from soils to plants (see Section 2.7), while iodine is also a phytotoxin to higher plants (Watanabe and Tensho, 1970; Yuita, 1994; Sheppard and Evenden, 1995), hence it seems likely

that under normal circumstances vegetable and plant material would provide only limited dietary iodine (e.g. Dahl et al., 2004). This would seem to be confirmed by studies on vegetarian and, in particular, vegan diets (Lightowler and Davies, 1998; Remer et al., 1999; Krajčovičová-Kudláčková et al., 2003; Leung et al., 2011), which will only contain sufficient iodine if iodised supplements are consumed or adventitious sources of iodine are included in the diet such as dairy produce or iodised salt (Fields and Borak, 2009; Longvah et al., 2013).

The general low iodine content of dietary vegetables is confirmed in most literature reviews of foodstuffs (e.g. Fordyce, 2003). However, it has been noted that leafy vegetables such as lettuce are somewhat richer than other vegetables (Fordyce, 2003; Haldimann et al., 2005; Uchida and Tagami, 2011). While some workers such as Dai et al. (2006) and Weng et al. (2013) have shown that iodine from root uptake is strongly concentrated in the leaves of leafy vegetables where exogenous iodine is added to soils, it is likely that the enrichment is due in part to the adsorption of atmospherically-derived iodine onto the leaf surface or incorporation through the stomata (Tschiersch et al., 2009). The enrichment of iodine in leafy vegetables may be of importance in near marine environments where the supply of atmospherically-derived iodine is likely to be relatively high, so giving rise to an iodine-rich dietary item.

While normal soils are, in most cases, unable to produce iodine-rich crops, it has been demonstrated by several workers that iodine-rich plants can be cultivated if iodine-rich algae fertilizers (e.g. Weng et al., 2013, 2014) or iodine-containing salts (Kiferle et al., 2013) are added to soils. As a result it has been suggested that exogenous iodine added to soils will be transferred to plants. It has been demonstrated that in coastal areas with high iodine inputs, plants are relatively enriched in iodine (e.g. Bowley, 2013). However, while crops grown in near coastal environments are likely to be relatively enriched in iodine, particularly leafy vegetables (see previous paragraph), the crops produced would be unlikely to be markedly enriched in iodine. While iodine-rich soils associated with volcanics are found in some rice paddies in Japan and have resulted in excessive iodine uptake by rice due to the occurrence of high I^- in the low Eh soils (Yuita, 1994), it is unlikely that the rare occurrence of such naturally iodine-enriched soils will have a great deal of influence on iodine in crops on a global scale. In addition, seaweed fertilizers have been used in coastal areas for some time and have likely influenced the iodine content of crops, however, there is little use of these fertilisers in inland areas.

3.1.2.2. Animal produce. From observations on radioactive isotopes of iodine released during nuclear accidents etc., it has been shown that iodine deposited on herbage can rapidly be incorporated into grazing animals and subsequently occur in milk (e.g. Burch, 1959; Dreicer and Klusek, 1988). It would appear likely then that where significant quantities of iodine are deposited onto vegetation, as in the near-marine environment, milk should be relatively enriched in iodine. This has been demonstrated in a study in Peru (Cárdenas et al., 2003). The mean iodine content of 27 samples of milk collected from the coastal area of Lima Province (154 m above sea level) was $216 \pm 199 \text{ mg L}^{-1}$ (median 170) while 62 samples from mountainous areas in Cajamarca Province in the north (2720 masl) and 44 samples from Arequipa Province in the south (2335 masl) showed mean values of 29 ± 20 (median 24) and 42 ± 27 (median 34) mg L^{-1} , respectively. This would suggest that the cows grazing in near-coastal areas produce milk which is considerable more iodine-rich than cows grazing in mountainous regions where there is limited marine iodine input.

The iodine content of milk will reflect the iodine content of the grazing material and fodder consumed so it is probable that high-

iodine containing milk and dairy produce will only occur where animals are grazing in areas of high-iodine input or where animals are fed iodine-enriched fodder (see section 3.1.3.2 below). Milk from cows grazing on low iodine pasture has been found to contain less than $20 \text{ } \mu\text{g L}^{-1}$ iodine (e.g. Grace and Waghorn, 2005; Kursu et al., 2005). However, it is likely that hay cut and stored for winter feed will have an increased iodine content as a result of drying and will, therefore, provide a richer iodine source when animals are fed indoors during winter, so producing iodine-enriched milk (Pauliková et al., 2008).

3.1.3. Adventitious sources of dietary iodine

3.1.3.1. Iodised salt. Iodisation of salt has been recommended by the World Health Organization (e.g. WHO, 1994) as an effective means of elimination of iodine deficiency by increasing dietary iodine in the world population, with iodised salt containing $15\text{--}80 \text{ mg kg}^{-1}$ iodine (Zimmermann and Andersson, 2012). According to Langer (1960) iodisation of salt as a means of boosting dietary iodine was first suggested by Boussingault (1831), based on observations on the use of natural iodine-rich salt to mitigate endemic goitre in parts of Columbia, and that subsequently this advice was also given by Grange (1849) in France. However, such a prophylaxis was not introduced until the 1920s when iodised salt was produced and distributed in the USA following the pioneering work of David Marine on the use of sodium iodide as a prophylactic for endemic goitre (e.g. Marine and Kimball, 1920). As a result goitre was eradicated from the major goitre belt of the USA (Pearce, 2007). Iodised salt was also introduced in Switzerland and parts of Italy in the 1920s. Subsequently, it has been introduced in many countries and, according to Andersson et al. (2012), some 71% of the world population are now exposed to iodised salt and in countries where it has been introduced it is suggested to be one of the main dietary sources of iodine. In China (Wu et al., 2012) and India (Longvah

Table 5
Iodine content of various food groups ($\mu\text{g kg}^{-1}$).

Food type	a	b	c	d	e	f
Bread	31	30 ¹	392 ²	–	140	40
Cereals	77	30 ¹	22	–	–	–
Potatoes	–	20	18	–	–	–
Vegetables	148	20	33	–	40 ³	–
Leafy vegetables	171	–	153 ⁴	–	–	–
Fruit	53	20	15	–	40 ³	–
Meat	90	37	20	–	100	–
Eggs	–	450	1620	600	400	520
Fish						
Marine	1300	650	1440 ⁵	–	1150	1610
Freshwater	102	–	205	–	–	–
Shellfish	–	–	–	–	900	2470 ⁶
Milk	–	150	675	300	250–400	300
Yogurt	–	80	556	600	335–670	270
Cheese	–	380 ⁷	396	990	375	300
		1290 ⁸				

a: Fordyce (2003) from literature data, median values.

b: Dahl et al. (2004) data for Norwegian foods, mean values.

c: Haldimann et al. (2005) data for Swiss foods, median values.

d: Food Standards Agency (2008) UK dairy produce, mean values.

e: Bath and Rayman (2013) compilation.

f: Scientific Advisory Committee on Nutrition (SACN) (2014) compilation of UK foods.

1: Bread and cereals combined.

2: Iodised bread.

3: Vegetables and fruit combined.

4: Salad vegetables.

5: Includes shellfish.

6: Mussels.

7: White cheese.

8: Whey cheese.

et al., 2013) for example most dietary iodine derives from vegetables cooked with iodised salt. The introduction of iodised salt in many countries has seen large drops in the percentages of populations suffering from iodine deficiency, none more so than in China where iodised salt was first introduced in 1995, resulting in the near elimination of IDD (Wu et al., 2012). In China it has been shown that iodised salt now provides 63.5% of food iodine to the population (Wu et al., 2012). However, as indicated by Li, W. et al. (2012), in some areas with elevated drinking water iodine ($>150 \mu\text{g L}^{-1}$), the combined effect of iodised salt and high iodine intakes from water has resulted in some 8% of schoolchildren having high-iodine goitre.

While the use of iodised salt has resulted in increased iodine intakes and, as a consequence, lowered the incidence of IDD, in many affluent countries much of the dietary salt consumed derives from processed foods (Andersen, L. et al., 2009; Ohlhorst et al., 2012). However, in many countries the salt used in food processing is not iodised (Charlton and Skeaff, 2011; Ohlhorst et al., 2012; Zimmermann and Andersson, 2012) and this has been suggested to be a major reason for iodine deficiency in industrialised countries (Zimmermann, 2010). In several countries, e.g. Switzerland (Haldimann et al., 2005), Denmark (Rasmussen et al., 2007) and India (Longvah et al., 2013), iodised salt is used in bread making and this has been identified as a major influence on dietary iodine in those countries. In addition, the introduction of mandatory use of iodised salt in bread making in Australia and New Zealand in 2009 has reversed the recent trends to low dietary iodine in those countries (Skeaff and Lonsdale-Cooper, 2013; Li, M. et al., 2014).

Given the drive towards lowering human salt intake it is possible that there could be a significant drop in iodised salt intake and a subsequent decline in iodine status of populations. This has been advanced as one possible reason for the lower iodine content of the USA diet (Pearce, 2007). This has also been suggested to be a possibility in The Netherlands (Verkaik-Kloosterman et al., 2010). However, Zimmermann (2010) states that any drop in salt intake can be countered by increasing the iodine content of salt. The problem could also be countered by introducing iodised salt into processed foods (Charlton and Skeaff, 2011).

3.1.3.2. From animal produce. From tables of data for various food groups it seems probable that animal produce are a richer source of iodine than plant produce (e.g. Fordyce, 2003; Dahl et al., 2004; see Table 5). While meat is regarded as a significant source of iodine in some diets (e.g. Lee et al., 1994; Pearce, 2007), with much of the iodine deriving from fortified feeds and supplements, it is not generally regarded as a rich dietary source. It has been shown that iodine in cattle-feed passes into milk to a far greater extent than into the organs and meat (Flachowsky, 2007; Meyer et al., 2008). As a result milk and dairy produce are, in general, rich dietary iodine sources.

It was realised in the first half of the 20th century that iodine supplementation of livestock improved their growth rate and productivity and as a result cattle-feeds and supplements are fortified with iodine (Phillips, 1997). As outlined in section 3.1.2.2., the iodine content of cow milk reflects the iodine intake of the cows with increased iodine in feeds strongly reflected by that in milk (e.g. Borucki Castro et al., 2011; Flachowsky et al., 2014). The iodine content of milk has been further enriched due to the use of iodophors as sterilants in the dairy industry, in particular their use in teat dips (e.g. O'Brien et al., 2013; Flachowsky et al., 2014).

The iodine content of milk is very variable but in general concentrations in excess of $100 \mu\text{g L}^{-1}$ are recorded for most countries, with values of over $300 \mu\text{g L}^{-1}$ being listed for the USA (Pearce et al., 2004), the Czech Republic (Kursa et al., 2005) and India (Longvah et al., 2013). Several workers have found significantly higher

iodine values in winter than in summer milk, reflecting indoor versus outdoor feeding (e.g. Dahl et al., 2003; Pearce et al., 2004; Flachowsky et al., 2014). The iodine content of conventionally produced milk has also been found to be appreciably higher than that of organically produced milk (e.g. Dahl et al., 2003; Bath et al., 2012; Köhler et al., 2012). In addition, it has been shown that heat pasteurisation of milk results in a drop in the iodine content (Norouzian, 2011).

Not surprisingly, the iodine contents of dairy produce such as yogurt and cheese are also elevated (Dahl et al., 2003; Haldimann et al., 2005) and are, therefore, important dietary sources of iodine.

Milk and dairy produce are major sources of dietary iodine in many countries and are particularly important sources for children and pregnant females (e.g. Dahl et al., 2004; Soriguer et al., 2011; Caldwell et al., 2013), while in some countries such as Norway (Dahl et al., 2004) and the UK (Bath et al., 2012) milk has been shown to be the principal source of dietary iodine. With regard to the latter, Phillips (1997) concluded that in the absence of mandatory salt iodisation in the UK, the increased iodine content of milk and dairy produce, as a result of changes in farming practice, and increased consumption, was the major reason for the elimination of endemic goitre in the 1960s.

Several authors have pointed to a decline in the iodine content of milk over recent years, mainly due to decreased iodine concentrations in feeds, in part due to concern over excessive dietary iodine resulting from consumption of dairy produce (Flachowsky et al., 2014). Li et al. (2006) have suggested that the reduced iodine content of milk in Australia was a major cause for the re-emergence of iodine deficiency there, however, they suggested that the low iodine in milk resulted from the replacement of iodophors in the dairy industry with non-iodine containing sterilants.

In addition to milk, eggs have been found to be a very iodine-rich dietary item again mainly as a result of iodine-enriched feeds (Flachowsky, 2007), the iodine being concentrated in the yolk (Haldimann et al., 2005; Flachowsky, 2007), with Travnicek et al. (2006) quoting median values of $487 \mu\text{g kg}^{-1}$ and $13 \mu\text{g kg}^{-1}$ iodine in yolk and albumen, respectively.

3.1.3.3. Other sources. In addition to the fortification of bread with iodine from the use of iodised salt, iodate has been used as a conditioner in bread making. Pearce et al. (2004) recorded iodine contents of up to 23mg kg^{-1} in bread samples from Boston, USA, as a result of the use of iodate as a conditioner, however, its use in bread making is being phased out.

The use of the iodine-containing red food dye erythrosine has been suggested to be a rich source of dietary iodine. However, the iodine in erythrosine has been found to have limited bioavailability (Pearce, 2007).

4. Role of environmental geochemistry in IDD

The historical distribution of endemic goitre generally suggests that most coastal areas are iodine sufficient with areas inland such as central continental regions and, in particular, rain shadow areas of high mountain ranges, being deficient (Kelly and Sneddon, 1960). This implies that in many coastal areas, there is sufficient intake of naturally occurring iodine. As indicated earlier (section 3), brown seaweeds are strongly enriched in iodine and have been shown to emit gaseous iodine, and, following a study of schoolgirls in a coastal area of Ireland, Smyth et al. (2011) have suggested that inhalation of iodine vapour from coastal kelp beds could provide an adequate intake in the immediate vicinity of the beds. Also in coastal areas seafood is likely to be more available than in inland areas and this could provide iodine-rich dietary items. However,

these sources are unlikely to be the major iodine providers for most coastal dwelling populations.

As outlined in section 3.1.2.1., as iodine incorporation into plants and vegetables is limited, they are not, in general, rich sources of dietary iodine (Fordyce, 2003). However, in near-coastal areas there is continual input of marine derived iodine and literature data reveals that plants growing in these areas are relatively enriched in iodine (Table 4). In addition, recent work in Northern Ireland, where there is a strong maritime influence, revealed a weak correlation between the iodine content of vegetation and soil (Bowley, 2013). It has also been demonstrated that leafy vegetables such as lettuce are richer in iodine than other vegetables (Fordyce, 2003; Haldimann et al., 2005; Uchida and Tagami, 2011). It is, therefore, possible that in coastal areas where there is a constant supply of iodine from precipitation and gaseous sources that such vegetables could provide a relatively iodine-rich dietary item.

Animal produce is considered to be a richer dietary iodine source than plant material (see section 3.1.2.2), this being particularly true of milk and dairy produce, with the iodine content of cow milk strongly reflecting iodine intake (Borucki Castro et al., 2011; Flachowsky et al., 2014). While modern agricultural practices, such as the use of iodine-fortified feeds and supplements etc., have resulted in iodine-rich milk, it is likely that where no such supplementation occurs, cattle grazing in areas where there is greater environmental iodine availability, such as the immediate coastal area will produce iodine-enriched milk. This would seem to be confirmed by the study of Cárdenas et al. (2003) which showed that in Peru, cow's milk from coastal Lima Province contained over six times as much iodine as that from cows grazing mountainous areas well removed from marine influence (see section 3.1.2.2).

Eggs are another iodine-rich dietary item, with iodine concentrated in the yolk (Haldimann et al., 2005; Travnicek et al., 2006; Flachowsky, 2007). As with milk, the high iodine content of eggs reflects iodine supplementation of feeds (Flachowsky, 2007). However, it is likely that without such feed supplementation, hens feeding on local foods in near coastal environments would also produce iodine-rich eggs.

However, while dietary items from near-coastal environments are likely to be somewhat enriched in iodine, the simple idea of iodine deficiency reflecting only areas remote from marine influence does not convey the whole picture. For example, in the UK, almost the whole of which is generally under a maritime influence, many areas have a history of serious endemic goitre and even endemic cretinism through to the 1950s. In addition, the areas that were seriously affected are frequently in close proximity to areas that were unaffected, which would seem to suggest that local environmental conditions are implicated in controlling iodine availability. This likely reflects the role of the iodine fixation potential of soils, with those having a high fixation potential strongly retaining iodine so making it almost totally non-bioavailable. While plants and vegetables are generally regarded as a relatively poor source of iodine for humans, as suggested above, it is probable that grazing animals would derive appreciable iodine from that incorporated into and on the surfaces of plants. The plant iodine would derive from that taken up by the roots and that volatilised from the soil and incorporated into and on the plant surfaces. Where soils have a high iodine fixation potential, very little iodine is going to be available for root uptake and, more importantly, for re-volatilisation.

Globally, it has been demonstrated that several serious endemic goitre occurrences were in areas underlain by limestone (e.g. Boussingault, 1831; Perel'man, 1977), while in the UK many of the badly affected areas are underlain by limestone, e.g. Derbyshire, the Yorkshire Dales and South Wales, which are underlain by Carboniferous limestone, and the area of North Oxfordshire, which is

underlain by Jurassic limestone. In contrast, the soil geochemical map of iodine for England and Wales shows iodine to be elevated over limestone areas (Rawlins et al., 2012). This implies that iodine in the soils over limestones is bio-unavailable. Iodide is more readily taken up from soils than IO_3^- and in alkaline and circum-neutral soils such as those in limestone areas, IO_3^- is likely to be more prevalent. In addition, and probably more importantly, in soils where IO_3^- is the dominant form of iodine there will be limited volatilisation (see Fig. 2), so depriving plants of a major pathway for iodine transfer.

Similarly, soils which are organic-rich have a very high iodine fixation potential so causing iodine to be very strongly retained. It is likely, therefore, that in such soils very little iodine is available for root uptake. In addition, as demonstrated by Bostock et al. (2003), there is limited iodine volatilisation from organic-rich soils, so depriving plants growing on such soils of a source of atmospherically-derived iodine.

Overall, because volatilisation from the marine environment is the major source of terrestrial iodine and the direct marine influence is confined to a relatively narrow zone in close proximity to the coast, this will have a strong influence on the distribution of IDD. However, volatilisation of iodine from terrestrial sources is also likely to be an important influence on the environmental distribution of iodine (Sive et al., 2007; Yokouchi et al., 2008). Where there is limited I^- in soil there is limited volatilisation of iodine so that a potentially vital pathway for transfer is missing. The authors would contend that while iodine in most soils shows poor bioavailability, in soils where iodine is not available for volatilisation, iodine deprivation would be extreme and, in the absence of adventitious sources in the human diet, would result in the occurrence of IDD.

It is probable that the historic distribution of iodine deficiency reflects the importance of local produce in the diet. Thus in areas where there is limited bioavailability of iodine, such as where limestone is the predominant lithology, or soils are organic-rich, endemic goitre occurred. With time, populations became less reliant on local produce and coupled with changes in agricultural practices resulting in iodine-rich dairy products, and the introduction of iodised salt, endemic goitre disappeared from the developed world. However, in recent times there has been a re-emergence of IDD in the developed world with Pearce et al. (2013) stating that the thirty countries that are currently iodine deficient include Australia, New Zealand and several Western Europe countries, with the suggestion that over 45% of schoolchildren in Europe are at least mildly iodine deficient.

Recently, Lazarus (2015) has suggested that the incidence of IDD bears little relationship to the environmental distribution of iodine. As stated above, the distribution and geochemistry of iodine was shown to be reflected in the historic incidence of IDD (Kelly and Sneddon, 1960; Dunn and van der Haar, 1990), the modern upsurge of IDD is more a reflection of dietary changes. The modern diet in developed countries is generally lower in milk and dairy produce (e.g. Vanderpump, 2012) than in the past and this is probably a significant factor in the re-emergence of IDD in developed countries. The increasing use of processed foods, frequently prepared with non-iodised salt is also likely to be a factor. It is also possible that the move to lower salt intake recommended by the medical profession, resulting in lowered use of iodised salt, may be a contributory cause of IDD in modern society. Indeed, Andersen et al. (2013), in a study of Danish pregnant women, have shown that even though salt is iodised there is sub-optimal intake of dietary iodine, leading those authors to suggest that the iodine content of salt in Denmark needs to be increased.

The current upsurge of IDD in many affluent countries should serve as a reminder that in the absence of adventitious sources of

dietary iodine, IDD has the potential to affect large numbers of the world population. It has been variously estimated that up to 30% of the world population are at risk of IDD (Hetzl, 1991; Stewart and Pharoah, 1996), however, the current authors would suggest that the potential for iodine deficiency in the world population has been underestimated. It is suggested that as most of the Earth's surface is iodine deficient, IDD has the potential to affect a very large percentage of the world population. It is then important to take account of and understand the geochemistry of iodine and it is the task of geochemists to delineate areas of iodine sufficiency and deficiency.

Acknowledgements

The authors thank Antony Smith, Department of Geography and Earth Sciences, Aberystwyth, for producing Fig. 3. We are also grateful to the reviewers for their time and effort.

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