



The geochemistry of iodine and its application to environmental strategies for reducing the risks from iodine deficiency disorders (IDD)

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The geochemistry of iodine and its application to environmental strategies for reducing the risks from iodine deficiency disorders (IDD)

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SUMMARY

The role of iodine in endemic goitre was the first recognised association between a trace element in the environment and human health. Medical intervention techniques such as salt iodisation have been successful in reducing the risks from iodine deficiency disorders (IDD) in many parts of the world. However, much of the effort in eliminating IDD proceeds without a sound understanding of its principal cause - a deficiency of iodine in the environment. This project funded by the UK Department for International Development (DFID) addresses the perceived need for a better understanding of iodine geochemistry so that we can ensure that the small amounts of iodine that are available in the environment are used in the most efficient way. Futhermore, iodine added through environmental supplementation techniques (e.g. adding iodine to irrigation waters) needs to be managed in an effective way to ensure maximum use is made of the added iodine through a better understanding of its geochemical behaviour.

This project uses data from BGS case studies in Sri Lanka, China and Morocco plus an extensive bibliography of iodine geochemistry. From this we have created databases on the iodine content of soils, food and drinking water.

The geochemistry of iodine in soils has been studied in detail as this is the vital link between the food chain and the environment. A model for the iodine content of soils is discussed based on locational factors, the iodine fixation potential of the soil and the important pathway of iodine from the ocean-atmosphere-land-plant-man. There is no simple correlation between the iodine content of a soil its distance from the sea, though the coastal zone is clearly a high-iodine environment which is reflected by the high levels of iodine in water, soil and crops in such areas. Climate, topography and parent material all contribute to the iodine status of a soil which is determined by the interaction of numerous physical and chemical parameters. The iodine content of a soil depends not only on the supply of iodine, or lack of it, but the ability of the soil to fix the iodine, i.e. its iodine fixation potential. Organic matter plays a principal role in retaining iodine but other factors will contribute including soil texture, iron and aluminium oxides, clay minerals, water-logging, microbial activity and Eh and pH.

The oxidation potential and pH are fundamental in determining the form and mobility of iodine in a soil system. It is the mobile or bioavailable iodine present in the environment that should be of prime concern. Iodide is considered to be the more mobile and volatile form within the soil and is favoured by acidic soil conditions. Iodate is the less mobile form of iodine in soil and is favoured by dry oxidising alkaline conditions such as those found in thin soils developed on limestone. Methyl iodide and other volatile organic complexes of iodine appear to be generated by microbial and root activity.

The atmophile nature of iodine is its most significant geochemical characteristic and the volatilisation of iodine from the soil-plant system is of far greater significance than previously believed. Direct adsorption of iodine on to plant leaves from the atmosphere can contribute to the total iodine content of plants and it is seen that, of the various plant parts, leaves tend to have the highest levels of iodine. The transfer ratio of iodine from soil to plant is low and with the exception of coastal zones it is suggested that most of the land surface is actually iodine-deficient in that locally grown crops alone cannot supply the recommended daily allowances to the local population. Industrialisation and development add adventitious iodine to the diet as well as the opportunity to eat foods from outside the local environment. Seafood is an external food source of major importance.

It is a fallacy to describe an area as iodine deficient purely because of a presence of IDD without citing levels for iodine in the local environment. This has rendered many mountainous and glaciated areas of the world iodine-deficient without any evidence to support this claim. Soils are not a good indicator of an iodine-deficiency because of their heterogeneous nature and the complexity of factors that determine their iodine status. The level of iodine in surface waters is a much better indicator of an environment's iodine status.

Environmental solutions to reducing the risks from IDD require that either the existing natural iodine is managed more efficiently or iodine is added from an external source. Measures to manage the local iodine balance more efficiently include: changing the crops grown; using grazing livestock to concentrate iodine; improving the soil's ability to fix the iodine; making the soil's iodine more bioavailable without losing it through volatilisation; finding alternative more iodine-rich water supplies; and preventing removal of iodine by flooding.

Although better control of iodine in marginally iodine-deficient areas may help to reduce the risks from IDD it is not likely to be appropriate in regions of extreme poverty and harsh environmental conditions where the local population have little or no scope for controlling their own environment. In such instances, environmental intervention techniques such as adding iodine to irrigation waters may be more appropriate. These have been shown to bring substantial benefits to the local environment as well as being cost effective with some benefits over the conventional salt iodisation strategies. However, such additions of iodine to the environment need to be managed carefully so the benefits of the added iodine are not lost through volatilisation and rapid migration of iodine out of the soil system in a relatively short period of time.

1. INTRODUCTION

We all face a danger if our diet lacks iodine and the consequence is a number of medical conditions grouped under the general heading of iodine deficiency disorders (IDD). Only a trace amount of iodine is required, as little as $100 - 150 \mu g$ is the recommended daily dose, less than 3 g of iodine during the course of a lifetime. Cretinism, mental retardation, decreased fertility, increased perinatal death and infant mortality will result from instances of severe iodine deficiency. As these disorders can be constantly present to a greater or less degree in any place where no intervention has occurred they are referred to as being endemic diseases. At least one billion people are estimated to be at risk from IDD and a combination of socio-economic and environmental factors will determine who is at risk and where.

An understanding of the role of iodine in endemic goitre was the first recognised association between a trace element in the environment and human health. Treatment of goitre using iodine rich seaweed has been used for thousands of years though it was not until the early 1900's that the need for iodine in the diet (specifically for its thyroid function) was recognised.

Currently the main thrust of effort to reduce the risks from iodine deficiency disorders has been coordinated by the International Council for the Control of Iodine Deficiency Disorders (ICCIDD)¹. This is *a non-profit, non-government organization for the sustainable elimination of iodine deficiency and the promotion of optimal iodine nutrition worldwide*". Much of the effort in eliminating IDD proceeds successfully without a sound understanding of its principal cause, a deficiency of iodine in the environment. There is a perceived need for a better understanding of the geochemistry of iodine so we can ensure that the small amounts of iodine that are available in the environment are used in the most efficient way. Where iodine is added directly to the environment by methods such as dripping into irrigation water we will be better able to ensure that this iodine reaches the food chain.

The aim of this project on "Environmental Controls in IDD" is to look at the factors controlling the bioavailability of iodine in the surface environment and to look at solutions to reduce the risk of IDD by supplementing medical intervention schemes where necessary. The output from the work is specifically aimed at informing the medical community about the geochemical behaviour of iodine in the environment. This project has been funded by the UK's Department for International Development (DFID) as part of their Knowledge and Research (KAR) programme which constitutes a key element in the UK's provision of aid and assistance to less economicallydeveloped countries.

This report is a synthesis of the data and information gathered by the project either from the project's bibliographic database (Johnson, 2003a) or from the two case study investigations in China (Fordyce et al, 2003) and Morocco (Johnson et al, 2002). This work does not intend to be an all embracing account of the geochemistry of iodine, that has been reported for example by Whitehead (1984), Fuge and Johnson (1986) and, more recently, by Fuge (2003). Here the geochemistry of iodine in soils is discussed in detail as this is a significant component of the pathway for this essential trace element in our diet. The iodine content of food and drinking water is also considered in Section 3 before strategies for reducing the risks of IDD are discussed.

The geochemistry of iodine is summarised in Figure 1.

¹ http://www.people.virginia.edu/~jtd/iccidd/



Figure 1: A diagram showing the general distribution of iodine in the environment (updated from Johnson, 1980)

2. A MODEL FOR THE IODINE CONTENT OF SOILS

2.1. Introduction

The iodine content of a soil can be considered by looking at the factors that are responsible for its composition, physical and chemical properties. These are the factors that will determine the soil type and will be responsible for regulating the input and output of the iodine from the soil. The first group of parameters can be considered as *locational factors* and would include geology and topography, climate and proximity to the sea. The soil is a dynamic system which will respond to changes in physio-chemical conditions. If these conditions remain stable over a period of time then elements in the soil will be at equilibrium. For a soil at a specific point in time the interaction of the physio-chemical properties will result in an *iodine fixation potential* for the soil. Iodine will be gained or lost through the soil through various *pathways* and the two most important pathways, ocean-atmosphere-plant/soil and plant/soil-man, will be discussed here. Finally, the anthropogenic impact on soil iodine needs to be discussed, as the way in which we use the land will ultimately impact on the pathway of iodine through our food chain. These four components can form the basis for the discussion of a model of the iodine content of soil (see Figure 2). The first three of these factors will be addressed in this section, anthropogenic activity will be discussed in the context of strategies for reducing the risks of IDD.



Figure 2: Four components of a model for determining the iodine content of a soil

2.2. Iodine content of soil

Before discussing the various components of the model it is worth considering the information on which our knowledge of the geochemistry of iodine in soils is based. Johnson (2003b) has compiled a database of published iodine results for soils from all over the world. This work is based on the earlier compilation of the Chilean Iodine Educational Bureau (CIEB, 1956) which is a very comprehensive account of soil iodine data pre-1956. The database of Johnson (2003b) has good representation of data drawn from the three main areas of research in this field. Most of the pre-1960 data are concerned with studies relating iodine deficiency disorders to human health and this interest has continued (for example Anke et al, 1995 and Fuge, 1996). In the 1970s and 1980s there was a renewed interest in iodine soil geochemistry because of its potential use as a pathfinder element in mineral exploration (Fuge et al, 1986). More recently there has been a developing and well-funded interest in the study of the behaviour of isotopes of iodine in the soil (for example, Schmitz and Auman, 1994; Sheppard et al, 1996; and Muramatsu and Yoshida, 1999) because of risks to human health posed by its radioactive isotopes (Zanzonico and Becker, 1993). Iodine is important because the very long-lived I-129 is the most critical component of low- or high-level radioactive waste management (Sheppard et al, 1993).

The main conclusions from Johnson (2003b) are:

- The average iodine content of soils is 5.1 µg/g (based on screened data of 2151 cited results). However, given the skewed nature of the distribution of results, the geometric mean of 3.0 µg/g is a more suitable value to quote for the level of iodine in soils.
- Using a classification based mainly on texture, the order for levels of iodine in soil has been determined as: peat (7.0) > clay (4.3) > silt (3.0) > sand (2.2). The figure in brackets is the geometric mean value in $\mu g/g$ for screened data (see Table 1).
- There is no simple correlation between the iodine content of a soil and the distance of the sample site from the sea coast. However, the highest levels of iodine are recorded in coastal zones (0-50 km from the sea) with a large range of results being reported (0.8 150 μ g/g) and a geometric mean of 11.6 μ g/g. Inland, at distances greater than 50 km, there is a much narrower range of results reported (0.4 14 μ g/g) with a lower geometric mean of 2.6 μ g/g.
- Unconsolidated and texturally coarse parent materials appear to produce low iodine soils, as do metamorphic bedrocks.

Soil Class	Unscreened data (µg/g I)					Screened data (µg/g I)						
	no.	mean	geo-	median	min.	max.	no.	mean	geo-	median	min.	max.
			mean						mean			
Peat	41	8.83	6.63	7.25	0.2	28	39	8.56	6.99	7.25	1.32	22
Silt	107	8.15	2.99	4.00	0.1	135	103	6.35	2.98	4.00	0.19	72
Clay	394	7.27	4.26	4.65	0.1	68.74	378	6.56	4.34	4.65	0.2	33.29
Sand	467	4.11	2.21	2.45	0.08	58	449	3.44	2.22	2.45	0.1	27.5
Undefined	1232	6.08	2.81	3.14	0.015	150	1182	5.02	2.84	3.14	0.14	36.29
All data	2241	6.03	2.93	3.15	0.015	150	2151	5.09	2.96	3.15	0.1	72

Table 1: Summary statistics for unscreened and screened data grouped by soil class (after Johnson, 2003b)

Most investigations have reported the total iodine content of soils. For human health studies the bioavailable iodine fraction of the soil is the most important consideration and workers in this field are urged to give this fraction of the soil iodine far greater attention. It should also be noted that much of the soil composition has been neglected. Figure 3 shows that for a generalised soil composition, approximately 50% of the soil volume is made up of air and water. These components of the soil are not completely by standard soil sampling methods yet they are of

fundamental importance in the migration of iodine through the soil. The size fraction of the soil is also an important consideration.



Figure 3: Volume composition of a loam surface soil (after Brady and Weil, 1999)

2.3. Locational Factors

2.3.1. Parent Material

The raw material and largest component of most soils is the inorganic minerals derived from the weathering of rock or the reworking of existing detritus. The nature of the parent material profoundly influences soil characteristics which in turn will determine the geochemical composition of the soil. For example, a weathered shale will produce abundant clay minerals and the soil will inherit a clayey texture. The texture will in turn influence the processes occurring in the soil such as water movement. The source of parent material is ultimately a consequence of location and the underlying geology.

The inorganic parent material may have formed by weathering in place or have been generated at one location and deposited at another. Soils formed in situ are generally referred to as residual. Parent material that has been transported is often classified by mode of placement to the current location, for example, alluvial, lacustrine, marine or glacial. The transport and deposition will greatly change the physical and chemical composition of the parent material resulting in the depletion or concentration of some inorganic components. The impact on the iodine content caused by transport and deposition of parent material is discussed later in this section after the direct iodine contribution of the bedrock is first considered.

Table 2 summarises the iodine content of common rock types. This shows that igneous rocks $(0.2 \ \mu g/g)$ contain less iodine than sedimentary rocks $(1-2 \ \mu g/g)$. (Note that metamorphic rocks are not included in this table because of the limited amount of reliable data - see Fuge and Johnson, 1986). There are some sedimentary rocks that are particularly enriched in iodine such as organic rich shales, e.g. Kimmeridge Shale, Dorset, England with 23.3 $\mu g/g$ (Fuge et al, 1978). However, these exotic rock types are relatively rare and with 95% of the Earth's crust being made up of rocks of igneous origin, an average estimate for parent material would be 0.25 $\mu g/g$ I. Most soils contain more iodine than this and are on average enriched by a factor of ten. The enrichment in soil relative to rock is also noted by Aston and Brazier (1979) and Muramatsu et al (1996). This is further illustrated with soil data from the CIEB (1956) shown in relation to the parent material from which they are formed (Table 3). Cohen (1985) concluded that sedimentary rocks were the principal and probably the prominent source of iodine in soils and

did not support the idea of an atmospheric origin for most of the soil's iodine. The overwhelming evidence from literature on atmospheric sources for iodine would no longer give credence to this standpoint.

Rock Type	Mean Iodine content (µg/g)
Igneous Rocks	
Granite	0.25
All other intrusives	0.22
Basalts	0.22
All other volcanics	0.24
Volcanic glasses	0.52
Sedimentary Rocks	
Shales	2.3
Sandstones	0.8
Limestones	2.7
Organic-rich shales	16.7

 Table 2: The iodine content of some common rock types (after Fuge and Ander, 1998)

Rock Type	Iodine in parent material (µg/g)	Iodine in soils derived from parent material (µg/g)
IGNEOUS ROCKS (ALL)	0.52	9.34
Basic	0.50	10.17
Intermediate	0.52	8.34
Acid	0.54	6.11
SEDIMENTARY (ALL)	1.55	3.85
Limestones	1.18	4.51
Sandstones	1.74	3.65
Shales and Argillites	2.18	2.22
METAMORPHIC ROCKS (ALL)	1.61	5.31

 Table 3 : Iodine content of rocks and of soils derived from them (after CIEB, 1956)

Whilst high-iodine bedrock can be a significant contributor to soil iodine, it is the numerous processes to which the soil is subjected that must be responsible for introducing additional iodine. The processes of soil formation are summarised in Table 4 along with a comment on how the iodine concentration of the soil may be enhanced or depleted. Any process that adds organic material to the soil, concentrates the finer clay fraction or introduces iodine rich seawater is going to lead to soils which are more iodine enriched. Processes that add no organic matter or concentrate the heavy mineral fraction or the coarse SiO_2 fraction of the soil are going to lead to iodine poor soils. Organic matter has a significant affect on accumulating iodine (see later) and, as most soil forming processes involve the accumulation of organic materials with time, the overall effect is an enrichment of iodine in the soil relative to its parent material.

Mode of Placement	Name	Consequence on soil iodine content relative to original bedrock
In situ	Residual	1, 2
Transported (Gravity)	Colluvial	4, 5
Transported (Water - river)	Alluvial	1, 2, 4, 5
Transported (Water - ocean)	Marine	1, 2, 3 , 5
Transported (Water - lake)	Lacustrine	1, 2, 4, 5
Transported (Ice)	Glacial	4, 5
Transported (Wind))	Eolian	4, 5
Accumulated Plant Debris	Organic	1

1. Increase in iodine content as organic material introduced to profile .

2. Any water soluble iodine fraction of the parent material lost.

3. Significant increase in iodine due to accumulation of iodine rich pore fluids.

4. Decrease in iodine due to accumulation of iodine poor heavy minerals or coarse

5. Increase in iodine due to concentration of finer clay minerals

 Table 4 : A summary of how the different modes of placement of parent material can affect the resulting soil iodine content

From Table 4 it may be deduced that fine grained marine parent material is likely to give rise to the most iodine rich soils. However, it should be noted that soils formed from marine material progressively lose their iodine with time. Reith (1933) showed that Dutch soils developed on what used to be the sea floor have been progressively losing iodine. Soils exposed since 1300, 1718, 1836 and 1923 contained 9.23, 9.45, 12.00 and 18.50 ppm I respectively. Futhermore, Anke et al (1995) note that Triassic sedimentary rocks that were formed in a marine environment are no longer enriched in iodine. The iodine is lost during the processes of rock formation.

Freshly ground rock powder deposited by glacial processes is often cited in the literature as being responsible for the low iodine status of glaciated terrains. Schnell and Aumann (1999) found that there was no major difference in soil iodine content in recently glaciated areas of Germany compared to those in similar geographical locations that have not been glaciated. Cohen (1985) was also unable to find a difference between glaciated and older non-glaciated soils. Whilst it is logically to assume a rock powder has the same iodine content of the original rock, the suggestion that such glacial soils are iodine-deficient takes no account on how fast a soil equilibrates in terms of its soil iodine balance. This misconception derives from the classic account on iodine geochemistry by Goldschmidt (1954): "...the frequency of goitre in a number of countries in Europe, North America, probably also Asia and New Zealand, shows a close relationship to the extent of Quaternary glaciation, that is the occurrence of soils which have not yet been sufficiently saturated with post-glacial air-borne oceanic iodine."

Recent research would suggest that iodine in soils equilibriates with the surrounding environment relatively rapidly and it is unlikely that glacial soils are still "under saturated" with iodine. The results of Schnell and Aumann (1999) show that present-day young soils of glaciated regions have had enough time to accumulate iodine solely through that supplied by rainfall. They estimate that, without loss of iodine from the soil, the present day inventory of iodine in the top 60 cm of soil would take 723 - 2146 years to achieve. Similarly, Whitehead (1979) calculates that for the UK with an annual rainfall of 900 mm, and an average rain water content of $1.5 \mu g/l$, iodine would be increased by $6 \mu g/g$ to a depth of 15 cm in 1000 years if all the iodine was retained. If the soil of glacial origin has the ability to retain iodine then there has been plenty of time since the last ice age (c.10,000 years ago) for equilibrium to have been reached. Any

quartz rich fraction.

deficiency of iodine in glacial soils is a result of the composition and texture of the soil rather than a function of time.

2.3.2. Climate

As climate determines the nature and intensity of weathering over large geographical areas it can be considered as one of the most influential factors in the process of soil formation. In particular, temperature and precipitation will affect the rates of both physio-chemical and biological processes which in turn will determine a soil's ability to retain iodine.

In arid alkaline environments iodine is found to occur as iodate minerals, the Chilean saltpetre deposits serving as an example of this (CIEB, 1956). Very insoluble iodide minerals have also been reported in the "weathered zones" of mineral deposits in arid environments (Burgess, 1911, 1917). These forms of iodine can be related to the unusual pH and Eh conditions of such a climatic zone.

Torrential rain in tropical environments is often cited as being responsible for leaching iodine from soils, for example in the "wet zone" of Sri Lanka (see Dissanayake and Chandrajith, 1996), and removal of iodine from soils during flooding. The cause of this could be due to the physical removal of the fractions that fix the iodine (e.g. organic matter and clays) as well as the dissolution of iodine (see Section 2.4.2). Unfortunately flooding will impact most on the "mobile iodine" fraction removing much of the bioavailable iodine from the food chain. Section 2.4.4 discusses the effect of water-logging on soil iodine content.

2.3.3. Topography

On apocryphal evidence it is frequently cited that mountainous areas are deficient in iodine. Goldschmidt (1954) discusses the possibility that because of the high atomic weight of iodine it may be distributed in the atmosphere according to some barometric formula. This led some workers to believe this was an explanation for the high prevalence of goitre in regions of high altitude. Whilst a high prevalence of IDD does occur in mountainous areas, it is the secondary factors associated with such areas that are likely to be implicated rather than the height factor itself. For example, soils developed on mountain slopes will often be thin, immature and with a high component of coarse rock fragments and consequently will have a low iodine fixation potential (see Section 2.4).

Conversely low lying ground will often be found in an iodine-rich environment because of proximity to the sea (see next section) or the low lying land has been subjected to marine incursions.

Topography will affect the local climate and will often be associated with rainfall zones. Fuge (2003) considers iodine in soils along a traverse from the Welsh coast over the Welsh Mountains (up to 350 m in height). The high values occur on the higher ground because of a combination of the greater degree of washout of atmospheric iodine due to increased rainfall in such areas, and the fact that the upland soils tend to be organic-rich and more able to retain the iodine. An associated consequence of this is the low supply of iodine in the rain shadow². This effect should be particularly pronounced in high mountainous areas such as the Andes and Himalayas.

² "**Rain shadow**" - An area having relatively little precipitation due to the effect of a barrier, such as a mountain range, that causes the prevailing winds to lose their moisture before reaching it.

2.3.4. Proximity to the sea

The majority of results quoted in the literature for iodine in soils do not give an indication of how far the soil sample site was from the coastline. Input of iodine from the atmosphere, either as wet or dry precipitation, is considered to be a major part of the iodine geochemical cycle and much of this iodine must be derived from the oceans (Fuge and Johnson, 1986). The proximity of the soil site to the sea is therefore of great interest. Johnson (2003b) has plotted iodine soil results for which there is "distance from the sea" information (75 records - Figure 4). This shows some very high results at locations near the sea and a generally higher than average level of iodine in the coastal zone 0 - 50 km. However, results in this coastal zone are not exclusively high and there are low levels of iodine also recorded for some soils. Moving well in land the average iodine content of soils does drop to low levels around 1 μ g/g and there is a much narrower range of results. Figure 4 does not include samples collected from the continental interior of Xinjiang province, China (Fordyce et al, 2003) so as not the compress the x axis. These samples were from at least 2,500 km from the nearest sea coast and had average iodine contents of 0.89 to 1.1 μ g/g.



Figure 4: Levels of iodine in soils plotted against their distance from the sea coast

There is no significant correlation between the iodine content of the soil and the distance from the sea coast (Pearson correlation coefficient = -0.18) but clearly soils in the coastal zone are subjected to a greater input of iodine. The level of iodine in the soil will depend on the ability of the soil to fix the iodine. A sample of beach sand collected within 200m of the sea at Agadir, Morocco contained only 0.59 µg/g I (Johnson et al, 2002). This sample was collected shortly after heavy rain and any salt or spray deposits had been washed from the sample. The prevailing wind direction is also of crucial importance to any comprehensive discussion of this topic, information that is lacking from most reports.

Fuge (1996) (for Wales, UK) and Johnson et al (2002) (for Anti Atlas Mts, Morocco) both report higher ranges of soil results in coastal areas declining to much lower and narrower ranges inland. It must be concluded that in coastal zones (0-50 km from the coast) there is a much higher input of iodine from the atmosphere that is directly related to migration from seawater to the land. There is a relatively rapid decline of iodine in soils moving away from the coast and soils, say for example in central England (< 4 μ g/g), do not have markedly different levels from soils of continental interiors e.g. Missouri 1.26 (μ g/g) (Fuge,1996). Evidence suggests that inland the mechanism for iodine transport via the atmosphere will be different and revolatilation from the soil-plant system to the atmosphere is possibly the most important factor in determining the soil's iodine status (Fuge, 1996).

The work of Schnell and Aumann (1999) is illustrates how the iodine content of soil does not necessarily decrease with increasing distance from the sea. In this instance the increased rainfall inland is shown to be responsible for delivering a greater annual amount of iodine than was found nearer the sea coast. Anke et al (1995) believe the geological origin of the soil has a much greater effect on the iodine content of flora and fauna than distance from the sea, although both effects cannot be separated entirely. Groppel and Anke (1986) note that the iodine content of red



clover and green rye nearer the sea coast is demonstrated in Figure 5.

Figure 5: A plot of iodine in clover and rye against site distance from the sea (data from Groppel and Anke, 1986)

2.4. Iodine Fixation Potential

Figure 6 illustrates a simple view of iodine interaction in a soil. The soil (A) will contain a component (B) that will interact with any introduced iodine through a pathway (C). Consider the circumstances that will give rise to a soil with low levels of iodine:



- a) The soil (A) has very low iodine in the parent material
- b) The output of iodine into the system exceeds the input
- c) The input pathway (C) has a small interaction with the soil (B)
- d) The output pathway (C) has a large interaction with the soil (B)Figure 6: Simple view of iodine interaction in a soil (see text for explanation)

Statement (a) concerning the parent material has already been discussed in Section 2.3.1. Statements (b) - (d) represent the more dynamic part of the soil processes and may change on a seasonal or even daily basis.

Soils are richer in iodine than the parent material from which they form (see Section 2.3.1) so the soil must have a capacity to fix more iodine input from an external source. In the early days of iodine geochemistry there was disagreement regarding the source of the additional iodine though it was accepted that an extraneous origin for most of it was required as the element cannot be concentrated as a relatively insoluble residual component from weathered primary rocks (Goldschmidt, 1954). The migration of iodine through the atmosphere is now considered to be the most important part of its geochemical cycle and this pathway is discussed in the next section. The exchange of iodine between atmosphere and soil makes the geochemistry of iodine unusual as there are few non-gaseous elements that exhibit atmophile behaviour.

A pathway with an abundant supply of iodine will not necessarily produce an iodine-rich soil. This is demonstrated by the beach sand sample collected by Johnson et al (2002) near the sea shore at Agadir, Morocco. With abundant sea spray there would have been a very high supply of iodine yet the total iodine recorded in this sample was only 0.59 μ g/g I. This sample which was almost pure sand, had little ability to fix the iodine which had clearly been washed away during heavy rain immediately prior to sampling. Johnson (1980) introduced the term **'Iodine fixation potential**" (ifp) that was defined as the total amount of iodine that can be fixed by the various fractions in a soil and is a characteristic of a soil in a given environment. A chemical or physical change in the environment will result in a new ifp for that soil. The combination of iodine supply and the ifp will give the **iodine status** of a soil. This idea of ifp can be represented by the following equation and the total iodine of a soil will reach the ifp if the supply of iodine is adequate:

$$I_{ifp} = I_1 + I_2 + I_3 + I_4 \quad \dots \dots I_{(n-1)} + I_n$$

or
$$I_{tot} = I_{ifp} = {}^n \sum_{1} I$$

where I_{ifp} is the iodine fixation potential of the soil; I_{tot} is the total iodine content of the soil; and $I_1 + I_2 + I_3 + I_4 \quad \dots \cdot I_{(n-1)} + I_n$ represents the iodine concentration of the different fractions of iodine in the soil resulting from different species of iodine associated with different components of the soil. In this context we must also include the soil gas and pore fluids. If we consider I_1 to be the most strongly fixed iodine fraction and I_n to be the most mobile, then the most bioavailable fractions are I_n , $I_{(n-1)}$, $I_{(n-2)}$ etc. and will be the first iodine components to disappear if processes acting within the soil cause the equilibrium to be disturbed so there is a greater output of iodine than there is input.

2.4.1. What is an iodine -deficient soil?

In the context of any discussion on IDD it is useful to consider what is meant by an iodinedeficient soil. Is it synonymous with an iodine-deficient environment? In the strictest sense, from the discussion above, an iodine-deficient soil will be one that has not reached its full ifp. As different soils will have different ifps then there is no single threshold below which a soil can be defined as being iodine-deficient. An iodine-deficient environment (of which soil will be an integral and important part) is one that cannot provide the sufficient daily intake of iodine for the local population or the livestock reared in it. The deficiency arises from low concentrations of iodine in the rocks, soil, vegetation, drinking water or atmosphere and the local population need an additional external supply of this essential element. This general definition of iodine deficiency would actually render most land areas of the world as being iodine deficient. The exception being coastal areas where adequate supplies of environment iodine are available because of the proximity to the marine environment, the single most important supply route in the iodine geochemical cycle.

The iodine status an area is usually implied by the iodine status of the local population as measured by medical parameters such as thyroid size or urinary iodine levels (see Table 5). The presence of IDD is used to state that environmental iodine levels are inadequate without such levels having been determined. This is an anthropological fallacy as an area cannot be described as environmentally iodine deficient purely on the basis of a presence of IDD (Stewart et al, 2003). The iodine status of a population may be related to the bioavailable iodine in the soil and not the total iodine content. Because of the heterogeneous nature of soils, the great variety of types and complex interaction of processes that determine the iodine content, using the total iodine of soils to describe the iodine status of an area is not considered a useful exercise. Surface waters are a better measure of an environments level of iodine deficiency (see Section 3.4).

Median Urinary Iodine Concentration (µg/L)	Corresponding Approximate Iodine Intake (µg/day)	Iodine Nutrition
<20	<30	Severe deficiency
20-49	30-74	Moderate deficiency
50-99	75-149	Mild deficiency
100-199	150-299	Optimal
200-299	300-449	More than adequate
>299	>449	Possible excess

 Table 5: Scale used by WHO/ICCIDD/UNICEF to relate iodine nutrition to urinary iodine concentration. (after http://www.people.virginia.edu/%7Ejtd/iccidd/aboutidd.htm)

2.4.2. Forms of iodine in a soil

Many analytical methods for iodine have limits of detection that are close to values for total iodine recorded for many soils. It is difficult to consider determining the smaller different iodine fractions and so there are not much data on the speciation of iodine in soils. Much is inferred by the extraction technique used in determining the iodine. For example, shaking the soil with cold water is believed to extract the more mobile fraction of the soil (the bioavailable iodine) leaving the more firmly fixed iodine behind.

Several workers have commented on the low percentage of water soluble iodine (I_{sol}) in soils. Magomedova et al (1970) found that in soils from mountainous Dagestan, (formerly USSR), only 1 - 12% of the total iodine was water soluble, and similarly Sinitskaya (1969) records only small amounts of water soluble iodine in Zeya-Bureya Plain soils, USSR. Whitehead (1973) found that from 23 analyses of some British soils 24% of the total iodine could be extracted by boiling water. Johnson (1980) in a study of nearly 200 mainly Welsh soils concluded that the cold water extractable fraction was generally less than 10% of the total iodine. Similar results are recorded by Johnson et al (2002) for 24 soils from the Atlas Mountains, Morocco where the I_{sol} is reported to be between 2 -10%. A notable exception to this was the beach sand for which a value of 35.4% was recorded.

In arid alkaline environments iodine is found to occur as iodate minerals, the Chilean saltpetre deposits are an example of this. Iodate minerals are soluble and should be easily extractable. Very insoluble iodides have also been reported in the "weathered zones" of some mineral

deposits in arid environments (Burgess, 1911, 1917). Such environments are characterised by their unusual pH and Eh levels to which the form of occurrence of the iodine can be related (see Figure 7). The iodide ion is reported as the dominant form of soluble iodine in acidic soils whilst in dry oxidising conditions iodate is the dominant soluble form (Yuita, 1992 and Fuge 1996).



Figure 7: Fields of iodine ions stability depending on the pH and Eh of the medium (after Vinogradov and Lapp, 1971). The field of the normal natural environment is shaded.

In acidic environments (i.e. low pH), Fe^{3+} and Mn^{4+} are oxidisers of iodine converting the I anion into molecular iodine (I₂) (Perel'man, 1977). An important geochemical barrier described by Fuge and Ander (1998) is in alkaline soils where the IO_3^- formed will not be revolatilised. This is a significant observation for two reasons. Regions of limestone (with the associated alkaline soils) are identified has high prevalence IDD areas (Fuge and Long, 1989). The implication is that iodine is fixed and not bioavailable. Secondly, such areas will be at greatest risk for thyroid cancer after the accidental nuclear release of radioisotopes of iodine. Because the natural sources of iodine are immobilised, people in these areas are more likely to take in a greater proportion of the more mobile radioisotopes of iodine with the associated higher risk of thyroid cancer.

Iodine forms a large univalent anion with a Pauling radius of 216 pm (cf 181 and 139 pm for CI and F respectively) and because of this large size it is unlikely that any crystal lattice would readily accept it as a substitute anion. When iodine accepts an electron it converts to Γ acquiring the stable configuration of an inert gas. As iodine's electron affinity is relatively small it easily loses the acquired electron to become the I₂ molecule.

Organic complexes of iodine are seen to be important in the atmospheric transfer of iodine (see Section 2.5.3) and these must be an important component of the iodine fraction in a soil.

Although different in many respects, geochemically iodine has more similarities to nitrogen than to the other halogens. Both are constituent parts of proteins and there is an anology between IO^{3-} and NO^{3-} in that IO^{3-} can be readily reduced to I_2 similar to denitrification.

2.4.3. Determining the iodine status of a soil

Johnson (1980) tried to represent the iodine status of a soil by plotting the ifp against supply of iodine in a semi-quantitative manner. This is shown in Figure 8 mainly with the purpose to emphasise that soils with a low supply of iodine can have a high iodine status if they have a high iodine fixation potential. It should be possible to determine the iodine status of a soil by more quantitative means. If the main supply of iodine is considered to be atmospheric then based on dry and wet precipitation rates an annual supply of iodine to the soil can be calculated though it may be difficult to model the distribution of the added iodine throughout the soil profile. The iodine fixation potential in Figure 8 is represented by soil texture which is taken to represent a summation of processes and components that contribute to determining the levels of iodine a soil.



Figure 8: Figure showing the iodine status of a soil in relation to the supply of iodine and the soils iodine fixation potential

Much can be learnt about the iodine fixation potential of a soil from studies of the migration of radioisotopes of iodine. Studies on I-129 in soils such as that described by Schmitz and Aumann (1994) could be used as a means of quantifying the ifp of a soil. An introduced radio-isotope of iodine added to the soil could be used to determine whether or not a soil has reached its iodine "saturation" point. If the soil has capacity to fix more radioactive iodine then its current total iodine content is below the ifp of the soil. However, it is unlikely that the addition of inorganic iodine in this way is truly representative of the natural situation where I-127 will exist in many different forms. Schmitz and Aumann (1994) observed that the water-soluble fractions of the natural I-127 ranged between 2.5 - 9.7% compared with 21.7 - 48.7% for the I-129. Yu et al (1996) report soils that lost added iodine as volatile species also had low natural iodine concentrations suggesting that the same processes that eliminate added iodide also account for the low natural concentrations.

2.4.4. Factors cited as influencing the fixation of iodine in soils

It must be assumed that under a specific set of conditions a soil will have a fixed number of sites at which iodine molecules or species can be absorbed or adsorbed. This will be determined by the presence of components in the soil such as organic matter, oxide minerals and clays that are capable of fixing the iodine. The chemical environment will determine the Eh-pH conditions of the soil and the activity of reducing bacteria which in turn will impact on the form of iodine in the soil. The form of iodine in the soil will influence the mobility of the element in the soil. Soil texture and water-logging will also impact on not only the chemical environment within the soil but also the pathways available for the removal or addition of iodine.

Organic matter. Organic matter plays a significant role in the retention of soil iodine and soil iodine can be correlated with the soil's organic content, particularly in surface soils. It is probably the single most important determinant in contributing to the total iodine levels in soil and sorption of iodine in soils is directly related to the organic matter content (Sheppard and Thibault, 1992). Peat soils are seen to be the most iodine-rich soils (Table 1).

Yu et al (1996) note that high-organic matter soils exhibited little volatility, presumably because they retain iodine in the organically bond state. Yamada et al (1999) found that a high proportion of the soil's iodine is organic iodine bound to fluvic and humic acids. Humic substances seem to play a considerable role in binding iodide (Lee and Dee, 1967 and Behrens, 1985). The incorporation of fallen plant material on which atmospheric iodine has been deposited is an important accumulation pathway in soils (Muramatsu and Yoshida, 1999). The iodide binding by humic acid was found to be inhibited when oxygen was depleted (Huang and Lu, 1991). The iodide in soils may be attracted to soil surfaces through weak electrostatic action but Sheppard and Thibault (1992) believe that the retention is primarily through physical association with surfaces. This would be entrapment in the micropores and structural cavities of the intricate fabric of the organic matter.

Sheppard et al (1996) from sortion/desorption experiments suggest that the oxidation of I to I₂ and complexation to organic functional groups or oxides are the major processes of iodine retention in Canadian Shield soils. Yu et al (1996) concluded from their experiments on the reactivity of I⁻ in volcanic soils that sorption of iodide in soils is primarily controlled by oxidation. Slow oxidation of I to $I_{2(aq)}$ is followed by $I_{2(aq)}$ or its hydrolysis product HOI_(aq) reacting with the soil organic matter.

Clay minerals. Clay minerals have been implicated in the retention of iodine in soils. The iodine adsorption capacity of soils is reported by the CIEB (1956) to depend on the amount of clay and colloids present. Hirai and Takagi (1937); Hamid and Warkentin (1967); Yeschenko and Trofimov (1970); Vinogradov and Lapp (1971); and De et al (1971) all cite research that implicates clays in concentrating iodine in the soil. However, Yu et al (1996) note that inorganic solutes Γ , IO_3^- and I_2 do not adsorb strongly to mineral surfaces of layer-silicate clays because these surfaces are commonly negatively charged. Fuge (2003) believes the evidence is not substantial and clay minerals are therefore not considered to be an important factor in soil iodine retention

Iron and aluminium oxides. Experimental evidence has shown that iron and aluminium oxides will retain iodine (Whitehead, 1973, 1979, 1984)) including iodate an ion not thought to be sorbed by organic matter. Shepphard and Thibault (1992) believe Fe-Mn-Al oxides may account for some of the neutral or positively charged species of iodine in the soil. Iodine is concentrated in iron-rich soils (Fuge and Ander, 1998).

Soil pH and Eh. The discussion on the form of iodine in soils has already mentioned that iodide is believed to be the dominant species in acidic soils whilst iodate will occur in alkaline soils. This demonstrates the importance of pH in determining the form of soluble iodine in soils. It has also been demonstrated that Fe^{3+} and SO_4^{2-} reducing bacteria in soils could also reduce iodate to iodide emphasising an Eh control on the form of iodine. The prominence of soluble iodide in acid soils and iodate in alkaline soils would also be suggested by the Eh-pH diagram of Figure 7.

The chemical form of the iodine in the soil must be fundamental in determining whether or not the iodine is mobile.

Soil texture. The variation in iodine content of soils with different textures has already been introduced in Section 2.2. Soil texture has a demonstrable affect on the iodine content of the soil because it is a reflection of both the components that make up the soil (e.g. clays and colloids) and it impacts on the volume of pore space in the soil. The latter must be of fundamental importance in the migration of iodine in the soil profile yet it is an area of iodine geochemistry that has received little attention. It may be supposed that compacted clay-rich soils with little pore space will not be liable to losing iodine through gaseous or water soluble forms via pore spaces because they simply do not exist. This must be a contributory factor to why sandy textured soils, with their abundant pore spaces, are generally iodine deficient.

Water-logging. The reducing conditions in flooded soils increases the dissolution of iodine in the soil and rice plants in Japan have been observed to display Akagare disease due to excessive absorption of the dissolved iodine (Yamada et al, 1999). Muramatsu and Yoshida (1999) compared andosol soils from forested and cultivated land. The process of reclamation and rice cultivation under flooded conditions reduced soil iodine levels by one tenth.

The effect of water-logging is threefold. Firstly, under flooding the increased water content of the soil provides a pathway for removal of the iodine and secondly, reducing conditions from flooding and microbial activity will result in more soluble forms of iodine. Thirdly the water may actually remove or decompose the materials responsible for fixing the iodine.

The mobilisation of iodine under flooding, as practiced with rice cultivation, is further demonstrated by Yuita (1994) who looked at the iodine content of rice straw. The average content of the straw was 290 μ g/g (dry weight) grown under flooded conditions but only 0.37 μ g/g (dry weight) under non-flooded conditions. This is nearly an eight hundred-fold increase to the straw iodine content because of mobilisation of iodine due to flooding.

Microbial activity. Products relating to microbial metabolism (e.g. organic acids, enzymes, Fe^{2+} and H_2S) may act to desorb iodine from the soil (Muramatsu et al, 1996). Autoclaving treatment of soils results in a significant decrease in the sorption of iodide (Muramatsu and Yoshida, 1999 and Yu et al , 1996) suggesting microbes must have a role in fixing the iodine. Behrens (1985) noted that in fresh surface waters and in soil water systems iodide is, to a large extent, converted by microbial action.

2.5. Pathways



Figure 9: The annual cycle of iodine (from data in Johnson (1980) based on cycle from Miyake and Tsunogai (1963))

Figure 9 shows estimates for the annual cycling of iodine. Estimates for transfers are from Miyake and Tsunogai (1963) whilst estimates for the abundances of iodine in the various earth environments are those of Johnson (1980). Miyake and Tsunogai (1963) recognised the importance of the pathway from ocean to the atmosphere. Although indicated on Figure 9 as "evaporation" the process is more likely to be photochemical oxidation. They estimated that less than 1% of this transfer could be attributed to sea spray.

Figure 10 from Kocher (1991) shows the global cycling of iodine between the atmosphere and surface soils. The deposition of iodine in this model (1×10^{11} g/year) is of the same order of magnitude as the figure used by Miyake and Tsungai (1963) (Figure 9). This is used by Kocher to give a predicted mean residence time for I-129 in surface soils of 4000 years.

from atmosphere



Figure 10: The terrestrial compartment for the global cycling of iodine after Kocher (1991)

2.5.1. Air-Sea Exchange of Iodine

Although rocks are the largest reservoir of iodine (see Figure 9), it is the hydrosphere (principally made up by the oceans) that is attributed to be the source of most of the iodine in the active geochemical cycle. Some iodine must be transferred from the ocean to the atmosphere as seawater spray but a mechanism is required to explain why the ratio of iodine to chlorine in the atmosphere is so much greater. A large percentage of the iodine is in gaseous form (Duce et al,1973) so the required mechanism must account for preferential volatilisation of seawater iodine. Duce et al (1965) report an I/Cl ratio for rainwater which is 500-1000 times higher than that for seawater. Wong (1991) also notes that relative to seawater the I/Cl ratio is higher in particulate and gaseous phases in the atmosphere, in rain and in river water.

Careful distinctions have to be made between iodine in aerosols and in air, the latter represents total iodine in the atmosphere and includes both aerosols and gaseous iodine. In the atmosphere aerosols can be up to 20 μ m in size and above this they are readily deposited (Junge, 1963). Johnson (1980) notes that recorded levels for iodine in aerosols (0.3 - 10 ng/m³) were very much less than those for air (0.1 - 48.6 μ g/m³) suggesting very little atmospheric iodine exists in aerosol form. However, much of the discrepancies in the early works could be explained by poor sampling methods and Vought et al (1970) comment that a better understanding of atmospheric iodine levels require the development of more sophisticated air sampling and chemical trapping methods.

More recent research has added to our knowledge of the transfer of iodine from the sea to the atmosphere. One of the driving forces behind this work has been the possible role of iodine in climatic change, particularly the control it might have on ozone cycling in the remote atmosphere. Macroalgae and phytoplankton play an important role in this transfer of iodine to the atmosphere. The biogeochemical cycle of iodine can be summaried as follows³:

- 1. Iodate (the most stable form of iodine in seawater) is reduced to iodide in ocean surface waters. Biological activity (phytoplankton/bacteria) are thought to be implicated in this process.
- 2. The iodide is taken up by seaweed and phytoplankton and released as iodine-containing organic gases such as CH_3I and CH_2I_2 .
- 3. The organic gases cross the sea-atmosphere boundary and iodine is released into the atmosphere by the action of sunlight.
- 4. Through complex chemical interactions the iodine in the atmosphere has a role in the destruction of ozone.
- 5. In aerosols iodine is present as: the inorganic forms iodide and iodate; soluble organic iodine compounds; an insoluble iodine fraction, which may be organic or inorganic; as well as several other forms which are only present for short periods, either because they are volatile or reactive.
- 6. The iodine is deposited back to the earth's surface either washed-out by rain or by dry depositions. This pathway from sea to land represents a major part of the iodine geochemical cycle.



Figure 11: The ocean - atmosphere - land part of the iodine cycle (updated from Fuge, 1996)

³ <u>http://www.uea.ac.uk/~e780/airseaiod.htm</u>

2.5.2. Precipitation of iodine on land

Evidence supporting the importance of the atmosphere to land plants pathway of iodine is given by Shacklette and Cuthbert (1967). Spanish moss with no attachment to the soil contained as much iodine as ordinary land plants and its only method of obtaining iodine would be direct from the atmosphere or rainwater. They suggested that direct adsorption of air-bourne iodine was an important source of iodine in land plants. A similar observation was made by Whitehead (1979) for lichens.

Figure 11 shows the ocean-atmosphere-land part of the iodine cycle. The transfer of iodine to land will occur through both wet and dry deposition and this will be highest in coastal zones. The influence on soil iodine content relative to distance from the sea has been discussed in Section 2.3.4. Iodide accounts for 50% of rainfall iodine with iodate as a secondary component.

Available data for rain and snow shows a range of values between $0.5 - 20 \mu g/l$ I. Dean (1963) found approximately 40% of the iodine in New Zealand rainwater was organically bound. Schutyser et al (1978) found that in rainwater samples from Belgium the concentration of the insoluble iodine fraction was similar to that found in dry deposition. This suggested that the insoluble fraction in rainwater originates mainly from atmospheric "washout".

Krupp and Aumann (1999) reported that the inorganic fraction of iodine predominated in rainwater from Germany (41-69%) and the concentration of iodine in rain near the coast was higher than further in land. However, the total annual deposition of iodine was not higher at coastal sites due to higher rainfall inland.

Fuge (2003) considers the pathway of direct absorption of iodine from the atmosphere to plants is more important than uptake of iodine from the soil through roots. Experiments using radioactive isotopes of iodine have shown that plant leaves can absorb iodine in this way (Cline et al, 1993 and Asprer and Lansangan (1986). Atmospheric iodine deposited on plant leaves must represent a significant source of iodine for grazing animals.

2.5.3. Soil-Plant-Atmosphere interface

Volatilisation of iodine from soils as gaseous forms is now thought to be a very important part of the iodine cycle (Fuge, 1990; Sheppard et al, 1993 and Muramatsu and Yoshida, 1995). The formation of $\frac{1}{2}$ from iodide in soils is suggested in to occur under oxidising and acidic conditions (Figure 7). Perel'man (1977) has also suggested that Fe³⁺ and Mn⁴⁺ could oxidise iodide under both acid and alkaline conditions. Figure 7 shows that volatilisation to $\frac{1}{2}$ is less likely at higher pH and therefore explain the reduced mobility, and hence bioavailability of iodine in soils over limestone and chalk areas.

The volatilisation of soil iodine as methyl iodide was seen by Muramatsu and Yoshida (1995) during radio-tracer experiments. This occurs under waterlogged and reducing conditions such as is found in rice paddies and is stimulated by the presence of plants. The role of plant roots in volatilising iodine from soil has also been noted by Wildung et al (1985). The methylation of the iodine is believed to be caused by the action of roots or micro-organisms and the gas produced was emitted from the plant shoot to the atmosphere.

Fuge (1996) believes that volatilisation of iodine from soils plays an important role in the iodine cycle and transfer to the biosphere. Iodine can migrate "stepwise" inland by repeated phases of deposition and revolatilisation with soils that fix iodine (e.g. organic-rich or alkaline soils) acting as barriers to migration (Figure 11).

Muramatsu et al (1995) looked at the soil-to-plant transfer ratio using I-125 in order to obtain information on the behaviour of I-129. This CR ratio (i.e. concentration in the plant over the concentration in the soil in which it was grown) varied widely with low values for tomato (0.003) and rice (0.0019) and the highest for *Brassica rapa L*. (0.016). In the Atlas Mountains of Morocco, Johnson et al (2002) report transfer factors of 0.0075 - 0.036 for various vegetables and crops. Muramatsu et al (1995) noted the following order for the concentration of iodine in plants:

older leaves > younger leaves > fruit/grain/beans

indicating little translocation from leaves where the iodine would be adsorbed to the other plant organs. Similar lack of translocation from the leaves is reported by Sheppard et al (1993). They also note that iodine in the soil was volatilised from the soil-plant system into the atmosphere as organic iodine.

The pathway soil-plant-man is discussed in the next section in the context of the iodine content of food.

3. IODINE CONTENT OF FOOD AND DRINKING WATER

3.1. Introduction

Whilst the determination and reporting of iodine in drinking water is relatively straightforward, it is not so for food. Determining the level of iodine in foodstuffs is more problematical and the reporting of results inconsistent. For example, reported data do not always include information on whether all or what part of a vegetable has been determined and results can be reported as dry or wet matter. Iodine contents have been shown to be subject to seasonal variations, and iodine can be lost or added during food processing, storage and cooking. It is a mistake to assume the iodine intake from a diet equates to the iodine content of the food.

A comprehensive account of iodine in foods was compiled by the Chilean Iodine Educational Bureau (CIEB, 1952). This project has also compiled a database of iodine in food and drinking water from available literature references (Fordyce, unpublished). More recent accounts of iodine in food and diets can be found in references such as Koutras et al (1970); Mahesh et al (1992); Lee et al (1994); Anke et al (1995); Kim (1998); and UK Food Standards Agency (FSA) (2000)⁴.

The relative contributions of food, air and water to the average daily iodine intake (for a developed country) are illustrated in Figure 12. This comprises of 156 μ g I per day from food (see below); 12 μ g I from drinking water (based on drinking 1.5 - 2 litres per day containing 5 - 10 μ g/l); and 0.3 μ g I from air breathed in (based on an air intake of 20 m³ per day (Vought et al, 1970) and average atmosphere iodine content of 10 -20 ng/m³ (Whitehead, 1984)). This shows the relative contribution of each source and, in particular, the minimal contribution from the air. Ignoring the negligible contribution from the air we breathe, drinking water will, in industrialised and developed countries, represent between 5 - 10% if the daily iodine intake. In undeveloped subsistence level economies reliant on the local environment for their food supply, drinking water will contribute a much higher amount, probably higher than 20% (see following discussions).



Figure 12: A figure showing the contribution to the daily iodine intake from food, water and air for a typical diet in a developed country

⁴ <u>http://www.foodstandards.gov.uk/science/surveillance/fsis-2000/5tds</u>

An example of a daily diet from the UK National Diet and Nutrition Survey of young people aged 4 - 18 years, 15-18 year group, (1997-1998) (taken from Expert Group on Vitamins and Minerals $(2002)^5$, Annex 2.) is given in Table 6 and shown in Figure 13.



Figure 13: A pie-chart showing the relative contribution to the diet of different foods (data from Table 6).

	µg/day	%
Cereal	20	6 17
Dairy products	6	6 42
Eggs	:	53
Fat spreads	;	3 2
Meats	1	1 7
Fish	1:	28
Vegetables	9	96
Fruits & nuts	:	2 1
Sugar & confectionery	:	53
Beverages	1	1 7
Miscellaneous	(6 4
	15	6 100

Table 6: An example of a daily diet based on data from the National [UK] Diet and Nutrition Survey of young people aged 4 - 18 years, 15-18 year group, (1997-1998) (taken from Expert Group on Vitamins and Minerals (2002).

The most recent total diet study (TDS) of iodine available to the project is that of the Food Standards Agency UK - 1997 Total Diet Study - Fluorine, Bromine and Iodine (FSA, 2000). Results from this are shown in Table 7. This study looks at trends in the UK and makes comparisons with other national total diets.

⁵ <u>http://www.foodstandards.gov.uk/multimedia/pdfs/evm0006p.pdf</u>

Food Group	lodine
-	Average concentration
	(mg/kg fresh weight)
Bread	0.14
Miscellaneous cereals	0.13
Carcass meat	0.09
Offal	0.09
Meat products	0.13
Poultry	0.10
Fish	1.30
Oils and fats	0.22
Eggs	0.48
Sugars and preserves	0.27
Green vegetables	0.03
Potatoes	0.07
Other vegetables	0.04
Canned vegetables	0.04
Fresh Fruit	0.04
Fruit products	0.09
Beverages	0.03
Milk	0.32
Dairy products	0.42
Nuts	0.25

Table 7: Average concentrations of iodine in the 20 food groups of the 1997 UK Total Diet Study (from FSA, 2000).

3.2. Iodine in food

The proceeding section lists results from total diet studies that give a good indication of the main sources of iodine in the diet. However, these do not show the importance of adventitious iodine (see Section 4.1) introduced during food production and manufacture. The two most important considerations in this respect are the use of iodophors as antiseptic cleansing agent in the dairy industry and red food colouring in meat products. Although milk is naturally enriched in iodine (see the data in CIEB, 1952) the use of iodophors has significantly increased the iodine levels in milk to such an extent that there has been concern about the toxic effects. Cows' milk is the major contributor to dietary exposure of UK consumers to iodine and in 1995 it was seen that milk contributed 41% of the total exposure (MAFF, 1999). Figure 13 illustrates that a significant proportion of the UK diet is composed of iodine from diary sources.



Figure 14: Tins of sardines - a rich sources of iodine in the diet

Fordyce (2003) reports on a database of results for the iodine content of foods and diets. Using a classification based on food type the following order for levels of iodine in food is determined (figure in brackets is the geometric mean):

Marine fish (1456 μ g/kg) > Freshwater fish (106 μ g/kg) > Leafy vegetables (89 μ g/kg) > Dairy (84 μ g/kg) > Other vegetables (80 μ g/kg) > Meat (68 μ g/kg) > Cereals (56 μ g/kg) > Fresh fruit (31 μ g/kg) > Bread (17 μ g/kg)

The results show that in general grain crops are poorer sources of iodine than vegetables ant that there is some equivocal evidence to suggest leafy vegetables contain higher iodine concentrations than other vegetables.

Sea foods are an important source of iodine in the diet and encouraging the consumption of tinned sea fish (e.g. sardines - Figure 14) is an important strategy for reducing IDD risks in iodine-deficient areas. Karl and Münkner (1999) present a comprehensive account of the iodine content of sea food including a study of the distribution of iodine in different parts of the fish. The work cites average iodine contents for sea fish ranging from 0.24 - 1.87 μ g/g (fresh weight). Karl et al (2001) report that iodine in the skin of marine fish can be up to twenty times the content of the muscle.

FSA (2000) notes that the iodine content of meat has declined in the UK TDS. This is attributed to decline in the use of iodine-containing red food colouring following legislation to restrict the use of erythrosine. Meats with such colouring added can add significant iodine in the diet in countries where such legislation does not exist.

3.3. Food as a source of iodine in iodine deficient areas

Soil to plant transfer ratios are low and the concentration in plants is a very small fraction of that found in the soil. The Moroccan case study (Johnson et al, 2002) describes values 0.0075 -0.0358 and Fuge (2003) cites that most values fall between 0.01 and 0.1. Whether the soil is considered to be depleted in iodine (say 1 μ g/g) or enriched (say 5 μ g/g), one hundredth of these values is not much iodine (0.01 and 0.05 μ g/g respectively). This difference approaches the sensitivity of many of the analytical methods used to determine iodine. If the diet is mainly one of eating grains (e.g. rice), which is the least enriched part of the plant, then cultures eating a predominantly cereal based diet will receive even less iodine. Mahesh et al (1990) estimates for a region in India that 75% of the dietary iodine is expected from cereals. Locally grown food from most areas of the world, except those in iodine enriched environments (e.g coastal areas) are not going to produce sufficient iodine to reach an adult's Recommended Dietary Allowance (RDA) of 150 µg/day. Take the typical UK diet shown in Figure 13, remove the diary produce, meat and fish' then the diet will be more like that from the developing world. This will yield a daily intake of less than 100 µg/day. It is only through the inclusion of iodine-rich seafood and the inclusion of adventitious sources of iodine introduced during the food processing that the levels of iodine can reach the recommended daily levels. We have become too obsessed with trying to attribute the status of iodine-deficiency to areas when in reality only a few areas of the world (e.g. coastal areas) are capable of producing an iodine sufficient diet.

The significance of soil contamination in animal fodder is discussed by Underwood and Suttle (1999). They cite an example where in a good season of pasture growth there is less opportunity for accidental soil ingestion than seasons of relatively low pasture production. Since most top soils are very much richer in iodine than the plants which grow on them (CR ratios 0.002 - 0.04,

see Section 2.5.3), soil ingestion greatly increases iodine intake. It can be stipulated that the same occurs in the human diet with accidental or even deliberate eating of soil contributing substantial additional iodine. For example, 100g of fresh lettuce would contain 1 - 2 μ g iodine (Anke et al, 1995) whilst just 1g of soil contamination would double that amount, particularly if it is an organic-rich compost.

When the locally grown food is an inadequate supply of dietary iodine, then the supply from the local drinking water becomes increasingly important.

3.4. Iodine in drinking water

Several investigators have suggested that the iodine content of surface waters can be used as an indicator of the environment's iodine status (Perel'man, 1977 and Koutras, 1986). The possible link between iodine in waters and endemic goitre is investigated by Fuge (1989). He concludes that although the iodine content of surface waters can give a general indication of the iodine status of the local environment, endemic goitre can still be prevalent in areas with relatively high iodine in the surface waters.

This project in the case study areas of Sri Lanka (Fordyce et al, 2000), China (Fordyce et al, 2003) and Morocco (Johnson et al, 2002) has found that the drinking water supply is an important factor in the aetiology of IDD. Areas of lower IDD prevalence were noted for their higher levels of iodine in the drinking water, particularly those from the ground water sources.

Levels of iodine in some drinking water are summarised in Table 8. The values for the iodine content of drinking water from this project's case study areas are given in Table 9. There is a wide range of results reported for the iodine content of drinking waters ranging from <0.1 to 150 μ g/l. The Sri Lankan drinking waters appear significantly higher than those from other areas, a fact noted for the Anuradhapura region by this project (see Table 9). Excluding the Sri Lankan waters, the average level of iodine in drinking waters reported in Table 9 is 4.4 μ g/l. From the studies that report results for a variety of water sources, it appears that artesian or deep water well supplies are most enriched in iodine. For natural waters Fuge (1989) records levels of 0.94 - 8.03 μ g/l I for rivers and lakes. Many authors note the relationship between the iodine water content and the proximity to the sea (Johnson et al, 2002 and Anke et al, 1993)

Pendersen et al (1999) note that drinking water samples from Denmark varied by more than one hundred-fold and suggest that changes in water supply and water purification methods may influence the population iodine intake and the occurrence of thyroid disorders. These workers also noted that preparation of coffee or tea did not reduce the iodine content of tap water that had initially a high iodine concentration.

Reference	Iodine (µg/l)		Country	Notes	
minimum maximum Av. (no.)					
Takaku et al (1995)	0.65	35.9	- (42)	Japan Northern Kanto area	
Jaffiol et al (1992)	1.0	9.2	- (10)	Togo	Lake Kara area
			0.92(1)	Morocco	Tenghourt
Aquaron et al (1993)	1.08	1.30	1.19 (2)	Morocco	Taourirt Aït Zaghar
			1.08	France	Marseilles
Bilabina et al (1994)			2	Togo	Gobe and Moretan
Larsen et al (1999)	2	8	-	Denmark	Jutand - tap water
	10	30	-	Denmark	Sealand - tap water
Longvah & Doesthale (1998)	3	31.5	7.38 (287)	India	82% of samples 5-10 µg/l
	0.1	139	- (55)	Denmark	Tap water
Pendersen et al (1999)			4.1	Denmark	Jutland
			23	Denmark	Sealand
Sharma et al (1999)	0.76	3.01	1.52 (108)	India	
	0.70	14.8	5.29 (10)	New Zealand	Artesian/bore
D_{22} (1963)	1.1	10.8	4.54 (11)	New Zealand	Upland surface
Dean (1965)	0.8	9.0	2.72 (13)	New Zealand	River
			3.1	New Zealand	Spring
Balauriva et al (1992)			15.6 (476)	Sri Lanka	Dug well
			37.4 (32)	Sri Lanka	Tube well
			20.6 (87)	Sri Lanka	Piped
			11.5 (14)	Sri Lanka	Other
Dissanayake and Chandrajith (1993)	15	150	55 (60)	Sri Lanka	water wells
	1.66	14.0	4.3 (11)	England	Spring/well - N England
	2.12	4.88	3.33 (3)	England	Spring/well - SW England
	1.18	7.30	4.17 (16)	Wales	Spring/well
Fuge (1989)	1.30	3.73	1.82 (9)	England	Piped - N England
	1.95	11.90	5.52(7)	England	Piped - E & S England
	0.50	3.80	1.89 (9)	Wales	Piped
			< 0.10 (1)	Canada	Piped - Calgary
			6.42	USA	Piped - Rolla, Missouri
			7.68	USA	Piped - Phoenix, Arizona
Anke et al (1993)	0.9	9		Germany	decreased with distance
					from the sea
Tan (1989)	5	50		China	

Table 8: Iodine in drinking water from literature citations

	CHINA ¹		SRI LANKA ²			MOROCCO ³		
Logation	Commune	Kuqa	Wushi	Anurad-	Kandy	Kalutara	Agadir*	Ounein
Location	148			hapura*				Valley
Number of waters	5	5	5	5	6	4	8	11
minimum	78	2.4	0.1	53.0	3.0	3.3	3.1	0.52
maximum	100	4.0	3.7	84.0	23.5	20.2	35.2	2.8
average	88.6	3.2	1.4	67.8	8.0	8.4	17.8	1.6
geometric mean	88.2	3.1	0.8	66.5	6.1	6.4	-	-

Table 9: Iodine in drinking water from BGS investigations. All locations (except those marked with *) have historical or present IDD incidence. All results in μ g/g. ¹Fordyce et al (2003), ²Fordyce et al (2000) (all shallow wells) and ³Johnson et al (2002).

The Chinese Atlas of Endemic Diseases and their Environments (Tan, 1989) states that in most areas of IDD the prevalence rate is negatively correlated with drinking water iodine. No threshold levels are stated but maps suggest IDD will occur at level of less than 5 μ g/l I. In early studies of goitre belts in the UK Murray et al (1948) noted the correspondence with low iodine in the drinking water. They recognised that other factors, e.g. water hardness could be correlated with goitre prevalence and suggested a "non-goitrous" level for the iodine content of drinking water at >5 μ g/l for hard water areas and > 3 μ g/l for soft water areas. They also give examples where changes to the water supply impacted on the goitre prevalence rates. Murray et al (1948) cite the work of McClendon and Williams (1923) who used data produced from the routine examination of 2.5 million US recruits for the 1914-1918 war. Their data (Table 10) suggests that areas with > 3 μ g/l I were practically goitre-free.

Other workers such as Coble et al (1968) and Kelly and Snedden (1960) relate goitre prevalence to iodine levels in the water supply. Fuge (1989) states that whilst the iodine content of surface waters can provide some indication of potentially goitrous regions he suggests caution in universally applying this as a fact.

Iodine in Water (ug per litre)	Goitre rate (per thousand
(1.9 I)	men)
0 - 0.5	15 — 30
0.5 — 2	5 — 15
3 and above	0.1

Table 10: Results from McClendon and Williams (1923) that showed the goitre rate amongst 2½ million recruits related to the iodine content of representative river waters

4. STRATEGIES FOR REDUCING THE RISK OF IDD

History and statistics demonstrate that urbanisation and development help reduce the risks of IDD. Whilst improvement of a nation's health and well-being can be considered as one of the driving forces behind industrialisation and development, it is not usually the prime reason but a consequence of such changes. When there is no prospect of development in the short-term, particularly as industrialisation tends to be regional rather than national neglecting remote rural areas, other measures are required to reduce the risks of IDD. These can be classified as medical intervention and environmental solutions.

4.1. Industrialisation and development

Industrialisation and development will generally lead to the improved nutritional status of a population. Historians and biologists can demonstrate this with reference to a height index as human height is a very sensitive indicator of nutritional status.⁶ A consequence of improved nutritional status is an increased level of iodine in the diet due to foodstuffs originating from outside the local environment. As the production of "manufactured" food increases there will also be more sources of "adventitious" iodine in the diet. That is iodine added to food but not for the purpose of iodine supplementation. Dunn (1996) describes the widespread but unregulated exposure to iodine in food as "silent prophylaxis". In industrialised cultures there are many adventitious sources of iodine in the diet (Koutras et al, 1980), for example:

- iodine content of poultry and eggs increased by the use of fish flour as chicken food
- iodoform used in water as a disinfectant
- iodates used as oxidants and sanitising agent in the bread making process
- use of iodophors as antiseptic cleansing agent in the dairy industry
- iodine-rich red food colouring erythrosine (2,4,5,7-tetraiodofluorescein) (e.g. in red glazed cherries)

In agriculture several I containing herbicides (e.g. ioxynil, ioxynil octanoate) and fungicides (e.g. benodanil) release iodine to soil as they decompose (Mynett and Wain, 1971).

4.2. Medical Intervention

Endemic iodine deficiency diseases (IDD), as the name would suggest, are mainly the result of an iodine deficiency. There are additional factors that, if not as a primary cause, are at least contributing ones in the aetiology of such diseases (Koutras, 1980; Fuge, 1996). These include goitrogens, other trace elements and excessive amounts of iodine. In this account it is the deficiency of iodine in the environment that is the prime concern and other contributory factors are not considered.

Earlier discussions have concluded that much of the earth's surface is iodine deficient and it cannot supply inhabitants with adequate iodine in either locally grown food or the drinking water (Section 3.3). Medical intervention techniques bypass natural means of delivering iodine by enhancing the level of iodine in the things we eat or drink (principally salt) or by direct delivery such as injection of iodised oil. In areas of high IDD prevalence in Europe iodine-enriched formula milk is recommended for bottle-fed babies (Delange, 1994). Salt iodisation for the elimination of iodine deficiency is comprehensively dealt with by Venkatesh Mannar and Dunn (1995).

⁶ Peter Kirby. "Human Heights and the Standard of Living"

http://oassis.gcal.ac.uk/teaching/historyweb/cdromteaching/SOCIAL/cores/kirbycor.htmfrom The TLTP History Courseware Consortium. Part of the "Social Aspects of Industrialisation". Accessed 10/02/03.

Such prophylaxes are subject to a combination of cultural, social, political, economic and legal forces that are every detailed bit as important as the knowledge pathological of the physiology or pharmacology behind these measures (Thilly and Hetzel, 1980 Lamberg, There is or 1993). an abundance of literature on medical intervention techniques and they will not be discussed here (see Stanbury and Hetzel, 1980). Much of this work is now coordinated by the International Council for the Control of Iodine Deficiency Disorders (ICCIDD).⁷ These methods are well established and have demonstrably resulted in large numbers of people being safeguarded from the risks of IDD (Matovinovic, 1980; Lamberg, 1993; and Table 11)

The nomenclature for iodine is sanctioned more by general use than chemical logic. The term "iodine" usually refers to the chemical element in a general sense without specifying its chemical form but it is also used to denote the form I₂. Occasionally salt or another vehicle is described as "iodated" when potassium iodate (KIO₃) is added, or as "iodinated" when iodine (I₂) is added to a vehicle such as water. Recently the World Organisation Health *(WHO)*, the International Council for Control of Iodine **Deficiency Disorders (ICCIDD) and UNICEF** have recommended that the term "Iodized" (also spelled "iodised") be used when iodine is added in any form. after Venkatesh Manner and Dunn (1995) BOX 1

Year	No. of persons	Prevalence(%)
	examined	
1952	38,632	38.0
1962	19,442	15.0
1964	3,253	7.2
1965	4,113	5.2

Table 11: Prevalence of endemic goitre in Guatemala 1952-1965 (after Thilly and Hetzel, 1980). These data illustrate a successful iodisation programme.

4.3. Environmental Solutions

A strategy based on controlling the iodine in an environment will require a two-fold approach. Firstly, any iodine that already exists should be managed efficiently. Processes that cause loss of iodine should be minimised so iodine is retained but as a bioavailable form. The processes that encourage the passage of iodine through the food chain need to be enhanced. However, there are some environments where the levels of iodine are so low that even efficient management of the iodine will simply not yield adequate levels for the local population. So secondly, in such instances, iodine in the environment needs to increased by adding additional supplies of iodine. Raising the environment's iodine levels in this way will lead to an increase in the iodine status of the local population who are part of that environment. The added iodine has to be managed effectively so it gives maximum benefit to the local population over a prolonged period of time.

⁷ <u>http://www.iccidd.org/</u>

Hartmanns (1974) reports that intensification of pasture use decreases the supply to grazing animals. Under such circumstances measures used that increase herbage iodine content are not efficient and other means (such as iodine rich cattle-licks) should be used. It should also be noted that not only is too much iodine toxic to humans, Braverman (1993) but it is also toxic to plants. In rice "Reclamation Akagare" disease is a physiological disorder caused by excessive iodine entering the flooded paddy fields of iodine rich soils (Tensho and Yeh, 1970 and Watnabe and Tensho, 1970).

4.3.1. Efficient management of the environment's natural iodine

Changes in agricultural practices will modify the pathways in which the iodine will pass through the food chain and the environment's ability to retain iodine. This is illustrated by the work of Lidiard (1992,1995). An agricultural area (40 km from the sea in SW England) originally covered in peat was "improved" by reclamation. Iodine deficiency problems appeared in the livestock where none had been seen previously. Fuge (2003) suggests the animals had previously obtained iodine from inadvertent intake of peat. An increase in the oxidation potential of soils draining reclaimed swampy areas will speed up migration of iodine from the original soil.

Efficient management of the environment's natural iodine requires a good understanding of its geochemical behaviour as discussed in Section 2 of this report. In iodine deficient areas improved agricultural management is unlikely to make major differences to the iodine levels of food simply because of the limited amount of iodine available. However, even small changes could lead to a significant impact on the iodine status of the local population. Applying a knowledge of iodine geochemistry the following strategies can be suggested:

Changing crops grown

There is no evidence to suggest that iodine fulfils any role in terrestrial plants. Section 3.2 would not suggest any major differences in vegetables, fruits and grains except that the latter are a poor source of iodine. If a major pathway for iodine into the plant system is through leaf adsorption then leafy vegetables must be considered to have an advantage in concentrating iodine. The iodine content of plants is seen to increase with the proportion of leaves (Anke et al, 1995).

Iodine is not mobile in plants and is not concentrated in the seed. Processing the seed for food consumption is likely to decrease the iodine content further. Seed crops such as rice and wheat cannot therefore be considered as good providers of iodine.

Variation in the iodine content of different strains of pasture grass have been noted (Butler and Johnson, 1957) though this requires more investigation before it can be stipulated that grasses that are better at concentrating the available iodine are grown in preference to low iodine species. Underwood and Suttle (1999) claim that in areas of marginally low soil iodine, the incidence and severity of goitre in grazing animals are influenced by the botanical composition of the herbage and problems are more likely to occur on grass than on mixed or leguminous swards.

With the exception of stating the fact that leafy vegetables are likely to provide more iodine in the diet than beans or grains, there is no evidence to suggest that a change in crops grown can bring about significant benefits. This really requires a change in eating habits and, if this is to happen, it is more beneficial to suggest people turn to eating sea fish than leafy vegetables (see Section 3.2).

An interesting approach in growing supplementary iodine food is suggested by Jopke et al (1996). Regularly eaten foodstuff could be grown in pots or trays to provide a prophylactic against iodine deficiency. They demonstrated the production of an iodine-rich cress ($30\mu g/g dry$ matter) fertilised with natural Caliche. In their experiment they used a sandy soil, a soil texture

that is very characteristic of many high risk IDD areas and a soil that has little fixation potential for iodine in an unclosed system.

It is interesting to note that the way food is processed might affect the content of the iodine. Zheng and Zu (1998) describe how corn and chilli dried over coal fires added iodine to the foodstuff from the combustion of the coal.

Using livestock grazing to "concentrate iodine"

In instances of fallout from nuclear plant accidents, e.g. Windscale, UK (Chamberlain and Dunster, 1958) and Chernobyl, Ukraine (Nishizawa et al, 1986), US nuclear test fall-out (Knapp, 1964) demonstrate how rapidly iodine passes from the atmosphere, to pasture, to grazing cattle and via diary products to human food. Futhermore, by grazing large areas of pasture the cattle are effectively concentrating the iodine precipitated on the grass, a fact consistent with the higher levels of iodine found in meat and diary products (see Section 3.2).

Dosing of animals to supplement their iodine intake is discussed by Underwood and Suttle (1999) and they demonstrate a linear increase in milk iodine in dairy cows in response to increased iodine supply.

Improving the soil's ability to fix iodine

The factors affecting the soil's iodine fixation potential were discussed in detail in Section 2.4. The measures taken to improve the soils ability to fix iodine can be summarised:

- improve the soil's organic content as the organic matter helps to retain any iodine. Grain crop stubble should be dug into the soil rather than burnt and adding organic materials that are already iodine-rich (e.g. seaweeds or peat) will have a significant impact on the iodine status of the soil.
- improve the soil's texture so it is more rich in clay or silt. Coarse sandy soils are generally low in iodine. The required change in soil texture is shown in Figure 15.



Figure 15: A figure showing soil texture classification and the direction needed to improve the soil's iodine fixation potential. Sandy soils (blue) are poor at retaining iodine, increasing the clay and silt content should help the soil retain more iodine.

Converting the soil's iodine to a bioavailable form

Improving the soil's ability to fix iodine can reduce the availability of the iodine in the food chain if the iodine is held so strongly it cannot pass along the food chain. The bioavailability of iodine will therefore depend on how strongly the iodine is fixed and in what form it exists. A balance therefore has to be achieved between fixing the iodine so it is not lost from the soil-plant system but fixing the iodine in such a way that it is still bioavailable. Earlier in Section 2.4.2 the possible forms of iodine in the soil were discussed. Bioavailable iodine is going to be the fraction of iodine that can be taken up into the food crops and ultimately digested by humans. This form will be iodide. Plants grown in solution culture were seen to take up iodine more readily in the form of iodate (Whitehead, 1975).

Moiseyev et al (1984) demonstrated that the introduction of organic matter to a soil can regulate the transfer of iodine from soil to plant and thus limit the amount of iodine in the food chain. Adding organic matter to a soil will fix the available iodine making it less readily available for root uptake. These workers also cite a reference from other work in the Soviet Union that showed the application of $CaCO_3$ (as ground lime) to a Sod-Podzolic clay loam lowered the iodine content in oat grain and straw by one-half. The addition of organic material to the soil can also help release iodine from the soil according to Muramatsu et al (1996). They observed that the desorption of iodine was enhanced markedly by the addition of organic substances (such as straw stubble) into soil. This was probably due to microbial activities in waterlogged soils stimulated by these organic substances. A change in the cation or anion ratios in soil solution in either direction produces a decrease in the coefficient of accumulation of iodine. Simpson (1930) reported that iodine in alkaline soils seemed to be of low availability while in acid soils it was readily available.

Factors that favour the existence of iodine in a bioavailable form, i.e. volatile and mobile forms such as I^{-} and I_{2} are to be encouraged if the soil iodine is to be managed efficiently. These can be achieved by:

- low pH and high Eh (see Figure 7)
- high level of microbial and root activity
- adequate pathways within the soil to allow migration of iodine (i.e. uncompacted soil with abundant pore space)
- flooding

The last point can be illustrated by Sheppard and Motycka's (1997)work on wild rice grown in flooded and non-flooded conditions. Rice grown under the former conditions demonstrated that flooding does enhance iodine uptake.

If the iodine supply to the soil is low, attempts to release iodine will only be short term and not sustainable. For example, the reclamation of peaty farmland may result in a large initial surge of bioavailable iodine but eventually the iodine will become depleted.

Reducing iodine volatilisation loss from the soil-plant system

Earlier discussions on iodine geochemistry concluded that volatilisation of iodine from the soilplant system is a very significant part of the iodine geochemical cycle. It is this volatile fraction that is also the bioavailable fraction that needs to be incorporated into the food chain. So while it is desirable to have the iodine in a form that is bioavailable (as described above), this has to be balanced against losing iodine from the soil-plant system to the atmosphere. It would be logical therefore to encourage volatilisation during the crop growing phase but take measures to retain the iodine when the ground is fallow. These measures would be the opposite to those listed above. Liming of agricultural soils reduces the level of iodine in the vegetation growing on the soil (Katalymov and Churbanov, 1960; and Katalymov and Shirshov, 1960). Whitehead (1974) found the addition of chalk to soils reduced the solubility of the iodine.

Finding alternative sources of more iodine-rich water

It has been noted by a number of workers, e.g. Shaohua and Delong (2000) and Fordyce et al (2003), both citing examples in China, where deeper water wells have yielded drinking water with more iodine. Seeking alternative water supplies that are richer in iodine is a further strategy that could be considered in an environment where surface waters are deficient in iodine. However, this must be done with caution as deeper water sources may also contain trace elements such as As and F present in toxic quantities. Murray et al (1948) record how changes to water supplies in England impacted on goitre prevalence as illustrated by the cessation of use of local wells in Derbyshire and Somerset.

It is also worth noting here that subsurface brines and thermal and mineral springs can be a rich source of iodine (Fuge and Johnson, 1986). Such iodine-rich brines are found associated with oil producing regions, for example, Collins (1969) reports oil field brines from Oklahoma, USA averaging 380 μ g/l I (range 23 - 1,400). In oil producing regions, the brines could be utilised to produce iodine for use in iodine deficient areas.

Preventing the removal of iodine by flooding

As previously mentioned at the start of this section, Muramatsu et al (1996) have shown how the flooding of paddy fields can mobilise iodine. In the iodine-rich environment of Japan the high concentrations of iodine in paddy flood waters has been seen to result in Reclamation Akagare disease caused by a toxic effect of excessive iodine on the rice plants. In Section 2.4.4 it was described how cultivation under flooded conditions can reduce soil iodine levels by one tenth. In iodine deficient environments the cultivation of crops involving flooding in the soils will further reduce the levels of iodine in the soil and if the supply of iodine is low paddy soils will remain depleted in iodine.

The impact of water movement on the soil will really depend on the form the iodine exists in the soil and the "fixing" of iodine has already been discussed previously. Peat soils are by far the most iodine-enriched soils yet they are usually associated with boggy waterlogged soil conditions. If a soil has a low iodine fixation potential then it might be anticipated that flooding will further deplete the iodine. Figure 3 shows the typical volume composition of a surface loam. Fifty percent of this is pore space a component of the soil greatly neglected in most investigations yet likely to be a very important pathway in the migration of iodine. A compacted soil or one with little pore space (e.g. a clay soil) will be less likely to lose iodine via flooding but for the same reason the iodine might be restricted moving through the food chain.

The management of soil iodine as described in this section is extremely complex and certain factors than can be cited as beneficial (e.g. flooding the soil makes the iodine more bioavailable) can also be seen to have deleterious effects (e.g. flood waters will deplete the soil's iodine). In areas of marginal iodine deficiency good management of the land will efficiently use available iodine and could make a significant difference in determining whether or not a population becomes iodine-deficient. Such procedures should be considered as measures to reduce the risks from IDD.

However, in environments of significant iodine-deficiency, where the local population have little or no scope for managing their own environment because of extreme poverty and harsh environmental conditions, adding iodine from an outside source is the only practical approach. Nonetheless, the measures discussed in this sub-section are important because any technique that adds iodine to the environment needs to use this essential trace element efficiently and not lose it in the groundwater or through volatilisation to the atmosphere.

4.3.2. Adding iodine to the environment

Iodination of drinking and irrigation water

In one of this project's case study areas there was the opportunity to work in an area where iodination of irrigation water had been trailed for several years (Fordyce et al, 2003). This was in the Xinjiang Province of China reported by Shaohua and Delong (2000) and discussed by Rengel et al (1999) as a possible agronomic approach for improving the iodine in crops. The iodination of irrigation water in the Xinjiang Uygur Autonomous Region increased soil, crop and animal iodine levels (Cao et al, 1994) and demonstrated this was an advantageous and cost effective method of supplying iodine to the environment. The work of Fordyce et al (2003) would suggest that the iodine does not persist in the soil as long as the six years speculated by Delong (2002). The Environmental Research Center of the Chinese Academy in Beijing is currently looking at the fate of added iodine to the soil (Delong, 2002).

Several workers have considered other ways of adding iodine to the drinking water supply and the work of this project concludes that the iodine in drinking water can be a significant factor in determining the iodine status of a local population.

Vigneri et al (1993) describe a project that supplemented the municipal water supply to a town in Sicily of approximately 13,000 people producing a water supply that averaged 46.5 μ g/l I. Foo et al (1996) report the delivery of an average of 139 μ g/l I in a village water supply in Sarawak. Both these studies comment on the cost effectiveness of this method of iodine supplementation and Foo et al note that such projects can be more rapidly implemented than salt iodisation programmes. It can be questioned whether iodine added to a municipal water supply is efficiently used as much of the water will not be used for drinking or cooking. However, if used for watering gardens and livestock it has wider benefits and not just to humans. More targeted approaches by supplementing drinking water in wells are described by Elnager et al (1997), Pichard et al (1993), and Fakhouri and Vergnaud (1994). The two former references describe the supplementation via iodine-saturated silicon matrices whilst the latter looks at the possibility of delivering iodine through wood saturated with iodine. Again, the investigators claim the methods to be cost effective and low maintenance. Elnager et al (1997) estimated an annual cost of US\$ 0.2 per person compared with US\$ 0.2 for iodised oil and US\$ 0.04 for salt iodisation.

Fertilisers

Contents of iodine in a variety of fertilizers are listed by Whitehead (1973) with levels ranging from less than 1 μ g/g in common nitrogen fertilizers to 79.5 μ g/g in Chilean nitrate. Phosphate fertilizers also contained relatively high levels of iodine (18.7 - 26 μ g/g I), presumable derived from high iodine phosphate rocks.

Application of Chilean nitrate or phosphate fertilisers is a means of adding to the iodine status of the soil (Itano and Yasuhiko, 1935 and Jopke et al, 1996). The affect of nitrogen fertilisers on the iodine status appears to be ambiguous (Moiseyev et al, 1984). Alderman and Jones (1967) demonstrated that the use of such fertilizers actually reduced the iodine content of grassland, presumably due to a dilution effect caused by the rapid growth of vegetation.

Herbage iodine concentrations can be increased by the use of fertilisers containing iodine (Underwood and Suttle, 1999). However, this method is described as inefficient because there is

low uptake by the herbage, although added iodate is much better absorbed than iodide, especially where liming is practiced (Whitehead, 1975). Adding iodine to the soil through the addition of fertilizer will only have a significant impact on the food chain if the iodine is retained in the soil as bioavailable iodine. Too much organic matter or liming will have the effect of fixing the iodine and this will not be made available to the food chain unless there is some process in the soil to release it. A sandy soil with no organic matter will not retain any added iodine which will be rapidly removed from the soil by volatilisation or washed away by soil water.

Gurevich (1964) describes the use of seaweed fertilisers as a prophylactic measure against endemic goitre. Seaweed ash was demonstrated to be the best way of applying the fertiliser with a content of 11,100 μ g/g (compared to 2,380, 250 and 22 μ g/g for natural seaweed, seaweed compost and fish meal respectively). A country with a coastline and one that has areas at risk from IDD could make use of the under-used resource of seaweed.

In practical and economic terms, the use of iodine-rich fertilizers requires the political will to implement such a system, and it must be demonstrated to be more effective than say for example using iodised salt. It is unlikely that the people of a remote rural location would be willing to pay the extra cost of using iodine-rich fertilisers.

5. COST-BENEFIT ANALYSIS

A cost-benefit study of iodine supplementation programmes for the prevention of endemic goitre and cretinism is presented by Correa (1980). The three main components summarized by Correa are:

- 1. The relationships existing between IDD, IQ and income of the populations with and without iodine supplementation programmes.
- 2. The cost of the various methods of iodine supplementation.
- 3. The relationship between the economic benefits estimated in (1) and the costs estimated in (2). From these, estimates of the rate of return of iodine supplementation programmes are obtained. These estimates are then compared with those obtained for other investments in human and physical capital.

In Correa's (1980) analysis:

- it is demonstrated that supplementation programmes reduce cretinism and can raise IQ levels by up to 10.92 points. Jiang et al (1997) report that iodine treatment in early pregnancy increased the IQ of 5 year olds by 14 points. (See Table 12 for IQ definition in terms of mental deficiency classification).
- there is a relationship between per capita income and IQ and this can be expressed as a regression equation in the form Y = mX + c where Y is the per capita income and X is the IQ.
- as an example, it was estimated that in Ecuador that a seven point increase in IQ (from 93 to 100) results in a per capita income increase of about 10%.
- there is a 15 year time delay after the start of the supplementation programme before the benefits can start to be realised
- the economic benefits that iodine supplementation programmes could have by improving the health of the livestock and poultry were not considered.
- the overall conclusion was that investments in iodine supplementation programmes are amply justified from an economic point of view.

Mental deficiency terminology and the relationship to IQ levels is summarised in Table 12.

To apply the cost-benefit analysis to environmental supplementation programmes is simply a case of modifying the estimates in item (2) of the list above. The Xanjiang iodine dripping into irrigation water project provides excellent estimates for this purpose with costs detailed by DeLong (2002) and Shaohua and DeLong (2000).

The point made about the economic benefits in improving the health of livestock and poultry is significant when considering environmental supplementation projects that will offer this as an additional economic benefit. DeLong (2002) notes improvements in animal production following the dripping programme in Xinjiang. In the most iodine-deficient areas Delong et al (1997) note that annual sheep production increased by 35 - 63% during the 3 years after iodination with a subsequent 5% increase in yearly income per person. Furthermore, such environmental supplementation programmes will yield results much faster than the 15 year time delay discussed by Correa. The estimated cost of the iodine-dripping programme is put at \$0.12 per person per year (DeLong, 2002). The affect of the iodine supplementation could persist over a number of years (though this has not been proven in the case of the Xinjiang dripping) which would reduce the cost further, e.g. if the iodine persists for three years the cost would be \$0.04. The current

estimated cost of salt iodisation is \$0.04 per person/ per year⁸. The dripping method of DeLong is therefore of comparable costs and the benefits are greater because of the improvements to livestock. Measures to ensure the efficient use of iodine as discussed in Section 4.3.1 may increase costs but would also maximise benefits.

Gutukunst (1993) has reported on the adverse consequences of iodine deficiency in Germany and considered the costs and benefits of iodine deficiency prevention. Based on 1992 figures, it was considered that Germany spent over 1 billion dollars per year (2 billion DM) for diagnosis, treatment and lost work time stemming from the effects of iodine deficiency disorders.

IQ Range	Classification
70-80	Borderline deficiency
50-69	Moron
20-49	Imbecile
below 20	Idiot

Table 12: Mental deficiency classified by IQ (after Reber, 1995)

⁸ http://www.people.virginia.edu/%7Ejtd/iccidd/aboutidd.htm

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