The role of volatility in the distribution of iodine in the secondary environment

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Abstract—Iodine in the secondary environment is derived from the oceans by way of the atmosphere and as a result near-coastal soils and surface waters are greatly enriched relative to central continental areas. However, it is likely that appreciable quantities of the I are re-cycled from soils and terrestrial waters by volatilisation. In acid soils and waters I is present as the I^- ion which can be oxidized to I_2 and volatilised. In alkaline conditions the I is more likely to be present as IO_3^-, which is not converted to I_2. Soils formed on limestone are enriched in I relative to soils formed over other rock types, and waters draining limestone areas are similarly enriched. Because plants, and possibly animals, are thought to derive much of their I by direct absorption from the atmosphere, the frequent association of I deficiency diseases with limestone areas could be due to the non-volatility of the element in the alkaline conditions.

INTRODUCTION

THE I CONTENT of the primary environment is low, with igneous rocks containing an average of 0.25 ppm (FUGE and JOHNSON, 1986). Sedimentary rocks are richer, with shales containing an average of 2.3 ppm, sandstones 0.8 ppm, and carbonates 2.7 ppm (FUGE et al., 1986), while some organic-rich sediments can contain extremely high contents of I (up to 44 ppm, FUGE and JOHNSON, 1986). However, it is generally accepted that little I occurring in the secondary environment derives from these primary sources.

Iodine has been variously described as a biophile, hydrophile and chalcophile element (RANKAMA and SAHAMA, 1950; GOLDSCHMIDT, 1954; FUGE and JOHNSON, 1984), however, the most significant aspect of the geochemistry of I is its volatilisation from sea water and as such it can be classified as an atmophile element. Most I occurring in the secondary environment derives from the oceans by way of the atmosphere and MIYAKE and TSUNOGAI (1963) estimated that 5×10^{11} g is transferred to the atmosphere annually. This atmospheric I reservoir results in soils showing considerable enrichment over parent material. Similarly, a large proportion of the I occurring in surface run-off derives from the atmosphere.

While the importance of the volatility of I from the marine environment has long been recognised, little has been written regarding its possible influence on the distribution of the element in the terrestrial environment. WHITEHEAD (1981, 1984) suggested that while I is volatilised from soils the degree of loss from topsoils is small, with even smaller losses from soils rich in organic matter and clays.

From a study based on data for I in soils and waters obtained over several years, the author suggests that I volatility in the terrestrial environment has a marked influence on the distribution of the element.

In the present paper, data is advanced to support this contention.

NATURAL FORMS OF IODINE AND THEIR TRANSFORMATIONS

As a member of the halogen group, I readily accepts an electron becoming the iodide anion, I^-, acquiring an inert gas configuration. However, because the electron affinity of I is low (295.5 kJ/mol, compared with chlorine 348.5 kJ/mol) the I^- anion easily loses the acquired electron to become the I_2 molecule. According to PEREL'MAN (1977) this transformation of $I^- \rightarrow I_2$ takes place in acid and alkaline environments due to the oxidative action of the Fe^{3+} and Mn^{4+} cations or free oxygen; however, in a reducing acidic medium I_2 is readily reduced to I^- (Fig. 1).

In addition to the I^- anion, I occurs as the complex iodate anion (IO_3^-). This is formed from elemental I in oxidizing alkaline environments: thus, in some hot arid deserts such as the Atacama, Chile, the caliche deposits are rich in IO_3^-. In acid conditions the oxidation potential for the reaction $I_2 \rightarrow IO_3^-$ is very high and it is therefore unlikely to occur.

In the marine environment I (average 58 μg/l, FUGE and JOHNSON, 1986) occurs predominantly as IO_3^- because this is the thermodynamically stable form (TSUNOGAI and SASE, 1969). Iodide is meta-stable in sea water (TSUNOGAI, 1971); similarly any elemental I produced biologically is unstable (TRUESDALE, 1974).

It has been suggested that IO_3^- is converted in the surface layers of sea water into I^- by the action of sunlight and also by organisms utilising the enzyme nitrate reductase (TSUNOGAI and SASE, 1969), MIYAKE and TSUNOGAI (1963) suggest that this I^- is
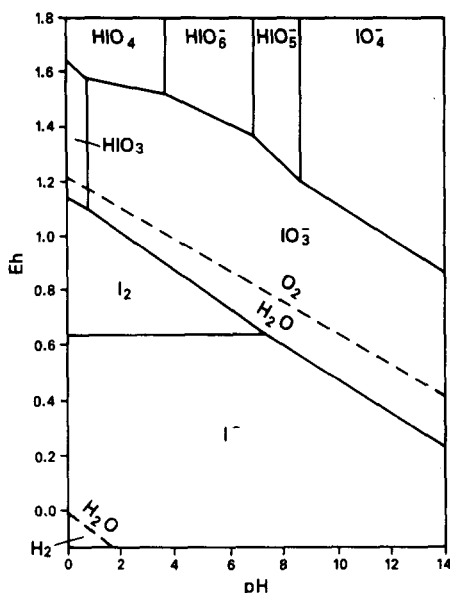
Fig. 1. Eh–pH plot for iodine (modified from Vinogradov and Lapp, 1971).

lost from surface layers by photochemical oxidation to I_2, which is volatilised. However, Whitehead (1984) is of the opinion that most I is transferred to the atmosphere as volatile organic iodides such as CH_3I.

Once in the atmosphere the I is available for transfer to the land masses by wet and dry precipitation. The recent work of Muramatsu and Ohmomo (1988) on radioiodine in rain suggests that I is present essentially as IO_3^- and I^-, with IO_3^- converting to I^- when samples were allowed to stand for several days.

IODINE IN SOILS

As would be expected, I is higher in near-coastal soils than those occurring inland, with central continental and mountainous regions having very low contents of I in soils. However, within the various regions there is frequently a considerable range of I depending on variables such as soil type. Fuge and Johnson (1986) have suggested that, in addition to proximity to a source of supply, the other important criterion in determining the status of I in a soil is its ability to retain it. These authors coined the term "I fixation potential" to cover the complex range of soil characteristics which govern its ability to retain that element. Among the factors which various workers have listed as important in I fixation are: pH, organic content, clay content, and the content of Al and Fe oxides.

The relative importance on soil I retention of each of the factors listed has been variously assessed by the different workers. Organic content appears to be one of the most important factors (Vinogradov, 1959), and Johnson (1980) found a strong correlation be-

tween organic content and total I in surface soils, while the correlation decreased with depth. Many workers have commented on the importance of clay particles and colloidal matter in the retention of I in soil (Vinogradov, 1959; Proskuryakova et al., 1969) while Irinevich and Fil'kov (1973) and Whitehead (1973) found little correlation between soil I and clay content. Whitehead (1973, 1979, 1984) obtained a good correlation between I and the Al and Fe oxides in soil and suggested that these oxides are important in retention of I. There is much conflicting evidence regarding the importance of pH in soil I retention.

VOLATILISATION OF IODINE FROM SOILS AND TERRESTRIAL WATERS

It has been widely suggested that I is lost from soils mainly through leaching, the various factors listed above merely serving to prevent this. However, from a consideration of the Eh–pH diagram for I (Fig. 1) it seems likely that in acid conditions the I^- ion, the likely predominant species of I, will be readily converted to I_2 which will be volatilised. As has been suggested by Perel'man (1977) this oxidation could be easily accomplished by the Fe^{3+} and Mn^{4+} cations. It is perhaps pertinent to mention here that McLendon (1939) suggested that KI added to acidic soils is converted to I_2 and is hence lost due to volatilisation. Under neutral and alkaline conditions I^- is less likely to be converted to I_2 and it is probable that much of the I is present as IO_3^-.

A recent study of I in the soils of Derbyshire, northern England (Fuge and Long, 1989), presented data for soils developed over a variety of bedrock including limestone. The results (Table 1) show that the I content of the near-neutral topsoils over the limestones is appreciably higher than that of the acidic topsoils developed over shales, sandstones and dolomites. Similarly, soils developed over a limestone in Missouri, U.S.A., contain 5.98 ppm I while topsoils developed over dolomite, shale and sandstone contained up to 2.90 ppm I, with a mean of 1.15 ppm (Fuge, 1987, and unpublished data).

It is possible that calcareous soils hinder the leaching of I and that this results in soils over limestone being enriched. However, many authors have suggested that a high pH does not favour retention of I (Hamid and Warkentin, 1967; Prister et al., 1977)

Table 1. Iodine in topsoils, Derbyshire, U.K.

Bedrock (No. of samples)	Iodine content (ppm)		
	Range	Mean	pH
Limestone (12)	2.58–26.0	8.20	6.0–6.9
Dolomite Sandstone Shale (15)	1.88–8.53	3.44	4.2–5.5

and the CHILEAN IODINE EDUCATIONAL BUREAU (1956) suggest that as lime-rich soils tend to break down humus they have a poor retentive capacity for I.

In addition, it is of interest to note that in a recent study FUGE (1989) found that surface waters draining limestone areas of northern England contained on average 3.71 $\mu g/l$ I while the average value for surface waters draining non-calcareous areas of the U.K. was 2.11 $\mu g/l$, many of these waters deriving from upland areas where waters are generally fairly acid. Waters draining limestone areas of Missouri have also been found to be relatively enriched in I (FUGE, 1989). It is likely that the more alkaline waters draining limestone areas tend to retain I which is probably present as the IO_3^- ion. Similarly, PEREL'MAN (1977) has suggested that high I in soda lakes is due to its presence as IO_3^- and its consequent non-volatility.

It has long been known that the nitrate deposits of the near coastal Atacama Desert, Chile are enriched in I (up to 0.6%, GOLDSCHMIDT, 1954) as the IO_3^- anion. Many researchers have invoked a marine origin for these deposits (CLARIDGE and CAMBELL, 1968). PEREL'MAN (1977) has suggested that the presence of IO_3^- is due to the strong oxidizing conditions prevailing in the desert environment. It is probable, then, that the enrichment of I in this desert environment is due to its immobilisation as the IO_3^- anion.

POSSIBLE IMPLICATIONS OF IODINE VOLATILITY

CHAMBERLAIN and CHADWICK (1953) demonstrated that plant leaves can absorb radioactive I, and SHACKLETTE and CUTHBERT (1967) have suggested that the atmosphere represents an important source of I for plants. AL-AJELY (1985) found no correlation of plant I levels with corresponding soils and WHITEHEAD (1984) suggests that the atmosphere is the predominant source of this element in plants. Similarly, it seems likely that atmospheric I may be an important direct source of I to humans and animals.

Thus it seems likely that in an environment where the predominant lithology is limestone, plants and, indirectly and possibly directly, animals may be deprived of an important source of I. In this context it has been suggested that limestone areas are prone to endemic goitre (BOUSSINGAULT, 1831; TAYLOR, 1958; PEREL'MAN, 1977); this has also led workers to suggest that Ca-rich hard waters are implicated in the disease (DAY and POWELL-JACKSON, 1972; MURRAY et al., 1948). On the evidence of the association of endemic goitre with limestone areas, TAYLOR (1954) has claimed that Ca is a goitrogen but HARRISON et al. (1967) have found no evidence of this in man.

Much has been written regarding the causes of endemic goitre and several workers have invoked the involvement of many elements and compounds in its aetiology (FUGE, 1987). However, it is generally considered that I deficiency in the diet is the chief factor. To this end it has been suggested that soils of goitrous areas are low in I; indeed, it has been further suggested that the I content of soil can be used as an indicator of potential deficiency problems. The north Derbyshire region was one of the most notorious areas of endemic goitre in the U.K. the disease being known as "Derbyshire Neck". However, the main endemia occurred in the limestone area where I values in soil range up to 26 ppm (mean 8.2 ppm). Work in progress has also indicated that the alkaline soils occurring over calcareous rocks in north Oxfordshire, U.K., another area where endemic goitre was very prevalent (KELLY and SNEDDEN, 1960), generally contain between 5 and 10 ppm I. These levels are considerably in excess of those found in the soils of goitrous central continental areas such as Missouri, U.S.A. (mean 1.26 ppm) and are not grossly lower than values for essentially non-goitrous areas such as coastal mid and north Wales, mean 14.7 ppm I (FUGE, 1987).

It is possible, then, that the association of endemic goitre with limestone and hard water areas is due to the neutral to alkaline soils over limestone, causing I to be non-volatile and, therefore, not available to plants and animals.

It is also interesting to speculate on one other aspect of the geochemistry of I which may be linked with its relative volatility. Iodine has been found to be strongly enriched in soils over sulphide mineral deposits (FUGE et al., 1986). ANDREWS et al. (1984) recorded values up to 149 ppm I over sulphide mineralisation, against a regional background in the range 15–30 ppm, in a near coastal environment in Wales. In continental areas I values over sulphide mineralisation are not nearly as high, however; FUGE et al. (1988) recorded values of up to 5.6 ppm I against a regional background of 1.2 ppm in the area of the Viburnum Trend, southeast Missouri.

The soils occurring over sulphide mineralisation are frequently quite strongly reducing and in such an environment the I^- ion is stable even in extremely acid conditions. Hence no I would be volatilised and thus as it is added to the soils from the atmosphere it becomes concentrated.

CONCLUSIONS

Surface soils occurring over limestones are generally richer in I than those occurring over other bedrock. Higher I values also occur in surface waters draining limestone areas. Iodine in acid soils and waters occurs predominantly as the I^- ion, which is easily oxidized to I_2 and volatilised. In neutral and alkaline soils this oxidation does not easily occur and, in addition, much of the I in alkaline soils is likely to be present as IO_3^-, which will not be converted to I_2. Thus neutral and alkaline soils are likely to retain

more I than acid soils. Because atmospheric I is an important source of I for plants and probably animals, the frequent association of endemic goitre with limestone areas may therefore be explained in terms of the lower degree of I volatility from the more alkaline soils of these areas.

The high I contents of soils occurring over sulphide mineralisation is possibly due to the retention of the I⁻ ion in the strongly reducing environment. In such an environment the I⁻ will be stable and not oxidized to I₂.

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