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11 Transfers of Iodine in the Soil–Plant–Air System: Solid–Liquid Partitioning, Migration, Plant Uptake and Volatilization Daniel J. Ashworth United States Department of Agriculture – Agriculture Research Services.

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Abstract

Human exposure to soil iodine depends on the partitioning of the iodine into the mobile (liquid and gaseous) soil phases. From the liquid phase, iodine can be transported to surface- and groundwaters, plant roots and, consequently, the human diet. From the gaseous phase, iodine can be transported to the atmosphere where human exposure may occur due to inhalation. The literature suggests that the vast majority of soil iodine is strongly bound by the soil solid phase, and hence is considered immobile. However, partitioning into the liquid and gaseous phases clearly does occur, primarily under anoxic conditions due to the presence of poorly sorbed iodine species. Under such conditions, iodine leaching, plant uptake (for plants with roots that can withstand anoxic conditions, e.g., rice) and volatile emissions to the atmosphere are likely to be increased, increasing the potential for human exposure to iodine.

Abbreviations

E _h	Redox potential
I^-	Iodide
I ₂	Elemental Iodine
IAEA	International Atomic Energy Agency
IO_3^-	Iodate
K _d	Soil solid–liquid partitioning coefficient
TF	Soil–plant transfer factor

Introduction

Iodine is an essential trace element for animals, including humans, but is considered nonessential for plants (Brady and Weil, 1996). It is ubiquitous in the biosphere (Sheppard *et al.*, 1994), and is capable of transferring between all three soil phases (solid, liquid and gaseous). Thus, its mobility away from the soil body in the liquid and gaseous phases has important implications in

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Figure 11.1 Schematic of potential transfers of iodine in the soil–plant–air system. Transfers, illustrated by arrows, between the solid, liquid and gas soil phases are: (a) volatilization; (b) dissolution; (c) adsorption; and (d) desorption and dissolution.

terms of human exposure. Its leaching into surface- and groundwaters, uptake by crop roots and volatilization into the atmosphere are all processes by which human exposure is increased, either through dietary intake or inhalation. The soil-plant-air system processes controlling the behavior of iodine are summarized in Figure 11.1 and discussed in detail in this chapter. Table 11.1 shows important iodine isotopes that are discussed in this chapter.

Iodine in Soils

Sources

The weathering of iodine-containing rock material leads to the enrichment of soils with stable iodine. Fuge and

Isotope	Radioactive?	Environmental significance?	Potential sources in soil
127	No, stable	Yes	Atmospheric deposition (marine- derived) – (Fuge and Johnson, 1986) Rock weathering – (Schmitz and Aumann, 1995; Muramatsu and Wedepohl, 1998)
129	Yes, 15.7 million year half-life	Yes	Atmospheric deposition (derived from 1960s atomic weapons testing and emissions from nuclear fuel reprocessing and waste solidification facilities) – (Robens and Aumann, 1988) Radioactive waste materials – (Nirex, 2003)
125	Yes, 60-day half-life	No	Not generally of concern in soils due to short half-life, but serves as very useful surrogate for ¹²⁷ I and ¹²⁹ I in laboratory experiments

Table 11.1 Important iodine isotopes discussed in this chapter

Notes: Of the other 21 iodine isotopes, all are radioactive and have half-lives measurable in minutes or days. Consequently, they are of little environmental significance and are rarely used as surrogates for ¹²⁷I or ¹²⁹I in laboratory soil-plant studies.

Johnson (1986) reported average values of $0.24 \,\mathrm{mg} \cdot \mathrm{kg}^{-1}$ for igneous rock, $5-200 \text{ mg} \cdot \text{kg}^{-1}$ for recent sediments, $2.7 \text{ mg} \cdot \text{kg}^{-1}$ for carbonates, $2.3 \text{ mg} \cdot \text{kg}^{-1}$ for shales, and $0.8 \text{ mg} \cdot \text{kg}^{-1}$ for sandstones. Soils become further enriched due to the deposition of marine-derived iodine onto the soil surface. Krupp and Aumann (1999) reported total annual deposition of stable iodine on the surface of German soils as between 2.3 $(\pm 0.6) \times 10^{-4}$ and 7.8 $(\pm 2.2)\times 10^{-4}g\cdot m^{-2}$ for the year 1994, and between 1.2 $(\pm 0.4) \times 10^{-3}$ and 2.2 $(\pm 0.6) \times 10^{-3} \text{g} \cdot \text{m}^{-2}$ for the year 1995. They further compared deposition on the soil in relation to distance from the ocean and found that, despite higher iodine loadings in rainfall near the coast, deposition loads on the soil were no greater. They attributed this to the lower rainfall at the coastal sites. For the same 2 years, Schnell and Aumann (1999) reported the iodine concentrations for the top 15 cm of 12 German soils as ranging from 0.4 to 6.5 mg·kg⁻¹. Again, these authors did not observe a relationship between soil concentration and distance from the coast.

Concentrations

Yuita (1994) reported that most Japanese soils (except paddy soils) are rich in iodine due to the wet, mild climate conditions that are conducive to the deposition of iodine derived from the surrounding ocean. For example, in forest and upland soils of Japan, Yuita and Kihou (2005) noted that iodine concentrations were highest in the oxic soil surface (0–0.3 m) layer, and ranged from 42 to 71 mg \cdot kg⁻¹. They further report that iodine concentrations fell markedly below the surface layer, particularly in the anoxic zone below the water table (at 2.5 m depth) where a concentration of around $0.1 \text{ mg} \cdot \text{kg}^{-1}$ was found. This highlights the importance of soil redox chemistry in controlling iodine behavior. In rice paddy soil, the same workers found iodine concentrations of around $12 \text{ mg} \cdot \text{kg}^{-1}$ in the oxic soil horizon (0.6-0.9 m depth) due to the accumulation of leached iodine from the anoxic (flooded) surface horizon above. This upper layer was shown to have an iodine content of 2.8 mg \cdot kg⁻¹.

The British Geological Survey soil iodine database (Johnson, 2003) gives a wide range of mean iodine concentrations (0.5-36.9 mg·kg⁻¹) for United Kingdom topsoils sampled from 80 sites between 1973 and 1999. The overall mean value was $8.8 \text{ mg} \cdot \text{kg}^{-1}$ (standard deviation $6.9 \text{ mg} \cdot \text{kg}^{-1}$). The same database gives an overall mean value for German topsoils of $2.2 \text{ mg} \cdot \text{kg}^{-1}$ (standard deviation $1.3 \,\mathrm{mg} \cdot \mathrm{kg}^{-1}$), which agrees with the values given for such soils by Schnell and Aumann (1999), and those for topsoils in neighboring Austria (Gerzabek et al., 1999). For Japanese topsoils, the database gives an overall mean value of $14.2 \,\mathrm{mg} \cdot \mathrm{kg}^{-1}$ (standard deviation 16.2 mg \cdot kg⁻¹), agreeing somewhat with the values of Yuita and Kihou (2005). For Russian topsoils, the database gives an overall mean value of $3.8 \text{ mg} \cdot \text{kg}^{-1}$ (standard deviation $2.8 \text{ mg} \cdot \text{kg}^{-1}$). For the Gandak Basin region of Bihar, India, Ghose et al. (2003) reported soil iodine concentrations of $3.65-12.59 \text{ mg} \cdot \text{kg}^{-1}$.

Behavior of lodine in the Soil-Plant-Air System

In common with other elements found in soils, a combination of physical, chemical, and biological processes controls the behavior of iodine. Iodine may distribute (or partition) between the solid, liquid, and gas components of a soil. The extent of this partitioning is critical since it, in turn, determines the environmental outcome of iodine. For example, a high degree of iodine sorption onto the solid phase of a soil suggests that it is likely to be immobile. In contrast, an affinity for the liquid or gaseous phases (low sorption) suggests a significant degree of mobility away from the soil body, e.g., uptake by plant roots, leaching into surface waters, or gaseous diffusion into the atmosphere. Under conditions such as these, human exposure to



Figure 11.2 Distribution of ¹²⁹I in different fractions of Chernobyl soil and Irish Sea sediment. From left to right, the fractions generally increase in the strength with which they bind iodine. *Source*: Hou *et al.*, (2003) reproduced with permission from Elsevier.

iodine is likely to be increased. In this section, literature pertaining to the soil processes controlling iodine sorption and partitioning are reviewed.

Sorption of iodine onto soil solids

A substantial amount of iodine present in a soil is likely to be adsorbed onto the soil solid phase. Hou et al. (2003) studied the fate of radioactive ¹²⁹I deposited on soils from the Chernobyl area and sediments from the Irish Sea, following the Chernobyl nuclear reactor accident. They found that around 75% of the soil ¹²⁹I, and around 90% of the sediment ¹²⁹I, was strongly bound to solid phases (metal oxide, organic matter and residual fractions). The data of Hou et al. (2003) are summarized in Figure 11.2. Many other workers have also reported the importance of organic matter in binding iodine (Whitehead, 1973; Bors et al., 1988; Yamada et al., 2002; Bostock et al., 2003), believed to be primarily due to the formation of covalent bonds between iodine and humic macromolecules (Mercier et al., 2000; Reiller et al., 2006). However, such sorption may relate only to well-degraded organic material (i.e., humic material) since Muramatsu et al. (1996) found that adding nonhumified organic substrates, such as straw and glucose, to the soil did not enhance iodine adsorption. Very much related to the turnover and sorption potential of organic materials in the soil are microbial processes. Studies have shown that a reduction in the microbial biomass of a soil (e.g., by autoclaving) can lead to a sometimes marked reduction in the sorption of iodine (Bunzl and Schimmack, 1998; Bird and Schwartz, 1996; Muramatsu

and Yoshida, 1999). In addition, however, microbes can themselves accumulate, or immobilize, iodine. Ban-nai et al. (2006) found that several strains of filamentous fungi could accumulate, in their hyphae, up to 40% of the ¹²⁵I present in a liquid medium. Inorganic solid phases (clay minerals) have also been shown to adsorb iodine via anion exchange processes and, possibly, covalent bonding. For example, Whitehead (1974) found that freshly precipitated hydrated ferric oxide substantially sorbed iodine at pH < 5.5. Dai *et al.* (2004a) found that adsorption of iodine correlated positively with the amounts of both iron and aluminum oxides in 20 Chinese soils. Similarly, Hakimi (1996) reported that laterite clay materials with varying contents of iron oxides and hydroxides could be used to sorb 90-97% of the ¹²⁵I in liquid hospital wastes, and could therefore be utilized in the cleanup of such wastes.

Effect of Time on Sorption Importantly, the adsorption processes are also influenced by time. Schmitz and Aumann (1995) used a sequential extraction procedure to compare the partitioning behavior of radioactive ¹²⁹I (which reached the soil relatively recently via the deposition of emissions from a nuclear fuel reprocessing plant) with that of stable, naturally occurring ¹²⁷I, and found that only a small fraction of the ¹²⁷I (2.5-4%) but a large fraction of the ¹²⁹I (38-49%) was water soluble. Although the influence of time over increasing iodine sorption has been observed through relatively short time periods (Ashworth and Shaw, 2006a), the data of Schmitz and Aumann (1995) suggest that time-dependent sorption continues to occur over extended periods - a process often termed "aging." This occurs as an element becomes increasingly associated with, and tightly bound by, surfaces such as metal oxides and humic matter, and suggests that the environmental mobility of recently added iodine is likely to be greater due to a lower degree of sorption.

Partitioning of iodine into the liquid phase of the soil

The proportion of total soil iodine partitioning into the liquid phase of a soil is often considered to be low due to high levels of adsorption onto solid-phase components. For example, Johnson (1980) analyzed 183 soil samples from the United Kingdom and found that water-extractable values could be $< 0.1 \text{ mg} \cdot \text{kg}^{-1}$, representing < 0.1% of total soil iodine. However, the full range of values for this set of soil samples extended to 13.6 mg $\cdot \text{kg}^{-1}$ in the liquid phase, equivalent to around 25% of total iodine. Similarly, Hou *et al.* (2003) found that readily available (the most environmentally mobile) ¹²⁹I (water-soluble and exchangeable fractions) accounted for around 20% of total ¹²⁹I in Chernobyl soil and around 10% of total ¹²⁹I in Irish Sea sediment (Figure 11.2). Therefore, appreciable quantities of iodine

may partition into the liquid phase. This partitioning is dependent on a number of geochemical processes.

Effects of Reduction-Oxidation (Redox) Potential Yuita et al. (2005, 2006) determined concentrations of iodine naturally present in soil solutions of forest, upland, and paddy field soils of Japan. Despite seasonal fluctuations of iodine concentration in precipitation at the various sites, these workers found no seasonal variation in soil solution concentration of the forest and upland soils at any depth. However, at shallow depths in the paddy field soil, floodirrigation conditions over the summer months induced a marked increase in iodine solution concentration (to around $50 \mu g \cdot l^{-1}$) when compared to pre-flood concentration (below $3\mu g \cdot l^{-1}$). This was attributed to the low redox potentials or $E_{\rm h}~(\sim -150-200\,{\rm mV})$ brought about by flooding of the soil. Flooding limits the diffusion of atmospheric oxygen into the soil pore space, leading ultimately to a "reduced" (low $E_{\rm h}$) soil (Sposito, 1989). This process is known to chemically reduce elements, such as iodine, leading to the production of different iodine species. For example, iodate (IO_3^-) may become chemically reduced to iodide (I^-) as E_h falls. Since different species have different solid-liquid partitioning behavior, the process of soil reduction has important implications for the subsequent mobility of iodine. Other workers have also demonstrated the control of $E_{\rm h}$ on iodine partitioning behavior. Muramatsu et al. (1996) showed that high desorption of radioactive ¹²⁵I from experimental soil samples occurred when soil $E_{\rm h}$ fell below around $-100\,{\rm mV}$. Similarly, Sheppard and Hawkins (1995) found lower soil adsorption of added ¹²⁵I under anoxic conditions than under oxic conditions, and Muramatsu and Yoshida (1999) noted that the microbially-driven lowering of soil $E_{\rm h}$ (i.e., inducement of anoxic conditions) produced a desorption of iodine from the soil solids into the liquid phase. Yuita (1994) reported that the iodine dissolution ratio (from soil solids) increased 1000-fold under anoxic conditions when compared to oxic conditions. More specifically, Yuita et al. (2005) found a clear negative relationship between the $E_{\rm h}$ of a paddy field soil and the iodine concentration in soil solution, with concentrations rapidly increasing when $E_{\rm h}$ fell below around 150 mV in the summer months following irrigation flooding of the soil (Figure 11.3). A similar relationship was observed in laboratory-based experiments by Ashworth and Shaw (2006a).

Iodine Speciation in the Liquid Phase of Soil Yamaguchi *et al.* (2006) further investigated iodine sorption behavior in relation to E_h by determining the speciation of the element in Japanese paddy field soils subject to oxic and anoxic conditions brought about by irrigation management. These workers observed the disappearance of added IO_3^- from anoxic soils as I^- concentrations in soil solution increased, i.e., the transformation from oxic to anoxic



Figure 11.3 Relationship between iodine concentration in soil water and redox potential (E_h) of paddy field soil. Closed round symbols represent flooded conditions during summer irrigation; closed square symbols represent flooded conditions during the winter period; open round symbols represent nonflooded conditions after drainage. *Source*: Yuita *et al.*, (2005) reproduced with permission from Blackwell Publishing.

iodine species. Out of the two major inorganic iodine species likely to exist in soil solution (IO₃⁻ and I⁻), Fukui et al. (1996) reported that the oxic IO_3^- form is likely to become more strongly adsorbed to soil than the anoxic, I⁻ form. Yamada et al. (1996) determined the speciation of iodine in water extracts of soil and concluded that of the three species determinable by their technique (IO_3^-) , I⁻, and organically bound iodine), the I⁻ ion was predominant. However, Sheppard et al. (1995) found that nonsorbed iodine in both an organic and a carbonated sandy soil was primarily associated with dissolved organic matter. The importance of dissolved organic matter in binding iodine in the soil solution was also reported by Muramatsu et al. (1996) and Yamada et al. (1996). Yuita (1992) reported that for Japanese soils, the oxic conditions of nonflooded soils led to an iodine speciation distribution in the soil solution that was dominated by IO_{2}^{-} (almost 90% of soluble iodine). In contrast, anoxic, flooded conditions were reported to result in a speciation dominated by (again, almost 90% of soluble iodine). Ι-

However, some workers have found the speciation of iodine in soil solution to be somewhat more complex,

	Summer irrigation period				Winter irrigation period			
Total I ($\mu g \cdot I^{-1}$)		Species (%)		Total I ($\mu g \cdot I^{-1}$)	Species (%)			
Depth of soil sample (m)		IO ₃ -	<i>I</i>	I ₂		10 ₃ -	Ι-	I ₂
0.2	26.6	47	52	1.0	2.4	75	24	1.0
0.5	30.5	42	58	0.3	1.8	78	21	1.1
1.0	10.6	42	58	0.4	1.7	78	22	0.3
2.0	-	-	-	-	2.8	71	28	0.7

Table 11.2 Mean concentrations and percentage speciation of iodine in soil solution samples from varying depths of Japanese paddy field soils under both summer and winter flood conditions

Note: The three iodine (I) species are iodate (IO_3^-), iodide (I^-), and elemental iodine (I_2). *Source*: Data taken from Yuita *et al.*, (2005) reproduced with permission from Elsevier.

with both IO_3^- and I^- present (in varying proportions) under both oxic and anoxic conditions. Yuita et al. (2005) found that the iodine present at relatively low soil solution concentrations (around $1.7-2.8 \mu g \cdot l^{-1}$) under oxic conditions was around three-quarters IO₃ and one-quarter I⁻. Under anoxic conditions, iodine concentrations in the soil solution increased to around $10.6-30.5 \,\mu g \cdot l^{-1}$ and the proportion present as the I⁻ species to just over one-half (52–58%) with much of the remainder as IO_3^- (Table 11.2). In addition to the shift in distribution of the IO_3^- and I^- species due to anoxia, these data illustrate that the concentration of both species increases under anoxic conditions. Thus, in addition to the potential for chemical reduction of IO_3^- to I^- , anoxia apparently induces the release of both species, but particularly I⁻, from the solid phase, thereby increasing total iodine concentration in the soil solution. It is possible that this release into the solution phase under anoxic conditions occurs due to geochemical processes that take place within soil as redox status changes. For example, the pH of acidic soils (the soil used by Yuita et al. (2005) had a pH of around 6) is known to increase to around neutrality as a result of anoxia (Rowell, 1994). This process, in turn, leads to a decrease in the net, negative, pH-dependent charge associated with soil solids. Thus, sorbed anionic (negatively charged) species may be electrostatically repelled into the solution phase.

Iodine Solid–Liquid Partitioning Coefficients (K_d **Values) in Soil** A useful approach for determining the partitioning of an element between the solid and the liquid soil phases is the partition coefficient, or K_d value, which is calculated as

$$K_{\rm d}({\rm l}\cdot{\rm kg}^{-1}) = \frac{ \begin{array}{c} {\rm Dry\ soil\ solid\ phase\ iodine\ concentration} \\ ({\rm mg}\cdot{\rm kg}^{-1}) \\ \hline {\rm Soil\ liquid\ phase\ iodine\ concentration} \\ ({\rm mg}\cdot{\rm l}^{-1}) \end{array}}$$

Thus, a high K_d value indicates a high degree of sorption onto the solid phase, and a low K_d value a high propensity

for the liquid phase. Ashworth and Shaw (2006a) used a mini-column approach to compare K_d values of ¹²⁵I in a sandy loam soil maintained at either nonsaturated or saturated moisture status. Over the first two weeks of the experiment, K_d values were below $11 \cdot kg^{-1}$ for both treatments, indicating a relatively low degree of adsorption onto the soil. After a 49-day period, K_d values in the saturated treatment equilibrated at over $21 \cdot \text{kg}^{-1}$, and, in the nonsaturated treatment, at almost $81 \cdot kg^{-1}$. Clearly therefore, the time-dependent sorption of the iodine in the drier soil was mitigated to some extent in the saturated treatment. Using field lysimeter experiments, Sheppard and Motycka (1997) also found lower iodine (¹²⁵I) K_d values in flooded soil (around $0.61 \cdot kg^{-1}$) than in drained soils (around 61·kg⁻¹). Bird and Schwartz (1996) reported average K_d values ranging from 0.1 to 0.51 kg⁻¹ for a sandy sediment under oxic conditions and with an equilibration period of 48h. Fukui et al. (1996) found average values of 2.2–4.01·kg⁻¹ for I⁻ and 4.2–201·kg⁻¹ for IO₃⁻ for a fine sand using a 14-day equilibration period. Bors et al. (1991) found K_d values of between 5 and 551 kg⁻¹ for a podzol (84% sand) using an equilibration period of at least 8 days. Compendia values for iodine K_d are also available. For example, in reviewing a range of literature sources, Sheppard *et al.* (2002) reported a geometric mean K_d value for sandy soils of $81 \cdot \text{kg}^{-1}$. However, the overall range of literature K_d values found for sandy soils by these workers was large (0.23-6951·kg⁻¹). IAEA (1994) reported values for a number of different soil types. These range from 1.3×10^{-2} to 8.5×10^1 for sandy soil, 8.2×10^{-2} to 2.4×10^2 for loam soil, 8.2×10^{-2} to 3.3×10^1 for clay soil, and 5.0×10^1 to 1.5×10^3 for organic soil. For each soil type, the iodine K_d values reported by IAEA (1994) are generally low compared to those of the other 32 elements listed in the document, suggesting that iodine may have a relatively high potential for liquid-phase migration through soil and uptake by the plant roots. Additionally, the K_d data suggest that such processes would potentially be most significant under anoxic soil conditions.

Migration of liquid-phase iodine through soil

Field Observations Numerous observations have led to the inference that anoxic conditions induce the migration of iodine through soil due to increased liquid-phase concentrations. Yuita et al. (2006) found that drainage of saturated, anoxic paddy field soil led to reduction in iodine concentration of surface soil due to leaching of soluble iodine with the drainage waters. Muramatsu et al. (1996) also found that the presence of iodine in soil solution under anoxic conditions led to a leaching of the element from the soil. Paddy soil was therefore found to have lower total iodine concentrations than forest and upland field soils. In agreement, Yuita (1994) concluded that the generally low iodine concentrations observed in Japanese paddy soils are likely to be a result of this dissolution and consequent leaching of iodine from the soil. Yamaguchi et al. (2006) further suggested that iodine leached in this way was in the form of the I^- ion.

Effects of Oxic-Anoxic Boundaries Ashworth et al. (2003) showed that iodine migration occurs more significant in anoxic, rather than oxic, soil. These workers found that ¹²⁵I added in the water table migrated to soil columns upward (due to an advective flux caused by evapotranspiration at the soil surface) through the saturated, anoxic soil zone at the base of the columns. Its migration was arrested at the boundary between the anoxic soil and the nonsaturated, oxic soil region above it. These findings were confirmed by Ashworth and Shaw (2006b) in similar experiments, but with a fluctuating water table depth. Under these conditions, the increased extent of saturated, anoxic soil gave rise to a similarly increased extent of ¹²⁵I migration. A comparison of the migration of ¹²⁵I for both fixed and fluctuating water tables is shown in Figure 11.4. Similarly, Thomson et al. (1995) demonstrated an accumulation of stable iodine occurring immediately above the anoxic/oxic boundary in deep-sea sediment cores. Sheppard et al. (1989) found that iodine released at the base of a



Figure 11.4 Upward soil migration of ¹²⁵I from a contaminated water table over a 6-month period. (a) The water table height was manipulated, in 0.5 cm increments, from 45 cm depth up to 30 cm depth (over the initial 3 months) and back down to 45 cm depth (over the latter 3 months). (b) The water table remained at 45 cm depth for the duration of the experiment. *Source:* Ashworth and Shaw (2006b) reproduced with permission from Elsevier.

Canadian peat bog migrated vertically over a distance of 1 m within a month and subsequently migrated no further. They also found that iodine K_d values generally decreased with depth. Their results imply that soil redox status may have played an important role in governing the extent of iodine migration. However, E_h was not reported in their paper.

Migration in Oxic Soils Overall, literature data regarding the migration of iodine suggest that the presence of anoxic conditions promotes elevated iodine concentration in the soil solution from where the element can migrate with the water flux. It is further evident that a boundary between anoxic and oxic soil (e.g., between groundwatersaturated soil at depth and surface soil above) represents a barrier to iodine migration. Accumulations of iodine observed in such regions suggest that iodine migration in oxic soil is very limited. This is confirmed by the findings of Kashparov et al. (2005) who undertook field studies to determine the downward migration of ¹²⁵I applied to the arable layer of a range of Russian soils (Figure 11.5). Under the oxic soil conditions of their experiments, less than 4% of the total applied iodine had leached down to below the 20 cm arable layer over a 269-day period. They attributed this to the high degree of adsorption of the iodine onto solid soil surfaces in the oxic, upper layer. Nevertheless, Ashworth et al. (2003) and Ashworth and Shaw (2006b) did note the upward movement of small amounts of iodine through the oxic soil zone in their experiments, indicating that even the relatively low amounts of iodine present in the liquid phase of oxic soils (Yuita et al., 2006) can also lead to migration (Figure 11.4).

Overall, iodine clearly has the potential to migrate through soils in the liquid phase. However, it is likely that

appreciable migration only occurs under anoxic conditions, indicating that iodine deposited onto the soil surface (e.g., aerially deposited) is unlikely to migrate deeper to any great extent. However, iodine potentially present below the water table (e.g., from rock weathering) is likely to exhibit relatively high mobility. It may, therefore, be transported to surface- and groundwaters, potentially increasing its contribution to the human diet through drinking water intake.

lodine uptake by plants

Plant root uptake of iodine from the liquid phase of soils is an important process, since it is a means by which iodine may subsequently enter food chains and be released to the atmosphere following conversion into volatile forms (see following section). Iodine is not categorized as an essential element for plant growth (Brady and Weil, 1996). Furthermore, at high concentrations in soil, iodine has been shown to adversely affect the growth of pak choi (Dai *et al.*, 2004b), spinach (Dai *et al.*, 2004b; Zhu *et al.*, 2003), and rice (Mackowiak and Grossl, 1999), indicating that its uptake has the potential to cause toxic effects in certain plants (Pel and Schuttelkopf, 1995).

Relationship between Soil Iodine Concentration and Plant Uptake Despite an apparently positive relationship between soil and plant iodine concentrations (Sheppard and Motycka, 1997; Weng *et al.*, 2003; Dai *et al.*, 2006), Yuita (1994) suggested that iodine uptake by plants is generally low. Although this worker found relatively high (compared to other parts of the world) soil iodine concentrations (average $43 \text{ mg} \cdot \text{kg}^{-1}$) across Japan, they also found that plant concentrations were only slightly higher



Figure 11.5 Vertical distribution of ¹²⁵I in soil profiles at various times after incorporation into the arable layer (0–20 cm). 1 – podzoluvisol, 2 – greyzem, 3 – meadow chernozem, and 4 – typical chernozem. *Source*: Kashparov *et al.*, (2005) reproduced with permission from Elsevier.

than other parts of the world. It was therefore hypothesized that the element largely occurs as an insoluble form that cannot easily be taken up by plants. This seems consistent with the observations that iodine in oxic soil regions is more strongly adsorbed, since the roots of most plants are only able to survive in oxic soils. In studying perennial ryegrass uptake of iodine, Ashworth et al. (2003) found that less than 0.1% of the total ¹²⁵I in soil column systems was associated with aboveground biomass of ryegrass, even after a 12-month period. In addition, Ashworth and Shaw (2006b) detected essentially zero transfer of ¹²⁵I from soil to aboveground perennial ryegrass biomass over 6 months. In both these experiments, the lack of transfer was primarily due to a limited overlap between the plant roots in the upper oxic region of the soil columns and the lower anoxic region where the majority of the ¹²⁵I was present.

Iodine Soil–Plant Transfer Factors The most convenient way to assess plant uptake of iodine is to consider the transfer factor (TF), since it inherently takes into account the relationship between soil and plant elemental concentrations. This is determined according to the formula

 $TF \text{ (unitless)} = \frac{Dry \text{ plant iodine concentration}}{Dry \text{ soil iodine concentration}} \\ (mg \cdot kg^{-1})$

Thus, high TFs indicate a high degree of transfer from the soil to the plant. Elements with a conservative, nonsorbing nature in soils, and which generally follow the water flux, exhibit exceptionally high TFs. For example, (radio) chlorine TFs (from soil to perennial ryegrass) of up to 785 were recorded by Ashworth and Shaw (2006b). In contrast, iodine TFs tend to be low. The IAEA (1994) compendium of TFs "expected" values of 3.4×10^{-3} for grass (95% confidence range of 3.4×10^{-4} to 3.4×10^{-2}) and 2×10^{-2} for an unspecified crop. Dai *et al.* (2004b) reported that iodine TFs increased with increasing soil concentration for a range of vegetables. At the highest soil addition of iodine in their work $(5 \text{ mg} \cdot \text{kg}^{-1} \text{ concentra-}$ tion of iodine in soil), fresh weight TFs from soil to edible parts of the vegetables ranged from around 0.1 to 10. These can be approximately converted to dry weight (so as to be comparable to other values that are usually expressed on a dry weight basis) by dividing by 10 (plant material is generally around 90% moisture) to give a range from 0.01 to 1. Their values followed the increasing order: carrot root = onion stem < celery shoot < water spinach shoot < pak choi leaf < spinach leaf.

Sheppard *et al.* (1993) reported iodine soil–plant TFs ranging from 0.024 to 0.19 for corn, beets, and cabbage. Kashparov *et al.* (2005) found ¹²⁵I TFs of 0.01–0.03 for radish roots and lettuce leaves, 0.003–0.004 for bean pods and 0.001 for wheat grains in podzoluvisol soil. Greyzem

and typical and meadow chernozem soils gave TFs around an order of magnitude lower for the same crops, suggesting that these soils adsorbed the iodine more strongly and limited bioavailability. Shinonaga et al. (2001) calculated soil to grain TFs for cereal grains cultivated at 38 locations in Austria and found values of 0.0005-0.02. These values correlated negatively with iodine concentration of the soils in which the cereals were grown, as well as with the amount of clay in the soils, again suggesting that soil characteristics (e.g., clay minerals) can increase soil adsorption, and reduce plant availability, of the element. Schmitz and Aumann (1994) found soil to pasture grass TFs for ¹²⁷I of $1.4 \pm 0.4 \times 10^{-1}$ and for ¹²⁹I of $9.0 \pm 2.8 \times 10^{-1}$. The difference between the two isotopes is consistent with the authors' data for water extractability of these isotopes, which was higher for ¹²⁹I.

Overall, TFs for iodine are low, indicating that the element is not readily transferred from the soil to plants. A probable reason for this is the strong soil adsorption of the element in the oxic region of soils where plant roots predominate. Therefore, the contribution to the human diet of iodine derived from crop plants is likely to be limited. However, plants with roots that are able to survive in anoxic soils, where iodine tends to be partitioned into the liquid phase to a greater extent, would therefore be expected to exhibit greater TFs. Indeed, Sheppard and Motycka (1997) noted that rice, the roots of which can tolerate anoxic soil, exhibited greater transfer of iodine from anoxic soil to the plant than under oxic conditions (TFs of 0.25 and 0.17, respectively). Cultures where rice is a staple food may therefore be exposed to the greatest plant-derived iodine loadings.

Partitioning of iodine into the gaseous phase (volatilization)

Conversion of Iodine into Volatile Forms Although the partitioning of iodine into the gaseous phase of the soil is thought to be influenced by factors such as organic and mineral adsorbing phases, pH, speciation, temperature and $E_{\rm h}$, the conversion of iodine into the volatile form is considered to be driven by microbial processes. Amachi et al. (2005) showed that I-oxidizing bacteria (which are distributed widely in the environment and oxidize I⁻ to molecular iodine) also produce volatile organic iodine, which they identified as diiodomethane and chloroiodomethane. The importance of microbes in iodine volatilization was also illustrated by Amachi et al. (2004) who found that, from seawater, only organic iodine volatilized. They noted that 1-2% of total iodine was volatilized as methyl iodide by isolated strains of bacteria. Volatilization did not occur when samples were autoclaved or passed through 0.22 µm filters, indicating that the bacteria were required to induce volatilization. In addition to bacteria, Ban-nai et al. (2006) reported that filamentous fungi strains volatilized "considerable" amounts (up to 3.4%) of ¹²⁵I in a liquid medium. Amachi *et al.* (2003) amended soil with I⁻ ions and found that iodine was emitted mainly as methyl I⁻, a process that was sometimes enhanced by the addition of glucose to stimulate microbial activity. The same workers also amended soils with ¹²⁵I, and again found that microbes played a significant role in iodine volatilization, since emissions were enhanced in the presence of yeast, but inhibited by autoclaving of the soil. Furthermore, antibiotics that inhibited bacterial growth strongly reduced iodine emissions, while a fungal inhibitor had little effect. The authors concluded that iodine-volatilizing bacteria that are ubiquitous in the soil are responsible for the formation of organic, volatile methyl iodide.

Volatile Iodine Species Sheppard *et al.* (1994) gave the different forms of volatile iodine as molecular iodine, I⁻ and IO_3^- (as hydrides, hydrogen iodide, or hydrogen IO_3^-), and methyl iodide. Taghipour and Evans (2001) reported that organic iodides dominate the airborne speciation of iodine. More specifically, Tessier et al. (2002) suggested that volatilization occurred due to the methylation of inorganic iodine forms and further identified up to eight volatile iodine species as alkyl iodides in European estuarine waters. Methyl iodide accounted for the majority, 40%, of the various species. Muramatsu and Yoshida (1995) also reported methyl iodide as the primary iodine species volatilized from a rice flooded soil system, and estimated the methyl iodide emission mass for rice paddies worldwide as around 2×10^{10} g·year⁻¹. Redeker *et al.* (2000) studied the influences on the emission of methyl iodide from rice paddies and calculated that up to 5% of atmospheric methyl iodide arises from rice fields. Methyl iodide is evidently the dominant iodine species leaving the soil-plant system in the gaseous phase.

Indirect Measures of Volatile Iodine Losses from Soil A number of studies have determined relatively large losses of iodine from soil systems, often based on a deficit in a system mass balance (i.e., the actual volatilization loss may not have been measured directly). Prister et al. (1977) found 55-60% loss of soil iodine over 10 days in the absence of irrigation. When soils were irrigated, the loss was around 20% over a 6-day period. Sheppard and Thibault (1991) reported a 21-26% iodine loss from spiked soil cores after a 4-year period. A 9% loss of iodine spiked near the surface of a sandy soil after 1 year was reported by Sheppard et al. (1987). The potential importance of iodine volatilization in determining the fate of environmental iodine is illustrated by the work of Sheppard et al. (1994). These workers undertook modeling simulations of iodine transport in soil-air systems and found that when the volatilization process was represented in the model, soil iodine concentrations were five times lower and air iodine concentrations were 25 times greater than when the process was not represented.

Direct Measures of Volatile Losses of Iodine from Soil Generally, workers who measure volatilization directly tend to report much lower values, particularly in organic soils where iodine becomes strongly adsorbed onto the solid organic phase. Sheppard et al. (1994) determined ¹²⁵I volatilization from peat soil in laboratory experiments and found a loss of just 0.07% over 66 days. Bostock et al. (2003) studied the soil-plant volatilization of ¹²⁵I from coniferous forest soil over a 22-day period and measured a total loss of 0.011%. The rate of emission of iodine was shown to decline over time and follow a double exponential model, i.e., declining very steeply initially, followed by a more gradual decline (Figure 11.6a). These authors further studied volatilization losses over the initial 48 h period following addition of the iodine to the coniferous forest soil and to a grassland soil (Figure 11.6b, c, respectively). In these cases, total volatile losses were measured as 0.011 and 0.004%, respectively, and emission rates declined over time according to a single exponential model. The authors attributed the low volatilization losses to the strong association they observed, in both soils, between iodine and the organic substances in the soil solid phase. Overall, the authors concluded that volatilization is not a significant pathway for the transport of ¹²⁵I in soil-plant systems.

Volatilization from Plants In addition to volatilization of iodine from the soil, plants can also convert the element into a volatile form that is emitted from the plant pores. Muramatsu and Yoshida (1995) reported that iodine emissions were highly stimulated by the presence of oats on nonflooded soil and, particularly, by the presence of rice on flooded soil where around 10% of the added ¹²⁵I was volatilized. Importantly, the authors reported that iodine emission from the shoots of the rice plants was significantly higher than that from the flooded soil surface alone. Muramatsu and Yoshida (1999) reported the volatilization of microbially generated methyl iodide gas from rice plants as a process by which iodine concentrations of soils may be reduced. Redeker and Cicerone (2004) showed that methyl iodide emissions from rice paddy soils are determined by the growth stage of the rice plant, with secondary influences of air temperature, soil iodine concentration, and soil moisture content. Muramatsu et al. (1995) also stressed the importance of rice plant growth in controlling iodine volatilization, with emissions markedly decreasing in the late cultivation period of the rice plants.

The process giving rise to enhanced methylation, and hence emissions, from rice-planted and flooded soil was postulated by Muramatsu and Yoshida (1995). This process entails the desorption of iodine from the solid phase of the soil due to low E_h and consequent predominance of I⁻ in the soil solution. I⁻ in the rhizosphere then becomes biomethylated by the effect of enzymes produced by soil microorganisms or roots (e.g., methyl halide transferase (Wuosmaa and Hager, 1990)). The methyl iodide produced



Figure 11.6 Volatile ¹²⁵I emission rates from soil. (a) Coniferous forest soils over a 22-day period. (b) Coniferous forest soils over a 48-h period. (c) Grassland soils over a 48-h period. Sample points are measured values. Lines are fits of the exponential equations shown. *Source:* Bostock *et al.*, (2003) reproduced with permission from Elsevier.

may then be transferred to the atmosphere by diffusion either through the soil pore space or, perhaps more significantly, through the intercellular gas space and aerenchym system in the plants. Alternatively, these authors propose that methyl iodide may be produced within the plant shoots from I⁻ taken up through the roots.

A mechanism exists by which soil iodine can become volatile and transfer to the aboveground atmosphere. A

pathway for human exposure thereby exists via inhalation. However, the low levels of iodine, which have actually been measured as soil-plant emissions, may significantly limit this exposure, particularly once this iodine-bearing air is diluted in the wider atmosphere.

Summary Points

- Iodine, an essential element for animals, including humans, is ubiquitous in the biosphere.
- Iodine partitioning between all three soil phases (solid, liquid, gas) leads to potential transfers away from the soil body, e.g., by leaching, plant uptake, and volatilization.
- The vast majority of soil iodine is most likely adsorbed to the soil solid phase, although appreciable amounts may be released into the liquid and gaseous phases, particularly under anoxic soil conditions.
- Under anoxic (low E_h) soil conditions, e.g., after flooding, the release of iodine into the liquid phase increases due to reduced sorption induced by changes in soil geochemistry and iodine speciation.
- Mobility of iodine under anoxic soil conditions is markedly greater than under oxic conditions. Accumulations of iodine at the boundary between anoxic and oxic soil regions are likely to occur.
- Mobility of iodine in oxic soils is low, leading to limited plant root uptake.
- Plants with roots able to tolerate anoxic conditions (e.g., rice) tend to take up greater quantities of iodine from the soil.
- Volatilization of iodine, primarily as methyl iodide, occurs from both soil and plants. Again, the presence of anoxic soil conditions is likely to enhance this process.
- Although the majority of soil iodine remains adsorbed to the soil solid phase, its release into the liquid and gaseous phases does occur, enabling potential transfer pathways that are likely to increase human exposure to iodine.

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