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Section 2

General Aspects of Iodine Sources and Intakes in the Diet, Main Routes of Iodine Metabolism, and Metabolic Roles
Section 2.1
Iodine Cycle and Chemistry
Abstract
As part of the biogeochemical cycle, the injection of iodine-containing gases into the atmosphere, and their subsequent chemical transformation therein, play a crucial role in environmental and health aspects associated with iodine – most importantly, in determining the quantity of the element available to the mammalian diet. This chapter focuses on these processes and the variety of gas- and aerosol-phase species that constitute the terrestrial iodine cycle, through discussion of the origin and measurement of atmospheric iodine in its various forms (“Sources and Measurements of Atmospheric Iodine”), the principal photo-chemical pathways in the gas phase (“Photolysis and Gas-Phase Iodine Chemistry”), and the role of aerosol uptake and chemistry and new particle production (“Aerosol Chemistry and Particle Formation”). Potential health and environmental issues related to atmospheric iodine are also reviewed (“Health and Environment Impacts”), along with discussion of the consequences of the release of radioactive iodine (I-131) into the air from nuclear reactor accidents and weapons tests that have occurred over the past half-century or so (“Radioactive Iodine: Atmospheric Sources and Consequences”).

Introduction
Iodine is an essential trace element in the endocrine system, necessary for the production of the hormones triiodothyronine (T3) and thyroxine (T4) in the thyroid gland. Mammals thus provide the termination step for the cycling of iodine in the biosphere. This biogeochemical cycle (Figure 8.1) involves processes of oceanic release, sea–air transfer, photochemical transformation, aerosol uptake, and deposition on the land where iodine is adsorbed onto the soil and vegetation (Fuge and Johnson, 1986).

The primary source of iodine is marine flora, with microalgae (phytoplankton and cyanobacteria) in open oceans and macroalgae (seaweed) in coastal areas releasing a range of gas-phase iodine-containing organic species, including methyl iodide (CH3I), diiodomethane (CH2I2), and molecular iodine (I2), to the atmosphere (Vogt, 1999; Carpenter, 2003). The predominant loss of these molecules occurs through photolysis, with subsequent oxidation by ozone (O3) and reaction with other atmospheric species (e.g., OH and NO2) in the marine boundary layer.

Abbreviations
BDE Bond dissociation energy
CCN Cloud condensation nucleus/nuclei
DMS Dimethyl sulfide
MBL Marine boundary layer
ppb Parts per billion
ppm Parts per million
ppt Parts per trillion
RGM Reactive gaseous mercury

Figure 8.1 Schematic of the production, transfer, and loss processes for atmospheric iodine.
MBl leading to the formation of iodine sinks in the form of more stable gas-phase species and aerosol particles (Vogt et al., 1999; McFiggans et al., 2000; O'Dowd and Hoffmann, 2005). There is, therefore, an intricate interplay between physical and chemical atmospheric processes prior to the eventual deposition of iodine on the soil and ultimate ingestion by animals and humans.

Sources and Measurements of Atmospheric Iodine

Despite the first detailed measurements of air-borne iodine dating back to the 1930s (Cauer, 1936, 1939) and observations of iodine enrichment (with respect to chlorine) in rainfall and aerosol (compared with seawater) in the 1960s (Duce et al., 1963), it was only a decade later, with the direct measurement of CH$_4$I in Atlantic water and air (Lovelock et al., 1973), that details of the origin and speciation of atmospheric iodine began to be resolved. Since then, and particularly in the last decade, there has been extensive research in this area, and the role and potential climatic effects of iodine in the atmosphere have been placed in a more accurate context (Kolb, 2002; von Glasow, 2005). A current estimate of the total emission rate of organo-iodide gases into the atmosphere lies in the range 2–4.5 Tg (10$^{12}$ g) per year (Saiz-Lopez and Plane, 2004a), with CH$_4$I and CH$_3$I accounting for > 90% of this atmospheric input. For comparison, the estimated input from the major anthropogenic source of iodine (fossil fuel burning) is some 2–3 orders of magnitude smaller (Vogt, 1999).

A number of organo-iodide species are of biological origin (Gribble, 2003) and have been identified at different locations around the globe – see Vogt (1999) or Carpenter (2003) for a summary of some of these more recent measurements. Measured atmospheric volume mixing ratios e.g., of CH$_4$I, show an order of magnitude increase at sea-weed-rich coastal locations compared with typical oceanic air values of 1–3 parts per trillion or ppt (1 ppt = 2.5 $\times$ 10$^{-12}$ molecules · cm$^{-3}$). Only very recently, molecular iodine (I$_2$) was measured in the MBl for the first time, at Mace Head, Ireland (53°N), with peak mixing ratios of 80–90 ppt at evening low-tide periods (Saiz-Lopez and Plane, 2004b) (Figure 8.2). These last two observations, along with reported correlations between measured gas-phase iodine oxide (IO and OIO) levels and rapid aerosol particle nucleation events or “bursts” (O’Dowd and Hoffmann, 2005), have established that the release of these iodine-containing gases into the marine air is initiated by a stress-induced biochemical pathway. For example, at Mace Head, the coastline is rich in the brown kelp, oarweed (Laminaria digitata). These accumulate very high concentrations of iodine within their structure (Leblanc et al., 2006) and recent laboratory studies have shown that light-, chemical-, and oxidative-induced stress in such seaweed species results in the release of gases including CH$_3$I and I$_2$ (Palmer et al., 2005). Saiz-Lopez and Plane (2004b) estimated an annual flux for I$_2$ of coastal origin of 0.5 Tg, assuming that 20% of the Earth’s total coastline (1.6 $\times$ 10$^6$ km) is habitable for these iodine-rich seaweed types.

In terms of the open ocean, while algal sources are most likely for the organo-iodides, a number of alternative processes have been suggested for volatilization of I$_2$ from seawater to the air. These include (i) the reduction of iodide ions (I$^-$) by UV photo-oxidation in the presence of O$_2$, originally proposed by Cauer (1939) and verified experimentally by Miyake and Tsunogai (1963); (ii) oxidation of I$^-$ by O$_3$ (Garland and Curtis, 1981); and (iii) decomposition of iodine-rich organics at the ocean surface and on the surface of sea salt particles, generated and passed into the air via wind-driven wave breaking (Moyers and Duce, 1972; Seto and Duce, 1972). Although estimates were made in the cited studies for likely global annual production rates of iodine from such mechanisms, (i) 0.4 Tg/year and (ii) 0.1 Tg/year, no concerted effort has been undertaken to more accurately characterize these processes and quantify the resultant gas emissions. Consequently, even though these sources are potentially far greater than the localized coastal emissions, due to the large sea surface area available, the contribution of the open ocean to the atmospheric iodine burden remains an unresolved issue.

Photolysis and Gas-Phase Iodine Chemistry

Sunlight (λ > 290 nm) penetrating down to the troposphere initiates the photo-oxidation of iodine-containing gases. Table 8.1 lists some of the precursor species along with key parameters associated with the photolysis process, which releases a reactive iodine (I) species in each case. The threshold wavelength ($\lambda_T$) corresponds to the minimum photon energy required to cause bond dissociation in the respective molecule, while $\lambda_{max}$ is the wavelength at which the absorption cross-section has its highest value ($\sigma_{max}$). Note that, although the organo-iodides have very similar bond dissociation energies (BDE), because the $\lambda_{max}$ values fall below the actinic cut-off wavelength of 290 nm for CH$_3$I, CH$_3$Br, and CH$_4$I, these molecules have comparatively small photolysis rates/long lifetimes in the lower atmosphere.

Figure 8.3 illustrates this point and shows the variation in the cross-section values for these molecules compared with a representative MBl solar (actinic) flux variation (values corresponding to cloud-free sky, overhead sun conditions – see Saiz-Lopez et al., 2004) with wavelength.

Clearly, the overlap between the flux and the cross-section profiles is greatest for CH$_3$I and I$_2$, which consequently have the shortest lifetimes of the iodine-containing gases emitted from the oceans (~2 min and 10 s, respectively).
Iodine in the Air: Origin, Transformation, and Exchange to Mammals

$$\text{CH}_2\text{I}_2 + h\nu \rightarrow \text{CH}_2\text{I} + \text{I}$$  \hspace{1cm} (8.1)

$$\text{I}_2 + h\nu \rightarrow 2\text{I}$$  \hspace{1cm} (8.2)

In the lower atmosphere, iodine destroys ozone via the reactions:

$$2(\text{I} + \text{O}_3) \rightarrow 2\text{IO} + 2\text{O}_2$$  \hspace{1cm} (8.3)

$$\text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I}$$  \hspace{1cm} (8.4a)

$$\rightarrow 2\text{I} + \text{O}_2$$  \hspace{1cm} (8.4b)

$$\text{IO} \text{ IO} \rightarrow \text{I}_2 \text{O}_2$$  \hspace{1cm} (8.4c)

Net: $$2\text{O}_3 \rightarrow 3\text{O}_2$$

The iodine monoxide (IO) self-reaction is relatively fast and yields mainly iodine dioxide (OIO) or I$_2$O$_2$ at the range of pressures in the lower atmosphere. The IO dimer formed via (8.4c) is likely to undergo photoysis, be taken up onto existing aerosol surfaces or take part in nucleation processes leading to the formation of new particles in coastal marine environments (O’Dowd and Hoffmann, 2002).

Figure 8.2 shows an example of the diurnal concentration profiles of I$_2$, OIO, and IO measured recently at the mid-latitude coastal marine location of Mace Head,

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Species} & \textbf{$\lambda_{\text{f}}$ (nm)} & \textbf{BDE$^b$} & \textbf{$\lambda_{\text{max}}c$ (nm)} & \textbf{$(10^{20}) \sigma_{\text{max}}^d$} \\
& & (kJ·mol$^{-1}$) & & (cm$^2$·molecule$^{-1}$) \\
\hline
\text{CH}_3\text{I} & 541 & 239 & < 290 & 112 \\
\text{CH}_2\text{I}_2 & 547 & 219 & 290 & 381 \\
\text{CH}_2\text{ICl} & 551 & 217 & < 290 & 122 \\
\text{CH}_2\text{IBr} & 559 & 214 & < 290 & 567 \\
\text{I}_2 & 792 & 151 & 525 & 285 \\
\hline
\end{tabular}
\caption{Molecular photolysis data}
\end{table}

Notes: Key parameters for consideration of the photolysis of iodine-containing gases in the air (data taken from the International Union of Pure and Applied Chemistry (IUPAC) Subcommittee for Gas Kinetic Data Evaluation online database: http://www.iupac-kinetic.ch.cam.ac.uk/).

- $\lambda_{\text{f}}$: Photo-dissociation threshold wavelength.
- BDE: Bond dissociation energy (298K).
- $\lambda_{\text{max}}$: Wavelength of maximum absorption.
- $\sigma_{\text{max}}$: Peak molecular absorption cross-section (298K).

Figure 8.3 Plot of molecular absorption cross-sections for the primary iodine-containing gases detected in the atmosphere, showing the relative overlap with the solar actinic flux in the MBL.
Ireland (Saiz-Lopez and Plane, 2004b). The correlation in the data with the tidal cycle is evident and gives strong support for a biological origin for the gases, as discussed previously.

The reaction of I\textsubscript{2} with the nitrate radical (NO\textsubscript{3}) during nighttime provides a nonphotolytic pathway to the formation of IO, and hence OIO (Saiz-Lopez and Plane, 2004b; Saiz-Lopez \textit{et al.}, 2006b).

\begin{align*}
I_2 + NO_3 &\rightarrow INO_3 + I \quad (8.5) \\
I + O_3 &\rightarrow IO + O_2 \quad (8.6)
\end{align*}

Iodine can have an effect on the oxidizing capacity of the atmosphere via modulation of the ratios of NO\textsubscript{2}/NO and HO\textsubscript{2}/OH. The ratio of NO\textsubscript{2} to NO in the atmosphere is controlled principally by the following reactions:

\begin{align*}
NO_2 + h\nu (\lambda < 398 \text{ nm}) &\rightarrow NO + O \quad (8.7) \\
NO + O_3 &\rightarrow NO_2 + O_2 \quad (8.8)
\end{align*}

In the presence of significant iodine concentrations, the ratio is shifted toward NO\textsubscript{2}:

\begin{align*}
IO + NO &\rightarrow I + NO_2 \quad (8.9)
\end{align*}

However, the HO\textsubscript{2}/OH balance will be shifted toward OH:

\begin{align*}
IO + HO_2 &\rightarrow HOI + O_2 \quad (8.10) \\
HOI + h\nu &\rightarrow OH + I \quad (8.11)
\end{align*}

Iodine can also participate in the removal of gaseous elemental mercury (Hg\textsubscript{0}) from the atmosphere. Hg\textsubscript{0}, a toxic pollutant of the environment, is emitted primarily from coal combustion (Lindberg and Stratton, 1998) and has an atmospheric lifetime of about 1 year, except in polar regions where reaction with halogen species converts it to reactive gaseous mercury or RGM (Hg\textsubscript{2}+) on a timescale of only a few hours (Calvert and Lindberg, 2004a). RGM will then deposit and accumulate in the snowpack as a bioavailable species, hence providing a pathway for the input of mercury to the Arctic biota (Brooks \textit{et al.}, 2006).

Over oceanic regions, iodine (in the form of IO) may oxidize dimethyl sulfide or DMS (Chatfield and Crutzen, 1990), a product of marine algae and the primary biogenic source of atmospheric SO\textsubscript{2} (and subsequently H\textsubscript{2}SO\textsubscript{4}), and hence be a possible route to the formation of cloud condensation nuclei or CCN (see “Aerosol Chemistry and Particle Formation” for further discussion). Although recent laboratory work indicates that this is unlikely to be significant over the open ocean (Gravestock \textit{et al.}, 2005), the higher measured iodine levels in the air at coastal sites may be conducive to this reaction pathway.

### Aerosol Chemistry and Particle Formation

The production of the gas-phase iodine oxides IO and OIO, as described in the previous section, initiates a number of possible processes that determine the ultimate speciation of iodine prior to deposition back on the land. These include (i) further gas-phase reactions, followed by (ii) uptake of the products onto existing background aerosol, primarily sea salt particles (Vogt \textit{et al.}, 1999), and (iii) resultant chemical cycling in the aerosol phase and activation of other halogens, followed by the release of the interhalogen species IBr and ICl, or (iv) further oxidation with O\textsubscript{3} to form higher oxides such as I\textsubscript{2}O\textsubscript{4} and I\textsubscript{2}O\textsubscript{5} (Saunders and Plane, 2005), leading to (v) the homogeneous nucleation of new particles in the atmosphere (O’Dowd and Hoffmann, 2005), and growth through condensation of other species or via Brownian collision-coagulation. Pathways (i–iii) are illustrated in Figure 8.4, which shows the overlap of iodine chemistry with that of chlorine and bromine in both gas and aerosol phases, and gives an idea of the complexity of the chemical transformation pathways for iodine while in the atmosphere.

In marine aerosol, iodine exists mainly in the inorganic forms, iodate (IO\textsuperscript{3–}) and iodide (I\textsuperscript{−}) (Baker \textit{et al.}, 2001), although recently the presence of soluble organic iodine, formed through the reaction of hypiodous acid (HOI) and organic matter, has also been identified in aerosol samples collected from air above the Atlantic Ocean (Baker, 2005).

A more recently studied phenomenon is that of new particle formation, reported at coastal sites possessing abundant iodine-rich seaweeds (O’Dowd \textit{et al.}, 2002). The episodic production of very high concentrations (>10\textsuperscript{5} cm\textsuperscript{−3}) of ultrafine aerosol over comparatively short periods of time (a few hours) has been shown to be correlated with daytime, low-tide conditions at these locations. This is consistent with the scenario of the photooxidation of iodine-containing gases, emitted by exposed marine flora. Subsequent laboratory and modeling studies have indicated that I\textsubscript{2} and CH\textsubscript{2}I\textsubscript{2} are the dominant precursor gases in this process, due to their relatively rapid photolysis in the MBL (O’Dowd and Hoffmann, 2002; McFiggans \textit{et al.}, 2004), and that the resulting particles are composed of polymeric iodine oxide structures consistent with either I\textsubscript{2}O\textsubscript{4} (Jimenez \textit{et al.}, 2003) or I\textsubscript{2}O\textsubscript{3} (Saunders and Plane, 2005) composition and possess nonspherical, noncompact structures with densities significantly lower than the respective bulk material value. Theoretical calculations (Saunders and Plane, 2005) indicate that the formation of these two iodine oxides in the gas phase is thermodynamically favored by a sequential oxidation route featuring more transient species such as I\textsubscript{2}O\textsubscript{2} and I\textsubscript{2}O\textsubscript{3} (Figure 8.5).

The precise mechanism responsible for the transition from gas to stable solid phase remains an area of some
uncertainty, although laboratory studies of I$_2$ photo-oxidation indicate that the homogeneous nucleation of either single I$_2$O$_5$ molecules or molecular clusters of the same species is a viable pathway (Saunders and Plane, 2006).

The subsequent fate of these particles is uncertain, although continued growth to larger sizes is likely to lead to either deposition or chemical modification through reactive uptake of species, such as water or sulfuric acid vapors. Another possibility is that the particles may grow to large enough sizes for them to bring about the activation of cloud formation, due to the ability of the particles to act as cloud condensation nuclei or CCN – "seeding" species that can initiate cloud droplet growth. The CCN potential of these particles is likely to be composition-dependent as I$_2$O$_4$ is nonhygroscopic while I$_2$O$_5$ is hygroscopic, and therefore aerosol composed of the latter species would be more likely to promote water uptake and condensation.
Finally, as with gas emissions to the atmosphere, the potential levels of and impacts from particle formation over open waters are far greater than for coastal locations. However, to date, this phenomenon has been exclusively observed at the latter; therefore, the global significance remains to be assessed.

Health and Environment Impacts

In the 1960s, a series of studies reported the beneficial role of iodine in the atmosphere with regard to issues such as the inhibition of urban photochemical smog production and artificial weather modification. Stephens et al. (1962) showed that addition of elemental iodine dramatically suppressed the formation of organic products, such as aldehydes and peroxyacetyl nitrate (PAN), produced from photochemical reactions between alkenes and NO₂, but concluded that the high concentrations of iodine required (parts per million, ppm) precluded any large-scale practical application for its use in smog reduction. Soon after, Hamilton et al. (1963) reported the effective inhibition of O₃ formation by trace amounts of iodine in a controlled smog-filled environment containing a mixture of car exhaust fumes and NO₂ and the resulting health benefits observed in test subjects exposed to the chemical pollutants. This method was suggested as a practical solution to the removal of ozone in supersonic aircraft, and indeed the authors subsequently took out a patent (3,084,024 – US Patent Office) on behalf of the Lockheed Aircraft Corporation.

Schäfer (1966) reported the activation of large numbers of ice nuclei on the addition of trace levels of iodine vapor to car exhaust (containing lead oxide nanoparticles) at temperatures from −3 to −20°C in the laboratory. The formation of lead iodide was concluded to have a “seeding” effect similar to that of silver iodide particles (Vonnegut, 1947), which had been used in an attempt to artificially modify cloud properties and enhance precipitation. Consequently this method was proposed as a means to remove harmful aerosol formed in polluted urban areas, and also in artificial weather modification. However, the development of unleaded fuels, for which no similar ice nucleating ability was shown to occur in the presence of iodine (Hogan, 1967), provided a better long-term solution to this problem.

Vikis and MacFarlane (1985) reported on reaction rates between I₂ and O₃ and the resultant formation of solid-phase iodine oxide aerosol. Coming from the opposite direction to the earlier work of Hamilton et al. (1963), this led the authors to suggest that the addition of O₃ to nuclear reactor environments should be considered as a practical route for the removal of air-borne radioactive iodine species produced as fission by-products (see “Radioactive Iodine: Atmospheric Sources and Consequences”).

Almost certainly however, the most important impact of the presence of iodine in the atmosphere is its potential for depletion of O₃ in the troposphere and lower stratosphere. Results of laboratory studies of the photo-oxidation of I₂ (Jenkin et al., 1985) supported the notion that oxidation of iodine released by photolysis of precursor gases would lead to a catalytic destruction cycle with the net result that two molecules of O₃ are converted to three molecules of O₂. Davis et al. (1986) predicted that, for equatorial to mid-latitude regions (0–42°), a total gas-phase iodine mixing ratio (∑I) of just 1.5 ppt in the upper troposphere would result in a 6% depletion of ozone, increasing to 30% for ∑I = 7 ppt. It should be noted that their calculations did not include an I₂ source from the oceans in addition to the organo-iodides. A decade later, with improved knowledge of reaction pathways and rate constants, a study by Saiz-Lopez et al. (2006a) of coastal, daytime I₂ emissions (average value of 6.5 ppt) at Mace Head, Ireland predicted an O₃ loss rate in the MBL, along a 4.2 km path length from the coast, of 1 part per billion or ppb (10⁻⁹) per hour, corresponding to an hourly depletion of ~4%. Modeling of iodine chemistry under a polar scenario (Barrow, Alaska 71°N), which included I₂ as a source, also predicted a significant O₃ depletion contribution in the springtime (Calvert and Lindberg, 2004b).

Solomon et al. (1994) implicated iodine in lower stratospheric ozone loss as a result of the rapid vertical transport of precursor gases via convection currents, resulting in photolysis and subsequent chemical transformations at altitudes up to 20 km, and concluded that this route would be 3 orders of magnitude greater than O₃ loss resulting from chlorine chemistry.

Radioactive Iodine: Atmospheric Sources and Consequences

The stable ¹²⁷I isotope constitutes 100% of naturally occurring iodine. However, a number of artificial, radioactive isotopes are formed as by-products of nuclear fission pathways (Figure 8.6). Of these, ¹³¹I is the most insidious in the biogeochemical cycle (via its transport in the atmosphere) due to its subsequent assimilation in the thyroid gland and relatively short half life of ~8 days.

Once released into the air, wind dispersal followed by deposition on the soil via rainfall and aerosol uptake and adsorption onto the vegetation (Chamberlain et al., 1960) leads to the primary source of ¹³¹I in humans originating from milk produced by grazing animals. Infants are therefore especially susceptible to the accumulation of this isotope to levels at which carcinoma can occur.

Jenkin et al. (1985) estimated that if radioactive iodine is released primarily as I₂, then during the daytime, 95% will be photolyzed within 1 min of release, and hence deposition during daylight hours is likely to occur in the form of species such as IONO₂ or aerosol, whereas at nighttime,
the major deposition channel is more likely to be in the elemental form.

The major atmospheric source of $^{131}$I originates from nuclear reactors in which the radioactive by-products are normally contained by the reactor coolant. However, since the first electricity-generating power plant went online in 1954, a handful of accidents resulting in the release of radioactive isotopes into the air have occurred, and subsequent instances of contaminated milk and cases of increased thyroid cancer have been well-documented. For example, the accident at the Windscale reactor in Cumbria, England, in 1957 is estimated to have released $2 \times 10^8$ Curies (Ci) of $^{131}$I into the atmosphere (Williams, 2006), equivalent to $\sim 7.5 \times 10^{14}$ disintegrations per second. Approximately 1 year after the accident, measurements of different radioactive isotopes collected in air filters and from grass samples showed that $^{131}$I had by far the highest activity (Chamberlain and Dunster, 1958). Wind dispersal carried the fallout along the coastline and further inland, i.e., to Leeds, Yorkshire, where subsequent studies indicated elevated $^{131}$I concentrations in milk and in infant thyroids (Burch, 1959).

However, this incident was dwarfed in scale by the meltdown that took place at the Chernobyl reactor in the former Soviet Union or modern-day Ukraine in 1986. Setting Windscale at 1 on an $^{131}$I release scale, Chernobyl comes in at $\sim 2300$ (Williams, 2006), and within a few years reports were made of a marked increase in cases of thyroid cancer in neighboring areas, such as modern-day Belarus (Kazakov et al., 1992). Studies of the aftermath of the incident continue today, although much uncertainty remains as to the long-term environmental and health effects (Baverstock and Williams, 2006).

Even greater than this event, in terms of radioactive iodine release, was the cumulative release (Windscale $\times 7500$) from the atomic weapons test program conducted in Nevada, USA, from 1951 to 1962. Again, fallout of the isotope was directly linked with radioactivity detected in cattle (Van Middlesworth, 1956), and in later studies, air trajectory calculations of fallout from underground explosions showed how effectively and rapidly air-borne $^{131}$I could be transported over large distances prior to deposition (Martell, 1964).

In conclusion, such relatively short-term studies only hint at the likely scale of effects possible following such incidents if fast, remediative action is not taken, and harmful levels of $^{131}$I are transported through the atmosphere prior to deposition back on the land and incorporation into the food chain. No further major reactor accidents have taken place since Chernobyl, and nuclear weapon tests are much less common than 40–50 years ago. However, in the light of the current build-up of such weapons in places such as North Korea, Pakistan, and the Middle East, and serious consideration, at least in the UK, of recommencing a program of nuclear reactor construction as a means of combating reliance on fossil fuel burning, lessons from the recent past must be kept in mind.

**Summary Points**

- The main sources of atmospheric iodine are biogenic, i.e., phytoplankton in the open ocean and certain seaweed species at coastal sites, with some likely contribution from chemical transformation of I$_2$ in seawater.
- These marine species release organic iodine gases (i.e., CH$_3$I and CH$_2$I$_2$) and molecular iodine (I$_2$).
- The total flux of these iodine-containing gases from the oceans into the air is $3.0–5.5 \times 10^{12}$ g/year.
- All of these gases are subject to dissociation in the atmosphere, primarily via photolysis, with I$_2$ having the shortest lifetime and therefore being the dominant source of reactive iodine, particularly in coastal locations.
- Oxidation of I atoms with ozone (O$_3$) in the lower atmosphere produces the IO molecule, which is subject to a number of subsequent reaction channels.
- These channels lead to further gas-phase reactions, aerosol uptake, and chemical cycling or particle nucleation, and ultimately deposition on the land via rainfall or aerosol.
- The chemical transformation of iodine overlaps with the chemistry of other halogen species, chlorine and bromine.
- The major impact of atmospheric iodine chemistry is the resultant depletion of O$_3$, while other consequences, such as enhanced cloud formation, remain to be established.
- The release of radioactive iodine isotopes, particularly $^{131}$I, into the atmosphere, and their subsequent transport and deposition, has conclusively been linked to increases in cases of infant thyroid cancer.
References