Methyl Iodide (Iodomethane)

RISK CHARACTERIZATION DOCUMENT FOR INHALATION EXPOSURE

Volume III

Environmental Fate

\[ \text{CH}_3\text{I} \]

External Panel Review Draft

Environmental Monitoring Branch
Department of Pesticide Regulation
California Environmental Protection Agency

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ENVIRONMENTAL FATE OF IODOMETHANE

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I. Chemical Description

\[
\begin{align*}
\text{H} & \\
\text{H–C–I} & \\
\text{H} &
\end{align*}
\]

Table 1. Physical /chemical properties of iodomethane

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Name</td>
<td>Methyl Iodide</td>
</tr>
<tr>
<td>CAS Registry Number</td>
<td>74-88-4</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>CH₃I</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>141.95</td>
</tr>
<tr>
<td>Color</td>
<td>Clear to light yellow; turns brown on exposure to light and moisture</td>
</tr>
<tr>
<td>Odor</td>
<td>Pungent, ether-like odor</td>
</tr>
<tr>
<td>Physical State</td>
<td>Liquid</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-66.5 °C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>42.5 °C</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>398 mmHg (25 °C)</td>
</tr>
<tr>
<td>Water Solubility</td>
<td>14.2 mg/mL (25 °C)</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.3 (20 °C)</td>
</tr>
<tr>
<td>Critical Temperature</td>
<td>254.8 °C</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>72.7 atm</td>
</tr>
<tr>
<td>Henry’s Law Constant (Kₕ)</td>
<td>0.0054 atm-m³/mol (25 °C)</td>
</tr>
<tr>
<td>Ozone Depletion Potential (ODP)</td>
<td>0.0015</td>
</tr>
<tr>
<td>Atmospheric Lifetime</td>
<td>5.2 days (average for all latitudes)</td>
</tr>
<tr>
<td></td>
<td>6.9 days (average for northern mid latitudes)</td>
</tr>
</tbody>
</table>

Iodomethane, an alkyl halide, is a colorless to pale yellow liquid with an acrid odor. It is stable at room temperature in sealed containers, non-corrosive to metals, and incompatible with strong oxidizing and reducing agents. On exposure to light and moisture, the color turns yellow, red or brown due to decomposition and the liberation of free iodine. When heated to decomposition in air at 270 °C, toxic iodine vapors are emitted. Iodomethane is soluble in water, and is miscible with alcohol and ether (DPR, 2002a; Lewis, 1991; Meister, 2004; O’Neil, 2001). Table 1 summarizes additional physical and chemical properties while Table 2 provides animal toxicity data.

Table 2. Acute toxicities of iodomethane in birds and aquatic animals. (DPR, 2002g)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bobwhite Quail oral LD&lt;sub&gt;50&lt;/sub&gt;</td>
<td>57 mg/kg</td>
</tr>
<tr>
<td>Bobwhite Quail inhalation LC&lt;sub&gt;50&lt;/sub&gt; (4 hr)</td>
<td>395 mg/L</td>
</tr>
<tr>
<td>Rainbow Trout LC&lt;sub&gt;50&lt;/sub&gt; (96 hr)</td>
<td>1.4 mg/L</td>
</tr>
<tr>
<td>Daphnia magna EC&lt;sub&gt;50&lt;/sub&gt; (48 hr)</td>
<td>0.57 mg/L</td>
</tr>
</tbody>
</table>

II. Regulation

Methyl bromide is scheduled for elimination as a soil fumigant and iodomethane has been proposed as an alternative (Ohr et al., 1996; Sims et al., 1995; U.S. Environmental Protection Agency, 1993; The United Nations Environmental Programmes, 1995). Based on the atmospheric lifetime, global warming potential, and ozone depletion potential, the U.S. Environmental Protection Agency (USEPA) has identified iodomethane as a reduced risk alternative to methyl bromide.

In October, 2007, the USEPA issued a one year time-limited registration of iodomethane. In April 2009, USEPA extended conditional registration of iodomethane without specifying any time limits. The USEPA website provides details of the registration (http://www.epa.gov/pesticides/factsheets/iodomethane_fs.htm). An application for California registration is currently being evaluated by DPR. Due to its acute toxicity, proposed products containing iodomethane are labeled as restricted use pesticides.

III. Use Profile

Proposed products will be applied to soil to control nematodes, weed and grass seeds, insects, and a broad spectrum of soil-borne diseases such as those caused by Phytophthora, Pythium, Fusarium, Verticillium and Rhizoctonia. Applications will be made as pre-plant soil fumigations to fields intended for the commercial production of strawberries, tomatoes, peppers, ornamentals, turf, tree and vine replanting, and to soils intended for strawberry nursery use. The proposed products are 100% iodomethane technical intended for the manufacture of end-use fumigant products, an end-use product containing 98% iodomethane with 2% chloropicrin as a warning agent, and several end-use products containing iodomethane and chloropicrin as active ingredients (Table 3).
Iodomethane is injected into soil by either shank fumigation (bed or broadcast/flat) using tractor mounted equipment with a mechanical tarpaulin layer or through chemigation (drip irrigation system). Application rates are summarized in Table 3. Besides soil fumigation, iodomethane can be formed in the environment of nuclear reactors and vented in exhaust gases (IARC, 1977). In addition, the general population may be exposed to iodomethane through ingesting seafood (Toxnet, 2009).

### Table 3. Application Rates of iodomethane products

<table>
<thead>
<tr>
<th>Product</th>
<th>Formulation</th>
<th>Application Rate lb/acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Midas@ 98:2</td>
<td>98% Iodomethane, 2% Chloropicrin</td>
<td>175</td>
</tr>
<tr>
<td>Midas@ 50:50</td>
<td>50% Iodomethane, 50% Chloropicrin</td>
<td>350</td>
</tr>
<tr>
<td>Midas@ EC Bronze</td>
<td>49.9% Iodomethane, 44.78% Chloropicrin</td>
<td>350</td>
</tr>
<tr>
<td>Midas@ 33:67</td>
<td>33% Iodomethane, 67% Chloropicrin</td>
<td>530</td>
</tr>
<tr>
<td>Midas@ EC Gold</td>
<td>33% Iodomethane, 61.7% Chloropicrin</td>
<td>530</td>
</tr>
<tr>
<td>Midas@ 25:75</td>
<td>25% Iodomethane, 75% Chloropicrin</td>
<td>700</td>
</tr>
</tbody>
</table>

a. Information derived from the U.S.EPA product labels.

### IV. Environmental Fate

The routes of iodomethane transport, dissipation, and transformation in the environment include volatilization from soil, oceanic sources or terrestrial plant surfaces with ensuing photolytic degradation, abiotic hydrolysis, aqueous photolysis, and biotransformation via soil microorganisms. The primary route of dissipation is volatilization with rapid photolysis, which releases active iodine (5.2 days half-life).

The rate of abiotic hydrolysis is slow at temperatures relevant to agricultural conditions, with a half-life of 113 days at 25 °C and pH = 7. The photolysis rate of iodomethane dissolved in water is faster (13.1 day half-life). Iodomethane displays low sorption to soil. Coupled with its high vapor pressure, iodomethane is therefore mobile in soil/water systems. It is quickly metabolized by soil microorganisms under aerobic conditions with an aerobic soil metabolism half-life of 2 hours. Under anaerobic conditions, the degradation rate is slower with an anaerobic soil metabolism half-life of 41.8 hours. An iodomethane terrestrial field soil dissipation study and concurrent volatilization study were conducted using tarped bare ground sites in a commercial strawberry production area of Watsonville, CA and a commercial strawberry/tomato production area of Dover, FL. Based on residues in a 0 to 24 inch soil sample core, the field dissipation half-life was 5.0 days. The highest levels of iodomethane in air occurred immediately after application, ranging from 0.01 to 0.065 ppm.
A. Fate and Persistence in the Aquatic Environment

A hydrolysis study was conducted using $[^{14}\text{C}]$ iodomethane in sterile pH 4, 7, and 9 aqueous buffers (DPR, 2002b). Samples were incubated in the dark at both 25 and 50 °C. Duplicate samples at each pH were analyzed at 0, 3, 14, 21, 28, and 30 days for the 25 °C incubation, and at time 0, 1, 2, 3, 4, 5, 6, and 7 days for the 50 °C incubation. The material balance at the sampling intervals was determined by liquid scintillation counting. The results are summarized in Table 3. The respective material balances for the 25 and 50 °C incubations were in the range of 91.3 – 107% and 91.9 – 105.6%, respectively. The major degradate at both temperatures was methanol.

Table 4. Hydrolysis of iodomethane at two temperatures (DPR, 2002b)

<table>
<thead>
<tr>
<th>pH</th>
<th>Hydrolysis half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>105 3.3</td>
</tr>
<tr>
<td>7</td>
<td>113 3.2</td>
</tr>
<tr>
<td>9</td>
<td>109 3</td>
</tr>
</tbody>
</table>

An aqueous photolysis study was conducted using $[^{14}\text{C}]$ iodomethane in a sterile pH 5 buffer at 25 °C (DPR, 2002b). The study duration was 15 days, and yielded a photolysis half-life of 13.1 days. The primary photodegradates were methanol and formaldehyde.

B. Fate and Persistence in Surface Water

Several factors make contamination of surface water unlikely. All iodomethane labels require applications to be tarped, minimizing any potential movement to surface water. In addition, by the time tarp removal occurs, most of the iodomethane will have dissipated.

Iodomethane is a replacement for methyl bromide, and the dominant soil types where methyl bromide is used are permeable soils with low runoff potential (sands, sandy loams and, to a lesser extent loams; Johnson and Spurlock, 2009). In contrast, very little fumigant use occurs in fine-textured runoff prone soils.

The two primary mechanisms for movement to surface water are storm water runoff and irrigation tailwater flow. Stormwater runoff occurs primarily in the winter months of Dec, Jan and Feb. Use during this time period is generally quite low. On a statewide basis less than 3% of methyl bromide field fumigations occurred during Dec, Jan and Feb. Consequently, off-site movement due to stormwater runoff is highly unlikely. Eighty-seven percent of methyl bromide field fumigations occurred during May-Oct. However, since iodomethane applications will be tarped (no irrigations), movement offsite in tailwater will not occur.
C. Fate and Persistence in Ground Water

Iodomethane shows chemical and structural similarities to bromomethane (methyl bromide). For example, both of these primary alkyl halides have high Henry’s law constants relative to other fumigants (Table 5). Consequently they have a strong tendency to volatilize from water and moist soil. In general, gas phase diffusion coefficients are approximately $10^4$ times greater than those in water (Lyman et al., 1990), and soil sorption coefficients for both fumigants are low (Ruzo, 2006). Thus, because of their volatility they both transport rapidly in soil. Note that iodomethane has a much greater Henry’s law constant than the two well-known fumigant ground water contaminants EDB and DBCP. The strong iodomethane tendency to partition into the gas phase as compared to the solution phase is a characteristic that reduces its ground water contamination potential.

Table 5. Henry’s law constant for selected fumigants.

<table>
<thead>
<tr>
<th>Fumigant Chemical</th>
<th>Dimensionless Henry’s Law Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>iodomethane</td>
<td>0.21</td>
</tr>
<tr>
<td>methyl bromide</td>
<td>0.24</td>
</tr>
<tr>
<td>chloropicrin</td>
<td>0.1</td>
</tr>
<tr>
<td>cis 1,3-dichloropropene</td>
<td>0.074</td>
</tr>
<tr>
<td>trans 1,3 – dichloropropene</td>
<td>0.043</td>
</tr>
<tr>
<td>propargyl bromide</td>
<td>0.046</td>
</tr>
<tr>
<td>methyl isothiocyanate (MITC)</td>
<td>0.01</td>
</tr>
<tr>
<td>ethylene dibromide (EDB)</td>
<td>0.029</td>
</tr>
<tr>
<td>dibromochloropropane (DBCP)</td>
<td>0.0008</td>
</tr>
</tbody>
</table>


While volatilization is the primary dissipation route of iodomethane in soil, three related degradation routes are known to occur in the soil-water environment. These are hydrolysis (Gan and Yates, 1996), nucleophilic substitution with other nucleophiles in solution such as thiourea (Zheng et al., 2003) and nucleophilic substitution with nucleophilic sites on soil organic (Paperniek et al., 2000). All of these degradation pathways yield iodide as a breakdown product. The methylation degradation reaction with nucleophilic sites in soil organic matter is considered to be largely abiotic as opposed to microbially-mediated. This conclusion is based on observations that degradation occurs with similar rates on sterile vs. non-sterile soil, and that rates of degradation increase markedly with increasing organic matter content (Guo and Gao 2009; Paperniek et al., 2000; Gan and Yates, 1997)

Iodomethane is more persistent than methyl bromide in soil and water. Gan and Yates (1996) reported half-lives ranging from 13 to 43 days in unsterilized soil, and neutral hydrolysis half-lives in the range of 50 – 113 days have been reported (Mabey and Mill, 1978; Schwarzenbach et al. 1993, DPR, 2002b). Initial investigations into the environmental fate of iodomethane recommended a cautious approach due to the potential for ground water contamination (Gan and Yates, 1996; Gan and Yates, 1997). However, USEPA concluded that “based on environmental fate data, the residual contents in soils (from field studies), and Tier I and II model estimated concentrations, the Agency does not expect iodomethane to adversely affect ground water.” Using empirical modeling, DPR also predicts essentially zero concentration of iodomethane in ground water.
water even under extreme irrigation conditions (Dias and Clayton, 2008). In contrast, the state of Florida required ground water monitoring for iodomethane as a condition of registration (FDACS, 2008).

Methanol is a degradation product of iodomethane hydrolysis, and methanol is known to be relatively susceptible to biodegradation (USEPA, 1994). In the case of iodomethane reaction with other nucleophiles, the degradation product would depend on the particular reactant. One potential source is agrochemicals such as thiourea (Zheng et al., 2003). Such chemicals are added as a fertilizer source and often are labile. Any potential for ground water contamination would require a very large initial thiourea (or other nucleophile) concentration and persistence of the resultant adduct. It’s not evident under what conditions, if any, this might happen in the field. Finally, methylation of soil organic matter would effectively eliminate the potential for organic portion of the iodomethane molecule to move to ground water. Thus, none of the three mechanisms appear to favor ground water contamination from the organic degradation portion of the iodomethane molecule.

All three of the iodomethane degradation routes yield iodide anion. Iodine/iodide has relatively complex environmental soil chemistry. In aerobic soils, iodine exists in inorganic and organic forms. In aerobic soils, iodide (I\(^-\), as opposed to iodate IO\(_3\)\(^-\)) is the dominant inorganic form based on iodine’s Pourbaix diagram (e.g. (Koch-Steindl and Prohl, 2001). Both iodide and iodate anions display low or no sorption to most clays, sands and pure minerals at neutral pHs (excluding acid systems containing sesquioxides and those containing illite) (Whitehead, 1974; Gu and Schulz, 1991; Kaplan et al., 2000). This suggests that iodide might be highly mobile in soil, similar to other halide anions such as chloride and bromide. In fact, Bowman (1984) suggested iodide for use as a tracer in soils. On the other hand, some data indicate that iodide has lesser mobility than the other two halides mentioned, largely due to iodide interactions with organic matter. Organic matter (soil humic material) plays an important role in iodide chemistry, and iodide-organic matter interactions appear to limit iodide mobility in many soils (Sheppard and Thibault, 1992; Fuge and Johnson, 1986). Actual iodination of soil organic matter can occur abiotically or biotically via microbial extra-cellular peroxidases (Santschi and Schwehr, 2004).

In summary, while organic matter is the dominant soil characteristic determining iodide sorption/reaction/mobility in natural soils, the nature of the interactions are unclear (Santschi and Schwehr, 2004). Several questions remain, including: To what extent is iodide sorbed or actually bonded? Are the interactions reversible? Can iodide be released from organic matter and be available for transport at a later time.

Some researchers have proposed a volatile iodide loss mechanism from soil, either after iodide conversion to a low molecular weight organo-iodine compound, hydroiodic acid (HI), or microbial conversion to I\(_2\) and subsequent volatilization (Whitehead, 1984). The role of hydroiodic acid is dubious because its pKa is less than zero, i.e it is ionic at environmental pHs. Data demonstrating this volatile iodide loss mechanism from soil are lacking; no studies supporting the hypothesis that volatilization is a general loss
mechanism for iodide in soil have included direct measurements of volatile iodine species.

For an evaluation of ground water contamination potential in California, the scenario of greatest interest is that where soils are known to be vulnerable to ground water contamination and ground water is shallow. These conditions exist on the east side of the San Joaquin Valley in Fresno County (Spurlock et al., 2006). In much of the area, soils are coarse to very coarse, ground water is shallow (5 – 30m), soils are aerobic and unconsolidated down to the water table. Organic matter contents in these vulnerable Fresno County coarse soils are quite low. Troiano et al. (1993) reported a mean soil organic carbon mass fraction ($f_{OC}$) of 0.0071 in the surface 0.0 - 0.15m segment, with $f_{OC}$ rapidly decreasing with depth to < 0.001 at the 0.5 m depth.

**Worst-Case Ground Water Scenario**

Under the assumptions that 50 percent of applied iodomethane volatilizes while the remainder stays in the soil and degrades quantitatively to iodide, an extremely conservative worst-case estimate of iodide loading to ground water is:

$$175 \text{ lbs max application/acre} \times 0.5 \text{ flux ratio} \times 0.112 \left(\frac{\text{g/m}^2}{\text{lb/acre}}\right) \times (127 \text{ g I})/(142 \text{ g CH}_3\text{I}) = 8.8 \text{ g I/m}^2$$

In the groundwater vulnerable area in Fresno County mentioned above, mean annual ground water recharge is on the order of 0.5m/yr (Spurlock et al., 2000). Based on the conservative upper bound iodide loading estimate above, an estimated ground water concentration is $$(8.8 \text{ g I/m}^2)/(0.5 \text{ m/yr}) = 18 \text{ g/m}^3 = 18 \text{ mg/L assuming yearly applications in all soil in the vulnerable area, and no other iodide losses or sinks are operative.}$$

This upper-bound estimate are almost certainly too high, and may or may not be appropriate to use for risk assessment. However, there are few data that would allow more realistic estimates. The post-application soil iodide data from the Florida and California iodomethane flux studies found only low levels of iodide in the soil, but the fate of the iodide was not determined. The most likely soil component responsible for whatever iodide transformation, sorption and or volatilization process that occurred is soil organic matter. Soils in California’s vulnerable ground water areas possess extremely low organic carbon contents as described above. Consequently, extrapolation of the iodide results from the Florida and California flux studies is inappropriate. It is not possible to determine if and how post-application iodide might dissipate in California’s coarse sandy low organic matter soils based on current data.

**D. Fate and Persistence in Soil**

The adsorption and desorption of $[^{14}\text{C}]$ iodomethane on five soil types was investigated using batch equilibrium methods (DPR, 2002c). The soil samples were sterilized using gamma radiation to eliminate microbial degradation reactions. The magnitude of the
resultant soil adsorption coefficients ($K_{oc}$) indicated that iodomethane is mobile in soil/water systems (Table 6).

Table 6. Summary of iodomethane soil adsorption coefficients ($K_{oc}$) and soil analysis data (DPR, 2002b).

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>$K_{oc}$ (cm$^3$/g)</th>
<th>% Organic Carbon</th>
<th>CEC$^a$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loam</td>
<td>28</td>
<td>1.76</td>
<td>10.43</td>
<td>7.0</td>
</tr>
<tr>
<td>Sandy Loam</td>
<td>61</td>
<td>1.02</td>
<td>9.72</td>
<td>6.3</td>
</tr>
<tr>
<td>Clay Loam</td>
<td>27</td>
<td>4.3</td>
<td>18.1</td>
<td>6.9</td>
</tr>
<tr>
<td>Sandy Loam</td>
<td>14</td>
<td>2.73</td>
<td>6.65</td>
<td>7.2</td>
</tr>
<tr>
<td>Silt Loam</td>
<td>43</td>
<td>1.95</td>
<td>11.18</td>
<td>5.42</td>
</tr>
</tbody>
</table>

$^a$ Cation exchange capacity

The distribution and leaching of iodomethane in soil after shank injection and subsurface drip application was investigated under laboratory conditions (Guo et al., 2004). Iodomethane was shank-injected or drip-applied at a 20-cm depth (178 pounds per acre) into stainless steel soil columns tarped with virtually impermeable film.

The route of iodomethane dissipation in soil is mainly volatilization, with minor contributions from microbial degradation processes and methylation of soil organic matter (Amachi et al., 2003; DPR, 2002c; DPR, 2002e).

The participation of microorganisms in the volatilization of iodine from soil has been investigated (Amachi et al., 2003). Soil from rice paddies, upland fields, forests, and wetlands were incubated with iodide ion (I$^-$) at 30˚C in the dark, and the volatile organic iodine species emitted determined by gas chromatography with an electron-capture detector. It was found that iodine was emitted as iodomethane, with no other alkyl iodides observed. Fourteen strains of bacteria isolated from the soils were found to volatilize significant amounts of iodomethane when cultivated with iodide ion.

The aerobic soil metabolism of iodomethane was examined using sandy loam soil from Watsonville, California (DPR, 2002c). Soil samples were placed in sealed glass columns and treated with [$^{14}$C] iodomethane at the maximum field use rate of 235 lbs/acre. Duplicate columns were connected to a flow-through volatile sampling assembly equipped with traps for collecting volatiles, and incubated in the dark at 20˚C. Soil samples were extracted and analyzed 0, 1, 2, 3, 4, 5, 6, 8, 24, 96, 168, and 288 hours by scintillation counting. Of the initial amount applied, more than 90% was lost through volatilization within 24 hours after application, a combined 1.2% was carbon dioxide and other unknown volatiles, 1.2% was non-volatile bound soil residues, and 0.8% remained in the soil as iodomethane. The aerobic soil metabolism half-life calculated was 2 hours.

The anaerobic soil metabolism of [$^{14}$C] iodomethane was investigated with soil-water systems treated with iodomethane at the maximum field use rate (DPR, 2002c). Flow-through duplicate test systems containing 3:1 (w/w) water/soil mixtures were anaerobically-incubated in the dark at 20˚C, and samples extracted and analyzed at 0, 4,
8, 24, 48, 72, 96, 168, 240, and 336 hours. Volatiles were analyzed at all sampling intervals except at time 0. The major route of dissipation was through volatilization, with minor contributions from microbial degradation to form methanol, carbon dioxide, other volatiles, and direct reactions with organic substances in the soil to form bound humic and fulvic compounds. The anaerobic soil metabolism half-life was 41.8 hours.

An iodomethane terrestrial field soil dissipation study was conducted using tarped bare ground sites in a commercial strawberry production area of Watsonville, CA and a commercial strawberry/tomato production area of Dover, FL (DPR, 2002e). The application method at the California site was broadcast flat fume shallow shank injection using a rate of 252 lb/acre. Iodomethane was applied to the Florida site via raised bed injection at the rate of 259 lb/treated acre (126 lb/acre effective broadcast rate). At the California site, soil sample cores were collected in 6-inch increments down to 24 inches on day 0, immediately after application, and days 1, 2, and 3, to 48 inches on days 8, and 57, and to 72 inches on days 15 and 28. The highest iodomethane residues were in the 0 to 12 inch soil sample cores at early sample times, with levels decreasing to less than or equal to 0.001 ppm by day 28. Residue levels in the soil sample cores collected at lower depths were highest at the earlier sample times. The field dissipation half-life determined in the California study was 4.8 days based on residues in a 0 to 24 inch soil sample cores. Soil sample cores at Florida site were collected in 6-inch increments down to 48-inch increments immediately after application, and on days 1, 2, 3, 5, 7, 14, 29, 59, and 90. Similar to California, iodomethane residues were highest in the 0 to 12 inch soil sample cores at early sample times, with levels decreasing to less than 0.001 ppm by day 90. The field dissipation half-life calculated was 5.0 days based on residues in a 0 to 24 inch soil sample core.

E. Fate and Persistence in the Atmosphere
The presence of iodomethane in the lower atmosphere is predominately due to biogenic processes of marine organisms, at least prior to its registration as a pesticide. These organisms release the metabolite into seawater with subsequent volatilization into the atmosphere (Lovelock et al., 1973; Singh et al., 1983). If released to air, iodomethane will exist solely as a vapor in the ambient atmosphere with a vapor pressure of 405 mm Hg at 25 °C (Toxnet, 2009).

The generation of halogenated metabolites in oceanic environments has been tied to the chemical defense mechanism of the organisms (Faulkner, 1980; Gschwend et al., 1985). Investigations have shown that iodomethane is produced by kelp (Lovelock, 1975), marine macroalgae (Chameides and Davis, 1980; Gschwend et al., 1985; Korzh, 1984; Schall et al., 1994; Theiler et al., 1978), and phytoplankton (Bassford et al., 1999; Oram and Penkett, 1994). Laboratory experiments by Moore and Zafirou (1994), however, showed that irradiated filtered seawater produced emissions of iodomethane via the photochemical reaction of methyl radicals with iodine atoms. The photochemical production mechanism was also supported through the correlation of iodomethane saturation anomalies and light intensity found in the Greenland/Norwegian Seas (Happell and Wallace, 1996), and by a modified sea-to-air flux model proposed by Yokouchi et al., (2001).
Organic iodine emissions from terrestrial sources have also been investigated. Iodomethane (along with carbon monoxide and carbon dioxide) has been shown to be emitted during biomass burning (Andreae et al., 1996; Blake et al., 1996). Emissions have also been reported from wood rotting fungi (Harper, 1985), soils, soil-plant systems, and vegetation. Iodine present in soil is methylated by soil microorganisms or plant roots, and emitted into the atmosphere (Amiro and Johnston, 1989; Amachi et al., 2003; Dimmer et al., 2001; Muramatsu and Yoshida, 1995; Redeker et al., 2000).

Estimated global atmospheric inputs of iodomethane from marine (oceans) and terrestrial sources are summarized in Table 7.

<table>
<thead>
<tr>
<th>Environmental Source</th>
<th>Global Emissions (Gg/year)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>Liss &amp; Slater, 1974</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>Rasmussen et al., 1982</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>Singh et al., 1983</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>Reifenhauser &amp; Heumann, 1992</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>Oram &amp; Penkett, 1994</td>
</tr>
<tr>
<td></td>
<td>214</td>
<td>Bell et al., 2002</td>
</tr>
<tr>
<td>Terrestrial</td>
<td></td>
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<tr>
<td>Biomass Burning</td>
<td>&lt;10</td>
<td>Andreae et al., 1996</td>
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<td></td>
<td>3.4</td>
<td>Blake et al., 1996</td>
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<tr>
<td>Peatland Ecosystems</td>
<td>1.4</td>
<td>Dimmer et al., 2001</td>
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<tr>
<td>Rice Paddies</td>
<td>20</td>
<td>Muramatsu &amp; Yoshida, 1995</td>
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<td></td>
<td>71</td>
<td>Redeker et al., 2000</td>
</tr>
</tbody>
</table>

Once a chemical is present in the atmosphere, it may be transformed and then removed through photolysis and/or reactions with atmospheric radicals (OH and NO$_3$) and ozone (O$_3$). The potential for human exposure to the chemical in the vapor phase and subsequent transformation products is therefore related to the atmospheric lifetime and reaction rates for removal from the atmosphere.

Several previous studies have identified photolysis as the main pathway of iodomethane removal from the troposphere (Chameides and Davis, 1980; Davis et al., 1996). Estimated atmospheric lifetimes with respect to photolysis ranged from 2 to 8 days (Calvert and Pitts, 1966; Chameides and Davis, 1980; Davis et al., 1996; DPR, Atmospheric and Environmental Research, Inc. 2000; Finlayson-Pitts and Pitts, 1986; Roehl et al., 1997; Solomon et al., 1994).

The Estimation Programs Interface (EPI) Suite™ is a Windows® based series of physical/chemical property and environmental fate estimation models developed by the EPA’s Office of Pollution Prevention and Toxics and Syracuse Research Corporation. AOPWIN™, an individual model in EPI Suite™, estimates the gas-phase reaction rate for the reaction between a chemical and OH, the most prevalent atmospheric oxidant.
Gas-phase O<sub>3</sub> reaction rates are estimated for only olefins and acetylenes. Atmospheric half-lives are automatically calculated using assumed average OH and O<sub>3</sub> concentrations. AOPWIN<sup>TM</sup> used for iodomethane produced an overall OH rate constant of 7.21 E-14 cm<sup>3</sup>/molecule−sec. The corresponding half-life was 148 days (12-hr day; 1.5E06 OH/cm<sup>3</sup>). The Experimental Database Structure Match respective values for the OH and NO<sub>3</sub> rate constants were 7.20 E-14 and 1.92 E-17 cm<sup>3</sup>/molecule−sec.

The iodomethane atmospheric lifetime and ODP has been estimated (Atmospheric and Environmental Research, Inc., 2000; Solomon et al., 1994). With the assumption that gases are emitted uniformly at all latitudes, the UV absorption cross-section for iodomethane and the OH radical reaction rate constant were used to calculate an atmospheric photolysis half-life of 5.2 days. Since photolysis is the main removal pathway of CH<sub>3</sub>I in the troposphere, the atmospheric lifetime was considered to be close to photolysis removal lifetime. The estimated ODP for stratospheric ozone depletion due to iodomethane photo-dissociation in the stratosphere was 0.0015.

Iodomethane field volatility was measured concurrently with a worker exposure study in Menteca, CA (Baker, 2001) and with terrestrial field soil dissipation studies in Watsonville, CA and Dover, FL (Baker, 2002). Application to the California sites was by broadcast flat fume shallow shank injection. The actual application rate at Menteca site was 242 lb/acre. Maximum residue in air around the plot was 0.31 ppm on the day of application around the perimeters. Higher concentrations (up to 1.51 ppm) were observed in the center of the plot. Application to the Watsonville site was at the rate of 252 lb/acre. Iodomethane was applied to the Dover site via raised bed injection at the rate of 258.8 lb/treated acre (126 lb/acre effective broadcast rate). In Watsonville and Dover, air samples were collected around the perimeter of the field 3 feet above the surface of the soil at the perimeter. At the Watsonville site, the highest levels were collected immediately after application, and ranged from 0.01 to 0.065 ppm. Iodomethane levels dropped to below the 0.0019 ppm limit of quantitation at most sample sites by day 6. The iodomethane volatilization half-life in air ranged from 1 to 2.5 days, with a mean of 1.3 days. At the Dover site, iodomethane levels were highest in the first 12 hours after application, with the highest level at 0.12 ppm. Iodomethane levels dropped to below the 0.0019 ppm limit of quantitation at all sample sites by day 10. The iodomethane volatilization half-life in air ranged from 1.3 to 2.8 days, with a mean of 2.0 days. Air concentrations and emissions measured in these studies are discussed in detail in the exposure assessment section.

V. Glossary

AOPWIN<sup>TM</sup> An individual model in EPT Suite<sup>TM</sup>

CAS Chemical Abstracts Service
CEC  Cation Exchange Capacity

CH₃I  Iodomethane

CH₃  Methyl-, a hydrophobic alkyl functional group named after methane (CH₄).

DPR  Department of Pesticide Regulation

EC₅₀  Median Effective Concentration. A statistically derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions.

EPI Suite  Estimation Programs Interface Suite™. A Windows® based series of physical/chemical property and environmental fate estimation models

f₅₀C  Mean soil organic carbon mass fraction

Hᵥ  The formula for a photon's energy in reactions.

I  Iodine

Kₒc  Soil Adsorption Coefficient. The partition coefficient of the pesticide in the organic fraction of the soil.

LC₅₀  Median Lethal Concentration. A statistically derived concentration of a substance that can be expected to cause death in 50% of test animals. It is usually expressed as the weight of substance per weight or volume of water, air or feed, e.g., mg/l, mg/kg or ppm.

LD₅₀  Median Lethal Dose. A statistically derived single dose that can be expected to cause death in 50% of the test animals when administered by the route indicated (oral, dermal, inhalation). It is expressed as a weight of substance per unit weight of animal, e.g., mg/kg.

NO₃  Nitrate

O₃  Ozone

ODP  Ozone Depletion Potential

OH  Hydroxyl radical

ppm  Parts Per Million
VI. References


DPR. 2002b. Environmental fate #2. Volume No. 52875-5, Department of Pesticide Regulation, Registration Branch, Sacramento, California.

DPR. 2002c. Environmental fate #3. Volume No. 52875-6, Department of Pesticide Regulation, Registration Branch, Sacramento, California.


DPR. 2002e. Environmental fate #5. Volume No. 52875-8, Department of Pesticide Regulation, Registration Branch, Sacramento, California.


DPR. 2002g. Ecological effects #7. Volume No. 52875-10, Department of Pesticide Regulation, Registration Branch, Sacramento, California.
DPR. 2002h. Product chemistry #2. Volume No. 52875-28, Department of Pesticide Regulation, Registration Branch, Sacramento, California.

DPR. 2002i. Calculation of Henry’s Law Constant of iodomethane. Volume No. 52875-36, Department of Pesticide Regulation, Registration Branch, Sacramento, California.


IARC; Some Fumigants, the Herbicides, 2,4-D and 2,4,5-T, Chlorinated Dibenzodioxins and Miscellaneous Industrial Chemical 15: 245-54 (1977)


