

Methyl Iodide (Iodomethane)

**RISK CHARACTERIZATION DOCUMENT
FOR INHALATION EXPOSURE**

Volume III

Environmental Fate

CH₃I

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ENVIRONMENTAL FATE OF IODOMETHANE

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I. Chemical Description

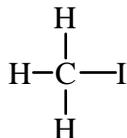


Table 1. Physical /chemical properties of iodomethane

Common Name	Methyl Iodide
CAS Registry Number	74-88-4
Molecular Formula	CH ₃ I
Molecular Weight ^a	141.95
Color ^b	Clear to light yellow; turns brown on exposure to light and moisture
Odor ^c	Pungent, ether-like odor
Physical State ^a	Liquid
Melting Point ^b	-66.5 °C
Boling Point ^a	42.5 °C
Vapor Pressure ^a	398 mmHg (25 °C)
Water Solubility ^a	14.2 mg/mL (25 °C)
Specific Gravity ^a	2.3 (20 °C)
Critical Temperature ^d	254.8 °C
Critical Pressure ^d	72.7 atm
Henry's Law Constant (K _h) ^e	0.0054 atm·m ³ /mol (25 °C)
Ozone Depletion Potential (ODP) ^f	0.0015
Atmospheric Lifetime ^f	5.2 days (average for all latitudes) 6.9 days (average for northern mid latitudes)

a. DPR, 2002a; b. Budavari, S. (ed.), 1996; c. NIOSH, 1997; d. Weast, R.C. (ed.) 1986-87; e. DPR, 2002i; f. Atmospheric and Environmental Research, Inc., 2000.

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)

Bobwhite Quail oral LD ₅₀	57 mg/kg
Bobwhite Quail inhalation LC ₅₀ (4 hr)	395 mg/L
Rainbow Trout LC ₅₀ (96 hr)	1.4 mg/L
Daphnia magna EC ₅₀ (48 hr)	0.57 mg/L

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^a.

Product	Formulation	Application Rate lb/acre
Midas@ 98:2	98% Iodomethane, 2% Chloropicrin	175
Midas@ 50:50	50% Iodomethane, 50% Chloropicrin	350
Midas@ EC Bronze	49.9% Iodomethane, 44.78% Chloropicrin	350
Midas@ 33:67	33% Iodomethane, 67% Chloropicrin	530
Midas@ EC Gold	33% Iodomethane, 61.7% Chloropicrin	530
Midas@ 25:75	25% Iodomethane, 75% Chloropicrin	700

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 [¹⁴C] 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)

pH	Hydrolysis half-life (days)	
	25°C	50°C
4	105	3.3
7	113	3.2
9	109	3

An aqueous photolysis study was conducted using [¹⁴C] 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.

Fumigant Chemical	Dimensionless Henry's Law Constant ^a
iodomethane	0.21
methyl bromide	0.24
chloropicrin	0.1
cis 1,3-dichloropropene	0.074
trans 1,3 – dichloropropene	0.043
propargyl bromide	0.046
methyl isothiocyanate (MITC)	0.01
ethylene dibromide (EDB)	0.029
dibromochloropropane (DBCP)	0.0008

a. Data for EDB and DBCP from Footprint European Pesticide Properties Database (<http://sitem.herts.ac.uk/aeru/footprint/>), all other data from Ruzo (2006).

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 (Dias and Clayton, 2008). DPR's modeling includes an assessment of extreme irrigation conditions, such as the use of post-fumigation water treatments to suppress air emissions.

In contrast, the state of Florida required ground water monitoring for iodomethane as a condition of registration (FDACS, 2008). No monitoring data is available yet. Moreover, if ground water contamination occurs, it will likely take several years to be measurable. Since methyl iodide has only been registered since 2007, any negative findings in the near future likely do not provide an adequate assessment of the potential for groundwater contamination.

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 degradate 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 I₂ 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.

Ground Water Concentration Estimates of Iodide Ion Breakdown Product

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:

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

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 $(8.8 \text{ g I/m}^2) / (0.5 \text{ m/y}) = 18 \text{ g/m}^3 = 18 \text{ mg/L}$ assuming yearly applications in all soil in the vulnerable area, and no other iodide losses or sinks are operative.

This upper-bound estimate is almost certainly too high, and may or may not be appropriate to use for risk assessment. 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.

Ground water monitoring in Florida includes iodide, but no monitoring data is available yet. In addition, any iodide detected could be due to naturally-occurring iodide as well as methyl iodide fumigations.

An alternative method to estimate iodide ground water concentrations is to use bromide ion as a surrogate. Methyl bromide has been used a soil fumigant for several decades in California. Methyl bromide and methyl iodide have similar use patterns (e.g., application rates, methods of application, regions of use). Since they are both halogenated methane compounds, they also have similar properties, including breakdown to the halogen anion (bromide ion and iodide ion). Under contract to the State Water Resources Control Board, the U.S. Geological Survey sampled 256 wells in California during 2004-2007 for multiple chemicals, including bromide ion (State Water Resources Control Board, 2009). Many of the sampled wells were located in areas of high methyl bromide use, including Monterey County. Bromide was detected in 246 of the 256 wells, with concentrations ranging from 0.01 mg/L to 13.3 mg/L, and a mean of 0.30 mg/L (Figure 1). Six wells had concentrations above 1.0 mg/L. Wells with higher concentrations were observed to be located outside of methyl bromide areas of use for 1994-2003. Since bromide occurs naturally, the contribution from methyl bromide fumigations cannot be determined. Potential ground water contamination of iodide ion may also be confounded by naturally occurring deposits. The U.S. Geological Survey detected iodide in 234 of the same 256 wells, with concentrations ranging from 0.001 to 2.4 mg/L, and a mean of 0.08 mg/L..

Figure 1a. Detections by the U.S. Geological Survey of bromide in ground water (2004-2007) and methyl bromide use (1994-2003).

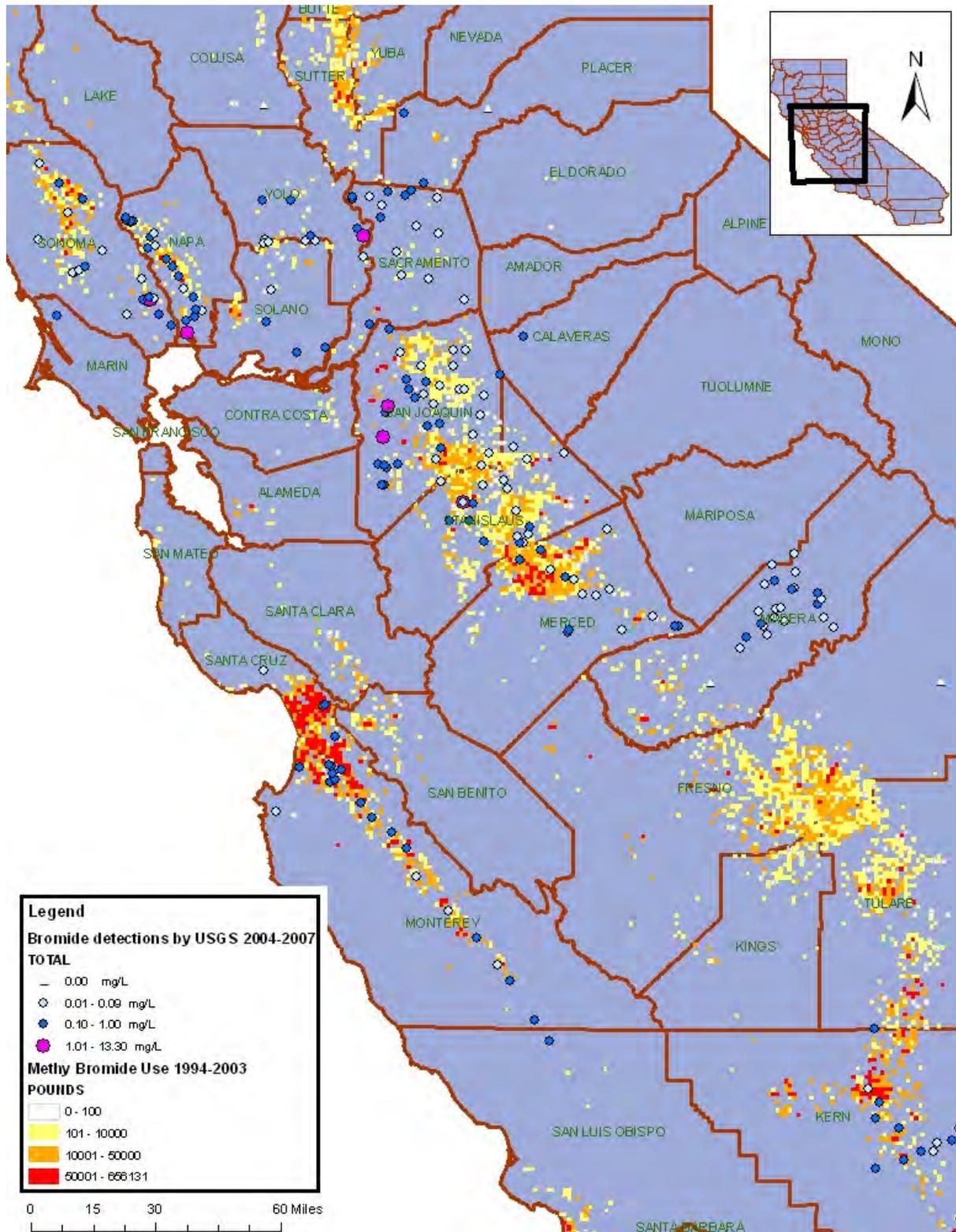
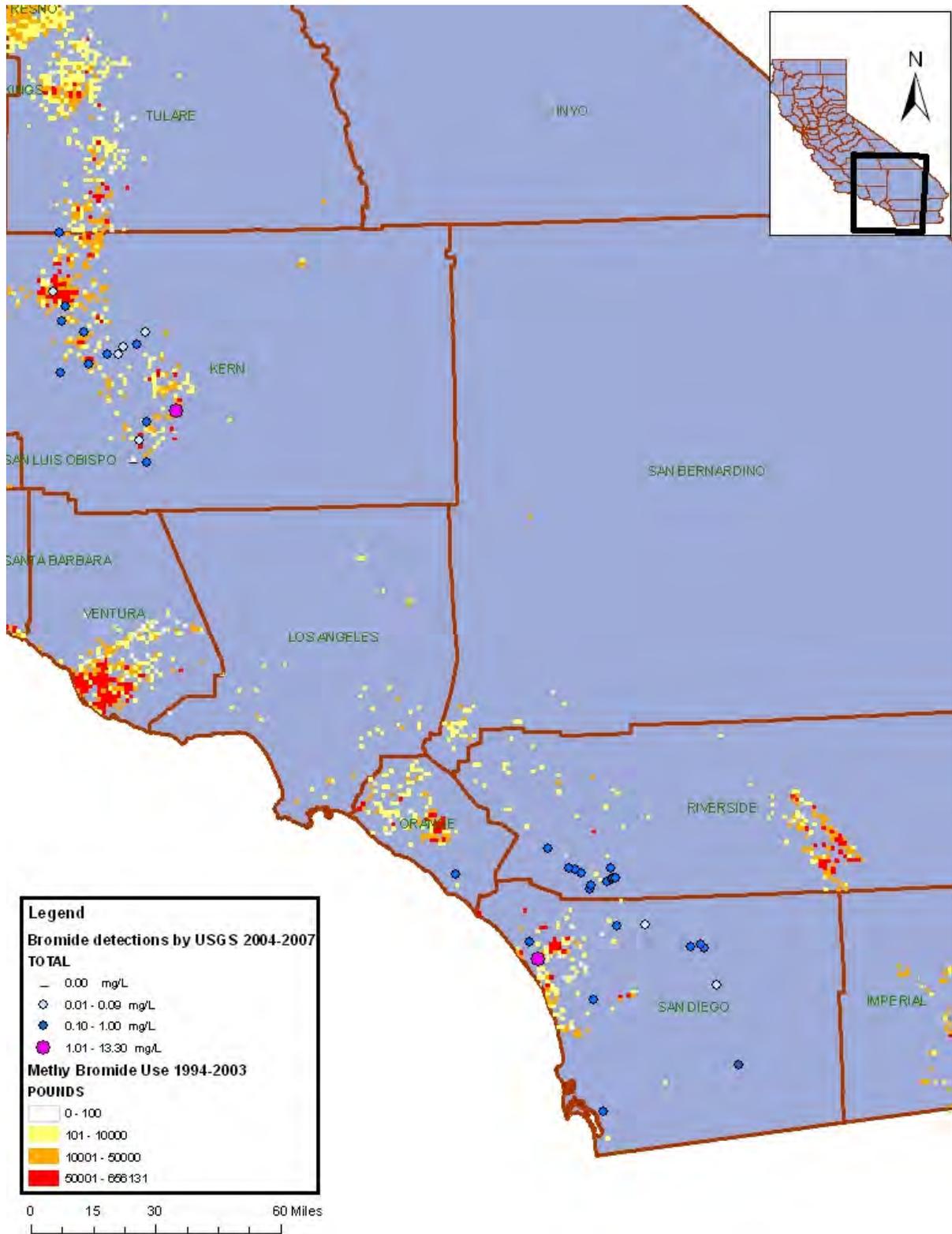


Figure 1b. Detections by the U.S. Geological Survey of bromide in ground water (2004-2007) and methyl bromide use (1994-2003).



D. Fate and Persistence in Soil

The adsorption and desorption of [¹⁴C] 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).

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

^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 [¹⁴C] 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 [¹⁴C] 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 7. Estimated global emissions of iodomethane from marine (oceans) and terrestrial sources into the atmosphere.

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

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 NO₃) and ozone (O₃). 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 (Meylan and Howard, 1993). Gas-phase O₃ reaction rates are estimated for only olefins and acetylenes. Atmospheric half-lives are automatically calculated using assumed average OH and O₃ concentrations. AOPWIN™ used for iodomethane produced an overall OH rate constant of 7.21 E-14 cm³/molecule–sec. The corresponding half-life was 148 days (12-hr day; 1.5E06 OH/cm³). The Experimental Database Structure Match respective values for the OH and NO₃ rate constants were 7.20 E-14 and 1.92 E-17 cm³/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 CH₃I 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.

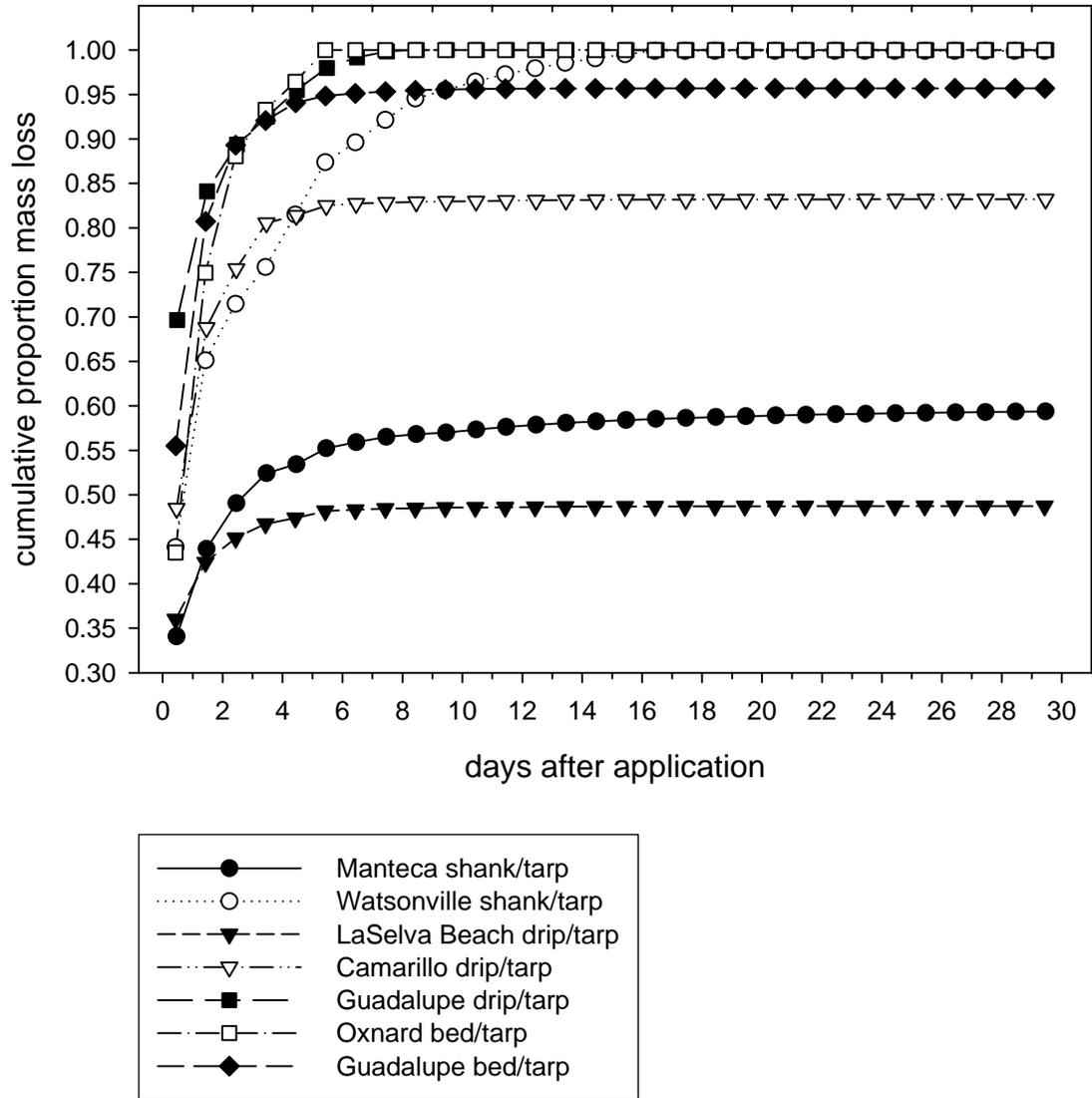
Iodomethane field volatility was measured concurrently with a worker exposure study in Menteca, CA (Baker, 2001) and with terrestrial field soil dissipation studies in Watsonville, CA and Dover, FL (Baker, 2002). Application to the California sites was by broadcast flat fume shallow shank injection. 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.

F. Mass Balance

There is insufficient data to estimate a complete mass balance, primarily due to lack of field dissipation data. However, most of the mass of methyl iodide applied volatilizes. Figure 2 shows the cumulative mass volatilized over time for all seven field volatility studies. Most of the volatilization and peak emissions occurred on the day of fumigation

and the day following fumigation. There was usually a slight increase in emissions following tarp removal (five days after application), relative to the day prior to tarp removal. However, emissions during tarp removal were much less than during the first two days. Total emissions ranged from 48% to 100% of the amount applied during the 30-day monitoring period.

Figure 2. Cumulative mass of methyl iodide volatilized during seven field volatility studies.



V. Glossary

AOPTWIN™	An individual model in EPT Suite™
CAS	Chemical Abstracts Service
CEC	Cation Exchange Capacity
CH ₃ I	Iodomethane
CH ₃	Methyl-, a hydrophobic alkyl functional group named after methane (CH ₄).
DPR	Department of Pesticide Regulation
EC ₅₀	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
f _{OC}	Mean soil organic carbon mass fraction
<i>Hv</i>	The formula for a photon's energy in reactions.
I	Iodine
K _{oc}	Soil Adsorption Coefficient. The partition coefficient of the pesticide in the organic fraction of the soil.
LC ₅₀	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.
LD ₅₀	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.
NO ₃	Nitrate
O ₃	Ozone
ODP	Ozone Depletion Potential

OH Hydroxyl radical

ppm Parts Per Million

VI. References

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