Degradation of Fumigant Pesticides: 1,3-Dichloropropene, Methyl Isothiocyanate, Chloropicrin, and Methyl Bromide

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ABSTRACT

Fumigant pesticides are frequently used in intensive agriculture to control nematodes, fungi, and weeds. Currently, four registered fumigants are available: 1,3-dichloropropene (1,3-D), methyl isothiocyanate (MITC), chloropicrin (CP), and methyl bromide (MeBr). The use of 1,3-D, MITC, and CP can be expected to increase after MeBr is completely phased out of production in the USA in 2005. In soil, the degradation of 1,3-D, MITC, CP, and MeBr occurs through both chemical and biological mechanisms. Repeated applications of the fumigants MITC and 1,3-D are known to enhance their biodegradation as a result of adapted microorganisms. Preliminary evidence suggests that the microorganisms responsible for enhanced degradation of MITC specifically target the isothiocyanate functional group. In the case of 1,3-D, a number of bacteria have been isolated that are capable of degrading 1,3-D and also using it as a sole C and energy source. Of the two isomers of 1,3-D, degradation of *trans*-1,3-D was found to be greater than that of *cis*-1,3-D in enhanced soil. Methyl bromide is mainly degraded chemically in soil by hydrolysis and methylation of nucleophilic sites on soil organic matter. Both degradation reactions occur via S_2N nucleophilic substitution. Methanotrophic and ammonia-oxidizing bacteria can co-oxidize MeBr during the oxidation of methane and ammonia, respectively. The microbiological degradation of MeBr is apparently catalyzed by methane and ammonia monooxygenase. Chloropicrin can be dehalogenated by *Pseudomonas* spp., with the major metabolic pathway occurring through three successive reductive dehalogenations to nitromethane.

The use of fumigants to control nematodes, fungi, and weeds is a common agricultural practice for maximizing the yield of various crops, especially in warm regions. In California and Florida, fumigants are extensively used to grow strawberry (*Fragaria* × *ananassa* Rozier) and tomato (*Lycopersicon esculentum* Mill.). Currently, there are only four registered chemical fumigants available: 1,3-D (marketed under the trade name Telone [DowAgroSciences LLC, Indianapolis, IN], which contains an equal ratio of *cis*-1,3-D and *trans*-1,3-D), MITC (primary breakdown product of metam-sodium [sodium methyldithiocarbamate]), CP (trichloronitromethane, often formulated with Telone and metam-sodium), and MeBr. Figure 1 gives the structural formula of metam-sodium, MITC, *cis*- and *trans*-1,3-D, CP, and MeBr. However, in 2005, MeBr will be completely phased out of use in the USA because of its role in the depletion of stratospheric ozone. 1,3-D and MITC are considered viable alternatives for MeBr. Although 1,3-D is effective against nematodes, it lacks herbicidal activity, and is often formulated with CP (e.g., Telone C17 and C35, which contain 17 and 35% CP, respectively) to provide control of some fungal pathogens. Methyl isothiocyanate is effective against nematodes and a variety of weeds and fungal pathogens.

Application of the fumigants can be made using different techniques that depend on the formulation type, pest to be controlled, and timing of the application (Lembright, 1990). Usually the fumigants are injected anywhere from 30 to 60 cm below the soil surface. Methyl bromide is applied by shank injection as a liquid, but with a high vapor pressure of about 189 kPa at 20°C, the liquid MeBr quickly vaporizes and begins diffusing outward from the lines of injection through the soil air space. In the case of 1,3-D, metam-sodium, and CP, which have relatively lower vapor pressures and higher boiling points than MeBr (see Table 1 for a list of physicochemical properties), application of these fumigants using emulsified formulations through drip irrigation systems has been shown to be more effective and safer than traditional shank injection. During application, the irrigation water acts as a vehicle for pesticide distribution, which provides a more uniform distribution of the chemical in soil.

Since fumigants are highly volatile chemicals, a large percentage of the applied material is transferred to the atmosphere. It has been reported that as much as much as 21 to 87% and 32 to 77% of the applied mass of MeBr and 1,3-D, respectively, is released to the atmosphere (Basile et al., 1986; Yagi et al., 1993, 1995; Yates et al., 1997; Gan et al., 2000b; Wang et al., 2001). The emission of a fumigant from the soil surface is controlled by its rate of diffusion (gas- and liquid-phase) and degradation, with gas-phase diffusion being the dominant rate-controlling process. Degradation of fumigants is generally slow, with half-lives ranging from days to weeks (Table 2). The addition of organic amendments to soil, however, has been shown to accelerate their degradation (Gan et al., 1998a,b; Dungan et al., 2001, 2002, 2003). Apparently, organic amendments promote the growth and activity of pesticide-degrading microorganisms, and speed up chemical degradation reactions. The incorporation of organic amendments into the soil surface is potentially useful as a means to reduce atmospheric emissions of fumigants (Gan et al., 1998a,b), which have been linked to human health problems in fumigation areas (Baker et al., 1996).

It is well established that microorganisms contribute to the degradation of fumigant pesticides in soil (Ta-

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Published in Vadose Zone Journal 2:279–286 (2003).

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Abbreviations: CP, chloropicrin; MeBr, methyl bromide; MITC, methyl isothiocyanate; 1,3-D, 1,3-dichloropropene; 3-CAA, 3-chloroallyl alcohol; 3-CAAC, 3-chloroacrylic acid.

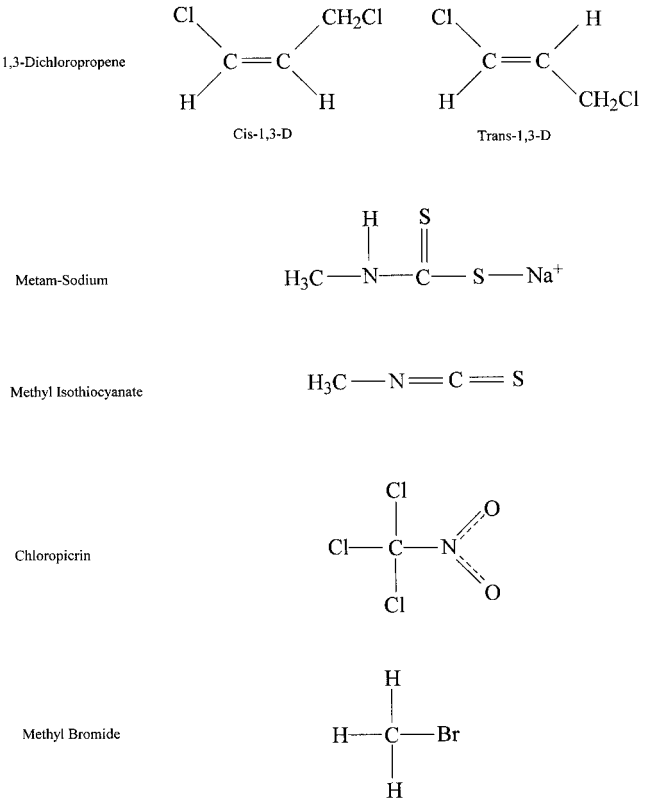

Fig. 1. The chemical structure of *cis*- and *trans*-1,3-dichloropropene, metam-sodium, methyl isothiocyanate, chloropicrin, and methyl bromide.

ble 3), but the contribution of biological mechanisms to the degradation of each fumigant does vary considerably. For example, in a sandy loam soil, only 9% of 1,3-D degradation was biologically associated (Dungan et al., 2001), while as much as 50% of MITC degradation was due to biological mechanisms (Dungan et al., 2002). Repeated applications of 1,3-D and MITC have been reported to enhance their biodegradation as a result of adapted microorganisms in the soil (Ou et al., 1995; Verhagen et al., 1996; Chung et al., 1999). Unfortunately, enhanced degradation of these pesticides can result in insufficient control of soilborne pathogens since less active product is available for control (Smelt et al., 1989a,b; Ou et al., 1995; Ou, 1998). The purpose of this review is to examine the degradation mechanisms of 1,3-D, MITC, CP, and MeBr in soil, since degradation plays a large role in influencing the transport of these fumigants and, ultimately, their effectiveness against soilborne pathogens. An emphasis is placed on the biological degradation of fumigant pesticides.

DEGRADATION OF FUMIGANT PESTICIDES

1,3-Dichloropropene

In soils from The Netherlands, where 1,3-D is extensively used to control nematodes, degradation rates between *cis*-1,3-D and *trans*-1,3-D were found to be similar (van Dijk, 1980; van der Pas and Leistra, 1987; Smelt et al., 1989a; Leistra et al., 1991). The rate of 1,3-D degradation increased with increasing temperature, and half-lives of the two isomers ranged from a few days to a few weeks (Table 2). Increased degradation of 1,3-D at higher temperatures, in some soils, is suspected to be a result of increased microbial metabolism, in addition to increased chemical degradation (Gan et al., 1999; Dungan et al., 2001). Soil moisture content, which is also known to influence microbial activity and pesticide degradation, had little effect on 1,3-D degradation in a sandy loam soil. However, in a loamy sand soil, degradation was 2.3 to 2.6 times faster (*cis*- and *trans*-1,3-D, respectively) at a soil moisture content of 16% than at 1.8% (w/w). In soils previously treated with 1,3-D, enhanced degradation of both isomers has been reported, and degradation of *trans*-1,3-D was found to be greater than that of *cis*-1,3-D (Ou et al., 1995; Ou, 1998; Chung et al., 1999). In field experiments with continuous potato (*Solanum tuberosum* L.) cropping it was found that sustained annual applications of 1,3-D led to insufficient control of potato-cyst nematodes [*Globodera rostochiensis* (Wollenweber)] (Lebbink et al., 1989). It was suggested that the adaptation of soils to 1,3-D was due to the selection of a microbial population with 1,3-D degradative capacity.

In soil, the degradation of *cis*- and *trans*-1,3-D is a combination of biological and chemical mechanisms (Ou, 1998; Gan et al., 1999; Chung et al., 1999). Both *cis*- and *trans*-1,3-D are initially hydrolyzed to corresponding *cis*- and *trans*-3-chloroallyl alcohol (3-CAA), which is mainly attributed to chemical mechanisms (Fig. 2) (Castro and Belser, 1966; Roberts and Stoydin, 1976; McCall, 1987). In enhanced soils, Ou et al. (1995) concluded that biological hydrolysis was the main factor in the initial degradation of 1,3-D, especially *cis*-1,3-D to 3-CAA. The isomers of 3-CAA are then oxidized to *cis*- and *trans*-3-chloroacrylic acid (3-CAAC), which are subsequently degraded to succinic acid, propionic acid, and acetic acid. The aliphatic carboxylic acids are finally mineralized to CO_2, H_2O, and Cl^-. The degradation of 1,3-D to 3-CAA is the most important detoxification step because 3-CAA is only weakly toxic to nematodes.

Several bacterial strains capable of degrading both isomers of 1,3-D, 3-CAA and 3-CAAC have been iso-

Table 1. Physicochemical properties of 1,3-dichloropropene (*cis*-1,3-D and *trans*-1,3-D), methyl isothiocyantate (MITC), chloropicrin (CP), and methyl bromide (MeBr).

Property	*cis*-1,3-D	*trans*-1,3-D	MITC	CP	MeBr
Density, g cm^{-3}	1.224 (20°C)	1.217 (20°C)	1.048 (24°C)	1.648 (20°C)	1.73 (0°C)
Molecular weight	111	111	73	164	95
Vapor pressure, kPa	4.5 (25°C)	3.1 (25°C)	2.8 (20°C)	2.7 (20°C)	189 (20°C)
Henry's constant (K_H)	0.074 (25°C)	0.043 (25°C)	0.01 (20°C)	0.1 (20°C)	0.24 (20°C)
Boiling point, °C	104	112	119	112	3.6
Solubility, % (at 20°C)	0.22	0.23	0.76	0.2	1.75

Table 2. First-order rate coefficients (k) and degradation half-lives ($t_{1/2}$) for 1,3-dichloropropene (1,3-D), methyl isothiocyanate (MITC), chloropicrin (CP), and methyl bromide (MeBr) in various soils.

Fumigant	k	$t_{1/2}$	Description	Reference
	d^{-1}	d		
1,3-D	0.037–0.164	18.7–4.2	Four soils at 15°C.	van Dijk, 1980
	0.021–0.07	33–9.9	Three soils at 15°C.	Smelt et al., 1989a
	0.018–0.019	38.5–36.5	Water-saturated subsoil at 10°C.	Leistra et al., 1991
	0.035–0.25	19.8–2.8	Enhanced degradation in previously treated surface and subsurface soils.	Ou et al., 1995
	0.15–1.88	4.6–0.37	Manure-amended soil at 25°C.	Gan et al., 1998a
	0.11–2.3	6.3–0.3	Effect of temperature, moisture content, and manure.	Dungan et al., 2001
	0.05–0.30	13.9–2.3	Manure-amended soil at 20°C.	Dungan et al., 2003
MITC	0.02–0.19	34.7–3.6	Three soils at 4, 13, or 21°C.	Smelt and Leistra, 1974
	0.07–0.21	9.9–3.3	Six soils at 20°C, 20% moisture.	Gerstl et al., 1977
	0.011–0.43	64–16	Four soils at 4°C.	Boesten et al., 1991
	0.21–13.5	3.4–0.05	Manure-amended soil at 25°C.	Gan et al., 1998b
	0.12–2.0	5.8–0.35	Effect of temperature, moisture content, and manure.	Dungan et al., 2002
MeBr	0.012–0.12	57.8–5.8	Four soils at different moisture contents.	Gan et al., 1994
	0.03–0.12	23.1–5.8	Three soils and potting mix at 24°C.	Gan and Yates, 1996
	0.06–1.24	11.6–0.56	Manure-amended soil at 25°C.	Gan et al., 1998b
	0.015–0.19	46.2–3.6	Two soils at 25°C.	Papiernik et al., 2000
CP	0.15	4.5	Sandy loam soil at 25°C.	Wilhelm et al., 1996
	0.16–23.7	4.3–0.03	Effect of temperature and moisture content in three different soils.	Gan et al., 2000a

lated (Belser and Castro, 1971; Lebbink et al., 1989; Hartmans et al., 1991; van Hylckama Vlieg and Janssen., 1992; Verhagen et al., 1995; Poelarends et al., 1998; Ou et al., 2001). Lebbink et al. (1989) isolated from an enhanced soil a *Pseudomonas* sp. that was reported to have the capacity to use 1,3-D as a sole C and energy source. Fifteen bacterial isolates with the capacity to degrade 1,3-D were isolated from five different enhanced soils (Verhagen et al., 1995). Six of the isolates (*Pseudomonas cichorii* I, *Alcaligenes paradoxus*, *Pseudomonas corrugate* (2 strains), *Pseudomonas putida*, and a *Pseudomonas* sp.) were found to harbor a plasmid that carried a *dhl*A (haloalkane dehalogenase)–like gene, which was suspected of being involved in 1,3-D degradation. Ou et al. (2001) enriched a bacterial consortium from an enhanced soil that was capable of cometabolically degrading *trans*-1,3-D in the presence of biodegradable substrates (e.g., tryptone, tryptophan, or alanine). A strain of *Rhodococcus* sp. (designated strain AS2C) was isolated from the mixed culture that cometabolically degraded *cis*- and *trans*-1,3-D to *cis*-3-CAA and *cis*-3-CAAC, and *trans*-CAA and *trans*-CAAC, respectively. Degradation of *trans*-1,3-D and *trans*-CAA was slightly faster than that of the respective *cis* isomer.

In contrast, *Pseudomonas pavonaceae* 170 [previously known as *Pseudomonas cichorii* 170 (Verhagen et al., 1995)] degraded *cis*-1,3-D faster than *trans*-1,3-D (Poelarends et al., 1998). The organism, isolated from soil in The Netherlands repeatedly treated with 1,3-D, could utilize low concentrations of 1,3-D as a sole C source and was also able to grow on 3-CAA and 3-CAAC. The organism produced at least three different dehalogenases: a hydrolytic haloalkane dehalogenase (DhaA) involved in the conversion of 1,3-D to 3-CAA and two 3-CAAC dehalogenases, one specific for *cis*-3-CAAC and the other specific for *trans*-CAAC. The haloalkane

Table 3. Microorganisms linked to the degradation of 1,3-dichloropropene (1,3-D), methyl isothiocyantate (MITC), chloropicrin (CP), and methyl bromide (MeBr).

Fumigant	Organism	Description	Reference
1,3-D	*Pseudomonas* sp.	Capable of completely metabolizing *cis*- and *trans*-3-CAA.	Belser and Castro, 1971
	Rhodococcus rhodochrous NCIMB13064	Can utilize 1,3-D as a sole C source, and can also grown on 3-CAA and 3-CAAC.	Kulakova et al., 1997
	Pseudomonas sp.	Preferentially degrades *trans*-1,3-D.	Lebbink et al., 1989
	Pseudomonas cepacia CAA1	Grows on *cis*-3-CAAC.	Hartmans et al., 1991
	Pseudomonas cepacia CAA2.	Grows on both *cis*- and *trans*-3-CAAC.	
	Pseudomonas cichorii		
	Alcaligenes paradoxus	Contain a *dhl*A-like gene, which is suspected of being involved in 1,3-D degradation.	Verhagen et al., 1995
	Pseudomonas corrugata		
	Pseudomonas putida		
	Pseudomonas sp.		
	Pseudomonas pavonaceae 170	Low concentrations of 1,3-D utilized as a sole C source, and can grow on 3-CAA and 3-CAAC. Produces at least three different dehalogenases.	Poelarends et al., 1998
	Rhodococcus sp. AS2C	Cometabolically degrades *cis*- and *trans*-1,3-D to *cis*-3-CAA and *cis*-3-CAAC, and *trans*-CAA and *trans*-CAAC, respectively.	Ou et al., 2001
MITC	*Rhodococcus* spp.	Consortium enhanced the degradation of MITC when spiked into sterile soil.	Warton et al., 2001
	Bacillus spp.		
	Unidentified spp.		
CP	*Pseudomonas* spp.	Successive reductive dehalogenations to produce nitromethane.	Castro et al., 1983
	P. putida PpG-786		
MeBr	*Nitrosomonas europaea*	Consumes MeBr in the presence of aluminum chloride.	Rasche et al., 1990
	Nitrosolobus multiformis		
	Methyloccus capsulatus	Oxidizes MeBr in the presence of methane.	Oremland et al., 1994
	Gram-negative aerobe	Utilizes MeBr as a sole carbon and energy source.	Miller et al., 1997

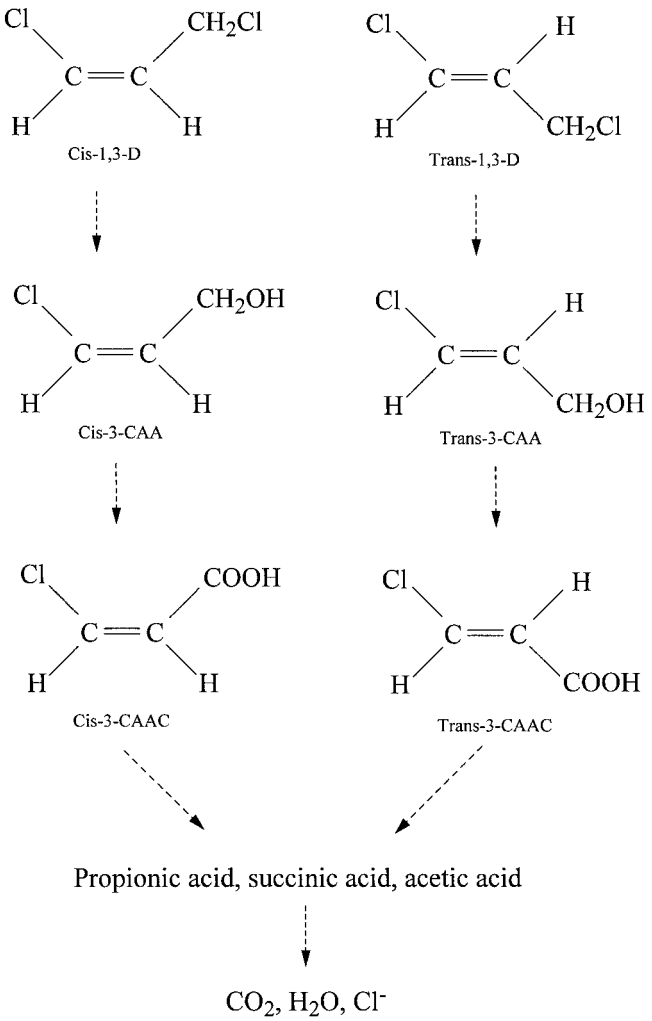

Fig. 2. The degradation pathway of *cis*- and *trans*-1,3-dichloropropene.

dehalogenase gene (*dha*A) turned out to be identical to the *dha*A gene of Gram-positive *Rhodococcus rhodochrous* NCIMB13064 (Kulakova et al., 1997). In contrast to the inducible production of DhaA in NCIMB13064, strain 170 constitutively produces DhaA. Belser and Castro (1971) isolated from soil a *Pseudomonas* sp. that was capable of completely metabolizing *cis*- and *trans*-3-CAA. Hartmans and coworkers (1991) isolated from soil two bacterial strains that used 3-CAAC as a sole C and energy source. Strain CAA1, a *Pseudomonas cepacia* sp., was capable of growth with only the *cis*-isomer of CAAC, while strain CAA2, a coryneform bacterium, utilized both isomers of CAAC as a sole C and energy source. Strain CAA1 contained a *cis*-CAAC hydratase, and strain CAA2 contained two hydratases, a *cis*- and *trans*-CAAC hydratase. The product of the hydratase activities with CAAC was malonate semialdehyde, which was subsequently decarboxylated by a cofactor-independent decarboxylase to acetaldehyde and CO_2.

Methyl Isothiocyanate

With respect to MITC, very little information is available on its degradation products in soil and toxicity in the environment. Methyl isothiocyanate is a skin and mucous membrane irritant, and high ambient levels have been detected in the air near metam-sodium application sites in California (Baker et al., 1996). During 1999, more than 7.7 million kg of metam-sodium were used in the production of agricultural crops in California (Trout, 2001). Although aqueous solutions of metam-sodium are stable for up to several weeks, it degrades rapidly in soils to MITC, which acts as a fumigant. Metam-sodium is formulated into the commercial product Vapam (AMVAC chemical corporation, Los Angeles, CA), which contains 42% of the active ingredient. The water solubility of metam-sodium at 20°C is 722 g L^{-1}, while that of MITC is 7.6 g L^{-1} (see Table 2 for more physicochemical properties). Turner and Corden (1963) found that low moisture content and high temperature increased the rate of metam-sodium transformation in soils. The time required for total transformation ranged from 2 to 7 h. In soil with moisture contents below saturation, the breakdown of metam-sodium to MITC was rapid, with a half-life generally <30 min (Gerstl et al., 1977). In a sandy loam soil, more than 87% of the metam-sodium was converted to MITC. Soils with high clay contents also exhibit higher transformation rates of metam-sodium.

In soil, the degradation half-life of MITC has been reported to range from a few days to weeks (Smelt and Leistra, 1974; Gerstl et al., 1977; Smelt et al., 1989b; Boesten et al., 1991; Dungan et al., 2002). The degradation of MITC is influenced by soil temperature, organic C content, moisture content, and texture (Smelt and Leistra, 1974; Gerstl et al., 1977; Smelt et al., 1989b; Boesten et al., 1991; Dungan et al., 2002). Of these soil conditions, temperature and organic C content often have the largest influence on MITC degradation. In a sandy loam soil, the degradation rate of MITC was about three times higher at 40°C than at 20°C (Dungan et al., 2002). When amended with 5% composted chicken manure, the degradation rate was about six times higher. Changes in the soil moisture content below saturation had little influence on the degradation rate of MITC in this soil, but in contrast to 1,3-D, degradation of MITC was 2.6 times slower at a soil moisture content of 16% than at 1.8% in a loamy sand soil (Gan et al., 1999).

Since degradation of MITC in sterile soil is significantly slower than in nonsterile soil, degradation of MITC can be attributed to biological and chemical mechanisms (Gan et al., 1999; Dungan et al., 2002). At 20°C, microbial degradation accounted for as much as 50 to 80% of the total degradation. The accelerated degradation of other carbamate pesticides by adapted microorganisms has also been reported (Rahman et al., 1979; Felsot et al., 1981). Smelt et al. (1989b) demonstrated that enhanced degradation of MITC occurred in soils that had been previously treated, which implies that microbial degradation of MITC is occurring. Verhagen and coworkers (1996) also confirmed that enhanced biodegradation of MITC did indeed occur in soils after intensive treatment (six consecutive treatments in 1 yr); however, enhanced degradation was less for MITC than for 1,3-D.

In the 10 different soils tested, enhanced degradation of MITC generally lasted for about 2 to 3 yr. In soil known to degrade MITC at an accelerated rate because of treatment with metam-sodium, the degradation of 2-propenyl isothiocyanate, 2-phenylethyl isothiocyanate, and benzyl isothiocyanate was up to 10 times faster than in a similar nondegrading soil, and up to 20 times slower in autoclaved soil (Warton et al., 2002). It was speculated that the microorganisms responsible for the enhanced degradation of MITC were specifically targeting the isothiocyanate functional group, which enabled them to degrade the three isothiocyanate compounds at an accelerated rate. Isolates resembling *Rhodococcus*, *Bacillus*, and unidentified spp. were obtained from the enhanced soil and were found to enhance the degradation of MITC when reintroduced into sterilized soil (Warton et al., 2001).

Unfortunately, there is little information available in the literature as to the nature of the breakdown products of MITC. Gas-phase photolysis of MITC results in the production of methyl isocyanide, sulfur dioxide, hydrogen sulfide, carbonyl sulfide, *N*-methylformamide, and methylamine (Geddes et al., 1995). Following a spill of about 72 000 L of metam-sodium in the upper Sacramento River (California) surface water showed the presence of carbonyl sulfide, methyl sulfide, and methyl amine in addition to MITC (Rosario et al., 1994). None of the breakdown products were detected 1 wk after the spill. Similar products may or may not be formed during the breakdown of MITC in soil, but additional research to identify the breakdown products is needed. This is especially important since the breakdown products could be more toxic and mobile than MITC. The effect of MITC on soil microbial activity and community structure has been investigated by several individuals (Sinha et al., 1979; Macalady et al., 1998; Toyota et al., 1999; Ellicott and Des Jardin, 2001). In general, microbial populations and activities were significantly reduced after fumigation, but recovered to levels similar to the control after several weeks.

Chloropicrin

Chloropicrin was first patented as an insecticide in 1908. As a soil fumigant, CP is typically used with MeBr as a warning agent or with 1,3-D for its broad biocidal and fungicidal properties. Chloropicrin is toxic to mammals, producing short- and long-term effects, and was used as a war gas during World War I. The mode of action in mammals is not well understood, but it is believed to be related to its metabolic dechlorination on reactions with biological thiols (Sparks et al., 1997).

Degradation of CP in soil follows first-order kinetics (Gan et al., 2000a). In Arlington sandy loam (coarse-loamy, mixed, active, thermic Haplic Durixeralf), Carsitas loamy sand (mixed, hyperthermic Typic Torripsamment), and Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludoll), the half-life of CP is 1.5, 4.3, and 0.2 d, respectively. After sterilization of these soils, the degradation half-life of CP increased to 6.3, 13.9, and 2.7 d, respectively, which suggests that soil microorganisms play an important role in the degradation of CP. On the basis of the difference in degradation rates between sterile and nonsterile soils, it was estimated that microbial degradation accounted for 68 to 92% of the overall CP degradation. Early studies showed that CP can be dehalogenated by *Pseudomonas* spp. that were isolated from soil (Castro et al., 1983). Work with *P. putida* PpG-786 revealed that the major metabolic pathway occurs through three successive reductive dehalogenations to nitromethane:

$$Cl_3CNO_2 \rightarrow Cl_2CHNO_2 \rightarrow ClCH_2NO_2 \rightarrow CH_3NO_2 \quad [1]$$

A small portion (about 4%) of the CP was also converted to CO_2. In a 24-d aerobic soil study, 65.6 to 75.2% of the applied [^{14}C]CP was converted to $^{14}CO_2$ (Wilhelm et al., 1996). A small amount of ^{14}C residues were also found in the fulvic (about 4%) and humic (<1%) acid fractions, as well as 14.7% as unextractable soil radiocarbon. The half-life of [^{14}C]CP was 4.5 d in a sandy loam soil at 25°C. In an anaerobic soil–aquatic system, [^{14}C]CP was rapidly dehalogenated to [^{14}C]nitromethane, with a half-life of 1.3 h.

Although a number of studies have been conducted on the efficacy of CP, little research has been completed on the fate of CP in the environment and its effect on microbial communities. As the use of CP will certainly increase in the coming years, it is necessary to expand our knowledge in these areas as rapidly as possible.

Methyl Bromide

Enhanced degradation of MeBr from repeated applications has not been reported to occur under field conditions, but a recent laboratory study established that repeated additions of MeBr resulted in higher rates of removal (Miller et al., 1997). In soil, MeBr is mainly degraded chemically, by chemical hydrolysis and methylation through a S_N2 nucleophilic substitution with water and nucleophilic sites on soil organic matter (OM), respectively (Gan et al., 1994):

$$CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^- \quad [2]$$

$$CH_3Br + OM \rightarrow CH_3OM + H^+ + Br^- \quad [3]$$

The addition of 5% composted manure to the top 5 cm of a packed soil column was reported to reduce MeBr emissions by 12% (Gan et al., 1998b).

Bacteria have also been implicated in the oxidation of MeBr (Rasche et al., 1990; Oremland et al., 1994; Miller et al., 1997; Ou et al., 1997). This reaction is believed to be catalyzed by monooxygenase:

$$CH_3Br + 1/2O_2 \rightarrow H_2CO + H^+ + Br^- \quad [4]$$

Rasche et al. (1990) found that two soil ammonia–oxidizing nitrifiers, *Nitrosomonas europaea* and *Nitrosolobus multiformis*, consumed MeBr only in the presence of ammonium chloride. Inhibition of biodegradation by allylthiourea and acetylene, specific inhibitors of the ammonia monooxygenase, suggests that the enzyme catalyzed MeBr degradation. Oremland et al. (1994) showed that a methanotrophic bacterium, *Methyloccus capsulatus*, was also capable of co-oxidizing MeBr when

incubated in the presence of methane. Methyl bromide did not support growth of the methanotroph. Miller et al. (1997), however, isolated a Gram-negative aerobic bacterium that was able to utilize MeBr as a sole C and energy source.

The degradation of MeBr was also reported to occur in a methanotrophic soil (Oremland et al., 1994). Under aerobic conditions with an application rate of 1000 mg kg^{-1}, MeBr was no longer present after 40 h, while in autoclaved soil only about 17% of the MeBr was removed during the same period. At a lower application rate of 10 mg kg^{-1}, MeBr had completely disappeared by 5 h, which was also largely due to biological mechanisms. However, in methanotrophic soil treated with 10 000 mg kg^{-1}, MeBr removal rates were comparatively slow and similar between live and autoclaved controls, indicating that degradation was a chemical rather than biological removal reaction. Apparently, the methanotrophs are inhibited by very high concentrations of MeBr. Ou (1997) found that MeBr was rapidly removed in soil (Arredondo fine sand [loamy, siliceous, semiactive, hyperthermic Grossarenic Paleudult], Gainesville, FL) that was continuously treated with methane for 1 mo. At a concentration of 20 mg kg^{-1} no MeBr residues were detected after 2 h of incubation, while at 50 mg kg^{-1} MeBr was completely removed after 3 d. It was postulated that the enhanced degradation in soil treated with methane was a result of stimulated activity of methanotrophic bacteria. Even though significant quantities of MeBr can be degraded in methanotrophic soils, it is likely that the biological oxidization of MeBr is of little significance in agricultural soils since most are not methanotrophic.

CONCLUSIONS

The fumigant pesticides 1,3-D, MITC, and CP are likely alternatives to MeBr after it is completely phased out of production by 2005 in the United States. In general, degradation of the fumigants occurs through both chemical and biological mechanisms; however, repeated application of 1,3-D and MITC is known to enhance their biodegradation as a result of adapted microorganisms. Enhanced degradation of these pesticides can result in insufficient control of soilborne pathogens since less active product is available for control. In enhanced soils treated with 1,3-D, the initial degradation of 1,3-D to 3-CAA occurs through biological hydrolysis. 3-chloroallyl alcohol is subsequently biodegraded to 3-CAAC, which is further degraded to propionic acid, succinic acid, and acetic acid, and finally to CO_2, H_2O, and Cl^-. Although MITC is subject to enhanced degradation, very little information is available on the mechanisms of MITC degradation, breakdown products, and the responsible microorganisms or enzymes. The degradation of MeBr in soils is believed to be catalyzed by a monooxygenase produced by methanotrophic and ammonia-oxidizing bacteria. The final degradation products are formaldehyde, H^+, and Br^-. Studies with CP showed that it can be dehalogenated by *Pseudomonas* spp., and work with *P. putida* PpG-786 revealed that the major metabolic pathway occurs through three successive reductive dehalogenations to nitromethane.

Since it will only be a very short time until use of 1,3-D, MITC, and CP dramatically increases as MeBr is phased-out, it is essential that the behavior of these fumigants in the soil environment is clearly understood. Although 1,3-D, MITC, and CP do not pose a specific threat to stratospheric ozone, atmospheric emissions near fumigant application areas may impact human and environmental health if not controlled. Given the relatively short half-life of these fumigants in soils, persistence in the environment should not be of major concern. Soil microorganisms, as discussed in this review, are very important in degrading these toxic fumigant pesticides to innocuous or less toxic substances. In the case of MITC and CP, further investigation is required. Degradation of the fumigants after application ultimately helps to reduce emission rates. However, since a large percentage of the fumigant is still lost after application, methods used to control fumigant emissions, such as tarping with an impermeable film (e.g., Hytibar, Hyplast, Hoogstraten, Belgium) should also be encouraged. Because more fumigant is contained within the soil profile under tarped conditions, less fumigant is required, and soil microbes also have more time to degrade the fumigants. On the other hand, increasing microorganisms' exposure to the fumigants may further result in enhanced degradation. One area that certainly requires further investigation is the impact that fumigant pesticides have on indigenous soil microbial communities and their recovery following fumigation. As of now, very few studies have been conducted. Microorganisms are not only important degraders of exogenous organic inputs, such as fumigant pesticides, but they also play a critical role in sustaining the health of natural and agricultural soil systems. Therefore, it should be of interest to optimize the application of fumigant pesticides to reduce their impact on soil microbial communities.

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