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Incompatibility of metam sodium with halogenated fumigants

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Abstract: Metam sodium (metam) is a widely used soil fumigant. Combined application of metam and other available fumigants is intended to produce synergic pesticidal effects for a broad spectrum of pest control in soil fumigation. This study aimed to test the compatibility of metam with the halogenated fumigants 1,3-dichloropropene (1,3-D), chloropicrin, methyl bromide, methyl iodide and propargyl bromide. Halogenated fumigants and metam were spiked simultaneously into organic solvents, water and moist soils, and metam-induced degradation of these halogenated chemicals was evaluated. In all three media, the halogenated fumigants were incompatible with metam and degraded via rapid chemical reactions. The degradation rate varied with halogenated fumigant species and increased as the amount of metam present was increased. In moist soil, 15–95% of the halogenated fumigants were decomposed within 72 h by metam at a 1:1 molar ratio. Combined application of Telone C-35 (62.5% 1,3-D + 35% chloropicrin) at 265 mg kg^{-1} and Vapam (42% metam) at 567 mg kg^{-1} in soil resulted in complete disappearance of the applied chloropicrin and 20–38% of the 1,3-D within 8 h. The results suggest that simultaneous application of halogenated fumigants and metam at the same soil depth will not maximize pest control. In practice, sequential treatment of soil or application at different soil depths is recommended when these two types of fumigants are used in combination.
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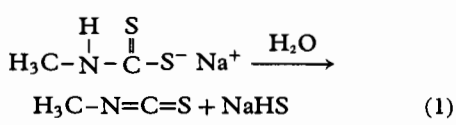
Keywords: Vapam; metam; methyl bromide; methyl iodide; 1,3-dichloropropene; chloropicrin; propargyl bromide; incompatibility

1 INTRODUCTION

Metam sodium (sodium *N*-methyldithiocarbamate, Fig 1) is a widely used soil fumigant that controls weeds, nematodes and pathogenic fungi in turf, fruit and vegetable production. The commercial products under trade names such as Vapam HL, Metam CLR, Nemasol and Sectagon 42 are generally liquid formulations containing 420 g kg^{-1} metam sodium (referred to hereafter as metam) as the active ingredient.

In moist soil, metam decomposes rapidly (half-life 0.5–4 h) to methyl isothiocyanate (Fig 1),[1] which is the primary biocidal agent. The major reaction can be described as:[2]



$$H_3C-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-S^- Na^+ \xrightarrow{H_2O} H_3C-N=C=S + NaHS \quad (1)$$

As methyl bromide is being phased out owing to its potential to deplete stratospheric ozone, only three additional chemicals are currently available for soil fumigation: 1,3-dichloropropene (1,3-D), chloropicrin and methyl isothiocyanate (Fig 1). Relative to standard methyl bromide–chloropicrin formulations, none of these registered fumigants alone has exhibited adequate broad-spectrum control of soil-borne pests.[3] The fumigant 1,3-D provides sufficient control of nematodes but is less effective against fungi, insects and weeds than methyl bromide.[4,5] Chloropicrin is highly fungicidal but may not have satisfactory efficacies against weeds and nematodes.[5–7] Methyl isothiocyanate has broad biocidal activity against plant pathogens[8,9] but does not penetrate perennial crop roots as well as methyl bromide and is not effective in controlling diseases such as those caused by *Fusarium* and *Verticillium* spp.[10] In addition, its disinfestation results can be inconsistent and are highly dependent on the proper application of methyl isothiocyanate generators such as metam.[11] To achieve adequate and broad-spectrum pest control, combined use of the currently available fumigants is a potential solution and warrants exploration. In practice, 1,3-D has been commonly used in combination

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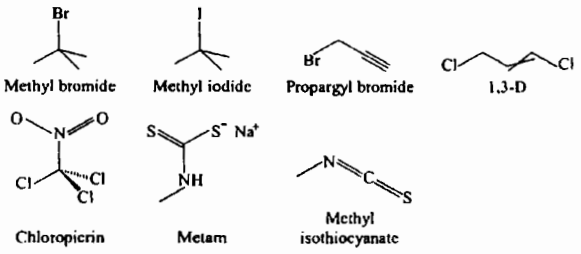

Figure 1. Molecular structure of test fumigants and chemicals.

with chloropicrin (eg Telone C35) or methyl isothiocyanate (eg Vorlex) to control soil-borne pathogens and weeds. Studies have shown that Telone C-35 (Dow Agrosciences, Indianapolis, IN), a mixture of 62.5% 1,3-D and 35% chloropicrin, is more effective in controlling soil-borne pathogens than either compound alone, and results in strawberry yields generally equivalent to those obtained with the standard methyl bromide–chloropicrin treatment.[12] Nevertheless, mixtures of 1,3-D and chloropicrin do not control weeds as well as methyl bromide–chloropicrin, and additional herbicides are required if weeds become a problem.[5,13] Given the high activity of methyl isothiocyanate against weeds, metam has been tested in combination with 1,3-D and chloropicrin for broad-spectrum pest control.[14–17] However, simultaneous or combined application of metam with these halogenated fumigants did not show the expected synergy. For example, drip application of metam together with Telone C-35 yielded significantly lower strawberry production than those treated with these fumigants individually.[15] Shank injection of 1,3-D + pebulate (*S*-propyl butyl(ethyl)thiocarbamate) combined with surface spray of metam produced worse nematode control and lower tomato yields than Telone C-35–pebulate combinations.[16] Combined use of 1,3-D or chloropicrin together with metam in drip fumigation did not provide additional weed-control benefit.[16] It is suspected that metam reacts with 1,3-D and chloropicrin in aqueous solution, since sequential application of metam via drip application two weeks following shank injection of chloropicrin or Telone C-35 provided a sterilization effect equivalent to the standard fumigation with methyl bromide–chloropicrin.[14] In a column study in which 1,3-D, chloropicrin and metam were applied simultaneously by either direct injection or sub-surface drip application, we noticed that gas-phase concentrations of 1,3-D and chloropicrin in the soil air were 10 to 100 times lower than those reported for an identical application rate of 1,3-D or chloropicrin alone under similar conditions. The chemical instability of 1,3-D and chloropicrin in the presence of metam has not been specifically reported in the literature. To develop effective fumigant application strategies, the compatibility of metam with other fumigants warrants detailed study. The objectives of this study were to investigate the compatibility of metam with halogenated fumigants and to examine the facilitated degradation of 1,3-D, chloropicrin, methyl bromide and other potential methyl bromide alternatives in the presence of metam.

2 MATERIALS AND METHODS

2.1 Chemicals and soil

The halogenated fumigants tested included 1,3-D, chloropicrin, methyl bromide, methyl iodide and propargyl bromide (Fig 1). Of these chemicals, methyl iodide and propargyl bromide are potential alternatives to methyl bromide which are not currently registered as soil fumigants. 1,3-D was provided by Dow Agrosciences Co (Indianapolis, IN) and contained 50.3% *cis*- and 47.5% *trans*-1,3-D. Chloropicrin (purity 99.9%) was received from Niklor Chemical Co (Long Beach, CA), and propargyl bromide (80% in toluene) from the USDA-ARS Water Management Research Laboratory (Fresno, CA). Methyl bromide (purity 99.5%) was obtained from Matheson Gas Products Inc (East Rutherford, NJ) and methyl iodide (purity 99.5%) from Aldrich Chemical Co (Milwaukee, WI). Metam (in dihydrous form) and methyl isothiocyanate (purity 99%) were purchased from Chem Service Co (West Chester, PA). Vapam (420 g kg^{-1} metam) was provided by Amvac Chemical Co (Newport Beach, CA), and Telone C-35 (62.5% 1,3-D + 35% chloropicrin) by Dow Agrosciences (Indianapolis, IN).

The soil used in this study was an Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralfs) collected from the University of California Agricultural Experiment Station in Riverside, CA. It had an organic carbon content of 9.2 g kg^{-1}, pH 7.20, and respective clay, silt and sand contents of 74, 180 and 746 g kg^{-1}. The soil was air-dried, sieved to <2 mm, and stored at 20 °C prior to use.

2.2 Stability of halogenated fumigants with metam in organic solvents

Organic solvents are generally used to extract fumigants from water and soil for residual concentration analysis. To find an appropriate solvent in which metam and halogenated fumigants are stable, the reactivities of the halogenated fumigants with metam in various organic solvents were determined. Stock solutions (1000–2000 mg liter^{-1}) of 1,3-D, chloropicrin, methyl bromide, methyl iodide and propargyl bromide in acetonitrile, acetone, ethyl acetate, methanol, hexane, benzene or toluene were prepared. Aliquots (5–10 μl) of the separate stock solutions were injected into 10-ml septa-sealed glass headspace vials that contained 3 ml of the corresponding organic solvents, followed by injection of 2 μl of Vapam. Concentrations of the halogenated fumigants in the vials were 18–30 μM (2.1–3.5 mg liter^{-1}) and molar ratios of halogenated fumigant/metam were 1:80–1:140. To verify that the effect of Vapam on the stability of halogenated fumigants was not caused by ingredients other than metam, the chemical metam was used in

place of Vapam to conduct the experiments (halogenated fumigant:metam 1:100–1:170). The stability of halogenated fumigants with methyl isothiocyanate in organic solvents was also examined by adding methyl isothiocyanate at 1:100 halogenated fumigant/methyl isothiocyanate molar ratio. Vials without simultaneous spiking of Vapam, metam or methyl isothiocyanate were treated as controls. The mixtures were shaken at 20 °C for 1 h, and analyzed using gas chromatography (GC) techniques for remaining halogenated fumigants. The stabilities of the halogenated fumigants with metam and methyl isothiocyanate were evaluated by comparing the contents remaining with those in control treatments. To test the stability of metam alone in these organic media, Vapam and the chemical metam were spiked separately into vials containing the test solvents, and production of methyl isothiocyanate determined.

2.3 Reactions of halogenated fumigants with metam in water

Aliquots (10–20 μl) of the fumigant stock solutions in ethyl acetate were injected into 5 ml of deionized water in headspace vials, followed by the delivery of 2 μl of Vapam. Concentrations of fumigants in the vials were 30 μM (2.85–4.93 mg liter^{-1}), and molar ratios of halogenated fumigant/metam were 1:50. Spiking of Vapam was further decreased to 0.16 μl to examine the effect of the molar ratio of halogenated fumigants to metam on their degradation rates. In addition, the chemical metam was used (45 μM) in place of Vapam to confirm the effect of metam on degradation of the halogenated fumigants. The compatibility of the latter with methyl isothiocyanate in water was also tested by spiking methyl isothiocyanate (300 μM) to give a halogenated fumigant/methyl isothiocyanate ratio of 1:10. Vials without simultaneous spiking of Vapam, metam or methyl isothiocyanate were treated as controls. Vials spiked with Vapam and the chemical metam alone were also included to test the stability of metam in water. The vials were shaken at 20 °C for 1 h, followed by extracting 0.5 ml of the mixtures with 3 ml of hexane with 3 g of anhydrous sodium sulfate. Preliminary tests showed that the halogenated fumigants were stable in hexane in the presence of metam. The hexane extracts were analyzed for the halogenated fumigants remaining and the methyl isothiocyanate produced. Compatibility of the halogenated fumigants with metam in water was assessed on the basis of the amounts remaining relative to the controls.

Degradation kinetics of the halogenated fumigants in water were determined by spiking the individual compounds (25 μM) and Vapam (metam 400 μM) into vials containing 5 ml of water, shaking the vials at 20 °C for scheduled times, and analyzing the residual halogenated fumigants in the vials. Reaction mixtures of individual halogenated fumigants with metam were analyzed by GC-MS (mass spectroscopy) and IC (ion chromatography) techniques to identify the degradation products.

2.4 Compatibility of halogenated fumigants with metam in moist soil

Arlington soil was adjusted to 10% gravimetric moisture content with deionized water, and aliquots (11.0 g) of the moist soil were weighed into 20-ml headspace vials. The vials were capped with Teflon-faced rubber septa and aluminum covers. In 'direct injection' that simulated shank application in the field, the fumigant chemicals chloropicrin, propargyl bromide, methyl iodide and 1,3-D were spiked into the vials with a 10-μl micro syringe, followed by injection of 10 μl of Vapam into each vial. Because methyl bromide is gaseous at 20 °C, its spiking was performed by injecting 40 μl of a 33 g liter^{-1} solution in ethyl acetate. Application rates of methyl bromide, methyl iodide, propargyl bromide, chloropicrin, 1,3-D, and metam were 1.4, 8.0, 5.6, 5.1, 5.5 and 3.8 mmol kg^{-1}, respectively. In 'water application' that simulated application of fumigants via irrigation systems, 3 μl of chloropicrin, propargyl bromide, methyl iodide or 1,3-D or 60 μl of 33 g liter^{-1} methyl bromide–ethyl acetate solution were separately mixed with 6 μl of Vapam in 3 ml of deionized water, and 0.5 ml of the mixture was immediately delivered (within 1 min) into vials that contained 11.0 g of moist soil. Application rates of methyl bromide, methyl iodide, propargyl bromide, chloropicrin, 1,3-D and metam were 0.35, 0.80, 0.56, 0.51, 0.55 and 0.38 mmol kg^{-1}, respectively. The low application rates ensured complete dissolution of the halogenated fumigants in water. In both 'direct injection' and 'water application', control vials without simultaneous spiking of Vapam were included. The vials were incubated at 20 °C for 72 h. After incubation, the vials were frozen at −76 °C overnight, and 6 g of anhydrous sodium sulfate and 10 ml of hexane were added immediately following decapping. The vials were recapped immediately and shaken at 20 °C for 4 h to extract residual fumigants. Concentrations of fumigants in the hexane extracts were analyzed using GC. The amounts of halogenated fumigants remaining in the soils in comparison with those in the controls were used to index their compatibilities with metam.

Additional experiments were conducted to investigate the effect of application rate and final moisture content on metam-induced degradation of the halogenated fumigants in soil. The halogenated fumigants were directly injected into soil (10% moisture content) at 2.0 mmol kg^{-1} in combination with metam (in Vapam) at 1.5 mmol kg^{-1}. The same amounts of halogenated fumigant and Vapam were delivered in 0.5 ml of water into vials containing 10.5 g of soil with 5% gravimetric water content, so that the final soil moisture content was 10%. The amounts of halogenated fumigant remaining after 24 h incubation at 20 °C were measured and compared.

The effect of moisture content on degradation of chloropicrin by metam in soil was tested by directly injecting chloropicrin and metam (in Vapam), each at 2 mmol kg^{-1}, into soils with moisture contents ranging from 0 to 20%. The soils were incubated at 20 °C for 24 h, and residual chloropicrin was measured. To investigate the effect of halogenated fumigant/metam molar ratio on degradation of the former in soil, chloropicrin was injected into 10% moisture soil at 2 mmol kg^{-1}, followed by delivering Vapam to give chloropicrin/metam molar ratios of 0, 2:1, 1:1, 1:2 and 1:5. Residual chloropicrin in soil was determined after 24 h of incubation. To test the compatibility of Telone C-35 with metam, Telone C-35 and Vapam were simultaneously spiked into moist soils at 265 and 567 mg kg^{-1}, respectively (molar chloropicrin:metam = 1:3.3, and 1,3-D:metam = 1:1.2), by 'direct injection' and 'water application'. The final soil moisture content was 10%. The soils were incubated at 20 °C for 8 h. Residual chloropicrin, 1,3-D and the generated methyl isothiocyanate were analyzed.

2.5 Fumigant analysis

All treatments were carried out in triplicate. Fumigants in organic solvents and hexane extracts were analyzed with a HP6890 GC system (Hewlett-Packard, Avondale, PA) equipped with a micro electron-capture detector (Φ-ECD, for halogenated fumigants), a nitrogen–phosphorus detector (NPD, for methyl isothiocyanate) and a DB-VRX capillary column (30 m × 0.25 mm ID × 1.4 μm film thickness, J&W Scientific, Folsom, CA). The carrier gas (helium) flow rate, injector temperature and detector temperature were set as 1.4 ml min^{-1}, 200 °C and 280 °C, respectively. The oven temperature program was: initially 45 °C, held for 1 min; increased at 2.5 °C min^{-1} to 80 °C; then at 35 °C min^{-1} to 120 °C, and held for 1 min. Under these conditions, the retention times for methyl bromide, methyl iodide, propargyl bromide, *cis*-1,3-D, *trans*-1,3-D, chloropicrin and methyl isothiocyanate were 2.7, 3.8, 6.7, 10.9, 12.2, 13.5 and 11.1 min, respectively.

Identification of reaction products of the halogenated fumigants with metam was carried out on a HP 5971 mass spectrometer equipped with a HP 7673 data system and coupled to a HP 5890 gas chromatograph with a DB-VRX capillary column. Helium was used as carrier gas. The mass spectra were recorded under electron ionization (EI) at 70 eV.

Inorganic anions including Cl^-, Br^-, and I^- were identified using ion chromatography (IC) (Dionex Series 100 with an AS40 autosampler, an IonPac AS14 ion exchange column and a UI20 conductivity detector; Dionex Corp, Sunnyvale, CA). An isocratic mobile phase comprising water, 7.5 mM sodium carbonate and 2.5 mM sodium bicarbonate was employed. The flow rate was 1.2 ml min^{-1} and run time was 10 min per sample.

2.6 Data analysis

The residual contents of the halogenated fumigants in each treatment in the presence of metam were measured and the mean of triplicates was calculated. The chemicals remaining in the controls without simultaneous spiking of metam were also analyzed and the mean determined. To exclude the effects of factors other than metam on the degradation of the test halogenated fumigants, data are presented as the percentage of the halogenated fumigants remaining in metam-spiking treatments relative to that in controls.

3 RESULTS AND DISCUSSION

3.1 Reactions of metam with halogenated fumigants in organic solvents

Approximately 1.9 mM of methyl isothiocyanate (identified by GC-MS and quantified by GC-NPD) was generated in 3 ml of acetonitrile, acetone, ethyl acetate or methanol spiked with 2 μl of Vapam alone, equivalent to 78% of that expected assuming a complete conversion of the metam to methyl isothiocyanate. In hexane, benzene and toluene, little methyl isothiocyanate (<0.03 mM) was detected. Generation of methyl isothiocyanate in vials spiked with the chemical metam had similar scenarios. Evidently, metam was unstable in polar solvents, and transformed spontaneously into methyl isothiocyanate and other products. In contrast, all test halogenated fumigants were stable in the organic solvents, and no concentration changes were observed over the experimental period. With the combined addition of Vapam, however, 65–100% of the spiked chloropicrin, methyl iodide, methyl bromide, propargyl bromide and 1,3-D in acetonitrile, acetone, ethyl acetate or methanol degraded within 1 h (Table 1), and about 1.9 mM of methyl isothiocyanate was also detected. In hexane, benzene or toluene, the halogenated fumigant concentrations remained unchanged (Table 1), and little methyl isothiocyanate was found. When the chemical metam was used in place of Vapam to conduct the experiments (halogenated fumigant/metam = 1:100–170), similar results were obtained: none of the halogenated fumigants were detected in acetonitrile, only 1,3-D (2–30% of the spiked amount) remained in acetone, ethyl acetate or methanol, and all halogenated fumigants were fully recovered from hexane, benzene or toluene. In the presence of methyl isothiocyanate at a 1:100 halogenated fumigant/methyl isothiocyanate molar ratio, concentrations of the halogenated fumigants changed little (98–101% recovery) in all test organic solvents, including acetonitrile, demonstrating their compatibility with methyl isothiocyanate.

Metam is an ionic salt (Fig 1). Its stability in organic solvents and reactivity with the halogenated fumigants is apparently controlled by its solubility. Of the test solvents, acetonitrile has an extremely high polarity and is infinitely water-miscible. Metam (in Vapam) is soluble in acetonitrile, and all the spiked halogenated fumigants disappeared within 1 h in the

Table 1. Residual percentages of halogenated fumigants[a] in organic solvents 1 h after the addition of Vapam

	% of control[b]					
Solvents	CP	MeBr	MeI	PgBr	*cis*-1,3-D	*trans*-1,3-D
Acetonitrile	ND[c]	ND	ND	ND	ND	ND
Methanol	ND	ND	ND	ND	2.9 (±0.2)	13.5 (±0.5)
Acetone	ND	ND	ND	ND	8.5 (±0.7)	20.1 (±1.8)
Ethyl acetate	ND	ND	ND	ND	15.3 (±0.9)	34.4 (±1.4)
Hexane	99.2 (±1.6)	101.4 (±1.5)	98.7 (±1.1)	101.2 (±2.8)	100.8 (±1.3)	101.1 (±2.0)
Benzene	101.5 (±2.0)	98.0 (±1.7)	99.9 (±2.1)	99.2 (±0.4)	101.5 (±2.6)	100.3 (±1.4)
Toluene	98.7 (±1.5)	102.4 (±2.3)	99.8 (±0.4)	100.9 (±1.6)	99.4 (±1.0)	99.6 (±1.5)

[a] CP: chloropicrin; MeBr: methyl bromide; MeI: methyl iodide; PgBr: propargyl bromide. Molar ratios of halogenated fumigant:metam were 1:85–1:140.
[b] Values in parentheses are standard error of triplicates. The test halogenated fumigants alone were stable in organic solvents. Recoveries ranged from 98 to 102% after 7 days of storage at 20 °C.
[c] Non-detectable.

presence of metam. In moderately polar solvents, including methanol, acetone and ethyl acetate, the spiked halogenated fumigants were also eliminated within 1 h by Vapam, except 1,3-D, of which 3–35% remained (Table 1). Methanol is water-miscible and has a greater polarity than acetone or ethyl acetate, and, consequently, less 1,3-D remained in methanol (Table 1). In non-polar solvents such as hexane, benzene or toluene, Vapam did not dissolve, and thus the halogenated fumigants remained unreactive in the presence of metam (Table 1). Given the stability of the halogenated fumigants with metam in non-polar media, hexane was used to extract water and soil samples in the following experiments.

3.2 Reactions of halogenated fumigants with metam in water

In water at 20 °C, the halogenated fumigants were relatively stable, nearly 100% of the chemicals being recovered from controls 1 h after spiking, and recoveries were 93–102% after 24 h of incubation. Relative to the controls, however, simultaneous application of Vapam at 1:50 halogenated fumigant/metam molar ratio resulted in disappearance of 55–100% of the halogenated fumigant within 1 h (Table 2). Meanwhile, 0.26–0.53 mM of methyl isothiocyanate was generated, in contrast to the small methyl isothiocyanate production (<0.04 mM) in applications of Vapam alone. This rapid disappearance was primarily a result of chemical reactions between metam and the halogenated fumigants. Other processes such as hydrolysis may have contributed, but this effect may not be significant, given the large half-lives (≥ 10 days) of these compounds in deionized water.[18,19] Methyl isothiocyanate was compatible with the halogenated fumigants in water, and the combined presence of methyl isothiocyanate at a 1:10 molar ratio did not affect degradation of the halogenated chemicals (Table 2).

Degradation rates of the halogenated fumigants were controlled by metam. In water at 20 °C, <47% of the spiked halogenated fumigants remained 1 h after the simultaneous application of metam at 1:50 halogenated fumigant/metam molar ratio (Table 2). The remaining portion increased to 79–94% (except chloropicrin) when metam was spiked at a 1:5 molar ratio, and to 90–99% (except chloropicrin) at a 1:1.5 molar ratio (Table 2). The degradation rate also varied with halogenated fumigant species. As illustrated in Fig 2, chloropicrin exhibited the highest reactivity with metam, and became undetectable within 2 h at a 1:16 molar ratio, whereas methyl iodide demonstrated the least reactivity, and 37% still remained after 20 h. With the same initial concentrations and halide/metam molar ratios, the relative degradation rate of the halogenated fumigants

Table 2. Residual percentages of halogenated fumigants[a] (HF) in water 1 h after addition of Vapam, the chemical metam or methyl isothiocyanate (MITC)

	% of control[b]					
Treatments	CP	MeBr	MeI	PgBr	*cis*-1,3-D	*trans*-1,3-D
Vapam (HF:metam = 1:50)	ND[c]	46.2 (±0.6)	39.3 (±1.1)	4.5 (±0.1)	15.7 (±0.1)	39.4 (±0.4)
Vapam (HF:metam = 1:5)	ND	92.5 (±0.7)	88.8 (±3.5)	79.4 (±1.8)	87.9 (±0.5)	93.7 (±1.1)
Metam (HF:metam = 1:1.5)	8.2 (±0.5)	94.0 (±0.3)	92.7 (±1.3)	90.0 (±0.7)	95.8 (±0.9)	98.4 (±1.4)
MITC (HF:MITC = 1:10)	103.0 (±6.1)	101.2 (±1.6)	101.3 (±1.6)	100.2 (±0.3)	98.2 (±1.7)	99.3 (±0.9)

[a] See Table 1 for nomenclature. Initial concentrations of halogenated fumigants were 30 μM.
[b] Values in parentheses are standard error of triplicates. No significant degradation of the halogenated fumigants in controls without the presence of metam was observed within 1 h, and the recoveries were nearly 100%.
[c] Non-detectable.

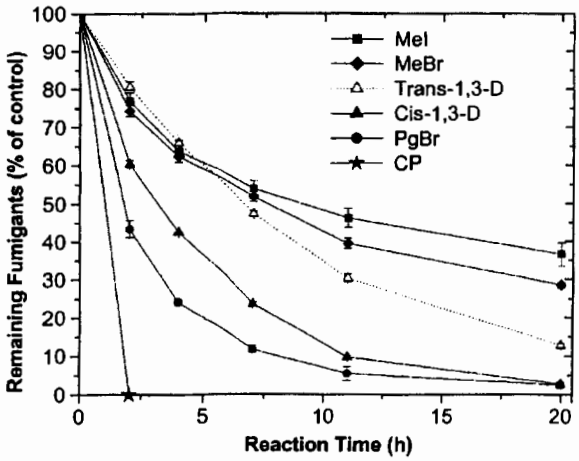

Figure 2. Promoted degradation of halogenated fumigants in water by metam. The initial concentration of halogenated fumigants was 25 μM, and the molar ratio of halogenated fumigant:metam was 1:16. Symbols represent mean of triplicate samples and error bars indicate standard deviation.

followed the order: chloropicrin > propargyl bromide > *cis*-1,3-D > *trans*-1,3-D > methyl bromide > methyl iodide (Fig 2).

Reaction mechanisms of metam with the halogenated fumigants are proposed as nucleophilic substitution (for 1,3-D, methyl bromide, methyl iodide and propargyl bromide) or redox reactions (for chloropicrin), following equations:

$$H_3C-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-S^- + R-X \longrightarrow H_3C-N=C=S + R-SH + X^- \quad (2)$$

where R denotes methyl (in methyl iodide and methyl bromide), propargyl (in propargyl bromide) or 1-chloropropenyl (in 1,3-D), and X represents Br (in methyl bromide and propargyl bromide), I (in methyl iodide) or Cl (in 1,3-D);

$$H_3C-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-S^- + Cl_3C-NO_2 \longrightarrow H_3C-N=C=S + Cl_2HC-NO_2 + S + Cl^- \quad (3)$$

$$H_3C-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-S^- + Cl_2HC-NO_2 \longrightarrow H_3C-N=C=S + ClH_2C-NO_2 + S + Cl^- \quad (4)$$

$$H_3C-\overset{H}{\overset{|}{N}}-\overset{S}{\overset{\|}{C}}-S^- + ClH_2C-NO_2 \longrightarrow H_3C-N=C=S + H_3C-NO_2 + S + Cl^- \quad (5)$$

In reacted aqueous mixtures of metam and the individual halogenated fumigants, the respective products, methyl isothiocyanate, R-SH (methyl mercaptan, propynethiol, and 1-chloro-3-thiolpropene), dichloronitromethane and chloronitromethane, were tentatively identified using GC-MS (Fig 3), and Br^-, Cl^- and I^- ions were detected using IC techniques. Since no molecular ions (M^+) of dichloronitromethane were detected using the described GC-MS techniques, the mass spectra (*m/z* 83–85 and 48–50) of its EI fragments without the $-NO_2$ group are seen on Fig 3. Castro *et al*[20] reported that molecular ions of the chloronitromethane family, including chloropicrin, chloronitromethane and dichloronitromethane, were hardly observed in EI mass spectra, while the de-nitro fragments were intensive. Mixing chloropicrin with Vapam in water resulted in the rapid formation of a milky turbid solution because of the production of colloidal sulfur. The same white precipitate was also observed when sulfide (S^{2-}) or thiosulfate ($S_2O_3^{2-}$) was acidified with dilute hydrochloric acid or oxidized with hypochlorite, indicative of sulfur formation. It is noteworthy that only the 3-Cl in 1,3-D is reactive and able to be substituted in the reaction with metam. Aqueous solutions containing 1,3-D and metam at molar ratios of 1:1 and 1:2 yielded equivalent moles of Cl^- after complete reaction (Table 3). All three Cl atoms in chloropicrin are reactive, and can be reduced to Cl^- if adequate metam is present. The yield of Cl^- in chloropicrin/metam water mixtures at a 1:2 molar ratio was twice that in mixtures at a 1:1 molar ratio with the same amount of chloropicrin (Table 3). At 1:2 chloropicrin/metam molar ratio, chloronitromethane (Fig 3) took place of dichloronitromethane and became the

Table 3. Methyl isothiocyanate (MITC) and chloride production from 1,3-dichloropropene and chloropicrin in water in the presence of metam at different molar ratios[a,b]

	1,3-Dichloropropene (2.20 mM)			Chloropicrin (2.06 mM)		
Treatments	Cl^- produced (mM)	MITC produced (mM)	Residual 1,3-D (mM)	Cl^- produced (mM)	MITC produced (mM)	Residual CP (mM)
Control (no metam)	0.44 (±0.02)	–	1.74 (±0.03)	0.00	–	2.04 (±0.04)
HF:metam = 2:1	1.40 (±0.03)	1.05 (±0.01)	0.72 (±0.02)	1.11 (±0.04)	0.88 (±0.00)	0.98 (±0.03)
HF:metam = 1:1	2.25 (±0.09)	2.16 (±0.06)	0.01 (0.00)	2.11 (±0.05)	1.83 (±0.00)	0.00
HF:metam = 1:2	2.29 (±0.09)	2.30 (±0.15)	ND[c]	4.23 (±0.11)	3.58 (±0.04)	ND[c]

[a] The water mixtures were shaken at 20 °C for 40 h prior to analysis. Initial concentrations of 1,3-dichloropropene and chloropicrin were 2.20 and 2.06 mM, respectively.

[b] Values in parenthesis are standard error of triplicate determinations.

[c] Non-detectable.

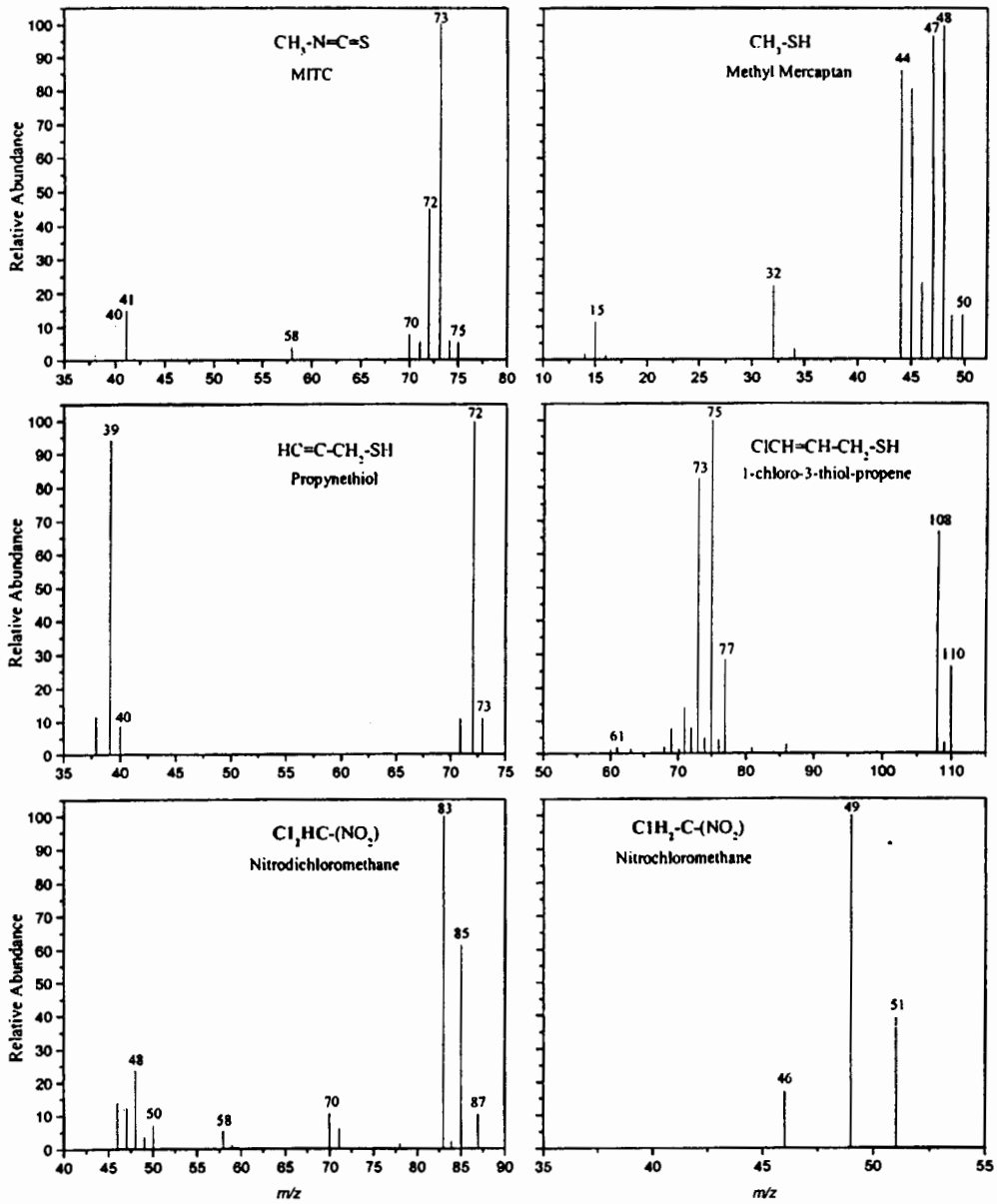

Figure 3. Mass spectra of products from reactions involving metam and the halogenated fumigants methyl bromide, methyl iodide, propargyl bromide, 1,3-dichloropropene and chloropicrin.

major chloropicrin transformation product. At 1:5 chloropicrin/metam molar ratio, neither chloronitromethane nor dichloronitromethane was detected, since the production of nitromethane was predominant (eqn (5)).

Major decomposition products of metam in water are methyl isothiocyanate and bisulfide (eqn (1)). Methyl isothiocyanate is compatible with the halogenated fumigants (Table 2), but bisulfide (HS^-) is a strong nucleophile and can react with halogenated alkanes via second-order nucleophilic substitution reactions.[21] The same degradation products (methyl mercaptan, propynethiol, 1-chloro-3-thiolpropene, dichloronitromethane and chloronitromethane) were identified when HS^- was used in place of metam to react with the test halogenated chemicals. One potential reaction process of metam with the halogenated fumigants is that metam first decomposes to methyl isothiocyanate and HS^- (eqn (1)), and then HS^- reacts with the halogenated fumigants. However, we observed that decomposition of metam in water was rather slow, generating merely 0.03 mM of methyl isothiocyanate and HS^- 24 h after spiking 2 μl of Vapam into 5 ml of water (metam 1.47 mM). Also, HS^- demonstrated lower reactivity with the halogenated fumigants than metam: under the same conditions and with equivalent initial molar concentrations of HS^- and metam, consistently

more halogenated fumigants remained in halogenated fumigant–HS^- mixtures than in halogenated fumigant–metam mixtures (data not shown). Metam evidently reacted directly with the halogenated fumigants following mechanisms described in eqns (2)–(5).

3.3 Promoted degradation of halogenated fumigants by metam in moist soil

In Arlington soil with 10% gravimetric moisture content, conversion of metam to methyl isothiocyanate was complete within 1 h, following either 'direct injection' or 'water application'. When halogenated fumigants were applied to the soil without Vapam, after 72 h incubation, 53–84% of the chemicals were recovered following 'direct injection', and 26–80% following 'water application' (Fig 4). With simultaneous application of Vapam at 1:3–2:1 halogenated fumigant/metam molar ratios, the fumigant remaining in the soil decreased dramatically, and the residual amounts following 'direct injection' and 'water application' were 19–36% and 3–60% of the spiked, respectively (Fig 4). Tests with metam in place of Vapam showed similar scenarios. The simultaneous presence of metam clearly promoted degradation of the halogenated fumigants in soil. In treatments with combined application of methyl isothiocyanate, degradation of the halogenated fumigants was not influenced relative to controls, indicating their compatibility with methyl isothiocyanate.

It appears that metam-induced degradation of the halogenated fumigants was greater following 'direct injection' than following 'water application', except for chloropicrin (Fig 4). This was because the former had much higher application rates, 10 times higher than the latter. With the same application rates, metam-induced degradation of the halogenated fumigants following 'water application' overweighed that following 'direct injection', owing to thorough mixing of the halogenated fumigants with metam. In a separate experiment, 1,3-D was applied to soils at 2 mmol kg^{-1} in combination with metam (in Vapam) at 1.5 mmol kg^{-1} following 'direct injection' and 'water application', and the final soil moisture content was the same (10%). After 24 h of incubation, 1,3-D remaining in soil following 'water application' was 63% (*cis*-1,3-D) and 82% (*trans*-1,3-D) of that following 'direct injection'. Similar results were obtained in tests with methyl iodide, methyl bromide and propargyl bromide. Evidently, prior mixing of the 'water application' treatment promoted degradation of the halogenated fumigants by metam.

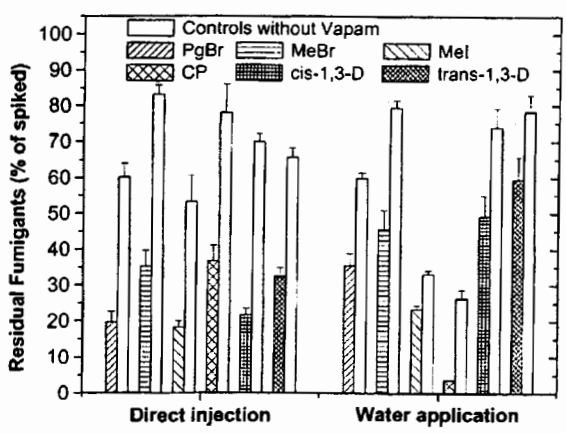

Figure 4. Degradation of halogenated fumigants in moist soil with combined application of metam following 'direct injection' and 'water application.' The soils were incubated at 20 °C for 72 h. Application rates of the chemicals were 130–840 mg kg^{-1} in 'direction injection' and 33–84 mg kg^{-1} in 'water application' treatments, and halogenated fumigant:metam molar ratios were 0.4:1–1.4:1. Error bars represent standard deviation of triplicate samples.

When Vapam alone was applied at 1.5 mmol metam kg^{-1} soil following either 'direct injection' or 'water application', equivalent contents of methyl isothiocyanate (1.18 mmol kg^{-1}) were detected in soils 24 h after incubation at 20 °C. When applied combined with 1,3-D, chloropicrin, propargyl bromide, methyl iodide or methyl bromide (2 mmol kg^{-1}), the same content of methyl isothiocyanate was measured following 'direct injection', but only 0.56–0.70 mmol kg^{-1} of methyl isothiocyanate was detected in soils following 'water application'. The significantly lower methyl isothiocyanate contents in soils following 'water application' may be attributed to the rapid formation of methyl isothiocyanate in mixing vials and its residence in the headspace. A range of 11–18 mmol $liter^{-1}$ of methyl isothiocyanate were detected in the solution phase immediately after mixing 8 µl of halogenated fumigant and 16 µl of Vapam in 2 ml water. The Henry's Law constant of methyl isothiocyanate (K_H, 20 °C) is 0.021,[22] and 0.23–0.38 mmol $liter^{-1}$ of the chemical was estimated in the vapor phase. The volume of the headspace was about 8 ml, and methyl isothiocyanate residing in the headspace accounted for 16–26% of the amount detected in soils (1.18 mmol kg^{-1}, 10 g soil) with application of Vapam alone at 1.5 mmol metam kg $soil^{-1}$. A fraction of methyl isothiocyanate might also have been lost during delivery of the water mixtures to soils.

As in water, the molar ratio of halogenated fumigant/metam controlled the degradation rate of the former in soil. When chloropicrin was injected into soil (10% moisture) at 2 mmol kg^{-1} in combination with metam, the amounts of chloropicrin remaining after 24 h of incubation were 91, 49, 23, 1 and 0% (non-detectable) of the spiked amount at chloropicrin/metam molar ratios of 0, 2:1, 1:1, 1:2 and 1:5, respectively. In addition, soil moisture content influenced the degradation rate of halogenated fumigants with metam. In the absence of metam, degradation of chloropicrin was independent of moisture content over a range of 5–20% in soil that had a field water-holding capacity of 20% (Fig 5). Approximately 91% of the spiked chloropicrin (2 mmol kg^{-1}) remained after 24 h of incubation for all soil moisture regimes.

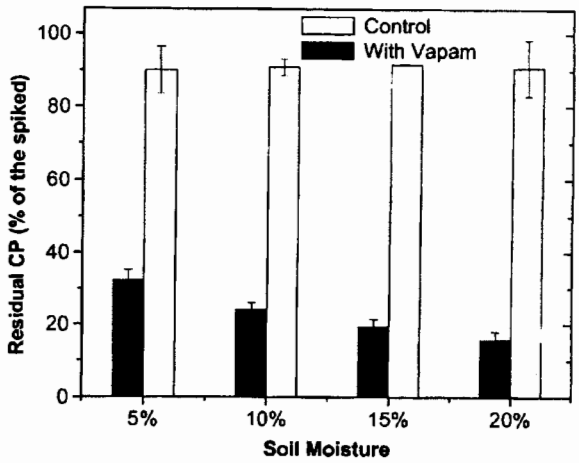

Figure 5. Effect of soil moisture content on degradation of directly injected chloropicrin with combined application of metam. The application rate of chloropicrin was 2 mmol kg^{-1}, and chloropicrin:metam molar ratio was 1:1. The soils were incubated at 20 °C for 24 h. Error bars represent standard deviation of triplicate samples.

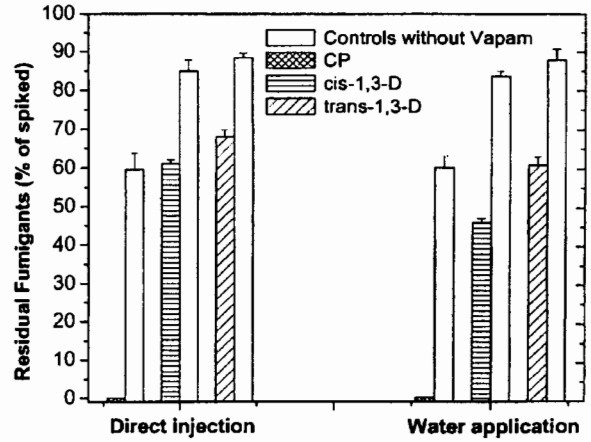

Figure 6. Promoted degradation of Telone C-35 in moist soil with combined application of Vapam. Molar ratios of chloropicrin/metam and 1,3-D/metam were 1:3.3 and 1:1.2, respectively. The soils were incubated at 20 °C for 8 h. Error bars represent standard deviation of triplicate samples.

With combined application of Vapam at 1:1 chloropicrin/metam molar ratio, however, only 16–32% of the chloropicrin remained, and the residual chloropicrin decreased as the moisture content increased (Fig 5). It is postulated that higher moisture contents promote dissolution of halogenated fumigants, enhancing their reaction with metam in aqueous media. Meanwhile, increasing moisture content slowed down decomposition of metam in soil,[2] which in turn, accelerated the halogenated fumigant degradation.

Considering that Telone C-35 is a widely used soil fumigant, its compatibility with metam was tested. In both 'direct injection' and 'water application' treatments, combined application of Vapam caused a significant decrease in Telone remaining in soils. The spiked chloropicrin (93 mg kg^{-1} or 0.56 mmol kg^{-1}) degraded completely within 8 h, but in controls without the combined application of Vapam, approximately 60% was recovered after 8 h of incubation (Fig 6). In 'direct injection', approximately 20% of the spiked *trans*-1,3-D and 24% of *cis*-1,3-D were degraded by metam, and in 'water application', the proportions were 27 and 38%, respectively (Fig 6). In addition, 1.48 mmol kg^{-1} of methyl isothiocyanate was detected in soils following 'direct injection', while in soils following 'water application', it was 0.79 mmol kg^{-1}. Clearly the chemical incompatibility of metam with 1,3-D and chloropicrin caused the poor pest-control effects when these chemicals were simultaneously applied by drip irrigation systems.[16]

4 CONCLUSION

Metam is not compatible with halogenated fumigants in polar organic solvents, water or moist soil. Simultaneous presence of metam and halogenated fumigants would give rise to rapid degradation of the halogenated fumigants and decomposition of metam to methyl isothiocyanate. Combined application of halogenated fumigants and metam at the same soil depth will result in low concentrations of halogenated fumigants in the soil and, consequently, poor pest-control efficacy of field fumigation. To obtain synergic disinfestation results, sequential treatment (ie 1-week interval) of soil or application at different soil depths (ie 10 cm distance) with the two types of fumigants is recommended.

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