Chapter 12

Natural and Synthetic Isothiocyanates for Pest Control in Soil

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Synthetic fumigants are widely used in agriculture to provide highly efficacious pre-plant pest control for high cash crops. However, stringent regulations aimed at controlling soil to air emissions govern fumigant use. This has led to increased interest in biofumigation using Brassica species which release volatile isothiocyanate (ITC) chemicals into the soil. These ITCs have a similar chemistry to the synthetic fumigant methyl isothiocyanate (MITC) and are, therefore, of interest in pest control. However, there are significant disadvantages to natural ITCs when compared to MITC; most notably, a relatively low release efficiency into the soil, and rapid degradation/sorption within the soil. The inconsistent pest control efficacy of biofumigation indicates a lack of robustness and suggests that non-organic growers may be reluctant to switch from traditional fumigants. MITC, despite being subject to regulations, offers efficacious pest control and its emissions to the atmosphere can be significantly reduced using plastic tarps or water sealing. Compared to other soil fumigants, MITC exhibits relatively low soil diffusion. Although this lower diffusion is advantageous in terms of limiting atmospheric emissions, it needs to be considered in relation to pest control, for example in the positioning of drip lines, emitters, or shank spacing, during application.

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Introduction

Both synthetic and natural isothiocyanates (ITCs) are volatile chemicals that are biocidal to a wide range of soil organisms, including nematodes, bacteria, and fungi (1, 2) and are therefore of use in the pre-planting control of soil pests. Synthetic methyl isothiocyanate (MITC) has long been widely used as one of the active ingredients in pre-plant soil fumigants in agriculture. Due to similarities in chemistry between synthetic and naturally produced ITC, there is increasing interest in the use of natural ITC as a biofumigation agent for pre-plant pest control in soils. Natural ITC is produced by certain plant materials; most commonly, Brassica species. Such plants can be used for biofumigation as rotation crops, or intercrops, by incorporating fresh, chopped plant material as green manure, or by incorporating processed plant products high in glucosinolates (GSLs) such as seed meal or dried plant material (3). Gas phase diffusion of synthetic and natural ITCs via the soil pore space affords a degree of pest control within the root zone of agricultural soils prior to the planting of a crop. In general, fumigants are used for high cash crops such as fruits, vegetables, and nuts.

Due to their potentially toxic nature, the use of chemical pesticides is strictly controlled within the USA and a pesticide must be registered by the US Environmental Protection Agency (USEPA) and an individual state before it can be used. In the case of fumigants, where their gaseous nature can lead to a relatively high degree of off-gassing from the site of application, regulations are in place to protect air quality and human health. For example, in California, fumigant labels (produced by CA Department of Pesticide Regulations, CDPR) generally require optimal soil and weather conditions at the time of application and may require the use of plastic tarp covering the soil surface to reduce the potential for soil to air emission and its associated risks. Moreover, certain areas of the state of California have been identified as “non-attainment” areas where additional regulations to reduce emissions are in place because these areas do not meet federal air quality standards for pesticide emissions (4). Due to these relatively strict regulations and registration requirements, there is a perceived need for alternative approaches to pest control. Biofumigation potentially addresses this need because the release of naturally produced gas into the atmosphere is not currently subject to regulation and no pesticide registration is required.

Traditional, synthetic, fumigants are typically either shank or drip applied as a liquid formulation. Upon entering the warm soil, they are converted to gas. The physical properties of this gas (particularly its Henry’s constant, vapor pressure, degradation half-life, and sorption potential) determine its fate and transport within the soil environment. Synthetic fumigants have a high Henry’s constant and vapor pressure, a long half-life, and low sorption potential, and so exhibit a high degree of soil diffusion (likely resulting in effective and uniform pest control), but also potentially high emissions from soil to air. Biofumigation can be considered a distributed source of ITC since the parent plant material is generally plowed into the surface soil. The plant material then undergoes chemical transformation to release ITC into the soil. The kinetics of this transformation, together with the potential for degradation and adsorption of the ITC, may have

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a significant bearing on ITC concentrations in the soil, subsequent pest control efficacy, and atmospheric emission potential.

In this chapter, the aim is to briefly review the use of natural ITC as a biofumigant and highlight some of the problems and limitations of this approach to pest control. The use of MITC will then be described, along with its environmental hazards. The concept of concentration-time index will be applied to demonstrate the relative efficacy of MITC in pre-plant pest control compared to other soil fumigants.

Natural ITC

Natural ITC is a by-product of GSL degradation. GSLs are sulfur-containing secondary plant metabolites that contain a β-thioglucose moiety, a sulfonated oxime moiety, and a side-chain derived from amino acid (5). They are found exclusively in dicotyledonous plants such as members of the order 

The Resedaceae, Capparidaceae and Brassicaceae families have been shown to contain the greatest concentrations of GSLs (6). Within the plant tissue, the GSLs are separated from the endogenous enzyme, myrosinase, which catalyses their hydrolysis (5). GSLs themselves are of limited biological activity (7). However, when GSL-containing plant tissues are disrupted (for example, pulverized and plowed into soil) the constituent GSLs are hydrolyzed to a number of breakdown products such as ITCs, thiocyanates, nitriles, and oxazolidines. ITCs have been shown to be toxic to a number of soil organisms, such as nematodes, bacteria, and fungi (1, 2). It is this production of ITC that has led to interest in the use of, especially Brassica, plant species as biofumigant amendments to soils. Because the production of GSL is greatest during flowering of the plant (8, 9), this often represents the ideal time to incorporate plant material for optimum generation of ITC and, hence, biofumigation potential.

Production of Natural ITC in Soil

The efficacy of biofumigation using fresh Brassica leaves depends on the rate of GSL conversion to ITCs, but also on the environmental factors controlling GSL availability in the soil matrix (10, 11). Omirou et al. (11) found that GSLs rapidly dissipated in clay loam soil with half-lives ranging from 3.2 to 15.5 h, and that increasing soil moisture increased the rate of dissipation. Similarly, other workers have found that ITCs and other GSL hydrolysis products degrade rapidly in soils, being present from as little as a few hours or days (5, 7, 12) to as much as 14 days (13). Hansen and Keinath (14) found that ITC concentrations were greatest after incorporation of mustard, intermediate with rapeseed, and lowest, or zero, with radish. Across the three crops and two experiments, these researchers found that when ITCs were detectable in the soil, mean concentrations ranged from 0.14 to 5.91 μg g⁻¹ dry soil. Highest concentrations were generally found after just 4 h and declined rapidly thereafter. Interestingly, they also found that ITCs were detected
at relatively low concentrations (< 0.17 µg g⁻¹ dry soil) in plots under plastic film even without prior plant material incorporation. Bangarwa et al. (15) found that the addition of allyl ITC at a rate of around 1000 kg ha⁻¹ under low density polyethylene was required to suppress weeds and produce marketable tomato yield equivalent to a standard methyl bromide application of 390 kg ha⁻¹, also under low density polyethylene. Assuming that one hectare of soil contains around 2 × 10⁶ kg soil in the plow layer (20 cm depth), this application of allyl ITC equates to a soil concentration of around 500 µg g⁻¹; two orders of magnitude greater than the highest values observed by Hansen and Keinath (14) following incorporation of Brassica species.

As reported by Motisi et al. (16), previous field studies indicate that the GSL content of plants is not well correlated with the efficacy of biofumigation for decreasing disease expression. Gimsing and Kirkegaard (5) attempted to relate GSL content of plant material to ITC concentrations in the soil following incorporation. They found that total GSL contents for ‘high GSL’ rape were 23.2 and 28.1 µmol g⁻¹ (for shoots and roots, respectively), and for ‘high GSL’ mustard were 31.3 and 13.7 µmol g⁻¹ (for shoots and roots, respectively). They also determined that between 10.4 µmol g⁻¹ (mustard roots) and 30.0 µmol g⁻¹ (mustard shoots) of these GSLs were ITC-liberating. In corresponding soils, these workers found that maximum total ITC concentrations were present just 30 min after incorporation of the green manure and were approximately 80 nmol g⁻¹ for mustard, and approximately 20 nmol g⁻¹ for rape. The GSL to ITC release efficiency after 30 min calculated for the ‘high GSL’ mustard was 56%, but it was only 26% for the ‘high GSL’ rape. By 6h, these values decreased to 23 and 10%, respectively.

Bangarwa et al. (10) evaluated the biofumigation potential of seven Brassica cover crops for weed control in plasticulture tomato and bell pepper. They found that GSL concentration and composition varied between crops and between roots and shoots. Total GSLs contributed to the soil by incorporation of Brassica cover crop tissues were between 47 and 452 nmol g⁻¹. These amounts of GSL contributed to the soil were then used to estimate maximum potential ITC release to the soil; ranging from 47 nmol g⁻¹ for oil seed rape (Brassica napus L.) to 237 nmol g⁻¹ for a blend of Indian mustard (Brassica juncea L.) and white mustard (Sinapis alba L.). However, actual measured ITC concentrations ranged from 1.6 to 28.4 nmol g⁻¹, indicating that the conversion from GSLs to ITCs was lower than expected. Actual conversion efficiencies were between 1 and 39% depending on crop. Highest ITC concentrations were measured 3 h after crop incorporation and declined over the following two weeks of monitoring.

**Pest Control Using Brassica Biofumigation**

The incorporation of seed meal or, particularly, chopped plant material (green manuring) are considered the most effective ways to induce a concentrated release of ITCs (3). For example, suppression of common scab disease was enhanced using dried and ground post-harvest residues of Brassica vegetables (17), bacterial wilt was reduced (40-50%) by a range of Brassica amendments to potato crops, and
the agents responsible for apple replant disease were suppressed by rapeseed meal (18). Rapeseed green manure was shown to be effective in controlling root-knot nematodes and in increasing yield of potatoes (17-25%), due to the role of GSLs (19). Green manures of Indian mustard, canola, and radish have been shown to be effective in controlling Verticillium dahlia (20), and a mustard green manure has also been used to suppress common scab (Streptomyces scabies) (21). Bangarwa et al. (10) noted that control of yellow nutsedge weed was < 53% at two weeks and declined to < 18% later in the season following incorporation of Brassica species, and they concluded that Brassica cover crops have only marginal potential for early season weed control and cannot be used as a weed control practice in commercial tomato and bell pepper production. As an alternative to incorporation of plant material into the soil, rotation, or intercropping, has also been used for biofumigation where above-ground plant material is harvested or left to mature above ground. This approach relies on ITCs entering the soil via root exudates of growing plants, leaf washings, or root and stubble residues decomposing in the soil after crop harvest (3). For example, ITCs have been detected in the rhizosphere of intact plants, and intercropping of strawberries with Brassica plants has been shown to control Verticillium wilt (22).

Motisi et al. (16) reported that field studies have generated conflicting data concerning the efficacy of biofumigation at the field scale, limiting the use of this technique. Indeed, in a broad review of the use of biofumigation these authors cite a lack of robustness with the technique as a major limitation to its widespread use. Although the biocidal effectiveness of ITCs has been clearly demonstrated in vitro (1), the many studies carried out in agricultural conditions have not systematically shown a pathogen-suppressing effect of the ITCs released by Brassica residues (16).

Advantages and Disadvantages of Biofumigation

Reducing emissions of synthetic MITC is a challenge for researchers and alternative, low emission approaches are required to satisfy increasingly stringent regulations relating to atmospheric emissions. In this regard, Trott et al. (23) measured air concentrations of natural ITCs during and after incorporation of mustard cover crops into soil. The maximum observed concentrations of allyl, benzyl, and phenethyl ITCs were 188.6, 6.1, and 0.7 µg m⁻³, respectively, during mustard incorporation. Based on measured concentrations, these workers concluded that airborne natural ITC concentrations did not appear to pose a human inhalation exposure concern to field operators and bystanders. Such regulatory advantages of biofumigation suggest that further research in this area, to find high GSL-yielding crops; increase rates of GSL to ITC conversion; and maintain higher concentrations of ITCs within the soil pore space over longer periods, is warranted.

In addition to the regulatory advantages of natural ITC, it also offers the advantages of improving soil texture and water holding capacity due to the addition of the plant material from which the ITCs are subsequently derived. Moreover, the addition of this material may also stimulate and improve the structure of the
existing soil microbial community, increase potentially mineralizable nitrogen in the soil, increase soil nutrient availability by mineral weathering, increase water infiltration rate, reduce soil erosion by wind, and reduce soil compaction (3). Thus, soils applied with plant material for the purposes of biofumigation are likely to be improved in terms of soil health and nutrition.

Conversely, a potentially major disadvantage of biofumigation with natural ITC may be limited pest control efficacy when compared to synthetic MITC. Because the production of natural ITC tends to be relatively low and subject to rapid degradation and/or sorption within the soil, a high level of soil diffusion may not be evident, resulting in a non-uniform distribution of the fumigant in soil. This is likely a primary reason for the lack of robustness of biofumigation noted by Motisi et al. (16). With MITC, a uniform concentration within the soil pore space can be more easily controlled and ensured, resulting in a more reliable degree of pest control. Further potential disadvantages of using natural ITC are the loss of crop production time that a grower experiences during the growing period of the biofumigation plants, and the possibility of the biofumigation crop hosting disease-causing organisms. Omirou et al. (24) reported that biofumigation by incorporation of Brassica plants into soil induced changes in the structure and function of the soil microbial community that were mostly related to microbial substrate availability changes derived from the soil amendment with fresh organic matter. Gilardi et al. (25) noted that soil amendments with Brassica products can enhance disease severity due to the increased pathogen inoculum potential when the substrate serves to sustain saprophytic growth of plant pathogens. In addition to these issues, there are also questions over the willingness of growers to accept non-traditional (non-chemical) approaches to pre-plant pest control, particularly if crop yield is adversely affected due to a lack of adequate pest control. Consequently, in California, the use of biofumigation is more likely utilized by organic growers while, in general, large scale production still relies on synthetic MITC or other fumigant chemicals.

**Synthetic MITC**

Methyl isothiocyanate (MITC) is a volatile organo-sulfur compound with pesticidal characteristics. In agricultural settings, MITC is generated following the degradation of the common soil fumigants metam sodium, metam potassium, and dazomet and is the active ingredient responsible for pest control via non-selective enzyme inhibition, when applying these compounds. The chemical structures of MITC, metam sodium, metam potassium, and dazomet are shown in Figure 1a-d. All three products are registered for use in the USA and are classed as non-selective fumigants for pre-plant application. In California, metam sodium and metam potassium are widely used. For example, in 2011, 4.91 and 2.58 million kg, respectively, were used to treat a total of 46.5 thousand hectares during 4300 agricultural applications (4). Metam sodium was ranked the fourth most used pesticide, and second most used fumigant (behind 1,3-dichloropropene) in California in 2011 while metam potassium was ranked eighth most used pesticide and fourth most used fumigant. This high level of use likely results in the release
of large quantities of volatile MITC into air. For example, California Department of Pesticide Regulations (26) estimated that an average of 9 million pounds per year of MITC were released into the air from agricultural applications of metam sodium in the 1995-2000 period.

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\begin{align*}
&\text{H}_3\text{C} \quad \text{N} = \text{C} = \text{S} \\
&\text{CH}_3-\text{NH}-\text{C} = \text{S}^{-} \quad \text{Na}^{+} \\
&\text{CH}_3-\text{NH}-\text{C} = \text{S}^{-} \quad \text{K}^{+} \\
&\text{H}_3\text{C} - \text{N} - \text{N} - \text{CH}_3
\end{align*}
\]

(a) (b) (c) (d)

Figure 1. Chemical structures of (a) MITC, and the three MITC pre-cursors (b) metam sodium, (c) metam potassium, and (d) dazomet.

In agricultural settings, metam sodium and metam potassium are applied to pre-plant soils as a liquid and convert to volatile MITC within the soil. They both exhibit fungicidal, herbicidal, insecticidal, and nematicidal properties. As dithiocarbamate salts, they breakdown in soil to produce volatile MITC which is capable of diffusing through the soil pore space and producing highly effective
pest kill. Metam sodium converts to MITC on a mole to mole basis, which based on the molecular weights of the two compounds results in a conversion rate of approximately 60% by weight (26). Zheng et al. (27) reported that this conversion to MITC was a rapid abiotic decomposition process and complete within 30 min for a sandy loam soil. Dazomet is applied to soil as dry granules that react with water to produce MITC. Water management is therefore critical to maintain appropriate MITC gas concentrations within the soil. Dazomet is used for the control of weeds, fungi, nematodes, and rhizomes (28, 29).

**MITC Properties**

In common with other soil fumigants, the adsorption of MITC to soil components is very low (30). MITC has a relatively high boiling point (119 °C), low density (1.05 g mL⁻¹ at 24 °C), intermediate water solubility (8200 mg L⁻¹ at 20 °C), low vapor pressure (19 mm Hg at 20 °C), and low dimensionless Henry’s constant (0.01 at 20 °C). The extent of pest control of a fumigant is largely controlled by its soil diffusion and, therefore, its Henry’s constant and vapor pressure for which higher values generally indicate a greater potential for diffusion through the soil pore space. Therefore, MITC is considered to have lower soil diffusion, potentially limiting the spatial extent of pest control, compared to other fumigants unless a more uniform application methodology is employed. However, these properties also indicate a relatively lower potential for soil to air emissions compared to other fumigants.

**MITC Toxicity**

MITC is acutely toxic by inhalation, injection, or dermal absorption (28). This chemical received publicity due to a spill of 19,500 gallons of 32.7% metam sodium into the Sacramento River in 1991 (26). Exposure of airborne MITC to local populations resulted in numerous complaints of eye and respiratory irritation, nausea, headaches, dizziness, vomiting, shortness of breath, and chemically induced asthma. Other accidental exposures have produced similar symptoms. Acute toxicity data for MITC were collated by CDPR (26). In humans, the no-effect air concentration for eye irritation was at 0.22 ppm (31). In rats, inhalation LC₅₀ was determined as 180 ppm for 4 h exposure (32) and 633 ppm for 1 h exposure (33). Oral LD₅₀ in rats was measured as between 50 mg kg⁻¹ (34), and 305 mg kg⁻¹ (35). Also in rats, dermal LD₅₀ was 181-225 mg kg⁻¹ (36), subcutaneous LD₅₀ was 60 mg kg⁻¹ (37), and intraperitoneal LD₅₀ was approximately 50 mg kg⁻¹ (37). Inhalation exposure is the principal concern with agriculturally applied MITC fumigants due to the potential for atmospheric emissions and the associated exposure risk to agricultural workers and local bystanders (27). However, the potential for MITC off-gassing to affect nursery seedlings in adjacent fields was also noted by Wang et al. (38).
MITC Degradation

The pest control efficacy of a fumigant is largely dependent upon the exposure concentration within the soil over time. Therefore, soil degradation kinetics of the chemical is a critical factor governing pest control since very rapid degradation may lead to poor efficacy. Conversely, very slow degradation may lead to relatively high concentrations of residual fumigant in the soil and the potential for atmospheric emissions over extended time periods.

In the absence of soil, the hydrolysis of MITC was investigated by Zheng et al. (39). In neutral aqueous solution, MITC was found to be stable with a half-life of 93 d. Hydrolysis products of MITC were identified by GC-MS as gas phase methyl isocyanate and liquid phase 1,3-dimethylthiourea. Zhang et al. (40) studied the half-life of MITC in nursery and forest soils at three application rates (195, 390, and 785 kg ha⁻¹ equivalent) and found that MITC degradation followed first order kinetics. In the nursery soils, half-lives ranged from 3.47 to 11.01 days across the three application rates, and in the forest soil from 3.14 to 11.20 days. Overall, these workers found no significant difference in MITC half-life across the three application rates or between nursery and forest soils. Dungan et al. (41) reported the effects of temperature and the addition of chicken manure on MITC degradation. In non-amended soil they found that half-life decreased from 5.8 days at 20°C to 1.8 days at 40°C. A similar temperature effect was observed for the chicken manure amended soils. The addition of the chicken manure also reduced half-life within each temperature treatment; for example, at 20°C, half-life decreased from 3.5 days at 1% manure addition to 2.2 days at 5% addition.

Zhang et al. (40) observed that enhanced degradation of MITC due to previous fumigation of the soil did not occur. Nevertheless, other workers have found that repeated fumigation of soil with MITC did lead to increased degradation rates, probably due to the increased potential for an adapted microbial community to persist (42, 43). Although, in soil, MITC degradation occurs via chemical and biological processes (28), Chellemi et al. (44) reported that biological mechanisms were most important. Therefore, an adapted or supplemented soil microbial population may be significant in enhancing MITC degradation. Indeed, the addition of organic materials has been shown to enhance MITC degradation (41, 45), probably due to the supplementation of the soil microbial community.

Soil-Air Emissions of MITC

Reducing soil to air emissions of agricultural fumigants such as MITC is critical to maintain air quality and to adhere to increasingly strict regulations regarding fumigant emissions. For example, in California, the Department of Pesticide Regulations places specific requirements on how fumigations must be performed, as well as prohibiting some high-emission methods, in five “non-attainment” areas of the state. The stringent regulations within these areas are due to a failure to meet federal air quality standards for pesticide volatile organic compound emissions. Scientific research in this area has focused on quantifying atmospheric emissions of fumigants and assessing methods to reduce these emissions. In addition to protecting air quality, some methods to reduce
emissions maintain fumigants within the soil environment; thereby, maximizing pest control potential. As such, a combination of field and laboratory (soil column) methods has been used to study MITC emissions.

The method by which a fumigant is applied to soil may have a strong bearing on its emission potential. Littke et al. (46) compared low-boom-height center pivot chemigation (surface application) with soil-incorporated shank injection for metam sodium and measured subsequent MITC emissions from the soil. They found that the estimated cumulative fumigant loss was 13% by shank injection compared with 47% by chemigation. A similar result was found by Saeed et al. (47). In part, the lower emissions for the shank injection were likely due to the increased path length between the site of application and the soil surface. However, Ajwa et al. (48) noted that emission reductions could also be associated with the improved design of shank injection systems that help to break up the soil voids after injection, and effective shank compaction of the soil. Similarly, Woodrow et al. (49) found that subsurface application potentially reduced MITC concentrations in air by four orders of magnitude when compared to application via surface irrigation water.

In raised-bed, plastic-mulched systems, Chellemi et al. (50) found that MITC emissions were < 6% under relatively impermeable films across three sites in Florida. With a more permeable film, emissions were <13% across three sites in Georgia state. In addition, peak emissions occurred much more rapidly with the more permeable film. Lower total emissions were found by Wang et al. (38) using high density polyethylene; 2.5-5.2%. Papiernik et al. (51) and Ou et al. (52) both found that virtually impermeable film not only reduced emissions to air but also retained MITC in the root zone longer, and at higher concentrations, compared to other plastic films. Agricultural films offer a benefit in terms of maintaining high soil gas concentrations and pest kill efficacy.

Using laboratory soil columns, Frick et al. (53) noted that MITC emissions were positively correlated with air-filled porosity and were suppressed by water application. Indeed, Wang et al. (38) found total MITC emissions of just 0.1 to 3.2% when applied with a water seal at the soil surface. Simpson et al. (54) compared various levels of irrigation water addition to the soil surface as an emission reduction strategy for MITC. These authors found that emissions were consistently reduced with increasing water seal application, with a 2.5-3.8 cm depth of water seal providing a 71-74% reduction in MITC emissions compared to no water seal. Zheng et al. (27) reported similar findings and suggested that water sealing, together with subsurface application, may be an effective and economical strategy to reduce MITC emissions while maintaining pest control efficacy. Sullivan et al. (55) found that intermittent water sealing significantly reduced off gassing rates of MITC for both shank injection and chemigation applications when compared to standard water sealing practices. Li et al (56) found that with surface drip irrigation of metam sodium under plastic tarp, MITC flux density showed a diurnal pattern with peak flux in the first 12 h after chemigation with a subsequent decline over time. During the first 60 h, 2.65% of the applied mass was lost via emissions suggesting that this drip application method (with tarp) offered relatively good control of MITC emissions from soil. In general, a water seal is considered the most cost-effective emission reduction strategy for MITC.

According to Henry’s law, the more water in the soil, the less MITC would be partitioned into the gas phase. Therefore, the relatively low (compared to other fumigants) Henry’s constant for MITC helps explain the observation of lower MITC emissions from irrigated soils.

MITC Soil Concentrations and Pest Control

In soil columns, Zhang and Wang (57) applied MITC at 20 cm soil depth at a rate of 170 kg ha⁻¹ under tarp without irrigation, with a tarp after limited irrigation, and 5 days of irrigation without tarp. During the first 24 h after application, soil concentrations of MITC were greatest in the 15-25 cm depth region and were relatively low closer to the soil surface throughout the experiment; presumably due to volatilization losses at the soil-air boundary. Peak concentrations of around 5, 3, and 2 µg mL⁻¹ were found for the tarp only, tarp with limited irrigation, and irrigation only treatments, respectively, soon after application (0.25 to 5 h). Peak concentrations, therefore, seemed to be inversely related to amount of irrigation water added which the authors suggested was due to MITC becoming solubilized in the water phase. This concurs with the low atmospheric emissions of MITC from irrigated soils found by these authors and others (discussed above).

In tarped (high density polyethylene) and water sealed plots, Wang et al. (58) measured MITC soil gas concentrations following application of dazomet (448-560 kg ha⁻¹ that was surface applied and then spaded into the top 20 cm of soil) and metam sodium (686 L ha⁻¹ of 0.5 kg L⁻¹ metam sodium solution that was surface applied and then roto-tilled into the top 12 cm soil). They found that MITC concentrations in the soil gas tended to decrease with depth and were generally higher under tarp than with water seal. With dazomet application at two separate sites, peak MITC concentrations were found in the top 5-10 cm and measured 2.14 and 1.17 µg mL⁻¹ at 1.17 and 0.3 days after application, respectively. With metam sodium application, MITC concentrations were lower, never exceeding 0.6 µg mL⁻¹. Overall, these authors concluded that, under tarp, MITC was concentrated in the upper 30 cm of the soil profile (i.e. the root zone of most crops) and the effect lasted about 3 days. With water seal, the lower concentrations were deemed to likely not provide sufficient exposure time in order to achieve desired pesticidal efficacy.

Candole et al. (59) studied MITC soil gas concentrations following drip application (drip lines at 2.5 cm depth) of Vapam (42% metam sodium) at 701 L ha⁻¹ to raised beds under low density polyethylene. MITC concentrations decreased over time and with lateral distance from the drip emitter. Higher amounts of MITC were detected at 20 cm below the emitter than at 10 cm, with a peak concentration of around 2.2 µg mL⁻¹ found at 20 cm below the emitter at 12 h after application. At 24, 48, 72, and 120 h, peak concentrations of around 1.6, 0.9, 0.6, and 0.1 µg mL⁻¹, respectively, were observed 20 cm below the emitter. These workers also determined the control of Phytophthora capsici Leonian, Rhizoctonia solani Kuhn, and Cyperus esculentus L. for two locations at 10 cm soil depth (both directly below the drip emitter and at a lateral distance of 20 cm away from the emitter). This was done for three rates of Vapam application (234, 468, and 701 L ha⁻¹). For each pest, survival was significantly lower at 10 cm below the emitter than at 20 cm away from the emitter. In general, organism
survival at 10 cm below the emitter was not significantly different from the survival in beds treated with a co-formulation of methyl bromide and chloropicrin (67:33) at a rate of 336 kg ha⁻¹.

Using a very similar approach but with application rates of 147 and 295 L ha⁻¹, the same workers (60) found that a higher rate of application resulted in higher MITC concentrations in the soil. Highest MITC concentrations were again found 20 cm directly below the emitter and lowest 30 cm laterally away from the emitter. MITC concentrations decreased with time and distance from the emitter. Peak concentrations of around 0.3 µg mL⁻¹ (lower application rate at 3 h) and 0.75 µg mL⁻¹ (higher application rate at 12 h) were found at 20 cm below the emitter. The authors also determined concentration-time (CT) index values (the integral of fumigant concentration in the soil over time) at each location. Lower MITC CT values at 20 and 30 cm laterally from the emitter resulted in lower mortalities of *R. solani* and *C. esculentus*. CT index values increased with time, particularly at the higher rate of application. At 240 h from application, CT values for this treatment were 62, 33, 10, and 0.8 µg-h cm⁻³ at 20 cm below the emitter, 10 cm below the emitter, 20 cm laterally away from the emitter, and 30 cm laterally away from the emitter, respectively. The results demonstrated that MITC can be delivered at lethal doses with drip applied water downward within beds. However, later diffusion of MITC from the point of application did not reach biologically active concentrations to affect the survival of *R. solani* and *C. esculentus*.

The concept of CT values is a useful one for predicting the degree of exposure of an organism to a fumigant and, consequently, for predicting pest control based on measured soil concentrations over time. The application of this concept is described further below.

**Predicting MITC Pest Control Using Concentration Time (CT) Index**

A 2-D chamber approach for measuring fumigant emissions, gas diffusion and pest control has been developed in this laboratory and was recently described by Luo et al (61, 62). Using this approach, moist soil is pre-mixed with plant pests of interest, such as fungi (coated onto millet seeds), weed seeds, and nematode-infested roots (e.g. chopped citrus roots). The soil mix is then packed into a stainless steel 2-D soil chamber in which fumigant volatilization, spatial and temporal distribution of soil gas concentration, degradation, and organisms’ survivability in the soil could be determined (63) (Figure 2). The soil chamber was fabricated from 0.5-cm stainless steel. The internal dimensions of the soil chamber were 60 cm x 60 cm x 6 cm so that typical agricultural management and practice methods within the root zone could be simulated. A total of 84 sampling ports extending radially from the central injection port were sampled to determine soil gas concentrations in real time after the fumigant was injected into the soil through the central port. These soil gas samples were taken at various times (e.g. 0.5, 1.5, 2.5, 3.5, 4.5, 6, 8, and 24 hr). At the end of the experiment, one side wall (60 cm x 60 cm) of the soil chamber was removed, and soil samples were taken with a stainless steel ring with a 4-cm diameter for pest survivability and residual fumigant determinations. In the case of citrus nematodes (*Tylenchulus semipenetrans* Cobb), for example, these were extracted from 50 g of soil using...
the Baerman funnel method (64). Extracted nematodes were then enumerated using a dissecting microscope. To quantify an organism’s exposure to pesticides, a concentration-time index, CT, the integral of concentration over time, is defined as:

\[ CT(t) = \int_0^t C_T(x, z, t) dt \]  

(1)

where: \( x, z \) are the spatial coordinates, \( C_T(x, z, t) \) is the total concentration \((=C_{gas} + C_{liquid} + C_{solid}) \) (µg mL\(^{-1}\)), \( t \) is time (h).

A logistic dose-response curve (Figure 3) is then used to describe the relationship between organism’s survival and concentration time index:

\[ \text{SURVIVAL} = \frac{100\%}{1 + (CT / CT_{50})^n} \]  

(2)

where: \( n \) is the slope at the inflection point of the logistic dose response curve.

Figure 2. 2-D soil chamber system for determining fumigant gas distribution, CT index, and pest control. Fumigant is injected at Port 0 (center) and soil gas distribution determined at selected ports over time. Atmospheric emissions are determined using a dynamic flux chamber covering the soil surface. Photo shows chamber laid flat for sampling of soil and determination of pest mortality.
Figure 3. Typical dose response curve for effect of fumigant CT index on citrus nematode (Tylenchulus semipenetrans Cobb) pest mortality. The solid line is derived from the survival model (Equation 2), with CT$_{50}$, n, and the regression $r^2$, respectively, 15.5 µg h cm$^{-3}$, -5.6, and 0.99. Error bars are one standard deviation.

This approach allows for prediction of pest control at various spatial coordinates throughout the 2D chamber. Surfer 8 (Golden Software Inc., Golden, CO) is used to map the distribution of soil gas-phase concentration, and mortality of organisms. The data are interpolated using a kriging method (65).

A prediction of pest control using this approach for MITC and two other fumigants (methyl iodide and propargyl bromide) is shown in Figure 4 for comparison. As mentioned previously, MITC exhibits low vapor pressure (19 mm Hg) and Henry’s constant (0.01) values compared to other fumigants. This is most noticeable in comparing MITC pest control with that of methyl iodide. For methyl iodide, the much higher Henry’s constant (0.22) and vapor pressure (400 mm Hg) values result in a high degree of gas diffusion (note the much greater soil diffusion coefficient, $D_s$) and, consequently, higher CT values throughout the chamber. This, in turn, gives excellent nematode control throughout the chamber. This degree of pest control is aided by the relatively long half-life for methyl iodide (~ 20 d). In comparison, for MITC the lower potential for gas diffusion throughout the chamber results in a radial pattern in MITC concentrations which decrease with distance from the application point. Consequently, CT values...
and nematode control exhibit a similar pattern. Indeed, complete nematode kill extends only within a ~5 cm radius from the application point, although fairly good control (> 60 % mortality) is seen to around a 15 cm radius. At the edges of the chamber, nematode control is relatively poor. This is likely exacerbated by the rather rapid soil degradation of MITC. For propargyl bromide, values for vapor pressure (94 mm Hg) and Henry’s constant (0.04) are intermediate between methyl iodide and MITC. Therefore, nematode control again shows a radial pattern, but extends further from the point of application; complete kill being observed to around a 15 cm radius and poor control only observed towards the soil surface. In all cases, volatilization of fumigant at the soil surface is seen to reduce concentrations in this region with a consequent reduction in nematode control. The concentration-time index approach also allows for determination of CT<sub>50</sub>, the effective CT required to give 50% pest mortality. Interestingly, the CT<sub>50</sub> for MITC (14 µg-h cm<sup>-3</sup>) is lower than for methyl iodide (19 µg-h cm<sup>-3</sup>) and propargyl bromide (16 µg-h cm<sup>-3</sup>) indicating its greater toxicity to nematodes in this work. Therefore, despite having a lower potential for soil diffusion, nematode control in regions close to the MITC application point is likely to be very good.

![Figure 4](image-url)

**Figure 4.** Citrus nematode mortality in the 2-D chamber for methyl iodide, propargyl bromide, and MITC. D<sub>s</sub> is soil diffusion coefficient, t<sub>½</sub> is degradation half-life of the chemical, and CT<sub>50</sub> is the effective concentration-time index that results in 50% nematode mortality.

### Conclusions

With increasingly stringent regulations governing the use of traditional, synthetic fumigants, there is clearly a need for non-chemical alternatives. However, such alternatives are only plausible if they can offer effective pest control and yields of economic significance. Although biofumigation using Brassica species offers a significant advantage over using synthetic fumigants...
in terms of regulations and air quality protection, its conflicting pest control efficacy under field conditions indicates a lack of robustness. The promise of biofumigation may be realized with further research, particularly in identifying high GSL crops in which the GSLs are efficiently converted to ITCs. Maintaining elevated ITC concentrations in the root zone of soils also appears to be a key challenge to increasing the efficacy of pest control. With synthetic MITC, maintaining elevated concentrations in the soil gas is relatively easy to control via application rate and the use of emission reduction strategies (especially tarping and water sealing). Maintaining MITC within the soil not only increases CT values, and hence pest control, but also partially addresses the issue of emissions regulations. With MITC, high pest control efficacy can be readily achieved; as evidenced by the widespread use of its precursor fumigants (metam sodium and metam potassium), particularly in California. Compared to other common soil fumigants, MITC exhibits relatively low soil diffusion and so pest control may not be as efficacious at distance from the point of application. Although this lower diffusion is probably advantageous in terms of limiting atmospheric emissions of MITC, it needs to be considered in the application of the chemical, for example in the positioning of drip lines, emitters, or shank spacing.

References

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