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Jiaye Gan
University of Miami

Sharon K Papiernik
United States Department of Agriculture

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Application of Organic Amendments To Reduce Volatile Pesticide Emissions from Soil

J. GAN,* S. R. YATES, S. PAPIERNIK, AND D. CROWLEY[†]

USDA-ARS, Soil Physics and Pesticides Research Unit, U.S. Salinity Laboratory, 450 Big Springs Rd., Riverside, California 92507, and Department of Soil and Environmental Sciences, University of California, Riverside, California 92521

Atmospheric emission of volatile pesticides such as soil fumigants contributes to air pollution, and feasible strategies to reduce their emission are urgently needed. In this study, we investigated the potential of applying organic wastes to reduce the emission of two important fumigants, methyl bromide (MeBr) and methyl isothiocyanate (MITC), by enhancing their degradation in surface soil. The degradation of both compounds was significantly accelerated in composted manure or biosolid-manure amended soils, and the enhancement was greater for MITC than for MeBr. The difference in degradation kinetics between sterile and nonsterile amended soils indicates that degradation of MeBr in amended soils was chemically mediated, while that of MITC was mainly a result of stimulated microbial degradation. Applying 5% of composted manure to the 5 cm surface soil in packed columns reduced MeBr emission by 12%, and almost completely eliminated the volatilization of MITC. As certain organic amendments can suppress soil pathogens on their own, integrating fumigation with organic waste application may potentially provide complementary pest control activity. The applicability and benefits of such integrations should be further evaluated under field conditions.

Introduction

Pesticide volatilization contributes to air pollution, especially in areas of intensive agriculture (*1*, *2*). Of all the pesticides, soil fumigants are potentially most volatile because of their high vapor pressures (*3*). Soil fumigation is used for controlling soilborne pathogens and parasitic nematodes, and the practice is essential for the production of high value crops such as strawberry and tomato, among many others. In a recent California Air Resources Board report, the concentrations of fumigants methyl bromide (MeBr), methyl isothiocyanate (MITC), 1,3-dichloropropene (1,3-D), and chloropicrin detected in the air near application sites in California were several orders of magnitude higher than that of the other pesticides (*2*). Because many fumigants have acute and chronic toxicity, genotoxicity, or carcinogenicity, their emissions have caused wide concern and frequently triggered a ban of their use. In particular, emission of MeBr from soil fumigation contributes to stratospheric ozone depletion, and a phase out in the U.S. by 2001 is currently mandated (*4*). On the other hand, current agricultural practices require fumigation as a core component of soil pest management (*5*, *6*). Under these circumstances, developing approaches to minimize fumigant emission without compromising pest control efficacy is highly desirable.

Volatilization of a fumigant from soil is controlled by its rate of transport and degradation in soil. The transport of fumigants in soil is very rapid because it is dominated by gas-phase diffusion (*7, 8*). The rapid transport is evident in that most emission loss occurs shortly after fumigation (*9−11*). In contrast to the rapid transport, the degradation of most fumigants is relatively slow, with half-lives ranging from days to weeks (*12−16*). Most of the known approaches to reduce fumigant emission, such as plastic tarping, deep injection, surface irrigation, and packing, are based on the suppression or delay of fumigant transport. Most of these methods, however, have been proven to be largely ineffective (*8−10*, *17−19*), partly because of the slow degradation. Conceivably, a fumigant's emission can be reduced if its degradation is significantly enhanced; and the negative effect on efficacy should be potentially small if the enhanced degradation occurs only at the soil surface.

Application of organic wastes to the soil surface is known to stimulate soil microbial activity (*20*, *21*), which could potentially lead to accelerated fumigant degradation. In a previous study, we observed that mixing 5% of a composted manure into a sandy loam resulted in a 4-fold enhancement of 1,3-D degradation, and incorporating 5% of the composted manure into the top 5 cm soil layer decreased 1,3-D emissions by 50% (*16*). Further, many organic wastes have been shown to suppress soilborne pathogens by promoting disease suppressive bacteria (*20*, *22−24*). Thus, integration of organic waste application with fumigation may not only reduce fumigant emission, but also provide complementary or better pest control. The compatibility and benefits of combining fumigation and organic amendment, however, are essentially untested.

The objectives of this study were to determine the effect of two organic amendments on the degradation of MeBr and MITC and the potential applicability for reducing their emissions from soil. Methyl bromide is widely considered as the most effective and difficult-to-replace fumigant (*6*), and any possible extension of MeBr use beyond the proposed phase-out date will likely depend on the availability of techniques for reducing its emission from soil (*11*, *25*). On the other hand, MITC and its precursors such as metam sodium and basimid are among the most important alternatives to MeBr (*6*). Because of its toxicity, MITC is classified as a Clean Air Act substance, and therefore, minimizing its atmospheric emission is also important.

Materials and Methods

Soil, Organic Amendments, and Chemicals. The soil used in this study, an Arlington sandy loam (coarse-loamy, mixed, thermic, Haplic Durixeralf), was obtained from the University of California, Riverside Agricultural Experiment Station. Fresh soil was passed through a 2 mm sieve without air-drying and stored at room temperature until use. The soil had a pH of 7.2 and organic matter content of 1.08%. Two different organic amendments, a composted steer manure (CM) purchased from a local supplier and a biosolid-manure mix (BM) obtained from a local municipal waste treatment plant (Recyc Inc., Corona, CA), were used. CM contained 25%

* Corresponding author tel: (909) 369-4804; fax: (909) 342-4964; e-mail: jgan@ussl.ars.usda.gov.

[†] University of California at Riverside.

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carbon and 2.4% nitrogen, and BM contained 15.4% carbon and 1.6% nitrogen.

Methyl bromide standard in a lecture bottle had a purity of 99.5% (Aldrich, Milwaukee, WI), and MITC standard had a purity of 99% (Sigma, St. Louis, MO). Before use, gaseous MeBr was chilled to liquid MeBr in a sealed vial on dry ice and stored at −15 °C. Vapam containing 45% metam sodium was provided by Zeneca (Richmond, CA) and was used in the column experiment.

Incubated Degradation Experiments. The first batch incubation experiment was conducted to determine MeBr and MITC degradation rates in soils that were amended with the organic wastes at different ratios. The amendment ratios (w/w) were 1:2, 1:4, 1:8, 1:20, 1:40, and 0 for CM and 1:2 and 0 for BM, where 0 served as the no-amendment control. To prepare the amended soils, amendment and soil were thoroughly mixed in a plastic bag, and the soil moisture was adjusted to 18% by adding deionized water. Ten grams (oven dried wt equivalent) of the amended soil was weighed into 21 mL headspace vials, and 5 μL of acetone solution containing 100 $\mu g\ \mu L^{-1}$ MeBr or MITC was added into the soil using a microsyringe. The treated vials were immediately capped with aluminum seals and Teflon-faced butyl rubber septa (Supelco, Bellefonte, PA). It was found in a preliminary experiment that the addition of 5 μL of acetone did not affect the degradation rate of MeBr or MITC in the soil. The treated samples were incubated at 25 ± 0.2 °C in the dark. At different times after fumigant application, three replicated vials from each treatment were removed and immediately stored at −15 °C. For fumigant residue extraction, the sample vials were opened while the soil was still frozen, and 10.0 g of anhydrous sodium sulfate and 10.0 mL of ethyl acetate were added to each vial, followed by immediate recapping. After the soil was thawed at room temperature (21 °C), the vials were mechanically shaken for 1.0 h, and an aliquot of the solvent supernatant was transferred to a GC vial and analyzed for fumigant concentrations on a Hewlett-Packard 5890 gas chromatograph (GC). An electron capture detector (ECD) was used for the detection of MeBr, and a nitrogen−phosphorus detector (NPD) was used for the detection of MITC. The GC conditions were 240 °C inlet temperature, 270 °C detector temperature, 1.1 mL min^{-1} column flow rate (helium), RTX-624 capillary column (30 m by 0.25 mm by 1.4 μm, Restek Co., Bellefonte, CA), 35 °C isothermal column temperature for MeBr, and 100 °C isothermal oven temperature for MITC. Decline of residual fumigant concentration in soil with time was subject to first-order fitting to obtain the degradation rate constant k (day^{-1}).

The second incubation experiment was conducted to determine the mechanisms of amendment-induced fumigant degradation. To distinguish between chemical and microbial degradation, fumigant degradation was determined simultaneously in nonsterile and sterile amended soils. Sterile amended soils were prepared by autoclaving the amended samples twice, 1.0 h at 121 °C each time, with a 24 h interval between the first and second autoclaving. The samples were treated with fumigants in the same way as described above, and the treated vials were incubated at 25 °C. Three sterilized soils were used for each fumigant: unamended soil, soil with CM at 1:2 (for MeBr) or 1:8 (for MITC), and soil with BM at 1:2. Residual fumigant concentrations were determined at various times, and the kinetics of fumigant degradation was compared between the nonsterile and sterile amended soils. In a separate experiment, the same soil matrixes were sterilized by adding 1000 mg kg^{-1} mercuric chloride (*26*), and the degradation of MeBr and MITC in the sterile matrixes was similarly followed.

Column Experiments. The effect of surface amendment on MeBr or MITC emission losses was studied using packed soil columns that were amended in the surface layer with or without CM. The columns (60 × 12.5 cm) were packed using the Arlington sandy loam, and the initial bulk density of the soil was 1.55 g cm^{-3} and the water content 0.20 $cm^3\ cm^{-3}$. The column system and sampling procedures are described in detail elsewhere (*27*, *28*). Briefly, the system consisted of the soil column and a 5 × 12.5 cm sampling chamber that was sealed onto the top opening of the soil column. After the fumigant was injected into the subsoil layer through a sampling port on the side of column, a continuous air flow (150 mL min^{-1}) in the sampling chamber was used to sweep fumigant vapor above the soil surface into charcoal tubes installed in line with the flow. Fumigant volatilization fluxes ($\mu g\ h^{-1}$) were obtained by periodically changing the sampling tubes and analyzing fumigant residues on the GC, and the cumulative emission loss was calculated by integrating volatilization fluxes over the sampling durations.

Four amendment treatments were used for MeBr: (i) no-amendment or control, (ii) 5% of CM mixed into the top 5 cm soil layer (5% CM-5 cm), (iii) 20% of CM mixed into the top 5 cm soil layer (20% CM-5 cm), and (iv) 20% of CM mixed into the top 10 cm soil layer (20% CM-10 cm). In MeBr-treated columns, the soil surface was covered with polyethylene film (0.0035 cm, Tri-Cal Co., Hollister, CA) to simulate tarped fumigation. Liquid MeBr (100 μL or 173 mg) was injected into the soil 30 cm below the soil surface using a chilled gastight syringe, and this rate was equivalent to 140 kg ha^{-1}. Two amendment treatments were used for MITC: (i) no-amendment or control, and (ii) 5% of CM mixed into the top 5 cm soil layer (5% CM-5 cm). No plastic cover was used for the MITC treatments. Vapam (100 μL) was injected at the 10 cm depth, and this rate was equivalent to 80 L ha^{-1}. Duplicate columns were used for each treatment. Fumigant volatilization was measured until the flux was no longer detectable.

TABLE 1. First-Order Degradation Rate Constants (k), Half-Lives ($t_{1/2}$), and Correlation Coefficients of Fitting (r^2) for Methyl Bromide Degradation in Arlington Sandy Loam Soil Amended with Different Ratios of Organic Amendments

matrix[a]	k (d^{-1})	$t_{1/2}$ (d)	r^2
soil (unamended)	0.06 ± 0.01[b]	12	0.93
CM-soil (1:40)	0.11 ± 0.01	6.2	0.98
CM-soil (1:20)	0.21 ± 0.01	3.30	0.99
CM-soil (1:8)	0.63 ± 0.03	1.10	0.97
CM-soil (1:4)	0.97 ± 0.02	0.71	1.00
CM-soil (1:2)	1.24 ± 0.02	0.56	1.00
BM-soil (1:2)	0.46 ± 0.05	1.50	0.90

[a] CM = composted manure; BM = Biosolid-manure mix; the ratio following CM or BM indicates the amendment-to-soil ratio in w/w. [b] Mean ± standard error of k.

Results and Discussion

Effect of Amendment on MeBr Degradation. Degradation of MeBr in soil was enhanced with the amendment of either CM or BM into the soil (Table 1). At the same amendment ratio, significantly ($p < 0.001$) more degradation occurred in the CM amended soil than in the BM amended soil (Table 1). When soil was amended with CM, as the amendment ratio increased, MeBr degradation rate also increased, and the half-life consequently decreased. For example, the half-life of MeBr in 1:40 CM amended soil was 6 days, but was reduced to about 1 day or less when the amendment ratio was 1:8 or more (Table 1). Regression analysis indicated that the MeBr degradation rate constant k (day^{-1}) in CM-amended soils was linearly related to soil amendment percentage CM% ($r^2 = 0.97$):

$$k = 0.068 + 0.0417\ (\mathrm{CM\%}) \quad (1)$$

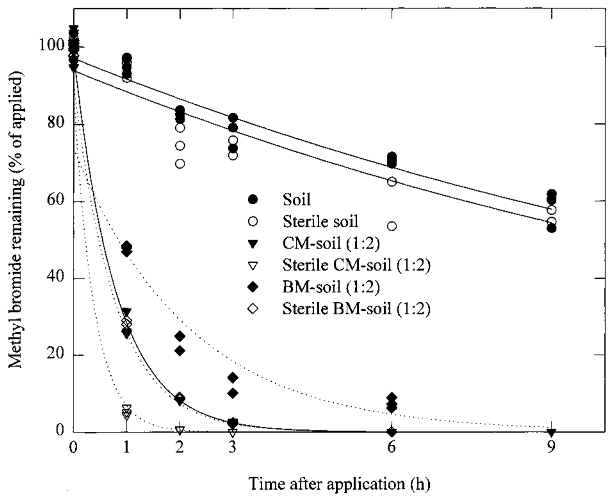

FIGURE 1. Degradation of methyl bromide in sterile and nonsterile Arlington sandy loam soil amended with different organic wastes. Symbols are measured values, and lines are first-order regressions.

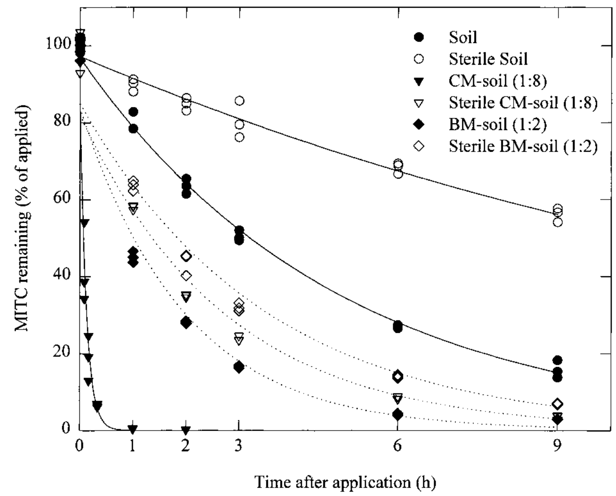

FIGURE 2. Degradation of methyl isothiocyanate in sterile and nonsterile Arlington sandy loam soil amended with different organic wastes. Symbols are measured values, and lines are first-order regressions.

TABLE 2. First-order Degradation Rate Constants (*k*), Half-Lives ($t_{1/2}$), and Correlation Coefficients of Fitting (r^2) for Methyl Isothiocyanate Degradation in an Arlington Sandy Loam Soil Amended with Different Ratios of Organic Amendments

matrix[a]	k (d^{-1})	$t_{1/2}$ (d)	r^2
soil (unamended)	0.21 ± 0.01[b]	3.4	0.99
CM-soil (1:40)	0.82 ± 0.03	0.8	0.99
CM-soil (1:20)	1.78 ± 0.05	0.4	0.99
CM-soil (1:8)	8.09 ± 0.56	0.1	0.95
CM-soil (1:4)	13.5 ± 1.06	0.05	0.94
CM-soil (1:2)	12.4 ± 0.36	0.06	0.99
BM-soil (1:2)	0.51 ± 0.02	1.4	0.99

[a] CM = composted manure; BM = Biosolid-manure mix; the ratio following CM or BM indicates the ratio of amendment to soil in w/w. [b] Mean ± standard error of *k*.

Microbial degradation of a pesticide in soil is traditionally based on a demonstration of inhibited degradation after sterilization. However, sterilizing amended soils resulted in an opposite effect on MeBr degradation: MeBr degraded faster in the sterile amended soils than in the nonsterile amended soils (Figure 1), and the difference was significant at the 5% level. In agricultural soils, MeBr undergoes both chemical transformations such as hydrolysis and methylation of organic matter (*14*, *15*) and microbial degradation (*29*, *30*). Methylation may occur with nucleophilic groups such as $-NH_2$, $-NH$, $-SH$, and $-OH$ on the organic matter, as illustrated from the reaction between MeBr and aniline (*15*). Although not experimentally confirmed, it is likely that autoclaving at high temperature and pressure may have caused a structural change of the organic matter and made the soil more reactive to MeBr, resulting in enhanced reaction between MeBr and the soil matrix. This was confirmed when chemical poisoning was used to sterilize the soils. In mercuric chloride treated soils, the degradation rate of MeBr was statistically similar to that in nonsterile soils. The effect of sterilization on MeBr degradation, along with the linear dependence of degradation rate on the amendment ratio, together suggests that MeBr degradation in the amended soils can mainly be attributed to chemical factors under the used experimental conditions.

Effect of Amendment on MITC Degradation. In the unamended soil, MITC had a half-life of 3.4 days (Table 2), which is in agreement with previously reported values (*12*). Compared to CM, addition of BM at the 1:2 ratio resulted in only a moderate enhancement (2.4 times) in MITC degradation, but addition of CM, even at low ratios, resulted in a substantial increase in MITC degradation (Table 2). For instance, at 1:40, the half-life of MITC was reduced to only 0.4 day, or the degradation was enhanced by a factor of 8.5 of that of the unamended soil. When the amendment ratio was >1:8, the half-life was <2 h (Table 2).

Sterilizing the amended soils significantly ($p < 0.001$) reduced the MITC degradation rate (Figure 2). For example, in nonsterile soil amended at 1:8, the k value was 8.1 day^{-1}, but after sterilization, it was reduced to 1.5 day^{-1} (Table 2). The inhibitory effect of sterilization on MITC degradation implies that the amendment-induced MITC degradation was primarily a result of stimulated microbial degradation. In a previous study, it was found that microbial degradation dominated the overall degradation of 1,3-D caused by organic amendments (*16*). On the other hand, the fact that certain amount of degradation of MITC still occurred in the sterile amended soils suggests that chemical degradation also contributed to the overall enhanced degradation (Figure 2). For instance, assuming chemical and microbial transformations are additive in the same matrix, from the k values (Table 2) it can be estimated that for the 1:8 amended soil, about 20% of the overall MITC degradation would be chemical degradation and 80% would be microbial degradation.

The mechanism for the stimulated microbial degradation of MITC in amended soils is not known. The overall soil respiration rate was found to increase greatly after the addition of organic amendments (*16*), which implies that the amendment may have brought into the soil a large population of degrading organisms or nutrients that could be used by the native soil organisms. Fumigation with MITC has been shown to cause temporary decreases in activity and population size of culturable heterotrophic microorganisms (*31*), and reduced microbial activity could result in slow fumigant degradation. The increase in biomass and microbial activity achieved by amendment addition may have counteracted this effect, leading to rapid fumigant degradation. As shown by this research, different organic amendments can have very dissimilar effects on fumigant degradation, which suggests that it may also be possible to identify compost properties (e.g., C/N ratio, microbial makeup, and maturity) that control fumigant degradation and to use these properties to attain a desired fumigant degradation rate.

Reduction of Fumigant Emissions by Surface Amendment Application. After injection at a depth of 30 cm, MeBr

TABLE 3. Measured Total Volatilization Losses (in Percent of Applied Chemical) of Methyl Bromide and Methyl Isothiocyanate from Packed Soil Columns under Different Surface Amendment Conditions ($n = 2$)

treatment[a]	methyl bromide	methyl isothiocyanate
control (no-amendment)	68.2 ± 2.5^b	21.3 ± 0.9
5% CM-5 cm	55.9 ± 0.5	0.3 ± 0.1
20% CM-5 cm	49.5 ± 2.3	
20% CM-10 cm	39.6 ± 2.3	

[a] CM = composted manure; percent following CM indicates the percentage of amendment in soil (w/w); the depth indicates the depth of soil layer that was amended with CM. [b] Mean ± standard deviation.

rapidly diffused through the soil column and volatilized from the soil surface. After 18 days, as much as 68% of the applied MeBr was lost via volatilization from the unamended soil columns (Table 3). Similar emission losses were measured under comparable conditions in a previous study (*28*), and the loss was also in agreement with recently reported field values (*9*−*11*, *17*−*19*). The high emission loss was apparently caused by the rapid diffusion of MeBr through soil, the relatively long persistence of MeBr in soil ($t_{1/2}$ = 12 days), and the high permeability of MeBr through the polyethylene film (*3*). Incorporating 5% CM into the top 5 cm soil layer reduced MeBr emission to 55.9% (Table 3). However, the difference between the amended and unamended treatments only represented a limited reduction (12%). Further increasing the amendment application rate resulted in further reduced MeBr emissions (Table 3). When 20% CM was incorporated into the top 5 cm soil layer, 49.5% of the applied MeBr was lost by emission; when 20% of CM was mixed into the top 10 cm soil layer, the emission loss decreased to 39.5%.

In practice, use of soil organic amendment will become infeasible if the application rate in the top 5 cm layer is more than 5%. Assuming that the 5 cm surface layer (bulk density is 1.3 g cm^{-3}) is amended, a 5% amendment application rate will translate into approximately 30 t of material per hectare. From the degradation experiments, the half-life of MeBr in the soil amended with 5% CM was 3.3 days. This persistence is apparently very long compared to the rapid diffusion. For instance, it is estimated that during this time, as much as 61% of the total volatilization loss had already occurred. Therefore, to achieve a greater reduction in MeBr emission, it is necessary to further increase either the degradation rate or the residence time of MeBr in soil. Recently, bacteria were isolated from fumigated soil which could grow on MeBr as a carbon source (*30*). Inoculation of such MeBr degrading organisms into the amendment may be one possible avenue for further increasing the degradation rate of MeBr under field conditions. Using less permeable films as surface tarps would increase the residence time of MeBr in soil, allowing more opportunity for degradation and less emission of MeBr (*11*, *25*).

After the injection of Vapam at 10 cm, MITC was formed and then gradually volatilized from soil surface, with the maximum volatilization occurring about 2−3 days after the application (Figure 3). Assuming 80% of the applied Vapam was converted to MITC under the experimental conditions (*12*), a total of 21.3% of the initially converted MITC was lost by emission after 202 h (8.4 days). Adding 5% CM into the top 5 cm soil layer, however, almost completely eliminated MITC volatilization (Figure 3). At the end of the experiment, a total of only 0.3% of the initially converted MITC was emitted. The negligible emission of MITC from the amended columns should be largely attributed to the rapid degradation of MITC in the top soil layer that was amended with CM. Other mechanisms, such as adsorption, should not contribute

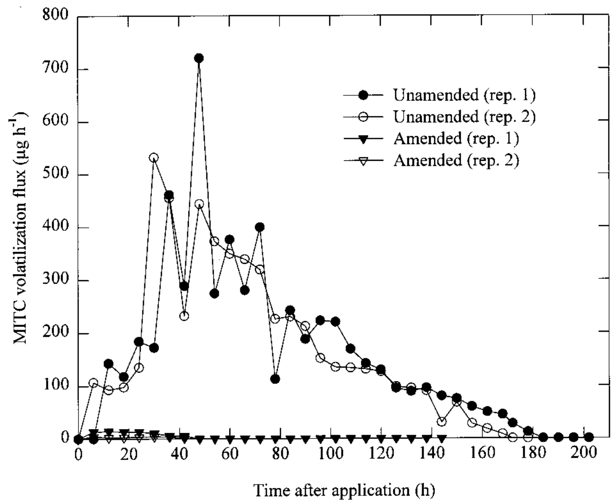

FIGURE 3. Volatilization fluxes of methyl isothiocyanate from control and amended soil columns after Vapam (metam sodium) was injected at the 10 cm depth. In amended columns, 5% of a composted manure was homogeneously mixed into the top 5 cm soil layer before fumigant application.

significantly because previous studies showed that fumigants are adsorbed weakly in soil (*7*, *12*, *15*).

Chemical fumigants have been used for several decades for soilborne pest management. However, under current practices, many of these fumigants can cause detrimental effects to the environment when they escape into the atmosphere. The results from our studies indicate that common organic wastes such as composted manure are capable of enhancing the degradation of major soil fumigants, and the enhanced degradation may be purposely employed to minimize fumigant emissions. Because many organic wastes also have the ability to suppress soil pathogens, the integration of fumigation with amendment application may potentially offer multiple benefits. It may not only reduce fumigant emission but also provide better pest control and, at the same time, provide additional nutrients for plant growth. In reality, however, as organic wastes exist in numerous forms and their physical-chemical properties also change greatly with origination and processing (*20*, *23*), the interaction of organic amendment and fumigant behavior should be studied in a case-by-case approach. Particularly, the effect on pest control efficacy and the effectiveness for reducing fumigant emissions should be evaluated under field conditions.

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