JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effect of Drip Application of Ammonium Thiosulfate on Fumigant Degradation in Soil Columns

RUIJUN QIN,*,†,‡ SUDUAN GAO,‡ BRADLEY D. HANSON,‡ JASON A. MCDONALD,‡ THOMAS J. TROUT,§ AND HUSEIN AJWA†

Department of Plant Sciences, University of California, Davis, 1636 East Alisal Street, Salinas, California 93905, U.S. Department of Agriculture-Agricultural Research Service (USDA-ARS), Water Management Research Unit, Parlier, California 93648, and USDA-ARS, Water Management Research, 2150 Centre Avenue, Fort Collins, Colorado 80526-8119

Low permeability tarps can effectively minimize fumigant emissions while improving fumigation efficacy by retaining fumigants under the tarp. However, when planting holes are cut through the tarps, high-concentration fumigants may be released and result in environmental and worker safety hazards. In a 11-day column study, we explored the effect of drip irrigation application of ammonium thiosulfate (ATS) on 1,3-dichloropropene (1,3-D) and chloropicrin (CP) degradation in soil. Decrease of 1,3-D and CP concentrations in soil-gas phase followed a three-parameter logistic equation for all treatments. It was slowest in the control with a half-life ($t_{1/2}$) of 86.0 h for 1,3-D and of 16.3 h for CP and most rapid when ATS was applied at 4:1 ATS/fumigant molar ratio with a half-life of 9.5 h for 1,3-D and of 5.5 h for CP. Our results indicate that applying ATS via the drip-irrigation systems to soil can accelerate fumigant degradation in soil and thus reduce emissions. This technical solution may be applicable in raised-bed strawberry production where drip-application of fumigants under tarps has become common.

KEYWORDS: 1,3-Dichloropropene; chloropicrin; ammonium thiosulfate; low permeability tarps; fumigant degradation; drip application

INTRODUCTION

California accounts for almost 90% of the U.S. strawberry (*Fragaria xananassa* Duchesne) fruit production (*1*). Most strawberry producers in California grow the crop using drip irrigation systems on raised beds covered with plastic mulch (*2*). Because strawberry is vulnerable to weeds, pathogens, and nematodes, preplant soil fumigation is used to achieve maximum yield. Drip fumigation, which utilizes emulsified formulations of fumigants applied via irrigation tubing (tapes) buried a few centimeters below the soil surface under plastic tarp, has been recently developed and is commonly used in California (*2*). About one third of strawberry fumigation treatments were drip fumigation in 2005, and this proportion is expected to increase due to generally lower emissions compared to shank-injections (*3*).

The fumigants 1,3-dichloropropene (1,3-D) and chloropicrin (CP) are important alternatives to methyl bromide, which has been phased out due to its effects on stratospheric ozone (*4*). The most common formulation of 1,3-D and CP for drip fumigation in strawberry raised-bed culture is InLine (a mixture of 61% 1,3-D, 33% CP, and 6% inert ingredients) (*5*). However, 1,3-D and CP are susceptible to rapid emission after being applied to soil. High levels of fumigant emissions may endanger the health of the workers and bystanders due to their acute toxicity. Their emissions also contribute to volatile organic compounds (VOCs) which impact air quality and the environment. Effective fumigation requires that the target pest receives sufficient time–concentration exposure to the chemical; thus, rapid emission loss of the fumigant from the soil may result in insufficient pest control unless high application rates are used. Because of environmental safety and economic concerns, it is essential to develop feasible agricultural practices to minimize fumigant emissions.

To enhance fumigation efficacy and reduce fumigant emissions, surface barriers such as plastic tarps are often used to retain fumigants within the soil for longer periods of time and minimize volatilization losses (*6–8*). Films with extremely low permeability such as virtually impermeable film (VIF) were reported to be one of the most effective tarps (*9–11*). Because VIF can retain the fumigants in soil at relatively higher concentrations and for longer periods of time, the fumigation efficacy on controlling pests and weeds may also be improved.

* Author to whom correspondence should be addressed. Tel: +1 559 596 2904. Fax: +1 559 596 2949. E-mail: rqin@fresno.ars.usda.gov.

† University of California, Davis.

‡ USDA-ARS, Water Management Research Unit, San Joaquin Valley Agricultural Sciences Center.

§ USDA-ARS, Water Management Research, Fort Collins, Colorado.

10.1021/jf071946w CCC: $37.00
Published on Web 09/12/2007

Another effective method to minimize fumigant emissions is to apply chemicals, such as ammonium thiosulfate (ATS) fertilizer, to the soil surface (*6*, *8*, *12*, *13*). Thiosulfate ($S_2O_3^{2-}$) has been known for its property to react with halogenated organic compounds through nucleophilic substitution (*14*). Thiosulfate can react with fumigants (e.g., methyl bromide, 1,3-D and CP) to form nonvolatile compounds, resulting in a substantial decrease in emissions (*12*, *15*, *16*). The application of ATS (at 15-cm depth) was found to decrease fumigant (e.g., 1,3-D and propargyl bromide) concentration of gas phase in crop root zones (20–80 cm soil depth) in river sand (*17*). Recent studies have shown the synergistic effect of controlling fumigant emissions by combining application of plastic tarp and thiourea solution to form a reactive surface barrier (*18*). In addition, as a source of fertilizer, ATS application can also provide N and S to strawberry and other plants.

However, if ATS application is made too soon after fumigant injection, the fumigant may react with ATS and fumigant efficacy may be impacted, so it is important to apply the ATS after efficacy is achieved. On the other hand, high retention of fumigants under low permeability tarps can have unfavorable consequences after the fumigation objective is achieved. For example, when planting holes for strawberry transplanting are cut in the tarps 2–4 weeks after fumigation, fumigants trapped under the tarp may be released immediately through the holes and contribute to emissions and endanger workers and bystanders. The residual fumigants may also harm crops by phytotoxicity (*17*) and also may contaminate groundwater by leaching (*19*).

To minimize risks from the accumulated fumigants under tarps after fumigation efficacy is achieved and before strawberry transplanting, we conducted a set of soil column tests with the objective to determine the potential of near surface drip-applied ammonium thiosulfate (ATS) for accelerating degradation of accumulated fumigants under low permeability tarps. The effects of ATS on fumigation efficacy on soil pests (e.g., nematodes and weeds) were also determined.

MATERIALS AND METHODS

Soil and Chemicals. A Hanford sandy loam soil (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) was collected from the topsoil (0–30 cm depth) at the San Joaquin Valley Agricultural Sciences Center, U.S. Department of Agriculture-Agriculture Research Service, Parlier, California. The soil had a pH of 7.2 and an electrical conductivity (EC) of 0.31 dS m^{-1} in 1:1 soil–water extracts, a cation exchange capacity (CEC) of 6.8 $cmol_c$ kg^{-1}, and an organic matter content of 0.72%. The soil contained 55.8% sand, 39.6% silt, and 5.6% clay. At 33-kPa suction, the soil–water content is about 17% (w/w) (*20*). The soil was air-dried to water content of 4.5% (w/w), sieved through a 4-mm mesh screen, and mixed before packing the soil columns.

cis-1,3-Dichloropropene (purity of 98.9%) was provided by Dow AgroSciences (Indianapolis, IN). CP (purity of 99.9%) was provided by Niklor Chemical Co., Inc. (Mojave, CA). ATS 55% (w/w) solution was obtained from Tessenderlo Kerley (Eufaula, AL). Ethyl acetate (pesticide grade), hexane (pesticide grade), and sodium sulfate anhydrous (Na_2SO_4, 10–60 mesh, ACS grade) were obtained from Fisher Scientific (Fair Lawn, NJ).

Soil Column Experiment. Soil was packed to a total depth of 22 cm into close-bottomed stainless steel columns (25-cm height × 15.5-cm i.d.). The short columns were used based on the premise that fumigant accumulation mostly occurs right under the tarp or near the soil surface where ATS applications would have the greatest effect. In this study, we used an impermeable surface seal and by sealing the soil columns with a glass cover (19 × 19 cm) using a silicone rubber sealant at the top.

The columns were packed in 5-cm increments to a uniform bulk density of 1.4 g cm^{-3}. Sampling ports for soil gases were installed at depths of 0 (above the soil and below the seal), 10 and 20 cm below the soil surface. A Teflon-faced silicone rubber septum (3-mm thick; Supelco, Bellefonte, PA) was installed in each sampling port. The septum was replaced with a new one after each sampling to avoid any potential gas leakage from the column. A Teflon tube attached to the inside of each sampling port extended to the center of the column. The experiments were conducted at laboratory room temperature (22 ± 3 °C).

One-hundred-forty microliters of fumigant mixture containing 100 μL (122 mg) of *cis*-1,3-D and 40 μL (66 mg) of CP (mixture similar to InLine soil fumigant), were injected into the column center at the 10-cm soil depth through an injection port using a long-needle syringe. The two isomers, i.e., *cis*- and *trans*-1,3-D have similar properties in terms of degradation and emissions (*21*–*23*). To simplify analysis, only the *cis* isomer was used in this study. The application rates were 21 mg kg^{-1} soil 1,3-D and 11 mg kg^{-1} soil CP (equivalent to 65 kg ha^{-1}1,3-D and 35 kg ha^{-1} CP), which is lower than normal field application rates of InLine, 236–393 kg ha^{-1} (*5*). This low rate achieved the desired soil gas fumigant concentrations at the time of ATS application in the short soil columns with impermeable surface seals.

For determining fumigant concentration in the soil-gas phase, 0.5-mL volume of soil gas was withdrawn from the sampling ports with a gas-tight syringe 3, 6, and 21 h after fumigant injection. After soil gas sampling at 21 h, six treatments in duplicate were drip applied to the columns immediately: 100 mL water (W1), or 100 mL ATS solutions containing ATS to fumigant (molar ratio) of 1:1 (ATS1:1/W1), 2:1 (ATS2:1/W1), or 4:1 (ATS4:1/W1), and 200 mL ATS solution at 2:1 (ATS2:1/W2), and an untreated control (CK). The water or ATS solution was applied over a 2.5-h period via Teflon tubing (1.6-mm i.d.) installed in the center of the column at a 3-cm depth, simulating the drip-tape in strawberry raised beds (*4*).

Soil Gas Sampling and Analysis. Following application of ATS, 0.5-mL volume of soil gas was withdrawn from the sampling ports with a gas-tight syringe 0, 3, 6, 9, 12, 48, 72, 120, 168, and 240 h after ATS treatment to determine fumigant concentration in the soil-gas phase. The gas samples were directly injected into the bottom of 20-mL clear headspace vials, and the vials were crimp-sealed very quickly with aluminum caps and Teflon-faced butyl-rubber septums (Supelco). This sampling technique was quantitative and reproducible (*24*). To avoid moisture effect on the fumigant stability, 0.2 g of anhydrous sodium sulfate was added to each vial before sample injection. Samples were stored in an ultra low temperature freezer (−80 °C) and analyzed within 72 h (*25*). Fumigants in the vials were analyzed on a GC-μECD (Agilent Technologies 6890N Network GC system with a micro electron capture detector) equipped with an automated headspace sampler (Agilent Technologies G1888 Network Headspace Sampler) system. A DB-VRX capillary column (30-m length × 0.25-mm i.d. × 1.4-μm film thickness, Agilent Technologies) was used. Conditions for the analysis were according to Gao and Trout (*26*).

Regression analysis using a first-order degradation model was initially used to describe the time-series soil gas concentration data; however, this model did not provide an adequate fit. Subsequent regression analysis was performed using a three-parameter logistic model (Sigma Plot version 10); $Y = a/[1 + (X/t_{1/2})^b]$, where Y is the fumigant concentration (mg L^{-1}), X is the time (h), a is the initial predicted concentration, $t_{1/2}$ is the half-life (h), and b is the slope of the line at $t_{1/2}$. This model used an iterative process to estimate parameters to best fit of fumigant concentration over time.

Residual Fumigant Extraction and Analysis. At the end of the experiment, soil samples from each column were taken at depths of 0−5, 5−10, 10−15, and 15−22 cm using a 2-cm diameter auger immediately after opening the glass seal. The soil was transferred to a 135-mL glass jar and sealed immediately to avoid loss of fumigants. The soil sample was used to determine soil–water content and residual 1,3-D and CP. The extraction procedure for soil residual fumigants followed Guo et al. (*19*). An equivalent dry weight of 8 g soil was added to a 20-mL clear vial containing Na_2SO_4 (amount at a 7:1 mass ratio of Na_2SO_4 to soil–water). After adding 8 mL of ethyl acetate to the vial, it was crimp-sealed with an aluminum cap and a Teflon-faced butyl-rubber septum. Then, the vial was incubated at 80 °C in a water bath over night (~18 h), the supernatant was settled, and a portion was transferred into a 2-mL amber glass vial for fumigant analysis

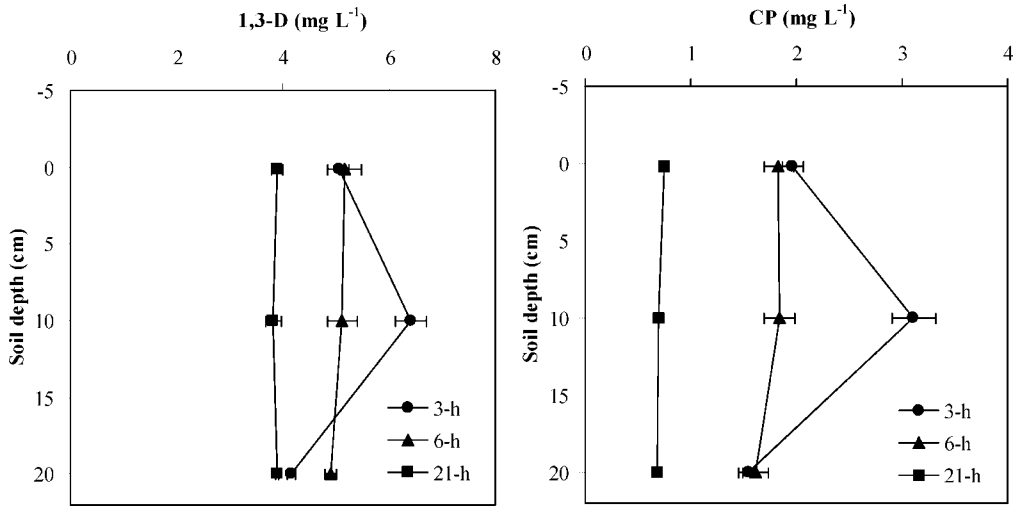

Figure 1. Average fumigant concentrations in soil gas (1,3-D and CP) after injection into soil columns and before drip application of ATS solution. Error bars represent standard error ($n = 12$).

using the GC-μECD with ethyl acetate solvent for the standards. The analysis of *cis*-1,3-D and CP in the extracts was according to Gao and Trout (*26*).

Tests on Nematodes and Weeds. To test potential effect of ATS application on fumigation efficacy, citrus nematodes (*Tylenchulus semipenetrans*) and two weed species, annual ryegrass (*Lolium multiflorum*) and common chickweed (*Stellaria media*), were buried in the soil columns. Nylon bags containing 10 g of soil with approximately 56 nematodes g^{-1} soil were buried at depths of 10 cm and 20 cm in the columns. Seed packets consisting of approximately 50 unimbibed seeds of each weed species sealed in a micropore plastic mesh bag (DelStar Technologies, Middletown DE) and placed at the soil surface and buried at 10- and 20-cm depths within the soil columns. At the end of the experiment, nematode bags and weed packets were recovered from the soil columns and the survival rate of the nematodes and weeds were determined. Nematodes were extracted using a Baerman funnel for five days and surviving nematodes were counted. Weed seeds were prepared with 5-min disinfection in a 2% bleach solution (v/v), rinsed well with distilled and deionized (DDI) water, and then placed in Petri dishes with filter paper moistened with 10 mL of 0.2% Captan + DDI water solution. Petri dishes were covered with parafilm and kept in the dark for three weeks. Germinated seeds were counted and removed twice per week and cumulative germination was determined.

Tests of nematode survival and weed germination in columns without fumigant injection were also conducted as a reference to the fumigated columns. Both the nematode and weed bags were placed in the unfumigated columns similar to the fumigated columns. One treatment was recovered just after packing of the soil columns to test whether the packing affected the survival of nematodes and the germination of weeds. Another two treatments were recovered at the end of the experiment similar to the fumigated columns (one with glass cover and the other without) to determine the potential impact of sealed columns on the nematodes and weeds. All treatments were run in duplicate. The procedure on processing the nematodes and weeds was the same as the fumigated columns.

RESULTS AND DISCUSSION

Fumigant Distribution in Soil Columns Prior to ATS Application. Fumigant concentration in the soil-gas phase between fumigant application and ATS treatment was monitored, and changes of the average concentrations are shown in **Figure 1**. The highest fumigant concentration was at the first sampling time (i.e., 3 h after fumigant injection) at the 10-cm soil depth where the fumigants were injected: 6.4 mg L^{-1} for 1,3-D and 3.1 mg L^{-1} for CP. A uniform distribution of 1,3-D and CP throughout the columns was established 6 h after application.

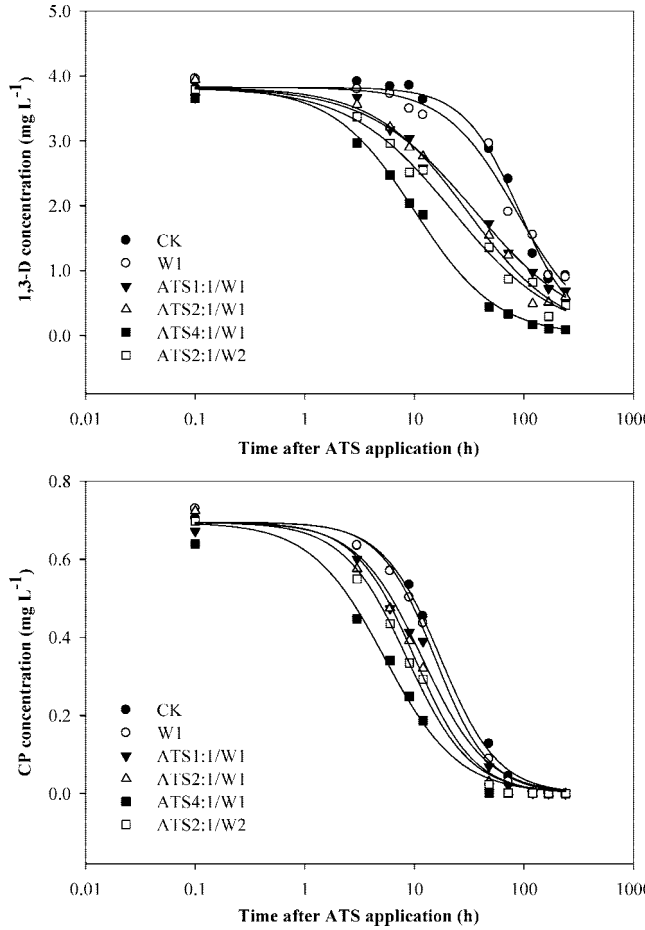

Figure 2. Fitted curves for 1,3-D and CP concentration data in the soil-gas phase at a soil depth of 10 cm in treated soil columns using a three-parameter logistic regression model. Symbols are the mean value of duplicate samples. (*The initial predicted concentration was forced through the time-zero average due to no significant difference).

Twenty-one hours after fumigant injection prior to drip application of ATS, both 1,3-D and CP were relatively uniformly distributed in all 12 columns at average concentrations of 3.9 and 0.7 mg L^{-1}, respectively (**Figure 1**). Note that the application rates of the fumigants in the column tests were lower compared to typical field application rates, but the fumigant concentrations before ATS application in the soil columns were

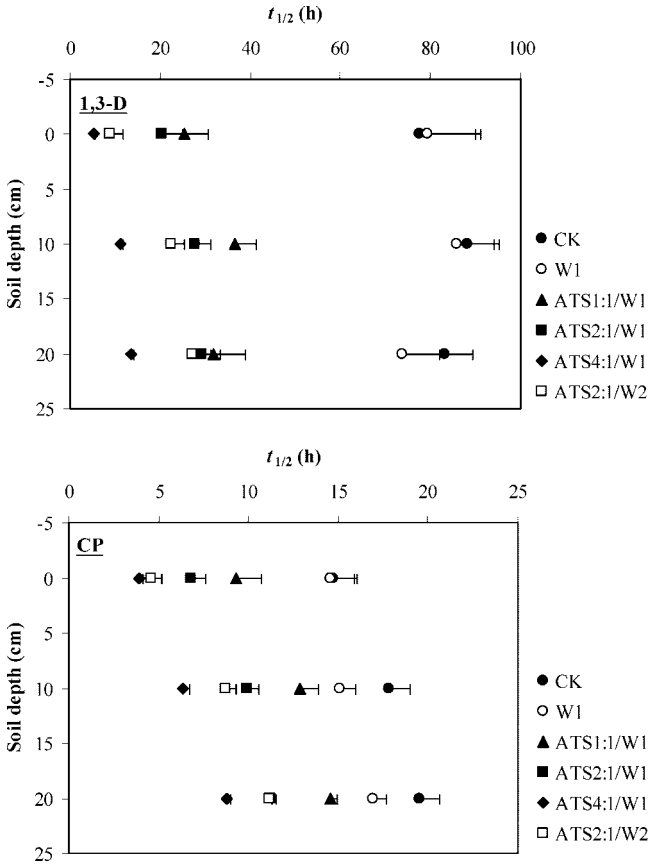

Figure 3. Calculated half-life (with standard error bar) of all the treatments on 1,3-D and CP degradation at each soil depth in the soil-gas phase based on a three-parameter logistic regression model.

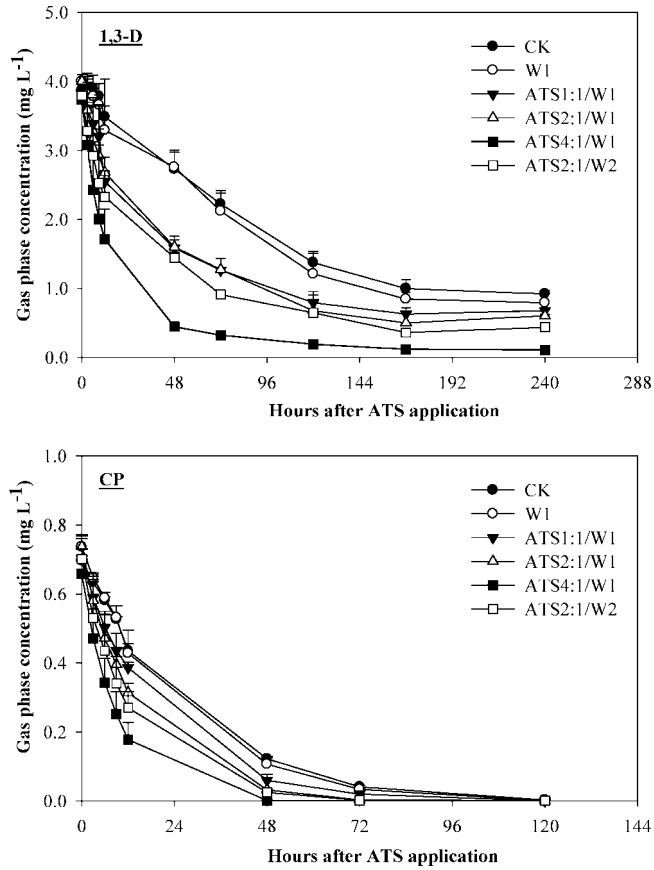

Figure 4. The effect of drip application of ATS solution on average 1,3-D and CP concentrations in the soil-gas phase in soil columns. Symbols are the mean value of six (three depths, duplicate samples) concentration values and error bars represent standard error.

typical of those found in fumigated field conditions several days after fumigation where surface emissions and natural degradation reduce the fumigant concentrations markedly.

Effect of ATS on Fumigants in the Soil-Gas Phase. Drip application of ATS near the soil surface significantly decreased the concentrations of 1,3-D and CP in the soil-gas phase throughout the soil profile. The greater the ATS application rate, the lower the concentration of fumigant over time (corresponding to rapid degradation) at all depths. To describe fumigant degradation pattern, separate regression analyses using a three-parameter logistic model were conducted on the soil gas measurements at each depth within each treatment. **Figure 2** illustrates the model fitting curves for the data at the 10-cm soil depth.

The half-life ($t_{1/2}$) of the fitted degradation curve is used for discussing the treatment effect on fumigant concentration decrease at the three sampling depths (**Figure 3**). Both the control and W1 had a similar half-life throughout the soil profile, which indicates that water application did not affect the degradation of 1,3-D and CP in the soil-gas phase. Compared to the control and W1, half-lives of 1,3-D and CP were consistently shorter at any soil depth in all ATS treatments ($P > 0.05$; **Figure 3**). Among the treatments of ATS application with same amount of water (W1 - 100 mL), the half-life decreased with increasing rate of ATS application. The ATS4:1/W1 resulted in a significantly short half-life compared to ATS1:1/W1 and ATS2:1/W1, which were not significantly different from each other. This confirms that ATS accelerated fumigant degradation and the amount of ATS affected the degradation rate.

The half-life of 1,3-D was significantly shorter at the soil surface than at deeper depths in the treatments of ATS2:1/W2 and ATS4:1/W1, whereas no significant difference was found in other treatments ($P > 0.05$) (**Figure 3**). The half-life of CP was generally shorter at the soil surface than the deeper depths in all the treatments, particularly in the treatments of ATS application. Because the ATS was applied near the soil surface, more ATS was available to react with 1,3-D and CP there than in the lower depths. The results indicate that the reaction of ATS with fumigants occurred fairly quickly.

Although there was a significant effect of soil depth on fumigant half-life, these differences were relatively consistent across treatments. Therefore, the decrease of average fumigant concentrations over soil depth (**Figure 4**), were fitted using the three-parameter logistic model to compare the effects of the treatments on fumigant degradation. The average $t_{1/2}$ (the half-life) is shown in **Table 1**. The control and W1 treatments had the slowest degradation rate with half-lives of 77.7 to 86.0 h for 1,3-D and 15.9 to 16.3 h for CP. The ATS4:1/W1 treatment accelerated the degradation of 1,3-D and of CP markedly and its half-life was the shortest among the ATS application treatments (9.5 h for 1,3-D and 5.5 h for CP).

CP concentration in the soil-gas phase decreased more rapidly than 1,3-D in this experiment, which has also been found in other research (*12, 16, 27*). The more rapid degradation combined with a lower application rate resulted in the early disappearance (by 100 h) of CP in the study, while 1,3-D was still present at the end of the experiment (**Figure 4**).

Effect of Water on Fumigants. Treatments with water or ATS solutions increased water content at soil surface, which gradually decreased with soil depth in the columns, while the control has the lowest water content (4.4%) throughout the soil

Table 1. Best-Fitting Three-Parameter Logistic Equation for 1,3-D and CP Concentrations in Soil Gas for All Depths Combined in the Column Study[a]

	1,3-D			CP		
treatment	*a* (mg L^{-1})	$t_{1/2}$ (h)	*b*	*a* (mg L^{-1})	$t_{1/2}$ (h)	*b*
CK	3.87 (0.08)	86.0 (5.6)	1.40 (0.14)	0.70 (0.01)	16.3 (0.7)	1.63 (0.08)
W1	3.87 (0.08)	77.7 (5.6)	1.39 (0.14)	0.70 (0.01)	15.9 (0.7)	1.73 (0.09)
ATS1:1/W1	3.87 (0.14)	33.6 (4.6)	0.98 (0.09)	0.70 (0.02)	12.0 (0.8)	1.51 (0.13)
ATS2:1/W1	3.87 (0.15)	30.4 (4.3)	0.96 (0.09)	0.70 (0.02)	9.8 (0.6)	1.57 (0.15)
ATS4:1/W1	3.87 (0.17)	9.5 (1.2)	1.18 (0.13)	0.70 (0.03)	5.5 (0.5)	1.38 (0.16)
ATS2:1/W2	3.87 (0.21)	20.3 (4.0)	0.88 (0.10)	0.70 (0.03)	8.1 (0.8)	1.43 (0.19)

[a] Parameters: *a*, the initial predicted concentration was forced through the time-zero average due to no significant difference; $t_{1/2}$, the half-life; *b*, the slope of the line at $t_{1/2}$. The range of the correlation (r^2) was 0.924–0.993. Values in parentheses are standard errors of duplicate column measurements.

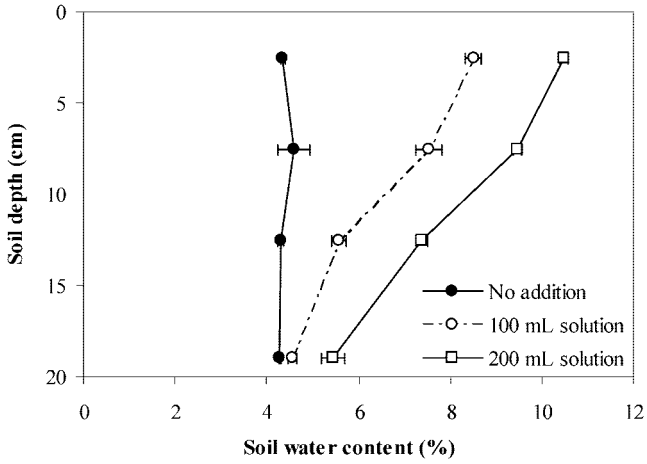

Figure 5. Soil–water content (%) in soil columns under various water/ATS treatments at the end of the experiment. Error bars represent standard error of duplicate column measurements except the 100 mL solution treatment, which was the average of four treatments with either 100 mL water or ATS solution.

column (**Figure 5**). Corresponding higher (with similar pattern) soil–water content was observed with higher amounts of water (W2 - 200 mL) application.

However, no difference between W1 and the control on fumigant degradation indicated that the effect of water application alone on fumigant concentration in soil-gas phase was minor in this study, and the enhanced fumigant degradation in ATS/W1 treatments was mainly due to ATS rather than water. Water can affect 1,3-D hydrolysis, which may result in a half-life of about 10 days (*21*). Compared to the ATS effect, the role of hydrolysis in fumigant degradation was small in our observations.

Similarly, a field trial showed that irrigation prior to fumigation increased soil–water content of topsoil (0–30 cm soil depth) but did not affect soil-gas 1,3-D and CP concentration in the soil profile compared to the control (no irrigation), indicating a limited impact of water on fumigant concentrations in the soil (*26*). The effect of soil moisture on 1,3-D and CP degradation seems inconsistent. A laboratory study showed the limited impact of water on CP degradation (*21*), while other studies reported that increasing soil moisture could accelerate the degradation of 1,3-D (*28*).

Similar degradation curves of 1,3-D and CP were observed from ATS2:1/W1 (low amount of water) and ATS2:1/W2 (high amount of water) (**Figures 2** and **4**), but ATS2:1/W2 had a slightly shorter half-life than ATS 2:1/W1 (**Table 1**). In addition, a significantly shorter half-life at the soil surface than at deeper depths was found in ATS2:1/W2 (**Figure 3**). This suggested that the water amount may contribute to ATS degradation of fumigants to some extent.

Residual Fumigant and Fumigant Degradation. At the end of the experiment, 1,3-D in the solid/liquid phase throughout the soil was low but clearly showed the effect of ATS. In all ATS treatments, less fumigant remained compared to the control and water application only (**Table 2**). CP residues in soil solid/liquid phase were found only in trace levels (<0.02 mg kg^{-1}).

Mass balance of the fumigants in the soil columns were conducted based on fumigant concentrations determined in soil-gas phase and extracted from soil samples. The difference between the applied fumigant and the amount measured in soil (including gas phase and solid/liquid phase) was assumed to be due to degradation as the soil column was a closed system. In ATS treatments, 94–98% of 1,3-D was degraded, compared to the 91% degradation when no ATS was applied. The positive effect of drip application of ATS on degradation of 1,3-D and CP demonstrated that ATS application through drip irrigation can be an effective and feasible method to minimize overall emissions and the potential for crop phytotoxicity, especially for the accumulated fumigants under low permeability tarps.

Efficacy on Weeds and Nematodes Control. Results from the unfumigated columns showed that both citrus nematodes and weeds were not affected either by packing or by time in the sealed soil columns. There were 58 nematodes per gram soil recovered and 90% of ryegrass and 58% chickweed germinated after the 11-day experiment from unfumigated columns. For all fumigated columns, however, citrus nematodes were all killed, and no weed seeds were viable.

Among the fumigated columns, calculated concentration–time index from all the treatments indicate that the highest exposure

Table 2. Fate of 1,3-D and CP in the Soil Columns at the End of the Experiment[a]

	1,3-D (% of applied)			CP (% of applied)		
treatment	gas phase	liquid/solid phase	degradation[b]	gas phase	liquid/solid phase	degradation[b]
CK	1.7 (0.0)	7.7 (0.7)	90.6	0.0	0.1	99.9
W1	1.4 (0.7)	7.3 (0.6)	91.2	0.0	0.1	99.9
ATS1:1/W1	1.2 (0.9)	5.0 (0.9)	93.7	0.0	0.0	100.0
ATS2:1/W1	1.1 (0.1)	4.5 (0.4)	94.4	0.0	0.1	99.9
ATS4:1/W1	0.2 (0.1)	2.1 (0.1)	97.7	0.0	0.0	100.0
ATS2:1/W2	0.8 (0.5)	3.9 (0.7)	95.3	0.0	0.0	100.0

[a] Values in parentheses are standard errors of duplicate column measurements. [b] Degradation calculated by difference of measured from applied to the column.

Table 3. Concentration–Time Index of 1,3-D and CP (mg h L^{-1}) in the Column Study[a]

treatment	1,3-D	CP
CK	532 (27)	52 (1.2)
W1	503 (24)	51 (0.5)
ATS1:1/W1	382 (18)	48 (0.3)
ATS2:1/W1	368 (9)	45 (1.0)
ATS4:1/W1	210 (12)	40 (1.5)
ATS2:1/W2	325 (14)	43 (1.7)

[a] The concentration–time index was calculated based on Wang and Yates (*29*) describing fumigant exposure; the exposure prior to dripping ATS (103 mg h L^{-1} for 1,3-D and 32 mg h L^{-1} for CP) was included in the calculations. Values in parentheses are standard errors of duplicate column measurements.

of fumigant in soil-gas phase was 532 (1,3-D) + 52 (CP) mg h L^{-1} in the control and the lowest exposure was 210 (1,3-D) + 40 (CP) mg h L^{-1} in ATS4:1/W1 (**Table 3**). According to a threshold soil 1,3-D concentration–time index which was only 12 mg h L^{-1} and achieved 100% efficacy controlling citrus nematodes in a field trial (*29*), the exposure index in our study is high enough to kill all the nematodes. Research by Klose et al. (*30*) reported that the fumigant concentration of InLine 780 μmol kg^{-1} (93 mg kg^{-1}) can control 90% chickweed after 24 h exposure in sandy loam soil. Although the fumigant amounts injected into our soil columns were considered low (approximate 32 mg kg^{-1} InLine), the pest exposure index was quite high. This resulted in complete control of nematodes and weed seeds in all columns; however, exposure index and pest control may differ in field applications.

However, compared to the control, the significantly reduced exposure of fumigants (mainly 1,3-D) with ATS application indicates a possibly reduced fumigation efficacy if the ATS or other amendment is applied too soon after fumigation. Some past studies have not showed an ATS affect on fumigation efficacy (*6*, *15*).

Practical Use of Dripping ATS in Fields. This study illustrated that drip application of ATS at 3-cm depth effectively reduced fumigant concentrations in the soil columns. The configuration is similar to drip irrigated beds, where tarps are commonly be used, as for strawberry fields. Drip application of ATS is expected to be practical and economical as it can use the existing irrigation system for both fumigation and ATS delivery. The effectiveness of ATS on degradation of residual fumigants in the soil would help shorten the waiting time between fumigation and planting as well as ensure the safety of workers and minimize environmental hazards when the tarp is perforated for planting.

Nonetheless, this process needs to be tested under field conditions to verify efficacy and reduced environmental risks, as laboratory findings can not fully represent field conditions. For example, field trials need to be carried out to determine the required ATS rates for specific fumigant formulation, the optimal timing of ATS applications, and potential technical obstacles that can only be experienced through field applications. As a fertilizer source, the ATS application rate should not be so high as to provide excessive amounts of N that may have a negative impact on plant growth and crop yields as well as potential leaching to contaminate ground water. To avoid potential problems with N, other thiosulfate formulations such as potassium thiosulfate (KTS) should be tested.

ABBREVIATIONS USED

ATS, ammonium thiosulfate; 1,3-D, 1,3-dichloropropene; CP, chloropicrin; $t_{1/2}$, half-life; VOCs, volatile organic compounds; HDPE, high density polyethylene; VIF, virtually impermeable film; Na_2SO_4, sodium sulfate anhydrous; W, water; KTS, potassium thiosulfate.

ACKNOWLEDGMENT

The authors appreciate the technical assistance from the personnel in Water Management Research Unit, USDA-ARS, Parlier, CA: Tom Pflaum, Robert Shenk, and Aileen Hendratna for assisting in experimental set-up and fumigant analysis; Nancy Goodell for nematode sample preparation and analysis; and Stella Zambrzuski for weed seed preparation and counting.

LITERATURE CITED

(1) United States Department of Agriculture. USDA-NASS. *Agricultural Statistics 2005*. http://www.usda.gov/nass/pubs/agstats.htm. 2005, pp V34–35.

(2) Ajwa, H. A.; Trout, T.; Mueller, J.; Wilhelm, S.; Nelson, S. D.; Soppe, R.; Shatley, D. Application of alternative fumigants through drip irrigation systems. *Phytopathology* **2002**, *92*, 1349–1355.

(3) Trout, T. J. Fumigant use in California - response to the phase-out. In *Proceedings of the Annual International Research Conference on MeBr Alternatives and Emission Reductions*. Orlando, FL, November 6–9, 2006. http://www.mbao.org/2006/06Proceedings/018TroutTmb-fumuse-06.pdf.

(4) Honaganahalli, P. S.; Seiber, J. N. Health and environmental concerns over the use of fumigants in agriculture: The case of methyl bromide. In *Fumigants: Environmental Fate, Exposure, and Analysis. ACS Symposium Series 652*; Seiber, J. N.; Knuteson, J. A.; Woodrow, J. E.; Wolfe, N. L.; Yates, M. V.; Yates, S. R., Eds.; ACS: Washington, D.C., 1997; pp 1–13.

(5) Ajwa, H. A.; Trout, T. Drip application of alternative fumigants to methyl bromide for strawberry production. *HortScience* **2004**, *39*, 1707–1715.

(6) Gan, J.; Yates, S. R.; Becker, J. O.; Wang, D. Surface amendment of fertilizer ammonium thiosulfate to reduce methyl bromide emission from soil. *Environ. Sci. Technol.* **1998**, *32*, 2438–2441.

(7) Gan, J.; Yates, S. R.; Wang, D.; Ernst, F. F. Effect of application methods on 1,3-D volatilization from soil under controlled conditions. *J. Environ. Qual.* **1998**, *27*, 432–438.

(8) Yates, S. R.; Gan, J.; Papiernik, S. K.; Dungan, R. S.; Wang, D. Reducing fumigant emissions after soil application. *Phytopathology* **2002**, *92*, 1344–1384.

(9) Nelson, S. D.; Riegel, C.; Allen, L. H.; Dickson, D. W.; Gan, J.; Locascio, S. J.; Mitchel, D. J. Volatilization of 1,3-dichloropropene in Florida plasticulture and effects on fall squash production. *J. Am. Soc. Hortic. Sci.* **2001**, *126*, 496–502.

(10) Papiernik, S. K.; Yates, S. R.; Dungan, R. S.; Lesch, S. M.; Zheng, W.; Guo, M. Effect of surface tarp on emissions and distribution of drip-applied fumigants. *Environ. Sci. Technol.* **2004**, *38*, 4254–4262.

(11) Thomas, J. E.; Ou, L. T.; Allen, L. H.; McCormack, L. A.; Vu, J. C.; Dickson, D. W. Persistence, distribution, and emission of Telone C35 injected into a Florida sandy soil as affected by moisture, organic matter, and plastic film cover. *J. Environ. Sci. Health, Part B* **2004**, *39*, 505–516.

(12) Wang, Q.; Gan, J.; Papiernik, S. K.; Yates, S. R. Transformation and detoxification of halogenated fumigants by ammonium thiosulfate. *Environ. Sci. Technol.* **2000**, *34*, 3717–3721.

(13) Gan, J.; Yates, S. R.; Knuteson, J. A.; Becker, J. O. Transformation of 1,3-dichloropropene in soil by thiosulfate fertilizers. *J. Environ. Qual.* **2000**, *29*, 1476–1481.

(14) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.

(15) Gan, J.; Becker, J. O.; Ernst, F. F.; Hutchinson, C.; Knuteson, J. A.; Yates, S. R. Surface application of ammonium thiosulfate fertilizer to reduce volatilization of 1,3-dichloropropene from soil. *Pest Manage. Sci.* **2000**, *56*, 264–270.

(16) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* **2000**, *29*, 1391–1397.
(17) Papiernik, S. K.; Ernst, F. F.; Dungan, R. S.; Zheng, W.; Guo, M.; Yates, S. R. Remediation of halogenated fumigant compounds in the root zone by subsurface application of ammonium thiosulfate. In *Pesticide Decontamination and Detoxification*; Gan, J. J., Zhu, P. C., Aust, S. D., Lemley, A. T., Eds.; American Chemical Society: Washington, DC, 2004; pp 169–179.
(18) Zheng, W.; Yates, S. R.; Papiernik, S. K.; Wang, Q. Reducing 1,3-dichloropropene emissions from soil columns amended with thiourea. *Environ. Sci. Technol.* **2006**, *40*, 2402–2407.
(19) Guo, M.; Papiernik, S. K.; Zheng, W.; Yates, S. R. Formation and extraction of persistent fumigant residues in soils. *Environ. Sci. Technol.* **2003**, *37*, 1844–1849.
(20) Skaggs, T. H.; Trout, T. J.; Simunek, J.; Shouse, P. J. Comparison of HYDRUS-2D simulations of drip irrigation with experimental observations. *J. Irrig. Drain Eng.* **2004**, *130*, 304–310.
(21) Gan, J.; Papiernik, S. K.; Yates, S. R.; Jury, W. A. Temperature and moisture effects on fumigant degradation in soil. *J. Environ. Qual.* **1999**, *28*, 1436–1441.
(22) Papiernik, S. K.; Yates, S. R. Effect of environmental conditions on the permeability of high density polyethylene film to fumigant vapors. *Environ. Sci. Technol.* **2002**, *36*, 1833–1838.
(23) Wang, D.; Yates, S. R.; Gan, J.; Kunteson, J. A. Atmospheric volatilization of methyl bromide, 1,3-dichloropropene, and propargyl bromide through two plastic films: Transfer coefficient and temperature effect. *Atmos. Environ.* **1999**, *33*, 401–407.
(24) Gan, J.; Yates, S. R.; Ernst, F. F.; Yates, M. V.; Jury, W. A. Laboratory-scale measurements and simulations of the effect of application methods on soil methyl bromide emission. *J. Environ. Qual.* **1997**, *26*, 310–317.
(25) Guo, M.; Zheng, W.; Papiernik, S. K.; Yates, S. R. Distribution and leaching of methyl iodide in soil following emulated shank and drip application. *J. Environ. Qual.* **2004**, *33*, 2149–2156.
(26) Gao, S.; Trout, T. Using surface water application to reduce 1,3-dichloropropene emission from soil fumigation. *J. Environ. Qual.* **2006**, *35*, 1040–1048.
(27) Dungan, R. S.; Gan, J.; Yates, S. R. Effect of temperature, organic amendment rate and moisture content on the degradation of 1,3-dichloropropene in soil. *Pest Manage. Sci.* **2001**, *57*, 1107–1113.
(28) Guo, M. X.; Papiernik, S. K.; Zheng, W.; Yates, S. R. Effects of environmental factors on 1,3-dichloropropene hydrolysis in water and soil. *J. Environ. Qual.* **2004**, *33*, 612–618.
(29) Wang, D.; Yates, S. R. Spatial and temporal distributions of 1,3-dichloropropene in soil under drip and shank application and implications for pest control efficacy using concentration-time index. *Pestic. Sci.* **1999**, *55*, 154–160.
(30) Klose, S.; Ajwa, H. A.; Fennimore, S. A.; Martin, F. N.; Browne, G. T.; Subbarao, K. V. Dose response of weed seeds and soilborne pathogens to 1,3-D and chloropicrin. *Crop Prot.* **2007**, *26*, 535–542.

Received for review June 29, 2007. Revised manuscript received August 15, 2007. Accepted August 16, 2007. This study was supported by the California Strawberry Commission and California Department of Food and Agriculture.

JF071946W