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Leaching Potential of Persistent Soil Fumigant Residues

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Persistent fumigant residues in soil resulting from agricultural pest-control practices may be released into water and leached to groundwater. In this study, the leaching potential of persistent soil fumigant residues was evaluated, and the effect of dissolved organic matter (DOM) and ammonium thiosulfate (ATS) amendment was investigated. A silt loam soil was incubated separately with the fumigants 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC) at 240−990 mg kg^{-1} for 35 d, followed by 48 h of evaporation. The soil was packed into stainless steel columns (1.4 cm × 10 cm) and leached with water, 5 mM ATS, and DOM solution (DOC 250 mg L^{-1}) by gravity. Residues of 1,3-D, CP, and MITC in the evaporated soil were 5.61, 11.38, and 1.83 mg kg^{-1}, respectively. Concentrations of 1,3-D, CP, and MITC in column effluents ranged from 0.05 to 0.73, 0.16 to 0.81, and 0.05 to 0.27 mg L^{-1}, respectively, when the soil was leached with 10 pore volumes of water. DOM did not promote the leaching of persistent fumigant residues, and ATS remarkably reduced the amount of 1,3-D and CP yet notably increased MITC recovered in the effluents. The results suggest that the leaching of persistent fumigant residues through soil to water is significant, and movement of fumigants in soil is not facilitated by DOM. Amending soil with ATS through irrigation is an effective method to remove persistent residues of halogenated fumigants. To reduce groundwater pollution risks posed by fumigation, persistent soil fumigant residues have to be considered.

Introduction

Chemical fumigants are widely used in agricultural production to control soil-borne pests and pathogens. After soil treatment, fumigants dissipate rapidly through volatilization and degradation. Due to the short lifetime of fumigants in soil, migration of the chemicals into groundwater is generally thought unlikely. However, fumigants such as 1,3-dichloropropene (1,3-D), chloropicrin (CP), and methyl isothiocyanate (MITC) have been detected in groundwater in the United States and other countries (*1*−*3*), despite that these chemicals may undergo hydrolysis in water. Among them 1,3-D is a drinking water contaminant candidate (*4*), and the California Environmental Protection Agency has developed a public health goal for 1,3-D in drinking water as 0.2 μg L^{-1} (*5*).

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Pesticides with a half-life >100 d in water and soil environments are categorized as persistent (*6*). Fumigants 1,3-D, CP, and MITC are nonpersistent (half-lives $t_{1/2}$ <10 d) in soil under normal conditions (*6*), but they may be entrapped in soil intra-aggregate micropores and form persistent residues (*7*). The persistent residues are resistant to volatilization and degradation and can remain in soil over years. For example, the half-life of CP in usual soils is less than 1 d (*6*), but residual concentrations of CP in the soil under a CP manufacturing facility of the Holtrachem Co. in Orrington, ME were found as 100−500 mg kg^{-1} 7 years after abandoning the factory. In previous studies, we defined persistent residues as the portion of fumigants remaining in soils >30 d after application followed by >20 h of evaporation (*7*). The contamination of groundwater by fumigants may be related to the formation of persistent residues in soil. Under conditions favoring leaching, such as over-irrigation or excessive rainfall, persistent soil fumigant residues may be released into water and leached to groundwater. Beneath the abandoned Holtrachem site in Maine, the groundwater had CP concentrations ranging from 10 to 150 mg L^{-1}.

Surface organic matter amendments have been suggested in soil fumigation practices to reduce fumigant atmospheric emissions (*8*), and this approach will result in an elevated DOM level in soil water. It is known that organic contaminants in aquatic systems are often associated with hydrophobic moieties of DOM (*9*), and movement of DOM in porous media facilitates the transport of associated pollutants (*10*). Predicting from its high mobility in soil (*11*), a high concentration of DOM would enhance the movement of pesticides through soil matrix. Nevertheless, the fumigants 1,3-D, CP, and MITC are weakly sorptive in soils, with log K_{OC} values <1.8 (*6*). Instead of being sorbed onto soil organic matter, persistent fumigant residues are entrapped in soil intra-aggregate micropores (*7*). The role of DOM in the mobility of persistent soil fumigant residues needs to be investigated.

In soil remediation and groundwater protection, the removal of persistent fumigant residues becomes essential. Wang et al. (*12*) reported that ammonium thiosulfate (ATS, an agricultural fertilizer) degraded halogenated fumigants (i.e. 1,3-D, CP, and methyl bromide) rapidly via nucleophilic substitution reactions and might be used as a soil surface amendment to reduce atmospheric volatilization of fumigants. In a sandy loam amended with ATS at 2:1 ATS/fumigant molar ratio, the half-life ($t_{1/2}$) of 1,3-D decreased from 162 to 29.7 h and CP from 139 to 30.1 h. The utility of ATS application to soil to eliminate persistent fumigant residues deserves tests. The objectives of this study were (1) to investigate the release of persistent fumigant residues 1,3-D, CP, and MITC from soil into water with batch extraction methods; (2) to evaluate the leaching potential of the fumigant residues using packed soil columns; and (3) to examine the effect of DOM and ATS application on the mobility of persistent fumigant residues in soil. These three fumigants are currently available biocides in soil fumigation, and they may form significant persistent residues in soils (*7*).

Materials and Methods

Chemicals and Soil Material. Three fumigants were included in this study: 1,3-D, CP, and Vapam (a precursor of MITC). The chemical 1,3-D was provided by Dow Agrosciences Co. (Indianapolis, IN). It contained 50.3% cis- and 47.5% trans-isomers. The CP (purity 99.9%) was obtained from Niklor Chemical Co. (Long Beach, CA), and the Vapam (42% of active ingredient metam-sodium) was received from Amvac Chemical Co. (Newport Beach, CA). In moist soils, metam-sodium

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breaks down rapidly ($t_{1/2}$ = 0.5−4 h) to MITC (a biocidal agent).

A Hagerstown silt loam (fine, mixed, semiactive, mesic Typic Hapludalfs) was collected from a fallow agricultural field in University Park, PA. The field was never treated with any fumigants. The air-dried soil was sieved to < 2 mm and stored at room temperature (20 °C) prior to use. It had a pH of 5.9 and an organic carbon (OC) content of 14.4 g kg^{-1} and contained 26.9%, 65.1%, and 8.0% of clay, silt, and sand, respectively.

A municipal compost (OC 176 g kg^{-1}) sampled from State College, PA was used as a DOM source. The compost was air-dried, passed through a 2-mm sieve, and stored at 20 °C.

Soil Incubation. Air-dried Hagerstown soil was adjusted to 10% gravimetric water content with deionized water, mixed well, and passed through a 2-mm sieve. The resieving process did not break original soil aggregates but ensured a homogeneous water distribution by breaking big soil chunks formed upon water addition. Aliquots (330 g) of the moist soil were placed in 500-mL conical glass flasks and spiked with 250 μL of 1,3-D, 150 μL of CP, or 250 μL of Vapam. The application rates of 1,3-D, CP, and MITC (1 g of Vapam will generate 238 mg of MITC assuming 100% transformation) were 995, 845, and 240 mg kg^{-1} soil, respectively. The flasks were sealed with one layer of Hytibar plastic film (Klerk's Plastic, Belgium), inverted, and incubated at 20 °C for 35 d. After incubation, soils were spread in a thin layer on aluminum foil in a fume hood, allowing 48 h of evaporation. The evaporated soils were then stored at 20 °C in flasks until further treatment.

Batch Experiments. Aliquots (10 g oven dry mass) of the treated soils were weighed into 20-mL headspace vials, and 8.00 mL of deionized water was added to each vial. The vials were sealed with Teflon-faced butyl rubber septa and aluminum covers and set at room temperature (20 °C) without disturbance. The extraction temperature was close to the mean annual temperature at 50 cm depth in the soil collection field (18.3 °C). A slightly higher temperature may promote fumigant degradation in water but has little influence on persistent soil fumigant residues. After 23 h of water wetting, the vials were shaken for 1 h, followed by centrifugation at 956 × g for 15 min. Supernatant (0.5 mL) was withdrawn from each vial with a 0.5-mL gastight syringe and extracted with 3.0 mL of ethyl acetate and 3.0 g of anhydrous Na_2SO_4 in a 8-mL septum-sealed headspace vial. The ethyl acetate extracts were then transferred into 2-mL GC vials and analyzed for fumigant concentrations by gas chromatography (GC). For each fumigant treatment, triplicates were performed.

The effect of ATS and DOM on the release of persistent soil fumigant residues was investigated by extracting the soils with 5 mM ATS solution or compost-water extract (1:10 w/w ratio, DOC 249.5 mg L^{-1}, pH 7.4, EC 1.0 dS m^{-1}) instead of deionized water using procedures described above.

After extraction, soils were removed from the headspace vials and air-dried for 48 h. Residues of fumigants remaining in the extracted soils were determined using the method described in Guo et al. (*7*). Briefly, aliquots (8 g) of the soils were weighed into 20-mL headspace vials, and 8 mL of acetonitrile plus 1 g of anhydrous Na_2SO_4 were added to each vial. The vials were sealed with rubber septa and extracted at 80 °C for 24 h.

Column Experiments. Soil columns were prepared by packing the fumigated soils into duplicate 1.4 cm i.d. × 10 cm length stainless steel columns. A total of 22.0 g (oven dry mass) of soil were packed in each column to give a bulk density of 1.38 g cm^{-3}. The pore volume of the soil columns was 7.8 cm^3. Both ends of the columns were capped with screw caps cushioned with porous polyethylene sheet (pore size 15−45 μm) to maintain the column shape. A stainless steel needle (1 mm i.d. × 6 cm length) was centered on the bottom cap to collect column effluent, and an acrylic tube (6 mm i.d. × 3 cm length) was installed on the top cap for water-loading purposes. Water (5 mM $CaCl_2$), 5 mM ATS solution (freshly made and changed daily), or compost-water extract was loaded to the column top at 0.05 mL min^{-1} using a peristaltic pump. The use of dilute $CaCl_2$ solution instead of deionized water was to reduce soil aggregate dispersion that may decrease the column flux. Batch extraction tests with these two solutions showed no differences in the release of persistent soil fumigant residues. A 1-cm constant water head was maintained on the column top by simultaneously pumping back any excess loading through a stainless steel needle installed on the side of the acrylic tube, resulting in a natural percolation of water through the columns merely by gravity. No pump pressure was exerted on the columns to promote the influent movement, and the effluent flux under the described conditions was 0.72 ± 0.11 cm h^{-1} (1.1 ± 0.17 mL h^{-1}). At a constant hydraulic head of 17 cm (1 cm pressure head and 16 cm gravity head), the saturated hydraulic conductivity (K_s) of the columns was 0.42 ± 0.06 cm hr^{-1}, and the saturated soil moisture content was 35.5 ± 0.8%. Effluents were collected at 7-mL increments in headspace vials sealed with aluminum caps and rubber septa, to a total of 10 pore volumes. Approximately 7 h were required to collect 1 pore volume of effluent. Extra fine (25 G) stainless steel needles were installed piercing through the septa to prevent air pressure from building up in the vials while minimizing fumigant emission losses. The fumigant recovery of this effluent collection method was >95%.

Fumigants in the effluents were extracted with ethyl acetate using procedures described above and analyzed by GC. At the end of the experiments, soil from the columns was air-dried and extracted with acetonitrile at 80 °C for 24 h to determine the remaining fumigant residues.

Chemical Analysis. Concentrations of fumigants in the samples were analyzed with an HP 6890 GC system (Hewlett-Packard, Avondale, PA) equipped with an electron capture detector (ECD, for 1,3-D and CP), a nitrogen phosphorus detector (NPD, for MITC), and an DB-VRX capillary column (30 m long × 0.25 mm i.d. × 1.4 μm film thickness, J&W Scientific, Folsom, CA). The carrier gas (He) flow rate was 1.4 mL min^{-1}. The oven temperature program was set as follows: held initially at 45 °C for 2 min; increasing at 2.5 °C min^{-1} to 76 °C and held for 0.3 min; then increasing at 35 °C min^{-1} to 120 °C and held for 1 min. Retention times for *cis*-1,3-D, *trans*-1,3-D, CP, and MITC were 11.5, 12.8, 14.2, and 11.6 min, respectively. The measured concentrations of MITC showed little signal on the ECD (also no signal of *cis*-1,3-D on NPD) so overlapping retention time windows did not interfere with accurate quantification.

Results and Discussion

Persistent Fumigant Residues in Soil. After 48 h of evaporation and more than 45 d of storage in unsealed flasks, residues of 1,3-D, CP, and MITC in the incubated soils were determined as 5.61 ± 0.33, 11.38 ± 0.53, and 1.83 ± 0.09 mg kg^{-1}, respectively, by extracting the soils with acetonitrile at 80 °C for 24 h. No fumigants were detected in the control soil without chemical treatment. Evidently, a small portion (0.5−1.5%) of the applied fumigants persisted in soil, resistant to degradation and volatilization. The persistent fumigant residues were retained in soil intra-aggregate micropores (*7*). Under certain conditions water may percolate into the micropores and mobilize the fumigant residues, posing groundwater contamination risks.

Water Release of Persistent Soil Fumigant Residues. In water extracts of the incubated soils at a 5:4 solid/water (w/w) ratio, concentrations of 1,3-D, CP, and MITC were 1.02 ± 0.04, 2.10 ± 0.18, and 0.42 ± 0.03 mg L^{-1}, respectively.

TABLE 1. Contents of Persistent Fumigant Residues Released into Water and Remaining in Soil[a]

	mg kg^{-1} soil									
		water			DOM solution			ATS solution		
fumigants	initial content	extract released[b]	soil remained[c]	mass balance[d]	extract released[b]	soil remained[c]	mass balance[d]	extract released[b]	soil remained[c]	mass balance[d]
1,3-D	5.61 (0.33)	0.82 (0.03)	3.05 (0.07)	−1.74 (0.43)	0.80 (0.04)	3.24 (0.27)	−1.57 (0.64)	0.47 (0.01)	2.59 (0.04)	−2.55 (0.38)
CP	11.38 (0.53)	1.68 (0.15)	3.14 (0.16)	−6.56 (0.84)	1.42 (0.08)	3.49 (0.35)	−6.47 (0.96)	0.63 (0.01)	0.89 (0.11)	−9.86 (0.65)
MITC	1.83 (0.09)	0.34 (0.03)	1.30 (0.22)	−0.19 (0.34)	0.39 (0.01)	1.36 (0.08)	−0.08 (0.18)	0.49 (0.03)	1.30 (0.07)	−0.04 (0.19)

[a] Data in parentheses are standard deviations of triplicate measurements. [b] The portion of persistent soil fumigant residues equivalent to the quantity recovered in the extracts. Multiply values by 1.25 for a conversion to concentrations of fumigants in the extracts in mg L^{-1}. [c] The content of persistent fumigant residues remaining in soil after extraction. [d] The content of persistent fumigant residues lost in the extraction process.

Although CP in groundwater has not been regulated, the detected 1,3-D and MITC in the water extracts were several orders of magnitude higher than the drinking water threshold (0.2 μg L^{-1} (*5*)) and ecotoxicological risk level (0.1 μg L^{-1} (*3*)). Although the release of persistent fumigant residues was significant, fumigants detected in the water extracts accounted for only 18−23% of the overall residues (Table 1), with a large portion remaining in soil that may release into water with further extraction. Residual contents of 1,3-D, CP, and MITC in the soils after the single-step water extraction were 3.05 ± 0.07, 3.14 ± 0.16, and 1.30 ± 0.22 mg kg^{-1} (Table 1), respectively, equivalent to 54%, 28%, and 71% of the overall residues. Approximately 28% of 1,3-D, 54% of CP, and 10% of MITC residues were lost during the experimental process. Degradation of these chemicals in the 24 h water-extraction process was only partially responsible for the loss, since determined half-lives of 1,3-D, CP, and MITC in the soil−water slurries (1:1 w/w ratio) were 9.9, 7.6, and 18.8 d, respectively. The majority of the loss should occur in the 48 h air-drying process following the extraction. The wet-dry cycle had broken a portion of soil aggregates and retained fumigant residues evaporated.

The effect of DOM on the partitioning of persistent fumigant residues was tested by extracting the incubated soils with a compost leachate that contained 249.5 mg L^{-1} of DOC. The contents of 1,3-D and MITC in the DOM extracts were fairly similar to those in the water extraction, and CP was slightly lower (Table 1). The lower content of CP was a result of chemical reaction with DOM. When CP was spiked at 2 mg L^{-1} in sterilized DOM solution and deionized water, after 6 h of incubation, concentrations of the chemical remaining in the former was 32% lower than in the latter. In soils after the DOM and water extraction, remaining fumigant residues showed little differences (Table 1). Evidently, DOM did not facilitate the release of persistent fumigant residues from soil. The three fumigants have low soil K_{OC} values (<62 L kg^{-1} (*6*)), implying their affinities for DOM constituents are even lower. Thus, the presence of DOM did not significantly influence the release of persistent fumigant residues.

When 5 mM ATS solution was used to extract the incubated soil, measured concentrations of 1,3-D and CP in the aqueous phase were 0.59 ± 0.01 and 0.79 ± 0.01 mg L^{-1}, respectively, much lower than those in the water and DOM extracts, while the concentration of MITC was 0.61 ± 0.04 mg L^{-1}, slightly higher than in the other two extracts (Table 1). The lower concentrations of 1,3-D and CP were a result of chemical transformation of the two fumigants by ATS. Thiosulfate is a nucleophile and can react with halogenated pesticides via bimolecular nucleophilic substitutions. The ATS-enhanced degradation of fumigants has been well studied. In water, half-lives of 1,3-D and CP at 20 °C decreased from 292 to 19.7 h and from 2009 to 30.1 h, respectively, with the presence of ATS at 4:1 ATS/fumigant molar ratio. In a sandy loam soil, half-lives of the two chemicals dropped by a factor of ~5 with ATS amendment at 2:1 ATS/fumigant molar ratio (*12*). Consequently, remaining residues of the two fumigants in soil after ATS extraction were notably lower than in soils after water and DOM extraction (Table 1). The lower contents of 1,3-D and CP in the aqueous extracts and extracted soils indicated that application of ATS may be an effective method to eliminate persistent soil residues of halogenated pesticides.

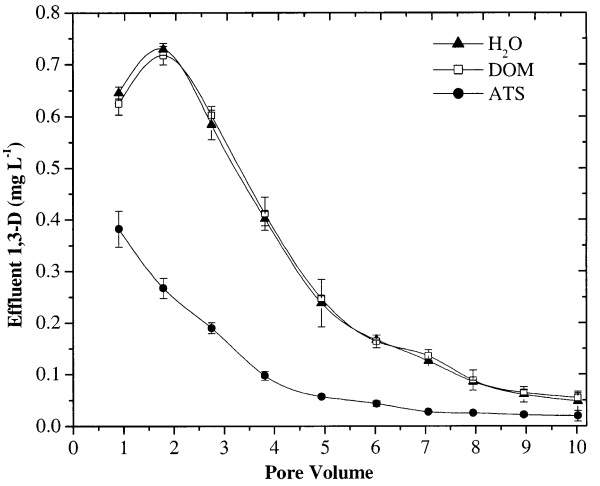

FIGURE 1. Concentrations of 1,3-dichloropropene (1,3-D) in effluents from soil columns leached with water, DOM, and ATS solution. Error bars represent standard deviations of duplicate measurements.

Leaching of Persistent 1,3-D Residues. Duplicate soil columns were leached with 5 mM $CaCl_2$, ATS solution, and DOM solution under 1-cm depth of water layer. The addition of $CaCl_2$ in deionized water was to minimize soil aggregate dispersion, and it did not affect the transport and degradation of fumigant residues. In effluents of water leaching, the concentration of 1,3-D increased as the leaching process progressed, maximized as 0.73 ± 0.01 mg L^{-1} at approximately 2 pore volumes, and then decreased gradually (Figure 1). There was apparently a lag (i.e. 1 pore volume) between the movement of the water-front and the dissolution of persistent fumigant residues that were entrapped in soil micropores, owing to a faster movement of water in inter-aggregate paths than in intra-aggregate pores (*13*). In general, leaching of persistent 1,3-D residues was significant. The cumulatively leached 1,3-D in 10 pore volumes was 1.17 ± 0.05 mg kg^{-1} soil (calculated by normalizing the sum of 1,3-D present in all effluents with the mass of soil in a column), accounting for 21% of the overall persistent residues in soil. Even after leaching 10 pore volumes of water, 1,3-D was still detectable in the effluents as 0.05 ± 0.02 mg L^{-1}, hundreds of times higher than the public health goal of 0.2 μg L^{-1} in drinking water (*5*). The residual 1,3-D in soil after water leaching was determined as 2.16 ± 0.07 mg kg^{-1}, 39% of the initial content. In field conditions with water percolating at a lower speed, continuous leaching of the persistent 1,3-D is expected. It

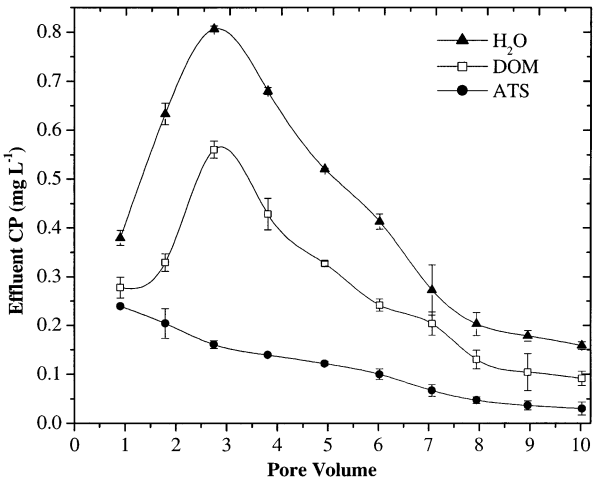

FIGURE 2. Concentrations of chloropicrin (CP) in effluents from soil columns leached with water, DOM, and ATS solution. Error bars represent standard deviations of duplicate measurements.

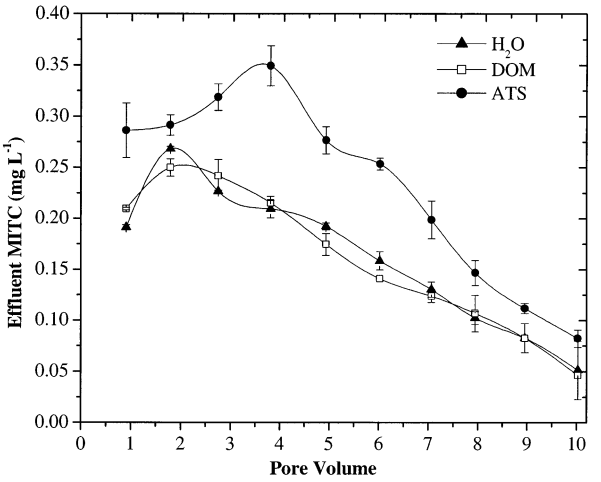

FIGURE 3. Concentrations of methyl isothiocyanate (MITC) in effluents from soil columns leached with water, DOM, and ATS solution. Error bars represent standard deviations of duplicate measurements.

may explain the detection of 1,3-D in groundwater, though the chemical hydrolyzes in water with a half-life of 10 d at 20 °C.

Leaching with the compost extract rather than water gave an identical concentration profile of 1,3-D in the effluents (Figure 1), demonstrating that DOM had little effect on transport and release of persistent 1,3-D residues in soil, in agreement with the results of batch extraction experiments (Table 1). Residual 1,3-D in the DOM-leached soil was 2.05 $\pm$ 0.13 mg kg^{-1}, close to that of water-leached soil (2.16 $\pm$ 0.07 mg kg^{-1}). Evidently, surface organic amendment will not facilitate 1,3-D residue leaching.

In effluents from columns leached with 5 mM ATS solution, concentrations of 1,3-D ranged from 0.02 to 0.38 mg L^{-1}, significantly lower than those in water and DOM effluents (Figure 1) because of rapid dehalogenation of 1,3-D by ATS. Different from water- and DOM-leaching, in which the effluent 1,3-D concentration peaked at ~2 pore volumes, the ATS-leaching gave the highest 1,3-D concentration in the initial effluents (Figure 1), suggesting the instability of early-loaded ATS in soil columns. Thiosulfate ($S_2O_3^{2-}$) is a reductive agent and can be oxidized rapidly to intermediates $S_4O_6^{2-}$ ($4S_2O_3^{2-} + O_2 + 2H_2O = 2S_4O_6^{2-} + 4OH^-$) and eventually to SO_4^{2-} ($2S_4O_6^{2-} + 4OH^- + O_2 = 4SO_4^{2-} + 4S + 2H_2O$) in soil (*14*). Air-dried soils employed in this study contained constituents such as O_2 and free metal oxides that could oxidize ATS to sulfate and sulfur (i.e. $2S_2O_3^{2-} + O_2 = 2SO_4^{2-} + 2S$). When the Hagerstown soil was added to 5 mM ATS solution at 1:1 (w/w) ratio, the concentration of $S_2O_3^{2-}$ decreased 40% in 2 h. Accompanying the $S_2O_3^{2-}$ decrease was the production of SO_4^{2-} (identified by IC techniques). A bright yellow color was noticed in the early effluents from ATS-leaching as extracted with ethyl acetate, indicating formation of sulfur at the beginning. Evidently, a large portion of the early-loaded ATS had been decomposed prior to its reaction with 1,3-D and thus resulting in the highest 1,3-D concentration in the initial effluent (Figure 1). Overall, ATS application remarkably decreased the content of 1,3-D in leachate and contaminated soil. The amount (equivalent to 0.37 mg kg^{-1} soil) of 1,3-D recovered in the ATS effluents was 32% of that from water leaching, and residual 1,3-D (1.37 $\pm$ 0.09 mg kg^{-1}) in soil after leaching was 63% of that remaining in water-leached soil. In practice, ATS solution with an appropriate concentration may be applied via irrigation to reduce soil 1,3-D residues if the water residence time is properly controlled.

Leaching Potential of Persistent CP Residues. The leaching pattern of persistent CP residues (Figure 2) from soil was comparable to that of 1,3-D (Figure 1). Concentrations of CP in the effluents resulting from water or DOM leaching increased initially, peaked at 3 pore volumes, and then decreased continuously, while in the ATS leaching it decreased gradually (Figure 2). Similar as in the batch experiments (Table 1), effluents from DOM-leaching had a lower CP concentration than that from water-leaching (Figure 2), a result of chemical transformation by certain DOM constituents. The concentration of CP in effluents from ATS-leaching ranged from 0.03 to 0.24 mg L^{-1}, significantly lower than that from water- and DOM-leaching, confirming the effectiveness of ATS in eliminating halogenated fumigant residues. Cumulative CP in the effluents from water-, DOM-, and ATS-leaching, on the soil mass basis, were 1.51 $\pm$ 0.06, 0.96 $\pm$ 0.07, and 0.40 $\pm$ 0.03 mg kg^{-1}, respectively, and the corresponding residual contents in the leached soils was 0.71 $\pm$ 0.08, 0.26 $\pm$ 0.01, and 0.04 $\pm$ 0.01 mg kg^{-1}. Approximately 80% of the overall CP residues (11.38 mg kg^{-1}) was lost during the water-leaching process, mainly due to microbial degradation. Chloropicrin is relatively stable in water but readily subject to microbial and organic degradation in soil. Half-lives of CP in most soils was <1 d (*6*). Despite the rapid degradation, the leaching of persistent CP residues was considerable. In field soils with less organic matter and decreased microbial activities at depth, leaching of CP to groundwater is of high potential. Contamination of groundwater by CP has been reported (*2*), and in the Holtrachem site in Maine, the concentration of CP in groundwater was 10−150 mg L^{-1}. It is noteworthy that nearly 100% of the persistent CP residues was removed from soil in the ATS treatment. Combined with the effect of ATS on 1,3-D leaching, it suggests that ATS amendment is an effective measure to eliminate persistent residues of halogenated pesticides. In fumigated fields, persistent fumigant residues mainly form at the application depth (e.g. 20 cm), and subsurface irrigation of dilute ATS solution is recommended for soil remediation.

Leaching Potential of Persistent MITC Residues. In effluents from water-leached and DOM-leached soil columns, concentrations of MITC ranged from 0.05 to 0.27 mg L^{-1} and followed a similar trend (Figure 3), strengthening our contention that DOM does not promote the release and transport of persistent fumigant residues in soil. The concentration of MITC in the effluents greatly exceeded its ecotoxicological critical level in water (0.1 μg L^{-1} (*3*)). Given its low soil K_{OC} value of 6 L kg^{-1} (*6*), MITC as persistent residues in field soils may leach to groundwater. In many states, MITC has been detected in groundwater (*1*−*3*). Cumulatively 0.57

± 0.03 mg kg^{-1} (equivalent to 31%) of the persistent MITC residues was recovered in the effluents, and 0.94 ± 0.03 mg kg^{-1} (~ 51%) remained in soil after leaching. Around 18% of the residues was lost during the leaching process, mostly due to microbial activities, which are the major degradation pathway of MITC in the environment. Gan et al. (*15*) found that the microbial contribution accounted for >80% of MITC degradation in a sandy loam, and >95% in a silt loam. The reported half-life of MITC at 20 °C in moist soils was 7 d (*6*).

Concentrations of MITC in effluents from ATS-leached columns increased initially from 0.28 ± 0.03 mg L^{-1} to 0.35 ± 0.02 mg L^{-1} at 4 pore volumes and decreased slowly to 0.08 ± 0.01 mg L^{-1} at 10 pore volumes (Figure 3). The concentration profile of MITC in effluents from ATS-leaching was distinctly different from those of 1,3-D (Figure 1) and CP (Figure 2) in similar treatments. This is because ATS is unreactive with MITC, and its instability in soil did not affect MITC leaching. Relative to water- and DOM-leaching, leaching with ATS solution resulted in higher concentrations of MITC in the effluents (Figure 3). Similar results were also obtained in batch extractions (Table 1). The higher concentration was not due to the "salt-out" effect but to inhibited microbial activities by ATS. When the soil was extracted simultaneously with deionized water, 5 mM $(NH_4)_2SO_4$, and 5 mM $(NH_4)_2S_2O_3$ for 24 h, concentrations of MITC in the former two solutions were comparable, both 18% lower than that in the third. Ammonium thiosulfate is a nitrification and urease inhibitor (*14*). The addition of ATS inhibited the activities of microorganisms that could use MITC as substrate, and less MITC released from the soil was degraded. As a result, the recovery of MITC in the ATS-leaching was 98% (45% present in effluents and 53% remained in the leached soil).

Results from this study demonstrate that leaching of persistent fumigant residues from soil is significant. The leaching process may last for a long time, depending on the amount of water passing through the soil profile. Dissolved organic matter has little influence on the mobility of persistent fumigant residues in soil, and it can decrease leaching of CP residues via chemical degradation. Amendment with ATS substantially decreased the content of 1,3-D and CP in leachate and treated soil. To protect groundwater resources, leaching of persistent fumigant residues should be considered.

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