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Phase partitioning, retention kinetics, and leaching of fumigant methyl iodide in agricultural soils

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ABSTRACT

Although it is not currently being sold in the USA, the recent US registration of the fumigant methyl iodide has led to an increased interest in its environmental fate and transport. Although some work has now considered its volatile emissions from soil, there remains a lack of experimental data regarding its ability to be retained in soil and ultimately become transported with irrigation/rain waters. Using laboratory batch and soil column experiments, we aimed to better understand the phase partitioning of MeI, the ability of soils to retain MeI on the solid phase, and the potential for leaching of MeI and its primary degradation product, iodide, down a soil profile. Results indicated that MeI was retained by the solid phase of soil, being protected from volatilization and degradation, particularly in the presence of elevated organic matter. Retention was greater at lower moisture content, and maximum retention occurred after 56 days of incubation. At higher moisture content, the liquid phase also became important in retaining MeI within soil. Together with low observed K_D values (0.10 to 0.57 mL g^{-1}), these data suggest that MeI may be prone to leaching. Indeed, in a steady-state soil column study, initially retained MeI was transported with interstitial water. The MeI degradation product, iodide, was also readily transported in this manner. The data highlight a potentially significant process by which MeI fate and transport within the environment may be impacted.

1. Introduction

The 2008 United States registration (USEPA, 2008) of methyl iodide (MeI, iodomethane, CH_3I) led to increasing interest in better understanding its potential for emission from soil to air (Luo et al., 2010; Ashworth et al., 2011; Luo et al., 2011). Despite the May 2012 decision by its manufacturer (Arysta Life Sciences) to stop selling MeI to the US market, its environmental fate and transport remains a research priority due to the potential for the manufacturer to recommence US sales of the product (under the existing registration), and its potential use in other countries. As a preplant soil fumigant, MeI was initially touted as a direct, non-ozone depleting, replacement for MeBr in the control of agricultural plant pests (Becker et al., 1998). However, concerns remain over the inhalation risk posed to agricultural workers and nearby populations during fumigation events. Indeed, as reported by Ashworth and Yates (2010), because of its toxicity the US registration of MeI proved to be controversial, particularly in California. Due to these concerns, regulations relating to the use of MeI and other soil fumigants exist, and aim to protect air quality. In addition to air quality concerns, some workers have highlighted the potential importance of residual MeI retained by soils which may be subject to leaching, e.g. during irrigation or rainfall (Gan et al., 1997; Guo et al., 2004).

In a recent paper (Ashworth et al., 2011), we reported that emissions of MeI from soil were very high (>80% of the total applied) if no mitigation strategy was employed. However, when the soil surface was covered with virtually impermeable film (VIF), emissions were reduced to <0.04%. Such dramatic reductions are the reason that USEPA regulations require the use of plastic film, typically high density polyethylene (HDPE), following MeI fumigation. In California, stricter regulations aim to better prevent MeI emissions from soil to air by specifying that the plastic film must be a VIF, and that it must cover the soil for 14 days following fumigation. During this time, MeI within the soil pore space is maintained at high concentrations (Gan et al., 1997; Ashworth et al., 2011) due to low emission loss and a relatively long degradation half-life of up to >40 days (Gan and Yates, 1996). Under such conditions, there is a potential for MeI to become physically or chemically associated with the soil solid phase (Guo et al., 2004), particularly in the presence of elevated organic matter content (Ashworth et al., 2011). Often, such a process is overlooked, or considered negligible, in relation to fumigant fate and transport but, importantly, these residues may be resistant to gaseous loss from the soil and, potentially, to degradation (Guo et al., 2004). Given the relatively high solubility of MeI (14 g L^{-1} at 20 °C) the residues may be prone to subsequent translocation with interstitial waters. In addition, soil degradation of

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MeI leads to the production of the iodide ion. In common with other biologically essential ions, iodide is considered a potential environmental contaminant at elevated concentrations and, due to its negative charge, is likely to be poorly sorbed to soil. Concerns over the risks of elevated concentrations of MeI (neurotoxicity and carcinogenicity in humans) and iodide (plant toxicity and inhibition of thyroid function in humans) suggest that the potential for soil fumigation to contribute to the MeI and iodide loading of soil water should be investigated.

Under field conditions with California regulations, MeI is maintained in the soil for 2 weeks by VIF covering which likely leads to very little MeI loss via gas phase emission (i.e. it can be approximated as a 'sealed' system). Following this time, the VIF must be ripped or removed to allow for 24 h venting of MeI gas before agricultural practices, such as planting and irrigation, can commence. Using these regulations as an example, we designed laboratory experiments that aimed to simulate such field conditions in terms of the contact time between MeI and soil and the time for venting of gas-phase MeI before agricultural use. The aim of the work was to gain an improved understanding of the solid–liquid–air phase partitioning of MeI in soil, the formation of MeI residues in soil, and to quantify the potential for leaching of MeI residues and the iodide produced during MeI degradation. The significance of soil organic matter in these processes was also given special consideration.

2. Materials and methods

2.1. Chemicals and soils

Methyl iodide standard (>99% purity) was obtained from Sigma Chemical Co. (St Louis, MO) and acetonitrile (HPLC grade) from Burdick and Jackson (Muskegon, MI). Soils (upper 15 cm) were collected from two fields on a farm near Buttonwillow, CA (thermic Typic Haplargids; Milham series). After collection, soils were sieved (<2 mm) and stored at 4 °C. Both were a sandy loam (around 60% sand, 30% silt, and 10% clay) of pH 7.8. The primary difference between the two soils was organic matter content since the farm owner had previously applied composted municipal green waste material to one of the fields (approximately 1 year before collection). Consequently, the organic matter content of this soil was increased from 2.09 to 3.16%. The soils are abbreviated here using the terms LOM (lower organic matter; essentially an untreated control) and HOM (higher organic matter). The degradation half life of MeI in the two soils was previously determined as 10.9 and 2.9 days for the LOM and HOM soils, respectively (Ashworth et al., 2011). A similar effect of organic matter on the half life of MeI was observed by Guo and Gao (2009).

2.2. Phase partitioning of MeI in soil

To determine phase partitioning of MeI in the soil, the method reported by Gan and Yates (1996) was used. In contrast to the slurry method for determining partitioning, this method allows partitioning at more realistic soil moisture contents during the equilibration. Here, we used both 2% (essentially air dry) and 10% gravimetric moisture contents, with the latter obtained by placing the soil in a plastic bag, spraying on the desired mass of deionized water, mixing well, leaving to equilibrate in the sealed bag overnight, and finally sieving to 2 mm. Triplicate 10 g samples of the moist HOM soil were weighed into 20 mL glass vials. A small volume (8 μL) of MeI solution was added to adjust the concentration of the soil to 37.0 μg g^{-1}. This concentration was similar to the theoretical average soil concentration for the upper 30 cm of soil (43.6 μg g^{-1}) when MeI is applied at the maximum US-permitted rate of 196 kg ha^{-1} (assuming 4500 Mg of soil in the upper 30 cm of 1 ha). Following application, the vials were sealed with a Teflon-faced septum, briefly shaken by hand, and placed at 25 °C for 24 h. After this time, a 100 μL subsample of headspace air was removed from each vial and injected into a GC vial containing 1 mL ethyl acetate. The measured headspace MeI concentration (C_A) was used in conjunction with the published Henry's constant (K_H) for MeI at 20 °C of 0.21 (Gan and Yates, 1996) to calculate the MeI concentration in the liquid phase (C_L). Using these concentrations and the volumes of the air and water phases within the vial, the amount of MeI within each phase was calculated. The amount of MeI in the soil solid phase was then determined by difference between the amount added and the combined amount in the air and liquid phases. The amount of MeI associated with the solid phase was corrected for degradation during the 24 h equilibration period using the previously determined degradation half life (Ashworth et al., 2011). Using the volume of the soil solid phase, the amount of MeI was converted to a concentration (C_S). Finally, K_D value was determined for the soil-containing vials according to Eq. (1).

$$K_D = C_S/C_L \quad (1)$$

Where: K_D is the distribution (partition) coefficient, mL g^{-1}; C_S is the solid phase MeI concentration, μg g^{-1}; and C_L is the liquid phase MeI concentration, μg mL^{-1}.

2.3. Retention kinetics study

To determine the kinetics of MeI retention on soils, a batch incubation study using the LOM and HOM soils was performed. Triplicate, 10 g samples of soil (2% gravimetric moisture content) were weighed into 20 mL glass vials and approximately 1000 μg MeI added, equivalent to 100 μg g^{-1} (a relatively high MeI concentration was used here to ensure that the, potentially small, level of MeI retention could be readily measured). Each vial was immediately sealed after MeI addition and, after brief shaking by hand, placed at a constant 25 °C. After 1 day, and 1, 2, 4, 8 and 20 weeks, soils were removed from the vials, thinly spread onto individual aluminum foil trays and allowed to vent in a fume hood for 24 h. After this time, soils were placed back into their original vial, and extracted, as described below, with either hot acetonitrile (total residual MeI content) or deionized water (water soluble MeI content).

2.4. Role of soil organic matter in MeI retention

To elucidate the potential role of soil organic matter in MeI retention by soil, a further batch incubation study was carried out. Initially, organic matter in samples of the HOM soil was removed by ignition at 375 °C overnight (Rowell, 1994). Triplicate, 10 g samples of this soil were then weighed into 20 mL glass vials and approximately 1000 μg MeI added to yield a concentration of 100 μg g−1. In addition, triplicate samples were established in the same way using the non-ignited, HOM soil (air dry). After immediate capping, all samples were incubated for 24 h at 25 °C before soils were removed from the vials, thinly spread onto individual aluminum foil trays and allowed to vent in a fume hood for 24 h. After this time, soils were placed back into their original vial, and the total residual MeI extracted using hot acetonitrile extraction (as described below).

2.5. Leaching studies

To determine the potential for soil-retained MeI to become subsequently transported with leachate water, a small scale steady-state column study was undertaken. In glass bottles, HOM soil (2% gravimetric moisture content) was treated with MeI at a rate of 100 μg g^{-1}, sealed with a teflon-faced cap, and incubated at 25 °C for 14 days. After this time, the soil was placed on a foil tray, spread to form a thin layer, and placed in a fume hood for 24 h to allow venting of gas phase MeI. Periodically, the soil was stirred to enhance this process. After this time, hot acetonitrile extraction of sub-samples of the soil (see below) was performed to determine the concentration of residual MeI retained

on the soil. Similarly, water extraction of sub-samples of the soil (see below) was performed to determine the initial iodide and chloride concentrations of the soil. The remaining soil was packed into a 70 mL graduated glass column (dimensions of 2.8 cm diameter × 11 cm length). The glass column had an outlet in the center of its base which was first covered by a disk of stainless steel gauze and then a layer of glass wool to prevent the outflow of soil particles during leaching. The soil was then packed onto the glass wool in 10 mL increments, to produce a soil column with a uniform dry bulk density of 1.47 g cm^{-3}. A disk of coarse filter paper was placed on the soil surface to aid the spreading of added leaching water. Deionized water was dripped onto the filter paper at a rate of 0.3 mL min^{-1}, and leachate collected at the base of the column in twelve, approximately 5 mL, fractions. As such, once wetted, the soil was leached at field capacity (steady state) and the effective pore volume of the soil column was calculated based on the mass of water within the column during the leaching process (i.e., 23 mL). Immediately after collection, a leachate fraction was weighed to determine the exact volume, and aliquots taken for determination of MeI, iodide and chloride concentrations. For the determination of MeI, 0.5 mL of the leachate was extracted by shaking for 1 h with 3 mL hexane. Supernatant solvent was removed to a GC vial for analysis of MeI. The efficiency of this extraction was determined in preliminary experiments as 90.6% and sample concentrations were adjusted to account for this. Concentrations of the conservative ion chloride were determined in the leachate to allow comparison of MeI movement with the movement of water.

2.6. Hot acetonitrile extraction

To determine the total concentration of MeI in soil samples, the method of Guo et al. (2003) was employed. According to Guo et al., this procedure was more effective in extracting fumigant residues than comparable procedures. To 10 g samples of soil weighed into 20 mL glass vials, 1 g anhydrous sodium sulfate and 10 mL acetonitrile were added before immediate capping with a Teflon-faced cap. MeI was then extracted from the soil by placing the vials in an oven at 80 °C. After 0, 3, 5 and 20 h of the extraction, samples were mixed for 1 min using a vortex mixer. At 24 h, the samples were allowed to cool and settle before a sample of supernatant was removed into a GC vial for MeI analysis. Extractions were performed in triplicate. This procedure was determined in preliminary experiments to extract 81.4% of the total MeI present in the soil, and therefore sample concentrations were adjusted to reflect this.

2.7. Water extraction

The water extraction of chemicals from soils is considered to be a useful measure of the fraction of the chemical available for processes such as leaching and plant uptake. To determine the water-extractable fraction of MeI in the soil, 10 g samples of soil were weighed into 20 mL glass vials and 10 mL deionized water was added. After immediate capping with a Teflon-faced cap, the samples were shaken for 1 h and then centrifuged for 10 min at 1000 g. A 0.5 mL sample of supernatant water was removed into a 10 mL glass vial containing 3 g anhydrous sodium sulfate and 3 mL ethyl acetate, and immediately sealed with a Teflon-faced cap. The MeI was then extracted into the solvent phase by shaking for 1 h. The resulting solvent supernatant was then placed into a GC vial for MeI analysis. Extractions were performed in triplicate. The extraction efficiency of this procedure was determined in preliminary experiments as 79.8%, and sample concentrations were adjusted to account for this efficiency.

2.8. Analysis

Iodide and chloride concentrations were determined using anion chromatography. For this, a Metrohm 861 Advanced Compact IC was used in conjunction with a Dionex AS5 column and the eluant 100 mM H_2SO_4. Under these conditions, the retention time for chloride was 2.44 min and for iodide was 7.89 min. Standards for each ion were prepared in deionized water and encompassed the range of concentrations observed in the samples. Methyl iodide concentrations of the solvent extracts were analyzed using a Hewlett Packard 7890A Gas Chromatograph (Agilent Technologies) equipped with a micro-electron capture detector. The capillary column measured 30.0 m × 0.25 mm × 1.4 μm (Agilent Technologies) running at a flow rate of 1.0 mL min^{-1} and using He as the carrier gas. The oven temperature was fixed at 60 °C, the inlet temperature at 240 °C and the detector temperature at 290 °C. Under these conditions, the MeI retention time was around 3.8 min, depending on solvent. Standards were prepared in the same solvent as the samples and encompassed the range of sample values.

3. Results and discussion

3.1. Phase partitioning of MeI in soil

The equilibrium phase distribution of MeI in the HOM soil at 2 and 10% moisture contents is shown in Fig. 1. At both moisture contents, the partitioning was dominated by the air phase (60–70% of the added MeI) reflecting the relatively high K_H value of MeI. In the liquid phase, the greater volume of water at 10% moisture content led to significantly greater (around 5.6 times) partitioning than was observed at 2% moisture content; presumably due to the greater volume of water acting as a solvent for the MeI vapor (Peterson et al., 1995). Inversely related to this, was partitioning to the solid phase which was much greater (around 2.9 times) at 2% than at 10% moisture content. Previous work has noted the role of soil moisture content in the retention of organic vapors on soils. It is considered that at increased moisture contents, water vapor competes with the organic vapor for retention sites on the soil solids; thereby limiting retention of the organic vapor (Ong and Lion, 1991). Since calculation of the liquid and solid phase MeI concentrations was based on measured air concentration and a literature K_H value of 0.21, the accuracy of this previously reported K_H value is of some significance. Therefore, it should be noted that this K_H value was based on MeI partitioning between pure water and air (Gan and Yates, 1996) and, as reported by Breiter et al. (1998), K_H values may increase in experimental systems containing soil solution, rather than pure water, possibly due to interactions with dissolved salts and organic matter. If this holds true for MeI in our system, using a K_H of 0.21 would result in partitioning to the liquid phase being overestimated, and partitioning to the solid phase being proportionally underestimated. Nevertheless, we believe that our simplified approach offers a useful estimation of MeI partitioning behavior.

The solid and liquid phase MeI concentrations determined from the phase partitioning study were used to calculate K_D values at the two moisture levels. These were 0.57 and 0.10 g mL^{-1} at 2 and 10%

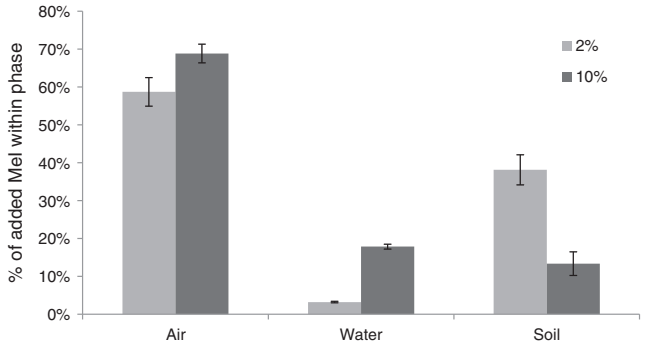

Fig. 1. Average (n = 3) and standard deviation of percentage distribution of MeI within soil (HOM) phases at 2 and 10% gravimetric moisture contents.

moisture contents, respectively. These values compare well to the MeI K_D values found for a range of soils by Gan and Yates (1996), i.e., from 0.08 to 0.46 mL g^{-1}. Compared to many soil contaminants (e.g. heavy metals) these values are low, indicating a small, but significant, degree of retention by the soil solids, and a large potential for MeI transport in the liquid phase. By conducting this experiment at 2 and 10% soil moisture contents, we aimed to encompass the range of relatively low values that might be typical of a fumigated soil under field conditions. Nevertheless, soil moisture can be extremely heterogeneous in such soils and, for example under conditions of drip irrigation/chemigation, much higher moisture levels may occur. The observed relationship between soil moisture content and solid–liquid partitioning suggests that with these higher moisture conditions, even lower K_D values (greater potential for partitioning into liquid phase) would be likely.

3.2. Retention kinetics study

The time-course concentrations of retained MeI for the LOM and HOM soils following 24 h venting are shown in Fig. 2. Because the phase partitioning experiment indicated that MeI retention was greater at low soil moisture content, we consider the use of 2% moisture content here to represent the upper end of the retention potential spectrum when considered in relation to the range of soil moisture contents that might be expected under field conditions (i.e. >2% moisture content). On the other hand, much research has demonstrated that in very dry soils (ranging from oven dry to air dry) solid phase retention increases by several orders of magnitude (Ong and Lion, 1991; Peterson et al., 1995); suggesting that if such conditions existed in the field (e.g. in surface soil during very hot, dry weather conditions), greater retention than we observed could be possible.

Although the two soils exhibited a very similar trend in MeI retention over time, the data strongly suggest that the additional organic material in the HOM soil was highly significant in facilitating MeI retention. Concentrations in the HOM soil were around two orders of magnitude greater than for the LOM soil (note use of double y axes in Fig. 2). Moreover, it is worth noting that the retained MeI concentration on the HOM soil at 140 days, despite having decreased significantly, was still an order of magnitude greater than the maximum concentration (Day 56) observed on the LOM soil. When the retained amounts of MeI are expressed in relation to the theoretical amount of MeI present in the system at a given time point (calculated based on degradation of the initial amount added), retention significantly increased with time (Fig. 3), indicating a strong time dependency for this interaction. Interestingly, at the later time points (≥28 days) in the HOM soil, the retained MeI amount was greater (and at the last time point dramatically greater)

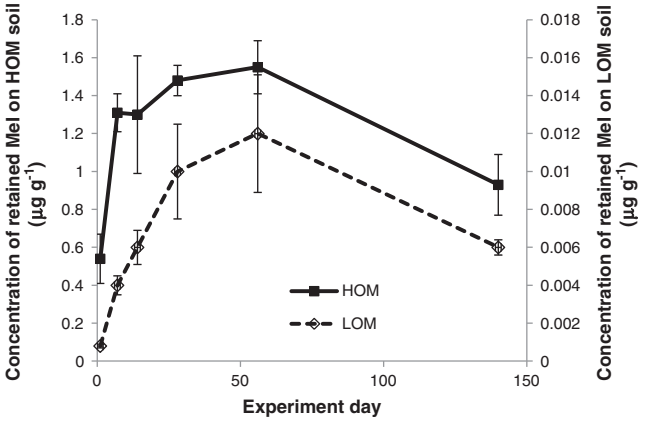

Fig. 2. Average (n = 3) and standard deviation concentrations of retained MeI on the HOM and LOM soils. Note use of double y axes and their two orders of magnitude difference.

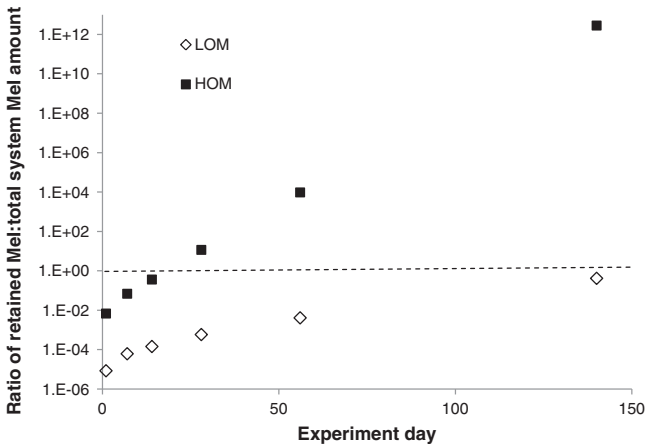

Fig. 3. Ratio of retained MeI:total amount theoretically present in the system (i.e. corrected for degradation) at each sample time. Values above the horizontal dashed line (ratio = 1:1) indicate that a greater amount was retained than was theoretically present, i.e. this MeI was protected from degradation. Note log y-axis.

than the theoretical determination of the total system amount. This indicates that the retained MeI was likely protected from degradation and the fact that this occurred only in the HOM soil suggests that the additional organic matter was responsible for this protection.

Given that the retained fraction of MeI was potentially resistant to both degradation and volatilization (i.e. was not lost during the venting period), an important consideration in relation to its fate and transport, is whether it has the potential to partition from the solid phase into the liquid phase. For the HOM soil, Fig. 4 shows the water extractability of the retained MeI. Peak MeI concentration of the water-extractable phase occurred on Day 7 and thereafter declined to non-detectable levels at Day 140. When considered as a percentage of the measured amount of MeI retained on the soil at each time point, the data demonstrate that water extractability decreased considerably over time, from 98% extractable at Day 1 to 0% at Day 140 (Fig. 4). This finding, in concurrence with the data presented in Fig. 3, suggests that the MeI became more strongly retained by the solid soil phase (i.e. decreasing environmental significance) over time.

3.3. Role of soil organic matter in MeI retention

Large differences in the ability of the LOM and HOM soils to retain MeI were observed (Fig. 2). To better understand the potential role of soil organic material in MeI retention, the HOM soil was subjected to removal of the organic material by ignition. With the organic material removed, retention of MeI after 1 day of incubation was dramatically reduced (almost 80 times) from 0.54 (±0.13) µg g^{-1} to 0.007 (±0.001) µg g^{-1}. This observation provides strong evidence for the

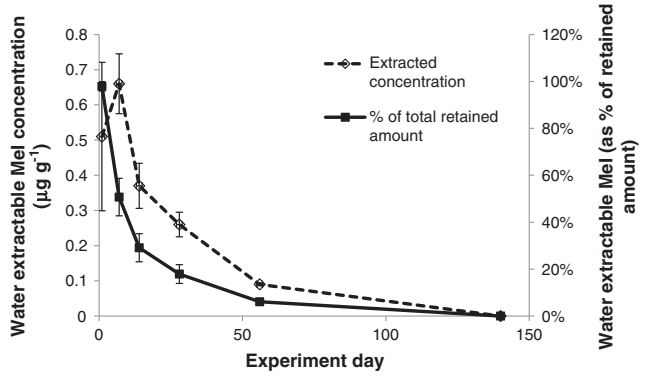

Fig. 4. Average (n = 3) and standard deviation water extractability of MeI retained on the HOM soil, expressed as both a concentration and as a percentage.

significant role of organic matter in MeI retention. Taking into account the relatively small difference in organic matter content of the LOM and HOM soils (2.09% compared to 3.16%, respectively), the retention result highlights that it was the organic material added to the HOM soil 1 year prior to soil collection that was significant in retaining MeI; probably via adsorption phenomena that have been previously observed for the fumigant 1,3-dichloropropene (Kim et al., 2003; Park et al., 2004). In contrast, the LOM soil, containing only native organic material, was highly ineffective at retaining MeI (0.0008 ± 0.0001 μg g^{-1} at Day 1; Fig. 2).

3.4. Leaching study

Its retention on the solid phase of the organically-amended soil during fumigation leads to the potential for liquid phase migration of MeI during irrigation or rainfall events. The low K_D values observed for MeI, particularly at high moisture content, suggest that leaching may be an important pathway in MeI fate and transport. Although soil fumigants are often not generally considered to be serious threats to ground water contamination, ethylene dibromide and 1,2-dibromo-3-chloropropane were banned in the United States during the early 1980s due to ground water contamination (Kloos, 1996). Years after the latter was no longer used, contaminated groundwater remained a problem in CA (Loague and Abrams, 1999) and has led to lawsuits against the manufacturer (Curtis and Profeta, 1993). Ground water contamination by 1,3-dichloropropene has also been a concern in Florida and other areas with sandy soil and shallow aquifers (e.g. Wisconsin) (USEPA, 1998).

Leaching the HOM soil (pre-contaminated with MeI) with deionized water resulted in the MeI leachate concentration profiles shown in Fig. 5. Also shown is the leachate concentration profile for iodide and the soil-conservative ion, chloride. For all analytes, concentrations were greatest in the initial leachate fraction and thereafter decreased over time, although the MeI curve showed extensive tailing that was absent for the anions. As would be expected for a solute with zero retardation, essentially all the chloride initially present within the soil column (based on extracted concentration) was leached from the column by 1 pore volume (110% recovery). Iodide showed strikingly similar behavior (105% recovery within 1 pore volume) indicating that it, too, was essentially conservative in this soil and would therefore possess a significant propensity for solute phase transport (leaching) and plant uptake. Because, in the absence of MeI addition, no iodide was detected in the HOM soil, all of the iodide leached from the soil column could be attributed to degradation of MeI during the incubation.

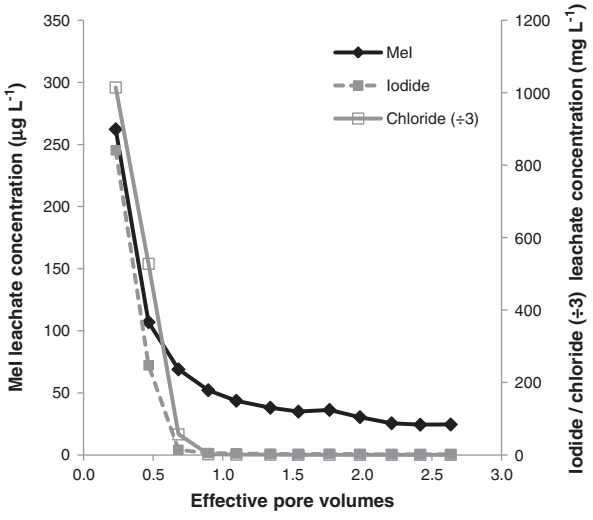

Fig. 5. Average (n = 2) HOM soil leaching profiles of MeI (primary y-axis), chloride (concentrations divided by three), and iodide (both on secondary y-axis).

Maximum concentration of iodide (around 840 mg L^{-1}) in the column leachate is very high (several orders of magnitude higher) when considered in relation to typical environmental levels. The World Health Organization (WHO, 2009) reported typical iodine concentrations of rainwater as ranging between 0.1 and 15 μg L^{-1}, depending on proximity to the ocean. Similarly, they reported surface water iodine concentrations of between 0.1 and 18 μg L^{-1}. In groundwater, the iodide concentration has been reported as around 1 μg L^{-1} (ATSDR, 2004).

The similarity in the nature of the MeI and chloride curves over the initial period indicates that MeI was also readily transported through the soil column with the movement of water. Although at one pore volume MeI was still present in the leachate (in contrast to chloride), the slope of the elution curve markedly decreased at this time, to produce the subsequent tailing. The extended tailing in MeI elution can be attributed to its interaction with the soil solid phase, which served to retard its movement through the column. Although the leaching experiment was ended after around 2.6 pore volumes, the shape of the curve suggests that significant tailing would have continued beyond this time. Guo et al. (2004) studied the potential for MeI leaching following application to large soil columns. These workers found a similar trend in MeI leaching, with initially high concentrations decreasing over time to produce extended tailing. Using an initial application rate to the column which was equivalent to 200 kg ha^{-1}, they reported peak, initial, MeI leachate concentrations of around 10 and 15 μg L^{-1} for drip and shank applications, respectively. Notwithstanding the fact that our columns were around one-sixth the length of those of Guo et al., our initial application rate was comparable, equivalent to 160 kg ha^{-1}, yet we recorded leachate concentrations around 20 times greater (up to 260 μg L^{-1}). We attribute this difference to the effect of the organic material in the soil we used for our experiments. As seen in the batch studies described above, this organic material had a significant impact, when compared to the non-amended LOM soil, in terms of retaining MeI that was subsequently leached.

The total mass of MeI leached from the column averaged 3.75 μg (± 0.31 μg). This equates to 0.038% of the total (acetonitrile extractable) amount of MeI initially added to the soil (i.e., present in the soil prior to incubation and venting). Compared to the mass of MeI in the soil when it was packed into the column (i.e. after venting), the leached mass represents 9.5% (± 1.2%) of the total (acetonitrile extractable) mass, and 25.6% (± 3.3%) of the water extractable amount. Analysis of the soil after the leaching experiment revealed that only non-detectable levels of MeI remained. Therefore, the mass balance indicates that a large proportion of the soil-retained MeI was lost by another route during the leaching process. Due to the relatively short duration of the leaching experiment (3–4 h), degradation of the MeI can be considered negligible and discounted. It seems most plausible that, although initially retained on the relatively dry soil, this MeI became subject to volatilization upon wetting of the soil and was lost via gas phase emission during the leaching process. This seems reasonable given that the K_D value within the relatively wet soil columns (final gravimetric soil moisture content of 24.3%) was very likely even lower than the values observed in the batch study (ranging from 0.10 to 0.57 mL g^{-1}); thereby effectively partitioning MeI into the liquid phase. From there, the relatively high K_H for MeI likely facilitated significant partitioning into the gas phase.

4. Conclusions

These experiments have demonstrated the potential for gas-phase MeI to become retained by the solid phase of soil following fumigation. In particular, the role of organic material in the soil, e.g. via the addition of composted green waste, significantly enhanced the potential for retention, most likely via physical or chemical adsorption. Retention apparently protected the MeI from volatilization and degradation. Low K_D values, coupled with a high degree of water extractability (especially at short time periods after fumigant application), indicated that MeI

could partition significantly into the liquid phase. Under field conditions, in the period immediately following fumigation, soils are typically irrigated extensively to facilitate growth of newly planted crops. The presence of MeI residues within the soil at this time may therefore lead to removal of MeI from the solid phase to the liquid phase. The presented data support such a hypothesis, perhaps suggesting a relatively weak interaction (i.e. physical, rather than chemical, adsorption) between the retained MeI and the soil surface. For example, the leaching studies indicated that when pre-contaminated soil was leached with water, relatively high concentrations of MeI and iodide ion were observed in the leachate water. Both analytes appeared to show a similar leaching trend to the soil-conservative ion chloride, indicating a potential for significant soil transport and/or plant uptake in the liquid phase. Use of highly impermeable films to cover/seal soil post-fumigation, although likely to reduce atmospheric emissions, may therefore significantly impact the sub-surface fate and transport of MeI. Overall, the data suggest that the potential for MeI and iodide contamination of surface and groundwater requires additional research consideration, including under field conditions. In particular, soil amended with organic materials, or with native organic material of a quality that engenders a propensity for retention of gas phase MeI, requires special consideration.

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References

Ashworth DJ, Yates SR. Methyl iodide. In: Krieger R, editor. Hayes' handbook of pesticide toxicology. Elsevier; 2010. p. 2307–17.
Ashworth DJ, Luo L, Xuan R, Yates SR. Irrigation, organic matter addition and tarping as methods of reducing emissions of methyl iodide from agricultural soils. Environ Sci Technol 2011;45:1384–90.
ATSDR Agency for Toxic Substances and Disease Registry. Toxicological profile for iodine. Atlanta: United States Department of Health and Human Services; 2004.
Becker JO, Ohr HD, Grech NM, McGiffen ME, Sims JJ. Evaluation of methyl iodide as a soil fumigant in container and small field plot studies. Pestic Sci 1998;52:58–62.
Breiter WA, Baker JM, Koskinen WC. Direct measurement of Henry's constant for S-Ethyl N, N-Di-*n*-propylthiocarbamate. J Agric Food Chem 1998;46:1624–9.
Curtis J, Profeta T. After silent spring: the unsolved problems of pesticide use in the United States. National Resources Defense Council; 1993.
Gan J, Yates SR. Degradation and phase partition of methyl iodide in soil. J Agric Food Chem 1996;44:4001–8.
Gan J, Yates SR, Ohr HD, Sims JJ. Volatilization and distribution of methyl iodide and methyl bromide after subsoil application. J Environ Qual 1997;26:1107–15.
Guo M, Gao S. Degradation of methyl iodide in soil: effects of environmental factors. J Environ Qual 2009;38:513–9.
Guo M, Papiernik SK, Zheng W, Yates SR. Formation and extraction of persistent fumigant residues in soils. Environ Sci Technol 2003;37:1844–9.
Guo M, Zheng W, Papiernik SK, Yates SR. Distribution and leaching of methyl iodide in soil following emulated shank and drip application. J Environ Qual 2004;33:2149–56.
Kim JH, Gan J, Farmer WJ, Yates SR, Papiernik SK, Dungan RS. Organic matter effects of phase partition of 1,3-dichloropropene in soil. J Agric Food Chem 2003;51:165–9.
Kloos H. 1,2-Dibromo-3-chloropropane (DBCP) and ethylene dibromide (EDB) in well water in the Fresno/Clovis metropolitan area, California. Arch Environ Health 1996;51:291–9.
Loague K, Abrams RH. DBCP contaminated ground water: hot spots and nonpoint sources. J Environ Qual 1999;28:429–46.
Luo L, Ashworth DJ, Dungan RS, Xuan R, Yates SR. Transport and fate of methyl iodide and its pest control in soils. Environ Sci Technol 2010;44:6275–80.
Luo L, Yates SR, Ashworth DJ. Predicting methyl iodide emission, soil concentration, and pest control in a two-dimensional chamber system. J Environ Qual 2011;40:109–17.
Ong SK, Lion LW. Effects of soil properties and moisture on the sorption of trichloroethylene vapor. Water Res 1991;25:29–36.
Park MK, Kim JH, Dungan RS. Sorption of the fumigant 1,3-dichloropropene on soil. J Environ Sci Health B 2004;B39:603–12.
Peterson LW, Moldrup P, El-Farhan YH, Jacobsen OH, Yamaguchi T, Rolsten DE. The effect of moisture and soil texture on the adsorption of organic vapors. J Environ Qual 1995;24:752–9.
Rowell DL. Soil science: methods and applications. Harlow: Longman; 1994.
USEPA. R.E.D. Facts. 1,3-Dichloropropene. Available at http://www.epa.gov/oppsrrd1/REDs/factsheets/0328fact.pdf1998. (Dec, 1998), Accessed Apr 10, 2012.
USEPA. Time-limited registration of iodomethane (methyl iodide). Available at http://www.epa.gov/pesticides/factsheets/iodomethane_fs.htm2008. (Oct 9, 2008), Accessed Jan 6, 2009.
WHO World Health Organization. Iodine and inorganic iodides: human health aspects. Geneva: WHO Press; 2009.