Impact of soil texture and organic matter content on mitc volatilization from soil columns

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Abstract
Metam sodium (MS; sodium N-methyl dithiocarbamate) has emerged as one of the most promising soil fumigants in the US to replace methyl bromide (MeBr). Metam potassium (MK; potassium N-methyl dithiocarbamate) and MS break down into the volatile gas methyl isothiocyanate (MITC) to control soil borne pests. While many studies have focused on MS, MK has not been studied as thoroughly. The objective of this research was to determine the effect of increasing organic matter (OM) treatments (10.9, 17.0, and 32.6% OM) and soil texture (sandy and sandy clay loam) to minimize the off-gassing of MS and MK. Bench-scale soil column studies were performed to simulate organic matter treatments that may decrease the volatilization loss of MITC. Incorporation depth of OM simulated surface tillage (0-15cm) practices. Soil was packed in steel columns and MS or MK was applied at a depth of 15 cm and MITC volatilization was measured using gas chromatography/mass spectroscopy. Volatilization of MITC was found to behave similarly for both MS and MK with MITC movement impacted significantly by soil texture with MITC volatilization lower from a sandy clay loam than a sandy soil type. Surface tillage incorporation of OM did not significantly decrease MITC volatilization. These results suggest that soil texture is the dominant factor reducing the off-gassing of MITC and prolonging the contact time needed to effectively control soil borne pests.

Key Words
Metam sodium, Metam potassium, Methyl isothiocyanate, Methyl bromide alternatives.

Introduction
The phase out of MeBr in 2005 due to its contribution to ozone depletion (USEPA 2009) has increased the use of MS to control soil borne pests. However, inconsistencies in pest control from such alternative chemicals have made it difficult to replace MeBr as a soil fumigant.the. Furthermore, these alternatives are still highly volatile and lead to high concentrations of these chemicals off-gassing into the atmosphere. Increased efforts to reduce these emissions are needed in order to improve their efficacy and reduce chemical exposure. Since 2005, MS has emerged as the most widely used soil fumigant for the control of soil borne pests (Kiely *et al.* 2004). MS and MK degrade readily into the volatile gas MITC shortly after their injection into the soil (Leistra and Smelt 1974). MS and MK are applied in liquid form and through shank injection or chemigation practices.

Fumigant volatilization is inhibited by the rate of degradation of the chemical and by the transport within the soil. Fumigants are transported quickly throughout the soil by gas-phase diffusion. This gas-phase diffusion is dependent on the movement towards the soil surface and is affected by the soil bulk density and water content. Many chemical and biological factors can affect the degradation of MITC, however, temperature and organic amendments are thought to have the greatest impact (Gan *et al.* 1998, 1999). Historically, soil organic amendments have been used to control soil pathogens (Muller and Gooch 1982). While more recently, organic amendments have been used in conjunction with soil fumigants in order to control soil borne pests and potentially reduce fumigant emissions (Gan *et al.* 1998; Dungan *et al.* 2001, 2002; Gao *et al,* 2008). With the addition of organic matter to the soil, MITC degradation can be significantly increased thereby decreasing volatilization loss (Dungan *et al.* 2003; Gan *et al.* 1999). The purpose of this study was to better understand the impact of varying soil type and organic matter additions on MITC volatilization after MS and MK application in soil columns, similar to columns used by Zheng *et al.* 2006.

Methods

Experimental design

Two bench-scale studies were set up aimed at understanding different aspects of MITC fate under differing soil properties with varying treatments. The purpose of the first study was to analyze the MITC volatilization of MS and MK from a sandy soil and a sandy clay loam soil. The second study focused on the MITC volatilization from a sandy clay loam soil with varying organic matter amendment rates after MK application.

Soil preparation

Two soils were used; one, a sandy soil type containing 2.8% organic matter, 93.5% sand, 2.5 % clay and 4% silt, obtained from the upper 30 cm of a sandy alluviated outwash soil collected at Premont, Jim Wells County, TX, USA (longitude 27º20', latitude 98º10'). The other an Orelia sandy clay loam (fine-loamy, mixed, hyperthermic Typic Ochraqualf) containing 2.3% organic matter, 55% sand, 33% clay, and 12% silt obtained from the upper 30 cm of farmland in Kingsville, Kleberg County, TX, USA (longitude W 097º 53', latitude N 27º 33'). Both soils were air dried, sieved to 2-mm and moisture level adjusted to 8% by adding deionized water prior to packing soil into steel soil columns. Soil organic matter was obtained from Brownville, Texas yardwaste compost, screened to 2.0 mm, and autoclaved for sterilization.

Chemical application

In all studies MS (Vapam 42% MS [0.121 g MITC equivalent], Dow AgroSciences LLC, Indianapolis, IN) or MK (K-pam HL 54% MK) was injected at a depth of 15 cm from the soil surface to the center of each column at a rate of 356.8 kg Met-Na/ha in a total solution of distilled water (116.3 mL) to simulate a 1.125 cm water application event.

Soil column setup

Steel soil columns (similar to those used in studies done by Gan *et al.* 1999 and Zheng *et al.* 2006) were used to model gas flow through the soil profile. Columns were 60 cm high by 12.5 cm inside diameter with side sampling ports located at the 15, 25, 35, 45, and 55-cm depths. A headspace sampling chamber (4 cm high by 12.5 i.d.) was placed on top of the steel columns and sealed with airtight aluminum tape vacuum system was set up to measure the volatilization of MITC from the soil. Charcoal ORBO-32 filters (Supelco, Bellefonte, PA) were attached to a vacuum source set at 10 mm Hg that was pulling air from each of the 6 columns at an average of 1.5 mm Hg per column. Vacuum-side charcoal filters were used to trap any volatile chemical flowing out of the columns headspace chamber. On the inlet side of the column, another charcoal filter was attached to allow air to enter the column without allowing backflow loss of chemical out of the column. In the first study, 7.5 kg of sand and sandy clay loam at 8% moisture was packed in triplicate replicated steel columns (as mentioned above) to a bulk density of 1.36 kg m^{-3}. In the second study, 3 columns were set up at varying OM rates (10.9, 17.0, and 32.6% OM) and packed to a bulk density of 1.35, 1.30, and 1.17 kg/m^3, respectively. The columns had OM mixed homogeneously in the upper 15 cm depth of the soil column to simulate surface tillage of the incorporated OM.

Chemical analysis

For all studies, 500 µL air samples were extracted from the center of the columns from the side-ports and injected into the gas chromatograph after 6 hours. Analysis of MITC concentration within the soil-air phase was performed via direct on-column injection of samples taken directly from the soil columns side ports (Figure 1, pg 25). The gas chromatograph used was a SRI 8610C equipped with a flame ionization detector. It was equipped with an Rtx-624 wide bore capillary column (30m x 0.53mm x 3.0µm manufactured by Restek Corp., Bellefonte, PA.). Air samples were taken every 24 hours for a 7 day period. During this period ORBO-32 filters were changed every 4 hours during the day, and backup filters were attached to the vacuum source during the experiment and overnight for a period of 8 hours to ensure that no MITC was lost due to break through off the first filter. ORBO-32 charcoal filters used to collect MITC emissions were collected, end cap sealed and stored in the freezer at -20°C until extraction procedure was done. Methanol solvent was used to extract MITC off of the charcoal filters. Analysis of MITC from charcoal carbon filters and residual soil MITC levels was done using an Agilent 6890N gas chromatograph equipped with a 5973 Network mass selective detector (mass spectrometer). Methanol extraction efficiency was evaluated and found to be approximately 100%.

Statistical analysis

The first study was performed with three replicates per treatment and differences of the means between treatments were subjected to F tests and paired t-tests. All error bars shown are ± standard error of mean.

Results

Results from the first study indicate that volatilization loss of MITC occurred mostly within the first 72 hours after MS and MK injection and was highly dependent on soil texture (Figure 1). MS and MK behaved similarly with respect to MITC volatilization loss. Lower MITC volatilization from the sandy soil compared to the sandy clay loam was due to further downward movement of MITC in the sandy soil (Figure 1). Residual MITC was found at deeper depths in the sandy soil than in the sandy clay loam soil, providing further evidence that soil texture was a major contributing factor to MITC fumigant movement within the soil profile. Results from the second study with increasing OM resulted in equivalent volatilization loss in all 3 treatments (Figure 2). This occurred regardless of varying differences in soil bulk density or high OM incorporation ranging between 10.5-32.6% OM content. The results of this study indicate that MITC is not highly attracted to soil OM and incorporation of compost or another organic carbon source to try to mitigate MITC loss will most likely not be an effective means of reducing fumigant release to the atmosphere.

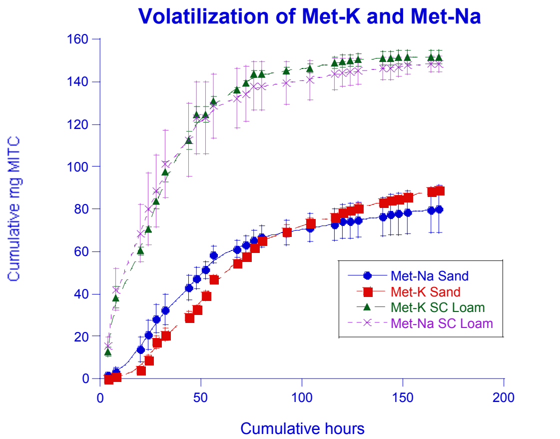

Figure 1. Cumulative volatilization of MITC by MS and MK in sandy soil vs. sandy clay loam.

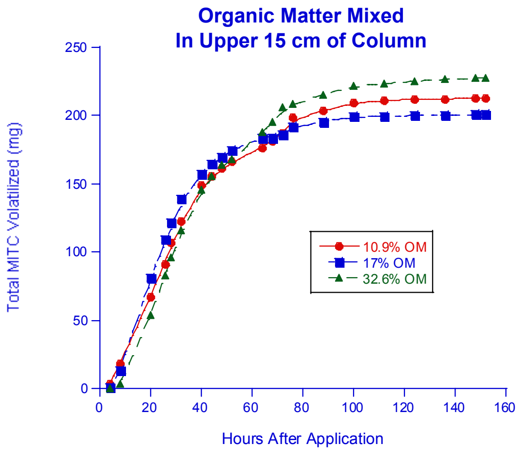

Figure 2. Total volatilization of MITC from sandy clay loam soil mixed with high organic matter content.

Conclusion

MITC emission into the atmosphere is highly dependent on soil texture, as sandier soils with larger pore space can lead to lower MITC volatilization as the fumigant penetrates deeper down in the soil profile, when compared finer textured soil with smaller pore space. Organic matter application to soils does not appear to be a productive method of suppressing MITC release from the soil as very high OM levels did not result in improved fumigant retention within the soil. The results of these column studies provide evidence that bench-scale laboratory studies can be performed prior to large and costly field scale studies. The results of this study if taken into consideration will allow researchers to focus on other factors besides OM additions at suppressing MITC fumigant release from the soil. Future studies that may possibly improve MS and MK application and its subsequent suppression of MITC volatilization may be enhanced using surface irrigation applications after chemical injection to provide a water seal to the soil surface. Similar column studies like these can be performed to evaluate at a relatively low cost in the laboratory setting if such ideas will work, prior to implementation at the on-farm level.

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