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Effect of films on dimethyl disulfide emissions, vertical distribution in soil and residues remaining after fumigation

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ABSTRACT

An improved understanding of the conditions that influence dimethyl disulfide (DMDS) emissions, distribution through the soil and residues remaining after treatment will help to optimise the use of this relatively new soil fumigant for the control of soil-borne pests and disease, and to improve the safety of DMDS use. Using soil columns in the laboratory, the cumulative emission of DMDS using doses of 40 and 80 $g\,m^{-2}$ were, respectively, 74.8% and 68.9% with bare soil, 4.2% and 9.6% with polyethylene (PE) film, 0.02% and 0.2% with Totally Impermeable Film (TIF). Six hours after injection DMDS was detected mostly 5 cm below the surface and very little at 25 cm when used on bare soil, compared with much higher and similar concentrations of DMDS 5 and 25 cm deep when films were used. DMDS at the injection port exceeded 1 $\mu g\,cm^{-3}$ for longer when a film was used instead of bare soil. The total DMDS soil residues remaining in the soil, as a percentage of the initial DMDS dose at 40 or 80 $g\,m^{-2}$ were, respectively, 1.17 and 5.58 with TIF, 0.91 and 1.18 with PE, 0.47 and 0.47 with bare soil. DMDS rose rapidly upwards and escaped from bare soil, whereas PE or TIF significantly reduced DMDS emissions, retained elevated DMDS concentrations in the soil for longer and distributed them more uniformly in the soil. TIF performed better in these respects than PE. TIF also reduced the potential environmental impact of DMDS more than PE, especially at the higher dose.

1. Introduction

Soil fumigants are important for controlling nematodes, pathogens and weeds in high-value crop production systems. Methyl bromide (MB) was once the most widely used soil fumigant, but its use was phased out in China in 2015 because it depleted stratospheric ozone (Mcavoy and Freeman, 2013a, 2013b; Yates et al., 2002). DMDS has recently been registered as Paladin® by the USEPA as a potential alternative to MB (Mcavoy and Freeman, 2013a, 2013b). DMDS is a natural biopesticide formed as a result of the decomposition of soil fungi and bacteria (Gu et al., 2007; Xu et al., 2004). Alliaceae and Brassicaceae plant families are also natural sources of DMDS (Auger et al., 1989; Wang et al., 2009). Importantly it does not deplete stratospheric ozone (Mcavoy and Freeman, 2013a, 2013b). DMDS is reported to control soil borne nematodes and insect pests by reducing neuronal activity through mitochondrial dysfunction and activation of neuronal K_{ATP} channels (Dugravot et al., 2003). In France, a DMDS dose of 80 $g\,m^{-2}$ had the equivalent effect on pathogenic fungi and strawberry yield as a dose of 50 $g\,m^{-2}$ of MB (Fritsch, 2005). DMDS control of nematodes resulted in increased yields of greenhouse melon, tomato, eggplant, pepper, and cucumber in field trials in Italy and Turkey (Heller et al., 2010; Leocata et al., 2014). DMDS mixed with chloropicrin and dazomet gave better control of soil borne diseases and insect pests than when these fumigants were used alone (Cebolla et al., 2010; Gilardi et al., 2017).

Effective fumigants are naturally volatile. To ensure fumigants are effective, they must volatilize, diffuse to the root zone and remain there for a sufficient time to control soil pests and diseases (Ou et al., 2005). The fumigant gasification rate, diffusion in soil and capability of binding to soil are all important factors affecting a fumigant's efficacy against pests. Emissions of fumigants to air will increase the exposure risk to people and environment, and reduce the efficacy of fumigants in the soil. The physicochemical properties of DMDS suggest that is less capable of spreading through the soil than MB because it is less volatile and it has a higher soil adsorption rate (Table 1).

Based on the information provided in Table 1, DMDS without any film might need to be applied at a high dose to obtain efficacy against pests equivalent to MB. A high DMDS dose without film increases the

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Table 1
Physicochemical properties of dimethyl disulfide and methyl bromide (Conkle et al., 2016; Ruzo, 2006).

Item	Dimethyl disulfide	Methyl bromide
Appearance	Colorless or light yellow transparent liquid	Colorless gas
Water solubility (mg/g)	558.6	1782.2
Boiling point (°C)	110.0	3.6
Density(g/mL)	1.06 (16 °C)	1.73 (0 °C)
Vapor pressure (kPa)	2.9 (20 °C)	213.3 (20 °C)
Henry's law constants (KH)	0.054 (20 °C)	0.240 (20 °C)

risk of DMDS exposure to people and environment, and increases the cost of DMDS fumigation (Conkle et al., 2016). Soil density, water content and surface containments will also influence the efficacy of DMDS (Zhang and Wang, 2007). For example, previous research showed that DMDS emissions were reduced by increasing the soil moisture content (Sumner and Culpepper, 2008).

Fumigants used to treat the soil in greenhouses or fields are commonly contained in the soil using a layer of film. The Mass Transfer Coefficient (MTC) is a measure of the permeability films to gases. Polyethylene film (PE) is the most commonly-used plastic film. Previous studies have shown PE film is an effective barrier to MB or chloropicrin (CP) fumigants, but less of a barrier to 1,3-dichloropropene (1,3-D) fumigant. In general PE does not effectively reduce emission of fumigants (Gao et al., 2011; Yates et al., 2002). On the other hand, Totally Impermeable Film (TIF) is an innovative film manufactured using advanced technology which is significantly less permeable to fumigants (Chow, 2008; Villahoz et al., 2008). TIF contains modified polyolefin with a functional group and special grade of ethylene vinyl alcohol copolymer (EVOH) which together form a five-layer barrier to fumigants (Austerweil et al., 2006; Qin et al., 2011; Villahoz et al., 2008). TIF is reported to have the lowest permeability to various fumigants (including DMDS), compared with other films (Qian et al., 2011); and to reduce emission loss, increase 1,3-D and CP retention, boost the pesticidal efficacy of fumigants and to improve crop yield (Fennimore and Ajwa, 2011; Gao et al., 2013; Qin et al., 2011; Stevens et al., 2016). Importantly, replacement of Virtually Impermeable Film such as PE by TIF may allow the DMDS dose to be reduced by 20–33% without any significant reductions in efficacy or crop yield (Mcavoy and Freeman, 2013a, 2013b; Gómez-Tenorio et al., 2015).

Little is known about DMDS atmospheric emissions and distribution in soil when the soil is fumigated without film (‘bare soil’). There is also little information on the effect of films on DMDS emissions, distribution in soil and soil residues after DMDS fumigation. Therefore, the objectives of this study were to determine DMDS emissions, vertical distribution in soil and soil residues when DMDS is applied to bare soil or when the soil is covered with PE or TIF under two DMDS dosages conditions. The results of our research will provide valuable guidance to fumigation experts and farmers on the effective application methods and rates for DMDS, and importantly how application of these methods will help to reduce the risk to people and the environment of DMDS emissions.

2. Materials and methods

2.1. Sources of chemicals, soil and films

An analytical standard of DMDS (99% purity) was purchased from Chengdu Best-Regent Co. Ltd. (Chengdu, China). The ethyl acetate (GC-MS/HPLC grade) was obtained from Thermo Fisher Scientific Co. Ltd. (Shanghai, China). Anhydrous sodium sulfate was obtained from Xilong Scientific Co. Ltd. (Shantou, China). Activated carbon adsorption tubes were obtained from Nantong Jin Nan Glass Apparatus Hardware Factory Co. Ltd. (Nantong, China).

Agricultural sandy loam soil (65.59% sand, 29.74% silt, 4.67% clay; 2.5% organic matter; pH 7.05) was collected from the upper 20 cm of a greenhouse in a suburb of Beijing (Shunyi, Beijing). Before being packed into soil columns, the soil was sieved through 2 mm mesh and air-dried at room temperature until the moisture content was 10%.

PE film was purchased from Shandong Longxing Science and Technology Co. Ltd. (Shandong Province, China). TIF was supplied by Nippon Synthetic Chemical industry Co. Ltd. (Osaka, Japan).

2.2. Film permeability

The equipment and methods used to measure film permeability followed those developed previously (Papiernik and Yates, 2001a, 2001b, 2002). Gastight stainless steel cylinders were constructed as two chambers of equal volume. A sample of the film was placed between the two chambers, which was made gastight using epoxy resin at the junction. Aluminum tape was also applied to the outside of the cylinder at the junction of the two chambers to ensure a gastight seal.

The cylinder was kept in a temperature controlled incubator at 25 °C (± 0.5 °C) and RH of 20–30% before DMDS was introduced to one of the chambers. Prior to each experiment a pure sample of DMDS (50 µl) was injected as the standard into a 150 mL Erlenmeyer flask with a mininert valve screw-cap to provide a vapor source. At beginning of each experiment, 50 mL of DMDS vapor was injected into one chamber in the cylinder using a gastight syringe. The excessive pressure was released through a small valve on the cylinder. Five hundred uL of gas sample were collected periodically from the receiving chamber in the cylinder using two gastight syringes. The contents of these syringes were injected into 20 mL headspace vials from which the DMDS concentration was immediately measured and recorded. The headspace vials were stored in a freezer at − 80 °C if the concentration in the vials could not be measured immediately. The concentrations of DMDS in all the headspace vials were analyzed within 72 h. The permeability tests were repeated three times for each film and the average of the triplicate at each time interval was used to calculate the film permeability (as the Mass Transfer Coefficient, MTC). Mass transfer follows Fick's laws; the resistive nature of barrier films can be described using mass transfer coefficient, $h = D_{film}/b$.D is the effective diffusion coefficient [$m^2 d^{-1}$] and b is the thickness of the membrane. The values of MTC were obtained by curve fitting to the raw data using the model described in Papiernik et al. (2001a, 2001b) and Origin Pro 8. (Pro 8.0; OriginLab; USA)

2.3. Soil column equipment

The equipment and methods used to monitor the distribution of a fumigant in a column of soil followed those developed previously (Ashworth et al., 2009; Gan et al., 2015; Gan et al., 2000; Wang et al., 2014). The column system comprised two parts: a stainless steel soil column [72 cm (h) × 15 cm (Internal diameter; ID), bottom closed] and a stainless steel flux chamber [5 cm (h) × 15 cm (ID)]. Six gas sampling ports were positioned 0, 5, 15, 25, 40 and 60 cm from the bottom of the column. The injector was located at 0 cm. The flux chamber was sealed onto the top of the soil column to collect any DMDS gas leaving the soil surface. The dried and sieved soil was loaded into the cylindrical stainless steel soil column to a dry bulk density of 1.30 g cm^{-3}, which was similar to the field soil bulk density. The study was conducted in a room held at 23–28 °C.

DMDS emissions, distribution in the soil and residues remaining in the soil were investigated using two doses of DMDS in combination with PE or TIF film, or without any film according to the following treatments:

(a) 40 g m^{-2} DMDS liquid injection with PE film.
(b) 80 g m^{-2} DMDS liquid injection with PE film.