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Henry's law constants and mass transfer coefficients for methyl bromide and 1,3-dichloropropene applied to Florida sandy field soil

John E. Thomas *, Li-Tse Ou, Leon H. Allen Jr., Joseph C. Vu, Donald W. Dickson

University of Florida, Gainesville, FL 32611, USA

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Abstract

Methyl bromide, a pre-emergent soil fumigant, is scheduled to be phased out in the US by 2005, with exceptions for critical use. Comparison of some of the physical constants related to distribution and retention for methyl bromide (MBr) to other fumigants yields a useful quantification of possible alternatives. In this study, the atmospheric and subsurface dissipation of methyl bromide as well as (*Z*)- and (*E*)-1,3-dichloropropene (1,3-D) isomers in Telone II were examined. The Henry's law constants of the three chemicals at soil temperature and their mass transfer coefficients for movement through an agricultural mulch of UV-resistant, high-density polyethylene (PE) were evaluated using field data. At the soil temperature of 16.4 °C, calculated Henry's law constant gave a fumigant ranking of MBr (0.21) $\gg$ (*Z*)-1,3-D (0.041) $>$ (*E*)-1,3-D (0.027). Since rapid subsurface distribution of a fumigant is highly dependent on the amount in the gas phase, the greater value for Henry's law constant implies faster distribution throughout the soil. After distribution through the soil, retention of the fumigant becomes imperative. Calculation of the fumigant's mass transfer coefficients through PE from field data gave a ranking of the three chemicals: MBr (1.08 cm/h) $<$ (*E*)-1,3-D (3.25 cm/h) $<$ (*Z*)-1,3-D (4.13 cm/h). With mass transfer coefficients of this magnitude, it was concluded that PE film was an inadequate barrier for retaining these fumigants in an agricultural setting.

Keywords: Methyl bromide; 1,3-Dichloropropene; Telone; Henry's law; Mass transfer coefficient; Polyethylene film; Emissions; Subsurface diffusion

1. Introduction

A vast amount of research has been conducted on alternatives to the pre-emergent crop fumigant, methyl bromide (MBr). Methyl bromide, originally slated to be phased out in the US by 2005 (UNEP, 1995), will continue to be used through critical use exemptions. The US has been granted an exemption for 8942 Mton for 2005 (UNEP, 2004). Even with a temporary use exemption, the investigation into alternatives continues to be highly relevant. One alternative fumigant, Telone II, is comprised of (*Z*)- and (*E*)-isomers of 1,3-dichloropropene (1,3-D) in a ratio comparable to that found in other 1,3-D products such as Telone C-35 and In-Line.

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* Corresponding author. Tel.: +1 352 392 1951.
E-mail address: thomas@ufl.edu (J.E. Thomas).

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In this investigation, the subsurface distribution and surface emissions of (*Z*)- and (*E*)-1,3-D are compared to those of MBr after fumigant application to a Florida sandy soil that is subsequently covered with UV-resistant, high-density polyethylene film (PE). For methyl bromide, the permeability of low-density polyethylene is greater than for high-density polyethylene which, in turn, is greater than for a virtually impermeable film that is made from co-extruded layers of polyethylene with a layer of copolymer ethyl vinyl alcohol in the middle (Yates et al., 2003). Evaluation of Henry's Law constant at soil temperature and the mass transfer coefficients of the fumigants through high-density PE enabled rationalization of the differing dissipation behavior among the fumigants. Previous studies have focused solely on the volatilization and subsurface distribution patterns of 1,3-D (Wang and Yates, 1999; Kim et al., 2003a,b; Thomas et al., 2004a) or methyl bromide (Jin and Jury, 1995; Gan et al., 1997; Gamliel et al., 1998) alone with no comparison between these fumigants under the same set of environmental conditions.

2. Experimental materials and methods

2.1. Plot preparation

A total of six beds (0.23 m height × 1 m width × 90 m length) were prepared on December 16, 2003 (when the soil temperature at 15 cm depth was 16 °C) at the University of Florida Plant Science Education and Research Unit (PSERU) located near Citra, FL. The soil has been mapped as Candler sand, a hyperthermic, uncoated Typic Quartzipsamments (USDA, 1979). Physical properties (pH, moisture, bulk density, and porosity) are given in Table 1. Three rows were fumigated with 67:33 methyl bromide:chloropicrin (MBr:CP) and three rows with Telone II which is comprised of 96% [52:48 (*Z*):(*E*) isomers] 1,3-D. Each row was considered a replicate. Subsurface fumigation was done by chisel injection to a depth of 30 cm. Application rates were 236 and 168 l/ha for MBr:CP and Telone II, respectively. All beds were covered with 0.025 mm thick high-density, UV-stabilized PE plastic film mulch (Sonoco Products Inc., Hartsville, SC) immediately following fumigant injection. The center section (40–60 m length) of the middle row of each treatment was sampled. Similar field set-ups were used on June 4, 2001 for Telone II (when the soil temperature at 15 cm depth was 30 °C) and on March 1, 2004 for MBr:CP (when the soil temperature at 15 cm depth was 21 °C).

2.2. Sampling

Surface emissions were measured using the static chamber method described previously (Thomas et al., 2004a). Fumigant off-gassing were measured by three chambers on the bed and one chamber in the furrow along the bed. Subsurface gases at ⩾5 cm depth were sampled through 0.32 cm OD stainless steel gas probes capped with bulkhead unions and TFE-lined septa. Gas was sampled from 0.5 cm below the plastic film by a needle that pierced a TFE-faced butyl rubber septa attached to the PE mulch. The 30 ml subsurface gas samples were taken at depths of 0.5, 10, 20, 30, 40, 60 and 90 cm at 0.5, 4, 20, 44, 68, and 140 h for MBr and 0.5, 19, 43, 67, and 139 h for 1,3-D after injection. All gas samples were collected on ORBO-32 activated coconut charcoal tubes (SKC Inc., Eighty Four, PA). The tubes were placed on ice after gas collection and transported back to the laboratory where they were transferred to a −78 °C freezer until later extraction for analysis.

2.3. Analysis

The ORBO-32 tubes with MBr:CP were analyzed by transferring the activated charcoal to a 22 ml headspace vial, adding 3 ml benzyl alcohol, crimping on a TFE-lined septa cap, and ultra-sonicating for 15 min (Gan et al., 1995). The sonicated vials were transferred to a

Table 1
Soil physical properties of Candler sand taken from PSERU at Citra, FL

Soil depth (cm)	pH			% H_2O (g H_2O/g dry soil)			Bulk density (g dry soil/cm^3)	% Porosity
	2001	2003	2004	2001	2003	2004	2003	2003
0–10	6.6	5.6	6.2	5.33	6.68	4.41	1.35	43.1
10–20	6.1	5.7	6.3	8.11	7.58	4.54	1.50	37.2
20–30	5.7	5.8	6.3	8.67	7.36	4.88	1.59	33.9
30–40	ND[a]	6.5	ND	ND	7.19	ND	1.67	30.2
40–50	ND	6.3	ND	ND	7.79	ND	1.72	29.2
50–60	ND	5.7	ND	ND	10.62	ND	1.76	24.3
70–80	ND	5.7	ND	ND	16.61	ND	1.79	25.5
80–90	ND	5.7	ND	ND	16.98	ND	1.84	23.4

[a] ND = not determined.