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Effect of deep injection on field-scale emissions of 1,3-dichloropropene and chloropicrin from bare soil

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HIGHLIGHTS

- Fumigant emissions can be reduced by deep injection into soil.
- Mass loss of 1,3-dichloropropene was approximately 15–27%.
- Mass loss of chloropicrin was less than 2% due to high soil reactivity.

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ABSTRACT

Fumigating soil is important for the production of many high-value vegetable, fruit, and tree crops, but fumigants are toxic pesticides with relatively high volatility, which can lead to significant atmospheric emissions. A field experiment was conducted to measure emissions and subsurface diffusion of a mixture of 1,3-dichloropropene (1,3-D) and chloropicrin after shank injection to bare soil at 61 cm depth (i.e., deep injection). Three on-field methods, the aerodynamic (ADM), integrated horizontal flux (IHF), and theoretical profile shape (TPS) methods, were used to obtain fumigant flux density and cumulative emission values. Two air dispersion models (CALPUFF and ISCST3) were also used to back-calculate the flux density using air concentration measurements surrounding the fumigated field. Emissions were continuously measured for 16 days and the daily peak emission rates for the five methods ranged from 13 to 33 μg m^{-2} s^{-1} for 1,3-D and 0.22–3.2 μg m^{-2} s^{-1} for chloropicrin. Total 1,3-D mass lost to the atmosphere was approximately 23–41 kg ha^{-1}, or 15–27% of the applied active ingredient and total mass loss of chloropicrin was <2%. Based on the five methods, deep injection reduced total emissions by approximately 2–24% compared to standard fumigation practices where fumigant injection is at 46 cm depth. Given the relatively wide range in emission-reduction percentages, a fumigant diffusion model was used to predict the percentage reduction in emissions by injecting at 61 cm, which yielded a 21% reduction in emissions. Significant reductions in emissions of 1,3-D and chloropicrin are possible by injecting soil fumigants deeper in soil.

1. Introduction

The use of biologically-active organic chemicals (e.g., pesticides, fumigants, etc.) has been essential in the production of an abundant, nutritious and low–cost food supply. Use of synthetic organic chemicals in agricultural production has also resulted in detectable concentrations of pesticides and other compounds of concern in air, soil and water resources.

Agricultural uses of volatile pesticides and soil fumigants may pose a significant threat to human and environmental health if these compounds are transported away from the target zones or persist in soil. Globally, the fumigant methyl bromide (MeBr) was scheduled for phase-out in the year 2005, due to its potential for depleting stratospheric (UNEP, 1992, 1995; Federal Register, 2000). In California, air emission inventories have shown that pesticides

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and fumigants are significant sources of air pollution. In Fresno County from 1976 to 1995, about 19 tons of pesticide chemicals were emitted into the atmosphere daily (ARB, 1978, 1997a, 1997b), which represents 16% of the reactive organic gas fraction in this region. Unexpectedly high air concentration measurements of an agricultural fumigant 1,3-dichloropropene (1,3-D) prompted a suspension in California between 1990 and 1994 (CDFA, 1990). Soil fumigants may also pose a risk to water supplies due to their generally low soil adsorption properties. For example, movement of 1,3-D to groundwater and fate in aquatic ecosystems have been addressed in several studies (Merriman et al., 1991; Obreza and Onterman, 1991; Yon et al., 1991; Schneider et al., 1995). Bystander exposures to pesticides can be a serious problem related to production agriculture, if not properly managed. With an improved understanding of the mechanisms and processes that affect pesticide transport and fate in soil—water—air systems, it becomes possible to reduce the harmful effects to non-target organisms, and maintain agricultural production, through development of new pesticide management strategies that minimize emissions.

Volatilization and soil degradation are two important routes of fumigant dissipation (Yagi et al., 1995; Majewski et al., 1995; Yates et al., 1996) and several methods have been developed and tested to lower emission losses from soil. These include surface diffusion barriers, such as agricultural films, water seals (Wang et al., 1997,Gao and Trout, 2006), surface soil amendments (Gan et al., 2000; McDonald et al., 2008; Yates et al., 2011), and deep injection (Yates et al., 1997), among others. Deep injection offers a low-cost approach to reduce emissions compared to the use of agricultural films, water seals, soil amendments, or any other approach that requires adding material to a field. With deep injection, emissions can be reduced by decreasing concentration gradients near the soil surface and increasing the soil residence time, which removes chemical fumigants from the soil zone via degradation.

Micrometeorological approaches have been frequently used to measure field-scale pesticide and fumigant emissions from agricultural fields (Glotfelty et al., 1984; Majewski et al., 1995; Yates et al., 1996, 1997; 2015) and include the aerodynamic, integrated horizontal flux, and theoretical profile shape methods. Regulatory approaches have also been used to calculate fumigant emission rates by fitting air dispersion models to measurements of the air concentration collected around a treated field. For example, the California Department of Pesticide Regulations (CDPR) continues to use the Industrial Source Complex Short Term model (ISCST3) (Ross et al., 1996; Barry et al., 1997) for calculating emission rates for regulatory purposes (CDPR, 2008). EPA recently replaced ISCST3 with AERMOD for regulatory use. However, CDPR conducted an analysis and found that the changes incorporated into the AERMOD model did not significantly improve fumigant emission estimates compared to ISCST3. Therefore, CDPR determined that ISCST3 remains appropriate, and their preferred approach, for estimating fumigant emission rates (CDPR, 2008). Other atmospheric dispersion models, such as CALPUFF (Johnson et al., 1999) can also be used to calculate fumigant emission rates.

The soil fumigants 1,3-D and chloropicrin are used to control nematodes and fungi in a variety of vegetable and tree crops. They have relatively high water solubility (~2 g L^{-1}) and short field half-life, and thus, planting can commence within weeks after fumigation. These fumigants also have a relatively high vapor pressure (18—28 mmHg) so that losses to the atmosphere can be significant. In a previous paper, Yates et al. (2015) reported on a field experiment conducted to measure the volatilization rate of 1,3-D and chloropicrin after application to a bare soil at 46 cm depth (SI) using a standard fumigation methodology. Using several methods for quantification, the reported total emissions of 1,3-D and chloropicrin, respectively, ranged from 16 to 35% and 0.3—1.3% of the applied fumigant.

The purpose of the present paper is to obtain emission measurements for soil fumigation employing deep injection, a proposed emission-reduction methodology. By comparison to the standard application methodology reported by Yates et al. (2015) an evaluation can be made to determine if deep injection effectively mitigates emissions.

2. Methods

The deep injection (DI) field experiment was conducted near Buttonwillow, CA in an agricultural field managed by the farmer. The methods for this experiment are the same as Yates et al. (2015) with the exception of injection depth. In brief, the soil is classified as Milham sandy loam (fine-loamy, mixed, thermic Typic Haplargids), with approximately 1% organic matter (upper 10 cm) and decreasing with depth. Two weeks before the experiment the field was disked, plowed and irrigated so that the soil condition was suitable for fumigation (i.e., water content was approximately 0.2 cm^3 cm^{-3} and a friable soil texture). The fumigation rigs had a 450 cm tool bar containing 9 shanks spaced in 50 cm increments laterally. The target depth of application for this field was 61 cm (i.e., 24 inches) and target Telone C-35 application rate was 240 kg/ha (i.e., 20 gal/ac). The field size was 2.8 ha area (178 m by 157 m) and was determined by visually tracking and marking the outside edge of the fumigation rig and tool bar. The total Telone-C35 mass applied to the field was 672 kg and was determined by weighing the tanks before and after fumigation. A chemical analysis of the formulation in the tanks revealed that 430 kg of 1,3-D and 242 kg chloropicrin were applied (see Table 1). After the field was fumigated, nothing further was done to the field and there was no precipitation during the experiment.

2.1. Measurement of 1,3-D and Chloropicrin

XAD-4 (SKC 226-175, SKC, Incorporated, Fullerton, CA) sampling tubes were used to collect 1,3-D and chloropicrin concentrations in the atmosphere at the field site. A charcoal backup tube (SKC 226-09, SKC, Incorporated, Fullerton, CA) was used to check for 1,3-D breakthrough for the field samples. Fumigant measurements were collected at 10, 40, 80, 150, 250 and 400 cm above the ground surface at field center by drawing air through the sampling tubes

Table 1
Application rates and field dimensions.

Experimental treatment	Soil type	Total *cis*-1,3-D applied, kg	Total *trans*-1,3-D applied, kg	Total chloropicrin applied, kg	Field area (ha)	North-South dimension (m)	East-West dimension (m)
Deep injection	Milham sl	215	215	242	2.80	178	157
Standard injection[a]	Milham sl	237	237	222	2.89	162	178

[a] Yates et al. (2015).