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Replicated flux measurements of 1,3-dichloropropene emissions from a bare soil under field conditions☆

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ABSTRACT

Field experiments offer the most acceptable approach to quantifying agricultural fumigant emissions but there is an absence of *replicated* field data in reported literature. Air concentration profiles of 1,3-dichloropropene (1,3-D) were determined on duplicate masts above the center of a treated field over 14 days. Meteorological parameters were also measured. Three meteorological approaches were then used to determine the total and flux density emissions of 1,3-D. Across the three calculation methods, the averages of the duplicated measurements showed total emission losses of *cis* 1,3-D ranging from 27% to 36% and of *trans* 1,3-D ranging from 18% to 24%. The replicate measurements differed by between 1.6 and 7.7 percentage points, which we consider to be excellent replicability. Flux densities over time showed maximum emissions during the first nighttime and early morning of the day following application. A general declining trend in emission fluxes was accompanied by nighttime peaks. Flux density curves during the experiment showed excellent agreement between replicates, with linear regression of the two data sets yielding r^2 values of 0.95–0.98 and slopes of 1.01–1.17. To our knowledge, this is the first time that replicated fumigant fluxes have been reported. The high degree of replicability indicates the robustness of the approaches and lends credence to previous non-replicated flux data.

1. Introduction

Despite their significantly beneficial impact on agricultural food production, pesticides can have detrimental impacts on environmental and human health. Fumigants are a class of pesticides that kill pests by diffusing through the soil pore space as a gas. In general, they are highly effective in the pre-plant control of pests such as nematodes, weeds, and microorganisms, and they are commonly used in the production of high-value crops. In California, the use of soil fumigants is significant and increasing. Pesticide use reports from California Department of Pesticide Regulation (CDPR, 2017) show that total fumigant use increased in CA from 17.3×10^6 kg (38.1×10^6 lbs) in 2007 to 20.7×10^6 kg (45.7×10^6 lbs) in 2015, with the treated area increasing from 135.9×10^3 ha (335.5×10^3 acres) to 164.2×10^3 ha (405.4×10^3 acres) over the same period. The soil fumigant 1,3-dichloropropene (1,3-D) is widely used for pre-plant pest control across a wide variety of commodity crops such as strawberries, almonds, and carrots (Dow Agrosciences, 1996). According to CDPR (2017), 1,3-D was the most highly used fumigant (based on mass applied) in CA from 2011 to 2015 and the third most highly used pesticide (based on mass applied) in 2015. Between 2007 and 2015, 1,3-D use in CA increased from 4.3×10^6 kg (9.5×10^6 lbs) to 7.2×10^6 kg (15.8×10^6 lbs), with the applied land area increasing from 21.8×10^3 ha (53.9×10^3 acres) to 32.2×10^3 ha (79.4×10^3 acres).

The volatile nature of fumigants facilitates their transfer from soil to the atmosphere, where their toxicity may be a direct inhalation hazard

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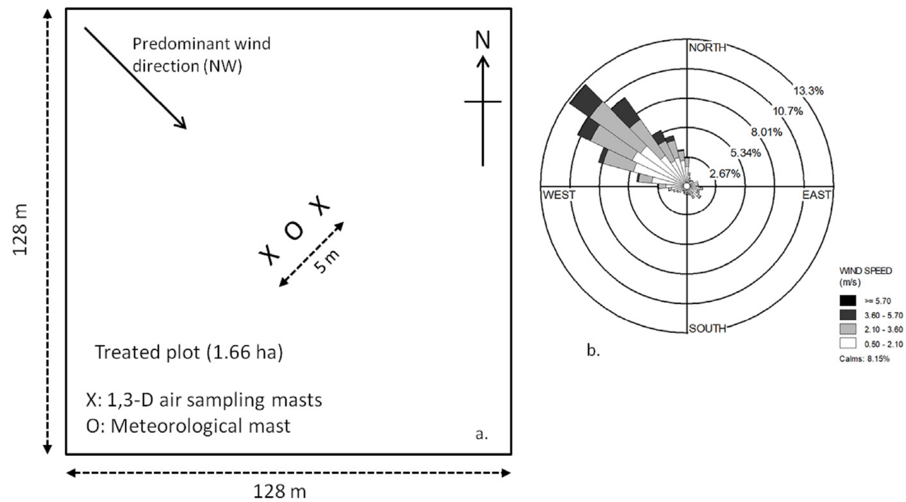

Fig. 1. (a) Plan view of experimental plot (not to scale) showing location of sampling masts, (b) wind rose diagram showing wind direction, wind speed, and frequency with which the wind occurred in a specific direction (measured at 240 cm height).

to local populations; moreover, they can also serve as the volatile organic compound (VOC) component of near-surface photochemical smog if sufficient NOx is available for reaction (CDPR (2010). Photochemical smog is a concern in relation to lung tissue damage, respiratory illness, and damage to crops (California Air Resources Board, 2016), and VOCs contributed by pesticides are tracked by CDPR as part of the state implementation plan (SIP) for VOCs. Therefore, understanding the emissions behavior of fumigants is a critical research requirement. A number of previous studies have quantified fumigant emissions under both laboratory and field conditions (Gan et al., 1997; Qin et al., 2007; McDonald et al., 2008; Luo et al., 2010). For 1,3-D, studies have generally found that emissions from bare soil range from 20 to 77% in laboratory columns and from 12 to 80% in field studies (Yates et al., 2015 and references therein). Field studies are of particular importance to regulators when assessing fumigant practices since they are conducted at the appropriate scale under realistic environmental conditions and should therefore provide the most accurate data. Although flux chambers have been used to estimate fumigant fluxes under field conditions (van Wesenbeeck et al., 2007; Gao and Trout, 2007), they suffer from a number of drawbacks such as their effect on temperature, water evaporation, and fumigant gas concentrations near the soil surface, which potentially compromises their accuracy in estimating emissions (Gao et al., 1997). Therefore, larger-scale, micrometeorological methods for estimating field-based emissions are preferred (i.e., the aerodynamic (AD), integrated horizontal flux (IHF), and theoretical profile shape (TPS) methods), which are typically used in fumigant flux studies (Yates et al., 2015, 2016a; 2016b). Micrometeorological approaches have long been used to measure field-scale pesticide and fumigant emissions from agricultural fields (Glotfelty et al., 1984; Majewski et al., 1995; Cryer et al., 2003; van Wesenbeeck et al., 2007). In previous field studies conducted by this research group, we studied the effects of irrigation and organic matter content on emissions of 1,3-D (Yates et al., 2008, 2011), and the effects of deep injection and ammonium thiosulfate application on emissions of 1,3-D and chloropicrin (Yates et al., 2016a; Yates et al., 2016b). However, only single (non-replicated) flux measurements were made in each of these reported studies. Indeed, we could find no reported field studies in which fumigant flux measurements based on micrometeorological approaches had been replicated. Field studies are expensive and time/resource-consuming compared with laboratory (soil column) studies or field-based flux chamber studies. Field studies using micrometeorological approaches also require specialized equipment and knowledge, together with access to a suitable field location. This explains the relatively low number of fumigant emission studies conducted under field conditions and the lack of replication in those that have been conducted. Replication is an important component in the assessment of data precision and accuracy; therefore, its application to fumigant studies is a clear research need, especially considering that such studies form the regulatory basis for protecting air quality from fumigant chemicals. For example, CDPR uses these studies to determine application factors (AFs) for tracking and enforcing maximum township caps for 1,3-D under the CDPR 1-3,D management plan and also to determine emission potentials for tracking pesticide VOCs under the SIP for VOCs.

Since fumigants are a critical component of agricultural production in many regions, information regarding their release to air under a range of soil and meteorological conditions is required, particularly at the field-scale. However, the lack of replication in previous studies leads to uncertainty in terms of the accuracy and precision of these flux measurements, which in turn can lead to uncertainty in the risk assessment of fumigant use. Therefore, the aim of this study was to assess the replicability of flux studies by making duplicate measurements at a single site. To the best of our knowledge, this is the first time that replicated field-scale fumigant fluxes have been reported. In addition, the study provides an additional set of 1,3-D flux data under field conditions that can be compared with previous data and assist in better understanding the impact of fumigant use on regional air quality.

2. Materials and methods

2.1. Field site

The field study was conducted at the US Western Research Center of Dow AgroSciences, LLC in Fresno, California between September 8 (Day 0) and September 22 (Day 14), 2016. A plot of approximately 128 × 128 m (1.66 ha) was used for the experiment (Fig. 1a). The loam soil within the plot is of the Pachappa series (UC Davis, CA Soil Resource Lab) and is classified by USDA/NRCS as a coarse-loamy, mixed, active, thermic mollic haploxeralfs. It was determined to have an organic matter content (loss-on-ignition) of 3.0% at 0–20 cm depth and 2.8% at 20–40 cm depth. Preliminary studies found that the degradation half-life of both *cis* and *trans* 1,3-D in the plot soil was 2.5 days. Approximately 1 week prior to the experiment, the plot was plowed, flood irrigated, and disked. At the time of application, the bulk density of the surface soil was approximately 1.2 g cm^{-3} and the volumetric water content was 0.1 cm^3 cm^{-3}. A standard Telone II (1,3-D CAS: 542-75-6) (Dow AgroSciences, Indianapolis, IN) application to the 1.66 ha plot was performed by a commercial applicator (TriCal, Hollister, CA).