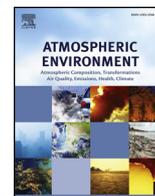




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# Replicated flux measurements of 1,3-dichloropropene emissions from a bare soil under field conditions<sup>☆</sup>

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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  $17.3 \times 10^6$  kg ( $38.1 \times 10^6$  lbs) in 2007 to  $20.7 \times 10^6$  kg ( $45.7 \times 10^6$  lbs) in 2015, with the treated area

increasing from  $135.9 \times 10^3$  ha ( $335.5 \times 10^3$  acres) to  $164.2 \times 10^3$  ha ( $405.4 \times 10^3$  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  $4.3 \times 10^6$  kg ( $9.5 \times 10^6$  lbs) to  $7.2 \times 10^6$  kg ( $15.8 \times 10^6$  lbs), with the applied land area increasing from  $21.8 \times 10^3$  ha ( $53.9 \times 10^3$  acres) to  $32.2 \times 10^3$  ha ( $79.4 \times 10^3$  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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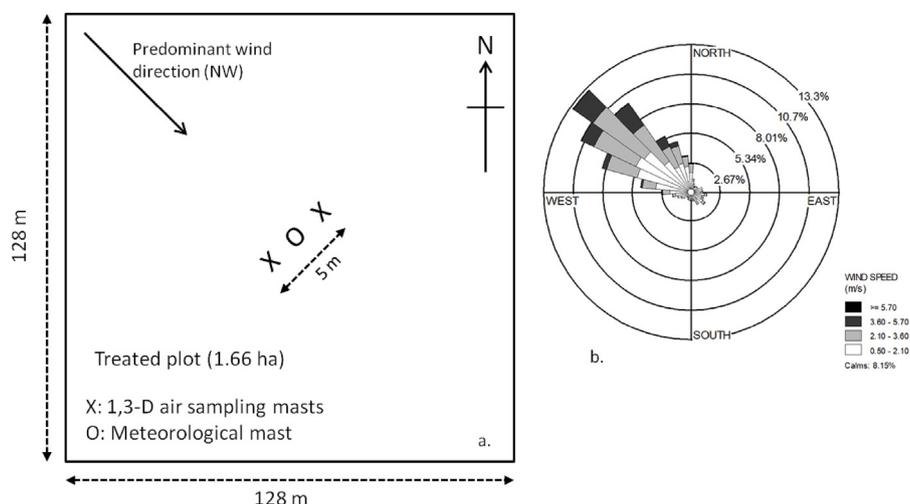


Fig. 1. (a) Plan view of experimental plot (not to scale) showing location of sampling masts, (b) wind rose diagram showing wind direction, wind speed, and frequency with which the wind occurred in a specific direction (measured at 240 cm height).

to local populations; moreover, they can also serve as the volatile organic compound (VOC) component of near-surface photochemical smog if sufficient NO<sub>x</sub> 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<sup>-3</sup> and the volumetric water content was 0.1 cm<sup>3</sup> cm<sup>-3</sup>. 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).

The injection rig consisted of seven shanks spaced at 50-cm intervals. The fumigant was injected at a target depth of 46 cm at a rate of 133 kg ha<sup>-1</sup>. The shank traces ran in an east–west direction. The total 1,3-D mass applied was 221.7 kg. The Telone II was applied as a 50:50 mixture of the *cis* and *trans* isomers. Application took place between 0720 h PST and 0820 h PST on Day 0, with 1,3-D air sampling commenced at 0930 h PST. No 1,3-D applications immediately upwind of the site were made during the study period.

## 2.2. Measurement of 1,3-dichloropropene in air

Duplicate sampling masts were placed in the center of the plot, approximately 5 m apart (Fig. 1a) and with the samplers pointing into the predominant wind direction (north-west). The concentrations of 1,3-D in air were determined at each mast by pumping air sampled at heights of 0.1, 0.4, 0.8, 1.5, 2.5, and 4.0 m above the soil surface through charcoal sampling tubes (SKC 226-09; 400/200 mg; SKC, Inc., Fullerton, CA). A pair of charcoal tubes (primary and backup tubes), connected in series, was used to sample the air each height. The target air flow rate at each sampler height was 150 mL min<sup>-1</sup>, provided by an AirChek 224-44XR pump. Actual air flow rates were recorded every 5 min by a datalogger (CR1000; Campbell Scientific, Logan, UT). After each sampling interval, pairs of tubes were immediately removed and replaced with new tubes. The flow rates were also adjusted to the target rate on each sampling occasion. Sampled tubes were then capped, placed into a sealable glass vial, bagged, and stored in a freezer at -20 °C. Initially, the sampling interval was 2 h during the day (07:00–21:00 PST) and 10 h at night (21:00–07:00 PST). Five days after application, the sampling interval was increased to 3 h during the day (07:00–19:00 PST) and 12 h at night (19:00–07:00 PST). At nine days after application, the daytime interval was increased to 4 h, and at 12 days after application, it was increased to 6 h. These increased intervals were used later in the experiment to ensure that sufficient mass was present on the charcoal tubes for 1,3-D analysis.

## 2.3. Meteorological measurements

Wind speed and direction were measured in the center of the plot (between the 1,3-D samplers; Fig. 1a) using a mast upon which were mounted Windsonic 2-D anemometers (Gill Instruments Ltd, Ly-mington, UK) at heights of 0.2, 0.4, 0.6, 1.5, and 2.4 m above the soil surface. Similarly, fine wire thermocouples (FW3, Campbell Scientific Inc., Logan UT) were mounted at heights of 0.2, 0.4, 0.6, and 1.5 m to measure air temperature. Sensors were pointed into the predominant wind direction (north-west). Using a CR3000 data logger (Campbell Scientific Inc., Logan, UT), wind speed, wind direction, and air temperature were measured every 30 s, with the average and standard deviation recorded every 5 min. Net radiation and incoming solar irradiance were measured at 30 min intervals with a net radiometer (CNR4, Kipp and Zonen, Delft, Netherlands) mounted 1.5 m above the field on a third mast located 48 m south east of the anemometer mast.

## 2.4. Analysis of charcoal tubes

The charcoal tubes were kept frozen during transport to the laboratory and during storage awaiting analysis. To extract 1,3-D, tubes were cut and the charcoal contents were transferred to a 10-mL glass vial. Immediately, 4 mL of acetone (Fisher Chemical, Fair lawn, NJ) was added and the vial was capped with a Teflon-faced septum and aluminum seal. Vials were shaken for 1 h before 1.5 mL of supernatant was transferred to an amber vial for analysis by gas chromatography (GC). Previous tests showed that the extraction efficiency of this procedure was 84 ± 7% for *cis* 1,3-D and 86 ± 7% for *trans* 1,3-D. GC analysis was carried out using an Agilent Technologies 7890C GC, equipped with a microelectron capture detector. The column was a DB-VRX 122-1534 with dimensions of 30 m × 0.25 mm × 1.4 µm (Agilent

Technologies) running at a flow rate of 1.6 mL min<sup>-1</sup> and with He as the carrier gas. The inlet temperature was 240 °C and the detector temperature was 290 °C. The GC oven temperature was maintained at 90 °C. The retention times of *cis* 1,3-D and *trans* 1,3-D were 4.07 and 4.51 min, respectively. Sets of analytical standards prepared in acetone and encompassing the range of concentrations in the samples were prepared from a certified Telone II reference sample (donated by Dow Agrosciences, IN). Standards were prepared in the same solvent as the samples. The analytical precision (based on repeated measurements of prepared samples) was < 5% discrepancy (n = 5). The limit of quantification and limit of detection were 0.05 µg per charcoal tube and 0.015 µg per charcoal tube, respectively.

## 2.5. Methods for measuring volatilization rates

Emission fluxes over time, together with total emission losses, were calculated using three meteorological approaches: the AD, IHF, and TPS methods. The derivation, equations, and assumptions of these methods are given in substantial detail by Yates et al. (1996) and Yates et al. (2003); therefore, only a brief overview is given herein. The AD method uses measured gradients of wind speed, temperature, and 1,3-D concentration over a relatively large and spatially uniform source area to calculate the 1,3-D volatilization rate (µg m<sup>-2</sup> s<sup>-1</sup>). It is worth noting that due to flow rate issues with the sampling of 1,3-D at 2.5 m on Mast 1 between 0.7 and 4.3 days, the gradients of 1,3-D concentration utilized in the AD method during this period were calculated with this sampling height excluded. In the IHF method, 1,3-D concentrations and horizontal wind speeds are used to determine fumigant flux based on a mass balance approach. Here, it is assumed that the mass of 1,3-D emitted from a spatially uniform surface area upwind of a sampling mast is equal to the mass collected through a vertical plane at the mast. The TPS method uses estimates of 1,3-D concentration and wind speed at a single height, with this height dependent on surface roughness and friction velocity. In the present study, we used a height of 2.13 m. In addition to the references above relating to the derivation and equations of these meteorological methods, further details on their application can be found in Parmele et al. (1972), Wilson et al. (1982), Majewski et al. (1995), and Yates et al. (2008).

## 3. Results and discussion

### 3.1. Meteorological conditions

Throughout the 14 days of the experiment, clear skies and relatively high daytime temperatures were observed. No precipitation fell during the experiment. At a height of 150 cm above the soil surface, air temperatures ranged from 7.9 to 39.7 °C overall. The hourly average temperatures at this height over the course of the experiment are shown in Fig. 2a and show general consistency over the first 4 days, ranging from approximately 12 to 35 °C. Lower temperatures were observed on day 5 before a warming trend through Day 11. Slightly lower temperatures were then observed for the last few days of the experiment. Overall, wind speed at 150 cm ranged from 0.07 to 8.61 m s<sup>-1</sup> over the course of the experiment. Hourly average wind speeds over the course of the experiment are shown in Fig. 2b and illustrate that relatively low winds (calms) were observed during nighttime periods and that relatively high values were observed on Days 4–5 and Days 13–14. The wind direction was predominantly from the north-west (Fig. 1b). Across all measurement heights during the course of the experiment, winds were from the north, north-west, and west 68% of the time. Fig. 2c shows the average diurnal cycle of net radiation and incoming solar irradiance measured at 150 cm. Maximum values of each were observed at around 1300 h PST, reaching 470 and 789 W m<sup>-2</sup>, respectively. The low confidence intervals suggest that for a given hour, conditions were relatively uniform throughout the experiment. Overall, the meteorological conditions illustrate typical conditions for the Fresno region, with high

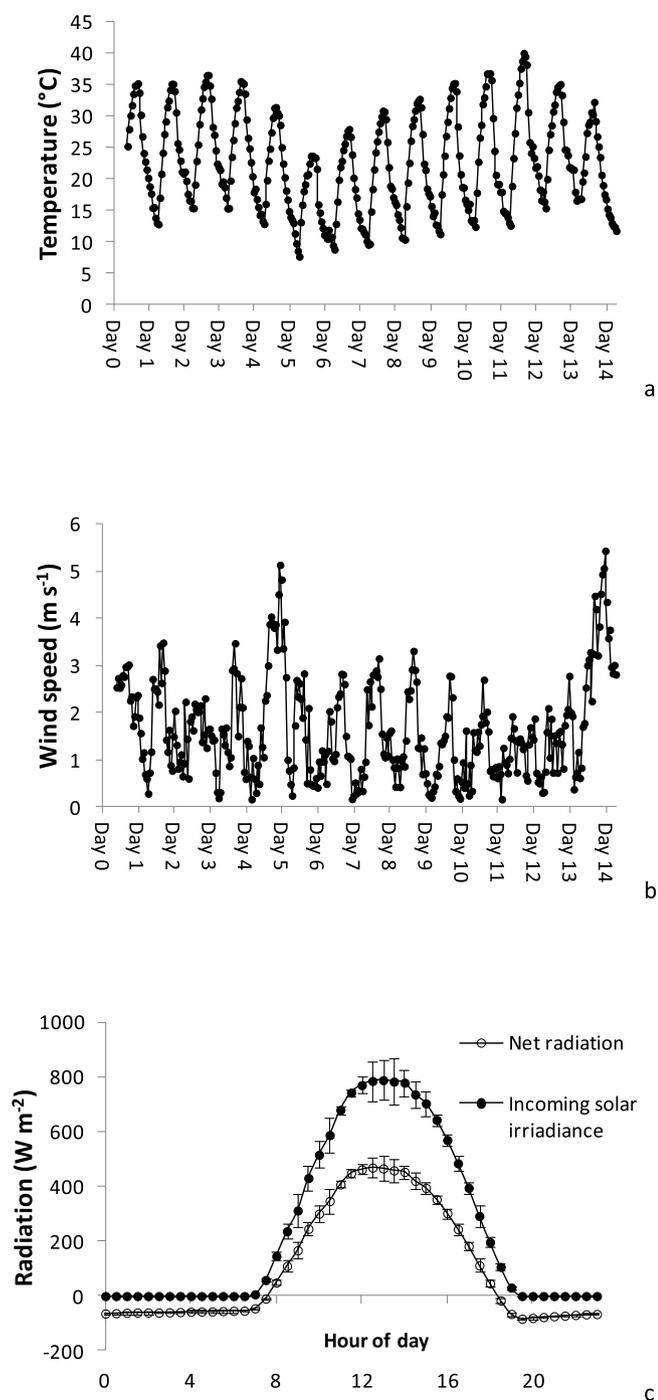


Fig. 2. Meteorological conditions during the experiment: (a) average hourly temperature at 150 cm height during each of the 14 days of the experiment, (b) average hourly wind speed at 150 cm height during each of the 14 days of the experiment, (c) average diurnal cycle of net radiation and incoming solar radiation. In (a) and (b), tick marks on the abscissa denote the start of each day, i.e., 0000 h. In (c), to calculate the confidence interval around each 30 min period for plotting the diurnal cycle, we used bootstrap sampling with replacement (1000 cycles) and set the 95% confidence interval around the middle 95% of the bootstrapped means. Times are PST.

daytime temperatures, sunny conditions, and a dominant wind direction between the north and west.

Based on previous field studies (Yates et al., 2015, 2016a; 2016b), it is considered that the meteorological measurements used in determining fumigant fluxes have a low degree of uncertainty, i.e.,

replicate measurements show very high concurrence. For example, the data recorded in those previous studies showed that 84.7% of triplicate wind speed measurements recorded hourly over a 16-day experiment were within  $0.5 \text{ m s}^{-1}$  of the hourly average values; similarly, 83.2% of triplicate air temperature measurements were within  $0.1 \text{ }^\circ\text{C}$  of the hourly average values. Therefore, in the present study, we assumed that the uncertainty in the meteorological measurements was negligibly small and instead focused on uncertainty in the 1,3-D air concentration profiles, which we expected to be greater owing to the significant potential for sampling and analysis errors.

### 3.2. Total emissions

In 2005, 2007, Yates et al. used several meteorological methods to quantify 1,3-D emissions under field conditions at a site near Buttonwillow, CA (Yates et al., 2008, 2011; 2015, 2016a; 2016b). These workers aimed to determine the effect of a range of emission reduction strategies on 1,3-D soil–air emissions. Under control (bare soil) conditions, they found 1,3-D emissions of 16–35%, depending on the calculation method used. Emissions were reduced when sequential surface irrigations (10–15%), green waste addition (3–8%), deep injection (15–27%), and ammonium thiosulfate addition (12–26%) were used as emission reduction strategies. Similarly, using a meteorological approach (AD method) van Wesenbeeck et al. (2007) reported bare-soil 1,3-D emissions of 26.5% for a field site near Douglas, GA. In the present study, we found that depending on the calculation method used (AD, IHF, or TPS), 79.9–107.5 kg of the total applied 1,3-D product (221.7 kg) was emitted from the soil over the entire experiment. This equates to percentage losses of 22.5–30.3% (Fig. 3). This range of values is broadly in line with percentage losses reported previously for bare soil and is also consistent with the 26% estimate for 1,3-D emissions from shank applications estimated by CDPR to calculate AFs for the 1,3-D management plan. Of this loss, 48.1–64.6 kg occurred as *cis* 1,3-D, representing total emissions of 27.1–36.4%; whereas 35.4–42.9 kg was lost as the *trans* isomer, representing total emissions of 17.9–24.1%, reflecting the greater vapor pressure of the *cis* isomer. On a daily basis, the day following application showed the highest level of emissions, with, on average, 8.1–12.2% of the total amount of applied *cis* 1,3-D, 5.4–7.2% of the applied *trans* 1,3-D, and 6.8–9.7% of the applied total 1,3-D emitted in this 24 h period (data not shown).

In comparing the two sampling masts in terms of total emissions, relatively good agreement is observed. With the AD method, the difference between the two masts was just 7.7, 5.1, and 6.4 percentage points for *cis*, *trans*, and total 1,3-D, respectively. For the IHF and TPS methods, the values were 5.0, 3.2, and 4.1 percentage points and 1.9,

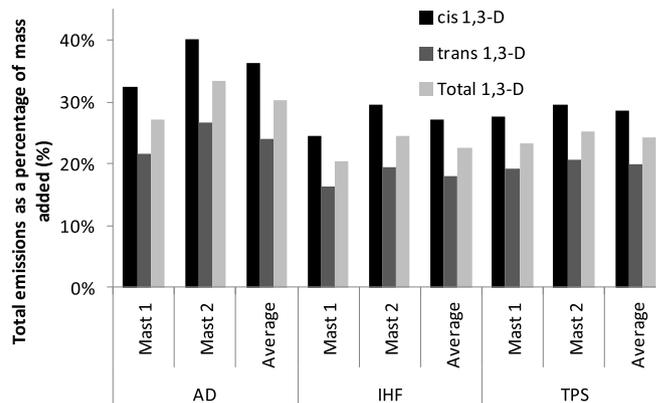


Fig. 3. Total emission losses of *cis*, *trans*, and total 1,3-dichloropropene over the entire experiment, expressed as a percentage of the total mass added, for each mast and each calculation method. The averages for the two masts are also given.

1.6, and 1.8 percentage points, respectively. The TPS method in particular yielded very similar emissions values between the two masts, suggesting a high degree of replicability when using this approach. Even the largest of these differences (AD method) are considered reasonable given that they are comparable with the variability in emissions observed in replicated soil column studies. For example, over the last decade, we have reported a number of highly controlled, highly uniform, replicated (duplicate or triplicate) laboratory soil column studies on fumigant emission fluxes (Ashworth and Yates, 2007, 2009; 2010, 2011; 2015). From these studies, if we consider only those data for bare soil treatments (i.e., those strictly comparable to the present field study) the range of total 1,3-D emission values across the column replicates ( $n = 2$  or  $3$ ) varied by between 0.6 and 12 percentage points for *cis* 1,3-D and by between 0.4 and 5.7 percentage points for *trans* 1,3-D. Across all these studies, the average difference across replicates was 6.1 ( $\pm 4.4$ ) percentage points for *cis* 1,3-D and 2.9 ( $\pm 2.1$ ) percentage points for *trans* 1,3-D. Given that these ranges for highly controlled soil column systems are slightly greater than those observed across the two replicate masts in the present field study, we consider that total emissions values for the two masts show very good replicability. This is highly encouraging given that the sources of variation in a field study of this scale are potentially very large.

### 3.3. Flux density over time

The flux densities of *cis* and *trans* 1,3-D over the course of the experiment, as calculated for each mast using each of the three methods, are shown in Fig. 4 (a–f). In each case, the fluxes of the *cis* isomer tended to be greater than those of the *trans* isomer, with maximum fluxes of the former typically at least twice those of the latter. This likely reflects the lower vapor pressure and Henry's constant of the *trans* isomer, and is consistent with previous laboratory and field studies. Overall, the three methods (AD, IHF, and TPS) produced similar flux profiles, particularly in relation to the timing of the flux peaks, i.e., the diurnal nature of the profiles. However, there are noticeable differences across the three methods in terms of the amplitude of the flux peaks. Some degree of divergence would be expected owing to the different measured/calculated parameters (each with their own level of uncertainty) used to determine the fluxes in each method; this is evidenced by the differences observed by other workers when comparing these three methods (Yates et al., 2008, 2011; 2016b). The most noticeable difference is that the AD method often yields higher fluxes than the other two methods. The AD method has long been recognized to heavily depend on stability corrections for heat and momentum (Halliwell and Rouse, 1989; Verma, 1990). In contrast, the TPS and IHF methods are not dependent on stability corrections (in the TPS method, the sensor is placed at a height that is relatively insensitive to atmospheric stability; in the IHF method, the calculations are based on principals of mass balance). Recent findings based on our research suggest that the AD flux method may be biased toward low stability values (Anderson, R; pers comm), which would result in a high bias in the resulting flux calculations.

The maximum flux rate is an important characteristic of a fumigant flux profile and is of interest to regulators since it represents the “source strength” used in air dispersion models and is therefore significant in establishing inhalation risks to bystanders and local populations. As calculated by the three methods, the maximum flux rate ranged from 9.95 to 15.37 (average 12.71)  $\mu\text{g m}^{-2} \text{s}^{-1}$  for *cis* 1,3-D and from 4.93 to 7.94 (average 6.71) for *trans* 1,3-D. When averaging the two replicate measurements, the AD method gave the greatest values for both isomers (*cis*:  $15.36 \pm 0.01 \mu\text{g m}^{-2} \text{s}^{-1}$ ; *trans*:  $7.67 \pm 0.28 \mu\text{g m}^{-2} \text{s}^{-1}$ ), followed by the TPS method (*cis*:  $12.39 \pm 0.59 \mu\text{g m}^{-2} \text{s}^{-1}$ ; *trans*:  $7.11 \pm 0.71 \mu\text{g m}^{-2} \text{s}^{-1}$ ) and then the IHF method (*cis*:  $11.47 \pm 1.52 \mu\text{g m}^{-2} \text{s}^{-1}$ ; *trans*:  $5.17 \pm 0.24 \mu\text{g m}^{-2} \text{s}^{-1}$ ). Based on these low ranges, it is considered that the two replicates showed very similar maximum flux rates to one another across both isomers and

each calculation method. In general, the timing of the maximum peak was also fairly consistent between the methods and between the two replicates; in each case, it was most frequently observed in the first nighttime sample (16.5 h after application) or in the morning of the day following application for both the *cis* and *trans* isomers.

After peaking relatively rapidly following application, the 1,3-D fluxes showed a general declining trend over time. In contrast to soil column emissions, which generally show a smooth decline in flux density over time after an initial peak (Ashworth et al., 2015), field data calculated using meteorological approaches tend to show numerous peaks over time due to the effects of environmental factors (van Wesenbeeck et al., 2007; Yates et al., 2016a). It is evident from Fig. 4 that emission peaks typically occurred during nighttime (indicated by vertical dashed lines). All else being equal, higher fumigant fluxes would be expected during daytime due to the higher temperatures facilitating evaporation (Majewski et al., 1995).

However, some studies have shown that high fluxes during nighttime and early morning can be observed under certain conditions, with low fluxes actually observed during the hottest part of the day. Spencer et al. (1969) showed that vapor phase adsorption strongly binds a volatile herbicide to soil particles as the water content decreases to low levels. As described by Yates et al., 2008; Yates et al., 2011; Yates et al., 2016b, this phenomenon may also relate to 1,3-D, with dry surface soil conditions during the hot daytime increasing gas phase adsorption and moist surface soil conditions during the colder nights and early mornings (e.g., due to dew formation) limiting vapor adsorption and thereby increasing emission fluxes. This relationship between vapor phase adsorption and water content has been reported by a number of workers (Goss, 1992; Goss and Eisenreich, 1996; Schneider et al., 2013; Garcia et al., 2014; Prueger et al., 2017) and helps to explain our observed trends in 1,3-D flux peaks over time.

In comparing the flux curves for Mast 1 and Mast 2 (Fig. 4 a–f), it is evident that at least visually, very good overlap/agreement is seen. Peaks and troughs in the curves from the two masts match well throughout the experiment and the magnitudes of the fluxes are also consistently very similar. In order to directly compare the fluxes from the two masts, the inset of each individual figure (a–f) shows the linear regression of the two sets of data (Mast 1 vs. Mast 2). In each case, the regression is very strong ( $r^2 = 0.94$ – $0.98$ ) and has a slope close to unity (1.01–1.17). Moreover, significance testing using the  $r^2$  values revealed that each correlation was very highly statistically significant ( $p < 0.00001$ ; degrees of freedom = 75). These results indicate that the two replicate measurements were highly similar. Good metrics against which to compare these values and demonstrate their replicability are the correlation coefficient and slope of the linear regression of flux densities obtained from replicated soil column experiments. Again using data from our previous soil column studies on 1,3-D emissions from bare soil (Ashworth and Yates, 2007; Ashworth et al., 2009, 2010, 2011, 2015), we find that  $r^2$  values of the linear regression of replicate pairs averaged ( $n = 7$ ) 0.90 for *cis* 1,3-D and 0.87 for *trans* 1,3-D, with standard deviations of 0.05 and 0.08, respectively. The slopes of these regression lines averaged 1.08 for *cis* 1,3-D and 1.00 for *trans* 1,3-D, with standard deviations of 0.23 and 0.22, respectively. Therefore, as for the total emission data, it is evident that the present field flux data show a degree of replicability that compares very favorably with that of highly controlled soil column systems.

Fig. 5 shows the differences between the flux measurements of the two masts for each of the 77 sample periods and each flux calculation method. Values above the abscissa indicate that the Mast 1 flux was greater than the Mast 2 flux (and vice versa); as such, it is apparent that Mast 2 typically gave the greater fluxes (93% of cases). It is noticeable that the largest differences were observed during approximately the first half of the experiment. One potential reason for this may be the flow rate issues observed for Mast 1 between 0.7 and 4.3 days (sample periods 4–32) at 250 cm height. It is possible that the elimination of this height from the flux calculations resulted in lower flux estimates for Mast 1. Across the three flux

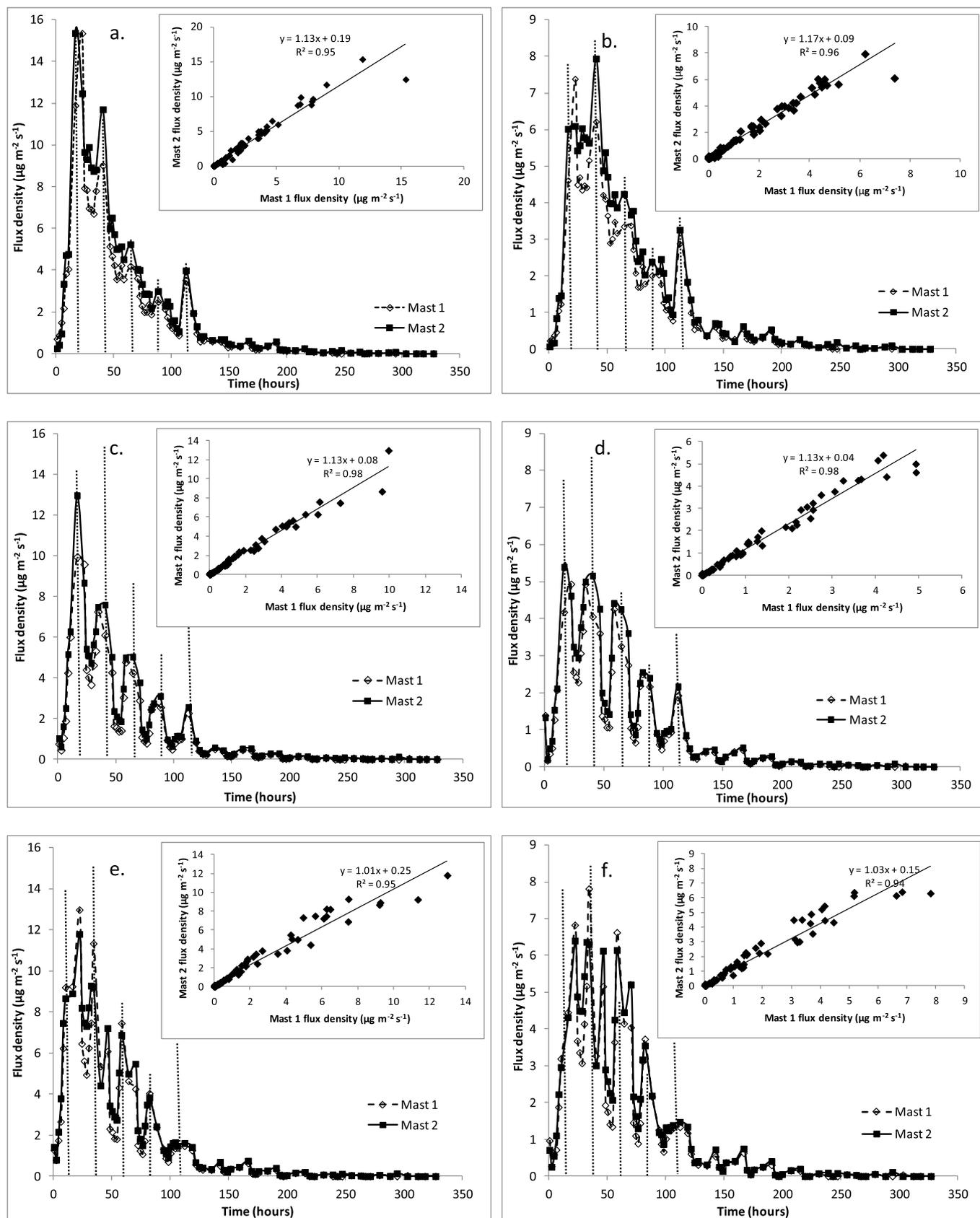


Fig. 4. Flux densities of *cis* (a, c, and e) and *trans* (b, d, and f) 1,3-dichloropropene from each mast over the course of the experiment, as calculated by the AD (a and b), IHF (c and d), and TPS (e and f) methods. Inset plots show the linear regression between the Mast 1 and Mast 2 data.

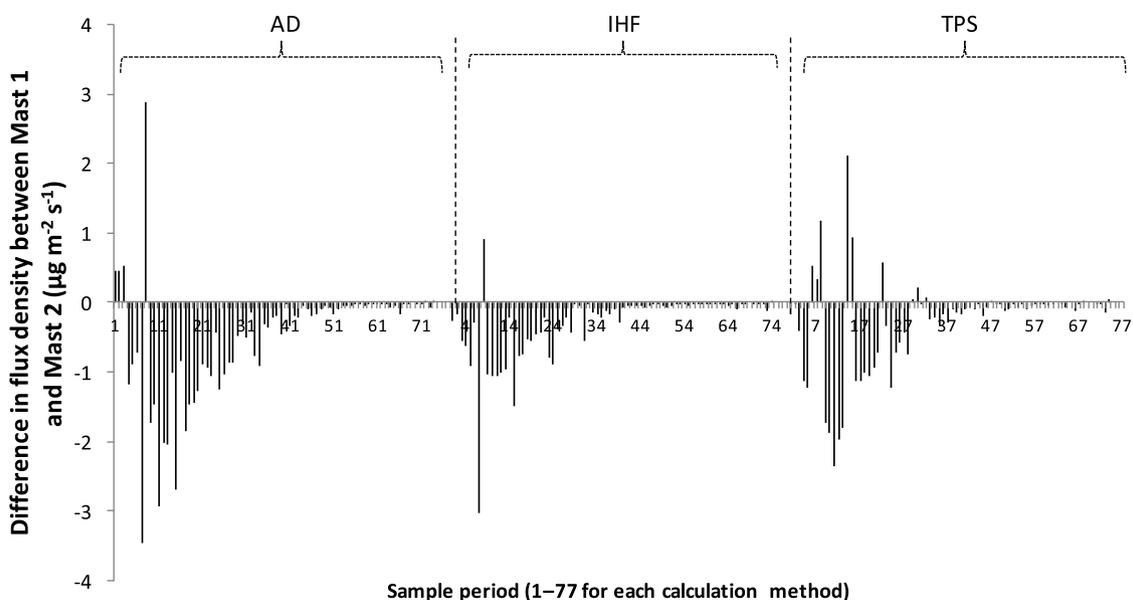


Fig. 5. Difference in *cis* 1,3-D flux density between Mast 1 and Mast 2 for each of the 77 sample periods and each calculation method (AD, IHF, TPS methods).

calculation methods, the average difference between the two masts followed the order: AD ( $0.60 \mu\text{g m}^{-2} \text{s}^{-1}$ ) > TPS ( $0.42 \mu\text{g m}^{-2} \text{s}^{-1}$ ) > IHF ( $0.30 \mu\text{g m}^{-2} \text{s}^{-1}$ ). Analysis of variance (ANOVA), followed by Tukey's honest significant difference (HSD) tests, was used to compare the methods in terms of the average flux difference given by each; this analysis demonstrated that the difference between the AD and IHF methods was significant ( $p < 0.05$ ). The plot of differences in *trans* 1,3-D flux data between the two masts (not shown) was relatively similar to that for the *cis* isomer, with 88% of the flux measurements being greater for Mast 2. The average differences across the methods followed the same order observed for the *cis* isomer but were smaller in magnitude: AD ( $0.39 \mu\text{g m}^{-2} \text{s}^{-1}$ ) > TPS ( $0.29 \mu\text{g m}^{-2} \text{s}^{-1}$ ) > IHF ( $0.20 \mu\text{g m}^{-2} \text{s}^{-1}$ ). As with the *cis* data, statistical (ANOVA/HSD) testing showed that a significant difference ( $p < 0.05$ ) was apparent between the AD and IHF methods. In contrast to the total emission comparisons above where the TPS method produced the best replicability, these results suggest that the IHF method produced the best replicability between the two masts in terms of flux density. Overall, the relatively "poorer" replicability of the AD method may be due to the greater level of complexity in its calculation, i.e., the greater number of parameters it requires (compared to the other methods) perhaps introduces additional potential uncertainties into the calculation. However, based on the very favorable comparisons with soil column data, we consider that all methods produced highly satisfactory replicability in relation to flux density.

#### 4. Conclusions

Herein, we have reported flux measurements of *cis* and *trans* 1,3-D over 14 days of a field experiment conducted near Fresno, CA in September 2016. Three meteorological methods were used to calculate fluxes and total emission losses. Some variation existed across the three calculation methods but the data were in line with losses reported in previous work. Compared with the other methods, it was noticeable that the AD method consistently gave the highest fluxes; it also yielded the highest total emissions percentage. This finding is consistent with previous studies. The AD method necessitates the accurate determination of stability corrections for heat and momentum; whereas the TPS and IHF methods do not. Having previously noted this discrepancy between the methods, we hypothesized that the method for determining stability parameters in the AD method may be subject to errors. Therefore, elucidating this phenomenon by additionally determining stability parameters based on entirely independent eddy covariance measurements was a secondary objective of the present

study; this will be presented in a subsequent paper. In contrast to all previous work (to our knowledge), our use of duplicate sampling masts allowed us to assess the replicability of the flux measurements. In terms of both total emission losses and flux density, the two masts yielded very similar data that compared very favorably with previous data obtained from highly controlled, uniform, replicated laboratory soil columns. In particular, linear regression of the flux density data from the two masts yielded very strong  $r^2$  (0.95–0.98) and slope (1.00–1.17) values. These findings suggest a high degree of replicability between the two masts and indicate that the meteorological methods offer a very robust approach to determining fumigant fluxes under large-scale field conditions, despite the potential for significant variation in environmental factors to occur in such studies.

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