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

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Brief:

Atmospheric emissions of 1,3-dichloropropene (1,3-D) and chloropicrin can be reduced by deep
injection into soil.

Short Title:

Effect of deep injection on emissions of 1,3-D and chloropicrin

33 ABSTRACT

34 Fumigating soil is important for the production of many high-value vegetable, fruit, and tree crops,
35 but fumigants are toxic pesticides with relatively high volatility, which can lead to significant
36 atmospheric emissions. A field experiment was conducted to measure emissions and subsurface
37 diffusion of a mixture of 1,3-dichloropropene (1,3-D) and chloropicrin after shank injection to bare
38 soil at 61 cm depth (i.e., deep injection). Three on-field methods, the aerodynamic (ADM),
39 integrated horizontal flux (IHF), and theoretical profile shape (TPS) methods, were used to obtain
40 fumigant flux density and cumulative emission values. Two air dispersion models (CALPUFF and
41 ISCST3) were also used to back-calculate the flux density using air concentration measurements
42 surrounding the fumigated field. Emissions were continuously measured for 16 days and the daily
43 peak emission rates for the five methods ranged from 13 to 33 $\mu\text{g m}^{-2} \text{ s}^{-1}$ for 1,3-D and 0.22 to 3.2
44 $\mu\text{g m}^{-2} \text{ s}^{-1}$ for chloropicrin. Total 1,3-D mass lost to the atmosphere was approximately 23–41 kg
45 ha^{-1} , or 15–27% of the applied active ingredient and total mass loss of chloropicrin was < 2%.
46 Based on the five methods, deep injection reduced total emissions by approximately 2–24%
47 compared to standard fumigation practices where fumigant injection is at 46 cm depth. Given the
48 relatively wide range in emission-reduction percentages, a fumigant diffusion model was used to
49 predict the percentage reduction in emissions by injecting at 61 cm, which yielded a 21% reduction
50 in emissions. Significant reductions in emissions of 1,3-D and chloropicrin are possible by injecting
51 soil fumigants deeper in soil.

52

53 KEYWORDS: soil fumigation, emissions, 1,3-dichloropropene, chloropicrin, bare soil, field
54 experiment, shank injection, Industrial Source Complex Short Term model (ISCST3), CALPUFF
55 dispersion model, aerodynamic gradient method, integrated horizontal flux method, theoretical
56 profile shape method

57

58 INTRODUCTION

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

63 Agricultural uses of volatile pesticides and soil fumigants may pose a significant threat to
64 human and environmental health if these compounds are transported away from the target zones or
65 persist in soil. Globally, the fumigant methyl bromide (MeBr) was scheduled for phase-out in the
66 year 2005, due to its potential for depleting stratospheric (UNEP, 1992; 1995; Federal Register,
67 2000). In California, air emission inventories have shown that pesticides and fumigants are
68 significant sources of air pollution. In Fresno County from 1976 to 1995, about 19 tons of pesticide
69 chemicals were emitted into the atmosphere daily (ARB, 1978, 1997a, 1997b), which represents
70 16% of the reactive organic gas fraction in this region. Unexpectedly high air concentration
71 measurements of an agricultural fumigant 1,3-dichloropropene (1,3-D) prompted a suspension in
72 California between 1990 and 1994 (CDFA, 1990). Soil fumigants may also pose a risk to water
73 supplies due to their generally low soil adsorption properties. For example, movement of 1,3-D to
74 groundwater and fate in aquatic ecosystems have been addressed in several studies (Merriman et al.,
75 1991; Obreza and Onterman, 1991; Yon et al., 1991; Schneider et al., 1995). Bystander exposures
76 to pesticides can be a serious problem related to production agriculture, if not properly managed.
77 With an improved understanding of the mechanisms and processes that affect pesticide transport
78 and fate in soil-water-air systems, it becomes possible to reduce the harmful effects to non-target
79 organisms, and maintain agricultural production, through development of new pesticide
80 management strategies that minimize emissions.

81

82 Volatilization and soil degradation are two important routes of fumigant dissipation (*Yagi et*
83 *al., 1995; Majewski et al., 1995; Yates et al., 1996*) and several methods have been developed and
84 tested to lower emission losses from soil. These include surface diffusion barriers, such as
85 agricultural films, water seals (*Wang et al., 1997; Gao and Trout, 2006*), surface soil amendments
86 (*Gan et al., 2000; McDonald et al., 2008; Yates et al., 2011*), and deep injection (*Yates, et al.,*
87 *1997*), among others. Deep injection offers a low-cost approach to reduce emissions compared to
88 the use of agricultural films, water seals, soil amendments, or any other approach that requires
89 adding material to a field. With deep injection, emissions can be reduced by decreasing
90 concentration gradients near the soil surface and increasing the soil residence time, which removes
91 chemical fumigants from the soil zone via degradation.

92 Micrometeorological approaches have been frequently used to measure field-scale pesticide
93 and fumigant emissions from agricultural fields (*Glotfelty et al., 1984; Majewski et al., 1995; Yates*
94 *et al., 1996; 1997; 2015*) and include the aerodynamic, integrated horizontal flux, and theoretical
95 profile shape methods. Regulatory approaches have also been used to calculate fumigant emission
96 rates by fitting air dispersion models to measurements of the air concentration collected around a
97 treated field. For example, the California Department of Pesticide Regulations (CDPR) continues
98 to use the Industrial Source Complex Short Term model (ISCST3) (*Ross et al., 1996; Barry et al.,*
99 *1997*) for calculating emission rates for regulatory purposes (*CDPR, 2008*). EPA recently replaced
100 ISCST3 with AERMOD for regulatory use. However, CDPR conducted an analysis and found that
101 the changes incorporated into the AERMOD model did not significantly improve fumigant
102 emission estimates compared to ISCST3. Therefore, CDPR determined that ISCST3 remains
103 appropriate, and their preferred approach, for estimating fumigant emission rates (*CDPR, 2008*).

104 Other atmospheric dispersion models, such as CALPUFF (*Johnson et al.*, 1999) can also be used to
105 calculate fumigant emission rates.

106 The soil fumigants 1,3-D and chloropicrin are used to control nematodes and fungi in a
107 variety of vegetable and tree crops. They have relatively high water solubility ($\sim 2 \text{ g L}^{-1}$) and short
108 field half-life, and thus, planting can commence within weeks after fumigation. These fumigants
109 also have a relatively high vapor pressure (18–28 mmHg) so that losses to the atmosphere can be
110 significant. In a previous paper, *Yates et al.* (2015) reported on a field experiment conducted to
111 measure the volatilization rate of 1,3-D and chloropicrin after application to a bare soil at 46 cm
112 depth (SI) using a standard fumigation methodology. Using several methods for quantification, the
113 reported total emissions of 1,3-D and chloropicrin, respectively, ranged from 16 – 35% and 0.3 –
114 1.3% of the applied fumigant.

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

119

120 **METHODS**

121 The deep injection (DI) field experiment was conducted near Buttonwillow, CA in an
122 agricultural field managed by the farmer. The methods for this experiment are the same as *Yates et*
123 *al.* (2015) with the exception of injection depth. In brief, the soil is classified as Milham sandy
124 loam (fine-loamy, mixed, thermic Typic Haplargids), with approximately 1 % organic matter
125 (upper 10 cm) and decreasing with depth. Two weeks before the experiment the field was disked,
126 plowed and irrigated so that the soil condition was suitable for fumigation (i.e., water content was

127 approximately $0.2 \text{ cm}^3 \text{ cm}^{-3}$ and a friable soil texture). The fumigation rigs had a 450 cm tool bar
128 containing 9 shanks spaced in 50 cm increments laterally. The target depth of application for this
129 field was 61 cm (i.e., 24 inches) and target Telone C-35 application rate was 240 kg/ha (i.e., 20
130 gal/ac). The field size was 2.8 ha area (178 m by 157 m) and was determined by visually tracking
131 and marking the outside edge of the fumigation rig and tool bar. The total Telone-C35 mass
132 applied to the field was 672 kg and was determined by weighing the tanks before and after
133 fumigation. A chemical analysis of the formulation in the tanks revealed that 430 kg of 1,3-D and
134 242 kg chloropicrin were applied. After the field was fumigated, nothing further was done to the
135 field and there was no precipitation during the experiment.

136

137 ***Measurement of 1,3-D and Chloropicrin***

138 XAD-4 (SKC 226-175, SKC, Incorporated, Fullerton, CA) sampling tubes were used to
139 collect 1,3-D and chloropicrin concentrations in the atmosphere at the field site. A charcoal backup
140 tube (SKC 226-09, SKC, Incorporated, Fullerton, CA) was used to check for 1,3-D breakthrough
141 for the field samples. Fumigant measurements were collected at 10, 40, 80, 150, 250 and 400 cm
142 above the ground surface at field center by drawing air through the sampling tubes using a vacuum
143 system at a nominal flow rate of $150 \text{ cm}^3 \text{ min}^{-1}$. Additional samples of the 1,3-D and chloropicrin
144 concentrations in the atmosphere were collected at 1.5 m above the soil surface at 12 locations
145 surrounding the field site (Figure 1) and had a nominal flow rate of 1.5 L min^{-1} . The sampling tubes
146 were stored in a freezer until chemical analysis.

147 Chloropicrin and 1,3-D concentrations in the soil gas phase were collected at two locations in
148 the field. The sampling protocol involved the use of stainless steel sampling tubes installed to 5,
149 10, 25, 50, 75 and 100 cm depths. During sampling, a gas-tight syringe was connected to the
150 stainless steel tube and 50 mL of the soil pore space air phase was drawn through an XAD-4 tube.

151

152 *Analysis of 1,3-D and Chloropicrin*

153 Sampling tubes were warmed to room temperature, cut and both sorbent beds were transferred
154 to separate 21-ml head-space vials. Then, 4 mL of n-hexane was added and the vials were
155 immediately sealed with a Teflon-lined septum and aluminum cap. The vials were shaken for 30
156 min, and then 1 mL of the supernatant was transferred into a 2-mL GC-vial, capped and then stored
157 at $-70\text{ }^{\circ}\text{C}$ until GC analysis.

158 The GC analysis was conducted using an Agilent 6890 series gas chromatograph (Agilent
159 Technologies, Palo Alto, CA) with a micro-electron capture detector (μECD). The column used for
160 the analysis was a $30\text{ m} \times 0.25\text{ mm}$ DB-VRX column (J & W Scientific, Folsom, CA). The oven,
161 inlet and detector temperatures were $90\text{ }^{\circ}\text{C}$, $240\text{ }^{\circ}\text{C}$ and $290\text{ }^{\circ}\text{C}$, respectively. The injection volume
162 was $4.0\text{ }\mu\text{L}$ and the makeup gas was nitrogen with a flow rate of 60 mL/min .

163 The limits of detection (LOD) and quantification (LOQ) were determined for XAD-4 tubes
164 using this analytical method. For 1,3-D, LOD and LOQ were $0.05\text{ }\mu\text{g/tube}$ and $0.14\text{ }\mu\text{g/tube}$,
165 respectively. For chloropicrin, LOD and LOQ were $0.004\text{ }\mu\text{g/tube}$ and $0.11\text{ }\mu\text{g/tube}$, respectively.
166 Further testing revealed that fumigant recovery by XAD-4 at an airflow rate of 0.15 L/min was $86 \pm$
167 5% (1,3-D) and $87 \pm 4\%$ (chloropicrin). An analysis of fumigant recovery from both sorbent beds
168 showed that 98% of the 1,3-D mass and 94% of the chloropicrin mass was found in the front bed.
169 Similar results for chloropicrin were found by Ashworth et al. (2008).

170

171 *Meteorological Measurements*

172 Wind speed and wind direction (heights 20, 40, 80, 160, 400 cm , Windsonic 2-D, Gill
173 Instruments, Ltd), net radiation (height 100 cm, Q-6, Radiation and Energy Balance Systems, Inc),

174 air temperature (heights 20, 40, 80, 150 cm, fine-wire thermocouples, FW3, Campbell Scientific,
 175 Inc.), air temperature and relative humidity (height 150 cm, CS-215, Campbell Scientific, Inc.) and
 176 barometric pressure (Vaisala PTA-427, Campbell Scientific, Inc.) were measured at the field center.
 177 Solar radiation (LI-200S, LI-COR, Inc.) and 10 m wind speed and wind direction (Wind Monitor,
 178 5305, R.M. Young, Traverse City, MI) were measured near the field (< 50 m). Using the 384
 179 hourly-averaged net radiation measurements collected during the experiment, an average and
 180 standard deviation was computed for each hour-of-day.

181

182 ***Methods for Measuring the Emission Rate from Soil***

183 Three on-field micrometeorological methods were used to measure the fumigant emission rate
 184 from the field: aerodynamic gradient (*Parmele et al., 1972*), theoretical profiles shape (*Wilson et*
 185 *al., 1982*), and integrated horizontal flux (*Denmead et al., 1977*) methods. The aerodynamic
 186 gradient method (ADM) utilizes the wind speed, temperature and fumigant concentration gradients
 187 to calculate an emission rate (i.e., flux density). The aerodynamic equation for the surface flux,
 188 $f_z(0, t)$, is (Rosenberg, et al. 1983)

$$189 \quad f_z(0, t) = \frac{-k^2 z^2}{\phi_m(t) \phi_c(t)} \left(\frac{\partial \bar{C}(t)}{\partial z} \right) \left(\frac{\partial \bar{u}(t)}{\partial z} \right) \quad (1)$$

or

$$f_z(0, t) = -k^2 \frac{[\bar{C}_2(t) - \bar{C}_1(t)] [\bar{u}_2(t) - \bar{u}_1(t)]}{\phi_m(t) \phi_c(t) \ln(z_2 / z_1)^2} = -\Omega_f \frac{[\bar{C}_2(t) - \bar{C}_1(t)]}{\ln(z_2 / z_1)}$$

190 where $f_z(0, t)$ is the interval-averaged vertical flux density at the soil surface [$\mu\text{g m}^{-2} \text{s}^{-1}$], k is von
 191 Karman's constant (~ 0.4), $\bar{u}(t)$ is the averaged wind speed [m s^{-1}], z is height above the soil surface
 192 [m] and $\bar{C}$ is the averaged concentration [$\mu\text{g m}^{-3}$] above the soil surface, ϕ is a stability correction

193 where the subscripts m and c indicate momentum and fumigant, and Ω_f is the contribution to the
194 flux from meteorological factors.

195 The ADM method requires a relatively large and spatially-uniform source area and the
196 sampling equipment is usually placed below a maximum height that is approximately 1–2% of the
197 upwind fetch distance, which for this experiments would be between the 80 and 150 cm. Empirical
198 relationships are used adjust the flux for stable and unstable atmospheric conditions (*Pruitt et al.*,
199 1973).

$$\begin{aligned} \phi_m &= (1 - 16R_i)^{-0.33} & \phi_c &= 0.885 (1 - 22R_i)^{-0.4} & R_i < 0 \\ \phi_m &= (1 + 16R_i)^{0.33} & \phi_c &= 0.885 (1 + 34R_i)^{0.4} & R_i > 0 \end{aligned} \quad (2)$$

201
202 where R_i is the Richardson's number ($g/T (\partial T/\partial z) [\partial u/\partial z]^{-2}$), g is the gravitational acceleration (i.e.,
203 9.8 m s^{-2}), and T is the absolute temperature. Other stability corrections have been proposed in the
204 literature (*Brutsaert, 1982; Rosenberg et al., 1983; Fleagle and Businger, 1980*). When calculating
205 the emission rates for this experiment, the wind speed and concentration gradients were determined
206 by linear regression (scalar vs natural logarithm of height) using the measurements between the
207 surface and a height of 150 cm.

208 The theoretical profile shape (TPS) method requires a measurement of wind speed and
209 fumigant concentration at one specific height in the field. The estimate of the volatilization rate is
210 obtained by dividing the product of the wind speed and concentration by a constant correction
211 factor, which is obtained using the trajectory simulation model of *Wilson et al. (1982)*. This
212 method can be used on smaller fields since the height of the sampling equipment is determined *a*
213 *priori* by conducting an atmospheric simulation of the field for a range of atmospheric conditions

214 and determining a height where the measurements used to obtain the emission rate are minimally
215 affected by atmospheric stability.

216 The integrated horizontal flux (IHF) method uses a mass balance approach to estimate the
217 emission rate, and requires fumigant concentrations and horizontal wind speeds measurements at
218 several heights above the soil surface (*Denmead et al., 1977*). This method assumes that emissions
219 are uniformly distributed in the treated area, but does not require corrections for atmospheric
220 stability.

221 In addition to the on-field flux measurements, two regulatory approaches based on fitting an
222 air dispersion model to air concentration measurements collected around a treated field were also
223 used to calculate the fumigant emission rate. A comprehensive non-steady state Lagrangian puff
224 atmospheric dispersion model, CALPUFF, was used to back calculate the fumigant emission rates
225 for this study (*Scire et al., 2000*). For computing the flux rate, CALPUFF v6.112 was used with a
226 2-min time step and an integrated puff sampling approach (i.e. MSLUG=0). In addition to
227 CALPUFF, the Industrial Source Complex Short Term model (ISCST3), which is currently the
228 preferred approach used by California Department of Pesticide Regulations (CDPR), was used for
229 back-calculating fumigant emission rate (*Ross et al., 1996; Barry et al., 1997; CDPR, 2008*). Even
230 though Gaussian plume air dispersion models are known to have limitations, which include errors
231 associated with changing meteorology and errors related to near- and far-field distance effects, etc.
232 (*Meroney, 1992*), CDPR's long history using these approaches for regulatory needs makes their
233 use in calculating fumigant emission rates relevant.

234 The total mass lost from fumigant emissions (kg) after application to soil, at a particular time,
235 was obtained by summing the product of the period emission rate, sampling period duration, and
236 treated area.

237 RESULTS AND DISCUSSION

238 Shown in Figure 1 is the site layout for the deep injection experiment. The treated field was
239 located about 0.85 km southwest of a standard-injection experiment reported by *Yates et al.*, (2015).
240 Figure 1 shows the layout of the plots and the position of the sampling equipment surrounding each
241 field. An additional air sampler was placed halfway between the two field plots to check for cross
242 contamination. For chloropicrin, all measurements between fields were below the analytical
243 detection limit. For 1,3-D, 14% of the measurements were below the detection limit and the
244 maximum measured concentration between the fields was $7.1 \mu\text{g m}^{-3}$, but this value was an order of
245 magnitude lower than near-field concentrations. For the samples above the detection limit, 8%,
246 58% and 20%, respectively were 4–9, 10–61 and 85–821 times lower than the near-field
247 concentrations.

248 Soil and environmental conditions at the deep-injection field site were very similar to the
249 standard-injection experiment. For the deep-injection experiment, the air temperature at 0.8 m
250 ranged from 10.2 to 35.5 °C and averaged 22.2 °C. The daily peak temperatures were relatively
251 warm with highs of 30.6 ± 3.6 °C and nighttime lows of 14.2 ± 2.5 °C.

252 The hourly mean and standard deviation of the net solar radiation (Q_{net}) during the deep-
253 injection experiment (Figure 2, solid bars), provides a measure of the energy available for soil
254 heating. The Q_{net} data was found to be smoothly varying throughout the day. This indicates
255 relatively continuous clear sky conditions. For comparison purposes, Figure 2 also shows Q_{net}
256 (crosshatched bars) for the standard-injection experiment conducted simultaneously in a nearby
257 field. In general, the differences between Q_{net} between fields are within one standard deviation
258 during any hourly period. The small standard deviation indicates that soil heating was relatively
259 uniform and predictable by daytime hour. The similarity in Q_{net} between field sites was anticipated

260 due to placement of field sites within the same soil type, and identical field and fumigation
261 management practices. For the deep-injection experiment, the maximum, average, and minimum
262 Q_{net} values, respectively, were 438 W m^{-2} , 88 W m^{-2} , and -72 W m^{-2} . While there are some slight
263 differences in the hour-of-day net radiation measurements between the field sites, the differences all
264 fall well within one standard deviation.

265 The wind speed at 0.8 m height ranged from 0.31 to 6.95 m s^{-1} and had an average of 1.5 m s^{-1}
266 and the dominant wind direction (i.e., average $\pm$ one standard deviation) was $344 \pm 66^\circ$. In this area
267 of the San Joaquin Valley, the regional wind patterns are affected by the geographic orientation of
268 the valley and surrounding mountains, and leads to winds coming predominately from the NW. The
269 wind rose diagrams (Figure 3) provide information about the direction of the wind speed, the wind
270 speed velocity and the probability that the wind speed comes from a particular direction. The wind
271 rose diagram reveals that between 14 % (10 m height) and 16 % (1.6 m height) of the time the
272 winds were from $360 \pm 11^\circ$. Averaging the high frequency measurements (i.e., 1 min data)
273 collected at 10 m, the resultant average wind direction and wind speed were 331° and 1.37 m s^{-1} ,
274 respectively. At 1.6 m, the resultant average wind direction and wind speed were 342° and 1.03 m
275 s^{-1} , respectively. The difference between the average wind direction at 10m and 1.6m was likely due
276 to deviations in the orientation of the sensors with respect to North. The diagram also shows that
277 wind speeds in excess of 5 m s^{-1} were observed infrequently, and tended to be from the NW and
278 WNW directions. On an hourly-averaged basis, the maximum wind speeds at 1.6 m were generally
279 below 4 m s^{-1} , with $3.4 \pm 1.4 \text{ m s}^{-1}$. The largest value at 1.6 m was 8.0 m s^{-1} , which occurred near
280 the end of the experiment ($t=14.7 \text{ d}$). The largest observed hourly wind speed at height 10 m was
281 8.8 m s^{-1} . During nighttime hours, wind speeds were commonly from 0.3 to 0.6 m s^{-1} .

282 Since two experiments were being conducted simultaneously, the orientation of the fields
283 were based on the highest probability that the observed wind directions (i.e., predominantly from
284 the northwest) would rarely lead to sampling interferences. Over the course of the experiment, the
285 predominant wind direction was indeed from northwest to the southeast (Figure 3) and rarely were
286 the winds from the NE (i.e., < 9% of time) or SW (< 3% of time). When this did occur, the NE
287 wind speeds were usually low; less than 2.5 m s^{-1} (6% of time).

288 The temperature gradient at 60 cm height above the soil surface is shown in Figure 4 (A) and
289 generally ranged $\pm 3^\circ\text{C m}^{-1}$ over the experiment. Negative values indicate higher temperatures near
290 the soil surface, which usually occur during unstable conditions (i.e., midday). Near neutral
291 atmospheric conditions occurred consistently near sunrise and sunset each day, and was also
292 observed occasionally at other times. At night, the temperature gradient is positive and is much
293 more erratic compared to daytime values. The gradient Richardson's number (Figure 4B) and
294 atmospheric stability parameter for momentum (Figure 4C) were calculated using the temperature
295 and wind speed gradients. The gradient Richardson number (Ri) is proportional to the temperature
296 gradient, and therefore is zero when the temperature gradient is zero. This provides a means to
297 determine the effect of thermal stability on atmospheric profiles and provides a means to compute
298 the emission rate. During nighttime hours, the momentum stability parameter, Φ_m , was commonly
299 from 2 to 4 with an average and standard deviation of the daily maxima of 2.63 ± 0.76 and during
300 daytime hours the average and standard deviation of the daily minima was 0.37 ± 0.08 .

301 The effect of atmospheric factors on the flux rate can be investigated using Ω_f (Equation 1).
302 Ω_f provides a means to compare the atmospheric stability differences of the deep-injection and
303 standard-injection fields by eliminating the confounding treatment effects introduced by the
304 concentration gradient. Ω_f provides a method to demonstrate the similarity, or dissimilarity, of the

305 fields and could be used to justify reliance on a single set of wind and temperature measurements in
306 field experiments with nearly identical soil, environmental conditions and field management
307 practices. The relationship shown in Figure 5 reveals that the soil and micrometeorological behavior
308 of the standard-injection and deep-injection fields were very similar for these experimental fields.
309 The slope of the regression line (solid) was 1.07 ($r^2 = 0.98$) which is close to the 1:1 line (dashed).

310 Air concentrations measured in the center of the field, and at surrounding locations 30, 90
311 and 120 m from the field edge showed expected behavior (Figure 6). During the first few days, high
312 atmospheric concentrations of 1,3-D were observed at the sampling locations. This is a
313 consequence of the larger chemical concentrations present in the soil shortly after injection,
314 concentration gradients moving fumigant toward the surface, and the rapid fumigant diffusion due
315 to the presence of soil fractures created during fumigation by the shanks. Using a fumigant
316 diffusion model, *Yates (2009)* showed that shanks produce a more uniform soil concentration and
317 higher concentrations near the soil surface shortly after fumigation, compared to fumigation without
318 a soil fracture. Excavation after fumigation clearly showed the presence of a significant fracture
319 zone (Figure S1). Air concentrations at later times decreased as the fumigant volatilizes and
320 degrades in soil, which reduce source concentrations and gradients. During the first couple of days,
321 the highest 1,3-D air concentration at 30 m from the field edge was approximately $170 \mu\text{g m}^{-3}$ and
322 after day 3, a steady reduction in air concentration occurred. At 90 and 120 m from the field edge,
323 the maximum air concentration was from approximately 80 to $110 \mu\text{g m}^{-3}$. After approximately day
324 6, and continuing until the end of the experiment, the daily maximum air concentrations for all
325 distances were an order-of-magnitude less than the earlier daily maxima. Unlike 1,3-D, chloropicrin
326 air concentrations were very low throughout the experiment (data not shown).

327 Also shown in Figure 6 is a comparison between 1,3-D concentrations in the atmosphere
328 and two injection depths. For standard injection at 46 cm (Yates et al., 2015), 1,3-D concentrations
329 were generally higher compared to deep injection (i.e., 61 cm) with maxima of approximately 200
330 $\mu\text{g m}^{-3}$ at 30 m and 120 $\mu\text{g m}^{-3}$ at 90 and 120 m from the field edge. After approximately 3 days, the
331 air concentrations became lower. By 14 days, air concentrations were negligible. The comparison
332 also reveals a similar temporal behavior for standard and deep injection.

333

334 *Direct Measurement of Fumigant Emissions*

335 Fumigant emission fractions are used by state and federal regulators to determine various
336 environmental risk endpoints. To reduce bystander exposure and protect public health, an
337 understanding of the transient emission rate is needed. Even infrequent high-level emission events
338 may lead to unacceptable exposure to fumigant vapors. Regulations to reduce near-surface ozone
339 levels also require an understanding of the total atmospheric loading of VOCs to provide an
340 estimate of soil fumigation's contribution to regional VOC.

341 Figure 7 shows time series of the emission rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) for the three
342 micrometeorological methods, which include the ADM (circles), IHF (triangles) and the TPS
343 (squares) methods. All the methods exhibit a similar pattern with daily maxima generally
344 coinciding and the peak emission rate (Table 2) for ADM and IHF occurring on day 3 of the
345 experiment, which is followed by very low rates after about 6 days post application. The only
346 exception to this trend was the peak emission rate for TPS occurring on day 1. Throughout the
347 experiment, emission rates calculated from the ADM method tended to be higher than the IHF and
348 TPS methods. In general, the single largest calculated flux, for each method, occurred during the
349 daytime hours at a time of typical atmospheric instability (i.e. morning or evening). But the other

350 daily maxima occurred at various times in response to atmospheric stability conditions in concert
351 with other soil and environmental factors that affect emissions (i.e., concentration gradients in soil,
352 soil drying, etc.).

353 For 1,3-D, the maximum emission rate of $32.3 \mu\text{g m}^{-2} \text{s}^{-1}$ was obtained with the
354 aerodynamic method, and occurred at 3.35 d. The largest emission rate for the IHF method (14.9
355 $\mu\text{g m}^{-2} \text{s}^{-1}$) also occurred during this time period. The maximum emission rate calculated with the
356 TPS method was $17.5 \mu\text{g m}^{-2} \text{s}^{-1}$ and occurred at 1.84 d and the emission rate at 3.35 d was $9.1 \mu\text{g}$
357 $\text{m}^{-2} \text{s}^{-1}$. Except for the maximum flux rate, the three methods provide similar behavior in the
358 average volatilization rates (see shaded areas), with increasing values to about 3 days then tailing
359 off afterwards.

360 The cumulative 1,3-D emission as a function of time after application is shown in Figure 7
361 (inset). At 12 d, the cumulative emission calculated with the ADM is 27 %, and the IHF and TPS
362 were lower at 19 and 15 %, respectively (Table 2). The ADM method yielded a cumulative
363 emission that was 42–80 % larger than the other methods, and was a result of consistently higher
364 emission rates throughout the experiment. When 1,3-D is applied at a depth of 46 cm (Yates et al,
365 2015) emissions calculated using the ADM were 35% (Table 2, SI). In previous research that used
366 these methods for calculating the fumigant emission rate, it was found that the ADM was
367 approximately 50% higher than the IHF and TPS methods (Yates et al., 2008). For this study, the
368 trend in total emissions was found to follow $\text{ADM} > \text{IHF} > \text{TPS}$.

369 For chloropicrin, emission rates were $< 1.5 \mu\text{g m}^{-2} \text{s}^{-1}$. The low emission rates were due to
370 high soil degradation rates observed for this soil type (Yates et al., 2015) and low chloropicrin
371 application rates, leading to relatively low soil concentrations (Ashworth et al., 2015). The total
372 chloropicrin emissions were found to be less than 1 % of applied for this study and less than 2%

373 when injected at 46 cm (Table 2, SI). This is consistent with the study by Ashworth et al, (2015)
374 which showed that chloropicrin emissions from a mixture of 1,3-D (65%) and chloropicrin (35%)
375 applied at a rate of approximately 157 kg ha⁻¹ resulted in <2% emission of chloropicrin. It was also
376 shown that the emission rate of chloropicrin drops dramatically at application rates below 100 kg
377 ha⁻¹ even in the presence of significant quantities of 1,3-D. The low atmospheric concentrations
378 measured for chloropicrin increases the uncertainty in the flux estimates, especially for the ADM,
379 which with uses the concentration gradient.

380 Short-term emission measurements tend to be highly variable during the day. Integrating
381 the short-term emission rates over a 24 h period produces smoothing and shows a more predictable
382 behavior that starts with an increase in the 24-hour emission rate after fumigation, reaching a
383 maximum on day 3, and is followed by a long period of decreasing values (see shaded areas in
384 Figure 7). The 24-hour emission rates could be mathematically modeled using conventional
385 transport approaches (Jury et al., 1983; Yates 2009; Yates et al., 2015).

386 The dynamics of the emission process changed with time after injection. Investigating the
387 behavior of the average emission rate (Figure 8), helps to reduce the variability as a function of
388 time, and more clearly reveals the underlying behavior of the volatilization process. Shortly after
389 injection the emission rate increased in response to large fumigant concentration gradients in soil,
390 and the peak emission rates occur near midnight, in an overall increasing pattern. Starting day 2,
391 the emission rates decrease during the early afternoon in response to evaporation reducing the water
392 content of the soil surface. The drying of the soil surface in response to solar energy inputs has
393 been suggested as a cause of reduced emission rate since very dry soil tends to have increased vapor
394 phase adsorption (*Spencer et al.*, 1969; *Glotfelty, et al.*, 1984; *Reichman et al.*, 2011; *Reichman et*
395 *al.*, 2013a,b). Vapor adsorption has been shown to strongly bind volatile pesticides to soil particles

396 in a highly nonlinear process (*Spencer and Cliath, 1973*), which reduces the vapor density in the
397 soil air phase.

398

399 *Indirect Measurement of Fumigant Emissions*

400 The emissions of 1,3-D obtained using the ISCST3 and CALPUFF (Figure 9) back-
401 calculation methods show similar behavior to the micrometeorological methods, with increasing
402 rates early in the experiment and decreasing rates after about 2 days. The peak emission rate for
403 CALPUFF and ISCST3 were 33 and 13 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively. The short-term emission rates
404 using ISCST3 were found to be consistently lower than estimates obtained using the CALPUFF
405 model (approximately 50% lower on average). The largest differences occurred after sunrise and
406 before solar noon, where the ISCST3 emissions could be as much as 90% lower than CALPUFF
407 values. The reported ISCST3 total 1,3-D volatilization losses were 39% lower than the CALPUFF
408 values. This is similar to the results reported by *Yates et al. (2015)* who found that the total
409 emission losses from ISCST3 were 40% less than CALPUFF. The 24 h averaged emission rate for
410 1,3-D revealed a similar pattern as shown in Figure 9 for the micrometeorological methods with an
411 increasing emission rate after fumigation, and decreasing emission rate after about 3 days.

412 For chloropicrin, the largest emission rates occurred during the first measurement period
413 with calculated CALPUFF and ISCST3 emission rates of 3 and 0.5 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively. This
414 was the period when fumigation was occurring and the high emission rates are likely associated
415 with fumigant losses when raising and lowering the shank injectors while turning the injection rig.
416 Compared to the micrometeorological methods, the total emissions were also estimated to be very
417 low, < 1.5% of applied. Total emissions from the ISCST3 method were 61% less than CALPUFF,
418 which is similar to *Yates et al., (2015)* who reported ISCST3 total emissions were 56% less than

419 CALPUFF. The measured emissions of chloropicrin during this study were different from emission
420 rates reported in the literature, which can exceed 30% of the applied fumigant. As discussed by
421 *Yates et al.* (2015), this was attributed to unusually high soil reactivity at the field site, and was also
422 verified by using a fumigant diffusion model.

423

424 *Fumigant Concentration in the Soil Gas Phase*

425 Figure 10 shows the 1,3-D (A) and chloropicrin (B) gas-phase concentration and the soil
426 water content (C) at several depths and times after application. Shown in Figure S2 is the soil
427 temperature during the experiment. For day 1, the concentration of 1,3-D and chloropicrin in the
428 soil gas phase at 0.5 m depth was approximately 14 and 5.5 $\mu\text{g cm}^{-3}$, respectively. It is evident that
429 diffusion in soil begins immediately after application and leads to increased concentrations with
430 depth. At later times (e.g., after ~ 6 days), the size of treatment zone increased and had a relatively
431 uniform concentration.

432 Two field experiments were conducted in 2005 in near-by fields, and with similar
433 experimental conditions. Field experiment 2005A (*Yates et al.*, 2008) studied the effect of surface
434 water seals on 1,3-D emissions and experiment 2005B (*Yates et al.*, 2011) studied the effect of soil
435 organic amendments on 1,3-D emissions. For both experiments, soil gas concentrations were
436 measured at a depth of 0.45 m for several days after fumigation. For 2005A, the measured soil gas
437 concentrations on days 1, 2, 3 and 4, respectively, were 29.0, 11.7, 4.57 and 2.05 $\mu\text{g cm}^{-3}$. For
438 2005B, the measured soil gas concentrations on days 1, 2, 3, 4 and 11, respectively were 25.5, 13.0,
439 6.6, 3.93, and 0.038 $\mu\text{g cm}^{-3}$. The higher soil gas concentrations during the 2005 experiments was
440 due to the depth of the soil gas samplers, which was 1 cm above the injection depth (0.46 m). For
441 the deep-injection experiment, the distance between the soil gas sampler and the injection depth

442 was 11 cm. To make a comparison with the soil gas concentration measurements from the 2005A
443 and 2005B experiments, a soil fumigant diffusion model (i.e., *Yates*, 2009) model was used to
444 estimate soil gas concentrations at 0.60 cm, 1 cm above the injection depth. Doing this leads to 1,3-
445 D concentrations of 27, 17, 12, and 9 g cm⁻³, which are similar to the measured soil gas
446 concentrations 1 cm above the injection depth during the 2005 experiments. The similarities
447 between experiments provide evidence that the observed differences in emission rates are due to
448 treatment effects (i.e., deep injection, water seals, and organic amendments).

449

450 **CONCLUSIONS**

451 One goal of this research was the comparison of emissions for several emission reduction
452 strategies, including deep injection. The similarities between measurements of soil and
453 environmental conditions across the treatments provide evidence that comparing emission rates and
454 total emissions would be valid. Using the micrometeorological and back-calculation methods to
455 estimate total emissions of 1,3-D and chloropicrin for the experiment, it was found that the methods
456 were in agreement to within approximately 20±6 % for 1,3-D and 0.6±0.3% for chloropicrin. The
457 reduction in total 1,3-D emissions by increasing the injection depth from 46 cm (*Yates et al.*, 2015)
458 to 61 cm (deep injection) ranged from 2% (ISCST3) to 24% (ADM) from a direct comparison of
459 experimental values. The reduction in emissions can also be predicted from a fumigant diffusion
460 model (*Yates*, 2009) by increasing the injection depth from 46 cm to 61 cm. Conducting this
461 analysis shows that the total 1,3-D emissions would be reduced by 21%, based on the predictions.
462 This suggests that the benefit from deep injection should be approximately a 20% reduction in
463 emissions, compared to standard fumigation; however, further research is needed to understand why
464 the back-calculation methods yielded low values compared to the micrometeorological and

465 predictive methods. A particular flux method produced relatively consistent maximum flux rates
466 for the SI and DI experiments (Table 2). The difference between methods, however, was found to
467 be greater. The ADM and CALPUFF methods produced Telone II flux rates between 25 – 33 μg
468 $\text{m}^{-2} \text{s}^{-1}$, whereas the IHF, TPS, and ISCST3 methods were 12 – 18 $\mu\text{g} \text{m}^{-2} \text{s}^{-1}$, or approximately 50
469 % lower rates. This has implications for risk assessment and for setting buffer zone sizes.

470 Additional research was conducted to further test these emission reduction strategies and for
471 additional verification of the field results. *Ashworth et al.*, (2009) conducted a laboratory study
472 using soil from the field site. An experiment was conducted using 1.5 m stainless steel soil columns
473 placed in a controlled temperature to simulate the temperature conditions observed at the field site.
474 This study reported that the total emissions of 1,3-D after injection at 46 cm was 41%. For deep
475 injection at 60 cm, total emissions of 1,3-D from replicated columns were found to be $26 \pm 2\%$
476 (unpublished data), which falls within the $20 \pm 6\%$ range. The laboratory value is also within 1% of
477 the ADM and CALPUFF methods. Comparing total emissions after fumigant injection at 46 cm to
478 deep injection (61 cm), led to a 36% reduction.

479 These results from the field experiments are consistent with two reports of the experimental
480 uncertainty inherent with the methodology for calculating emission rates, where the accuracy was
481 found to be from ± 20 to 50%. *Majewski (1997)* reported that the accuracy for emissions of methyl
482 bromide was approximately $\pm 50\%$ based on a regression analysis of the log-linear wind speed and
483 concentrations profiles with respect to height, which should also apply to other fumigants that have
484 log-linear concentration profiles. *Wilson and Shum (1992)* found that for appropriately large field
485 sites with surface roughness lengths below 10 cm the IHF method would have experimental
486 accuracy within approximately 20%. This analysis used a Lagrangian stochastic model and also
487 provides guidelines that can be used in the design of field experiments.

488 Our experiments reveal considerable variability between the methodologies used for
489 calculating the emission rate. However, it is difficult to state which method has the highest
490 likelihood of being most accurate. To do this quantitatively would require an absolute reference for
491 comparing each methodology. All the approaches used in this study require inherent simplifications
492 and assumptions that can affect the calculated flux rates. The ADM method requires a well-
493 developed surface layer for measuring gradients (concentration, wind speed, and temperature) and
494 the evaluation of an empirical term for stable and unstable atmospheric conditions, which could
495 introduce uncertainty. The TPS method does not require a large fetch, requires measurement of the
496 air concentration and wind speed at a single height and uses a sensor height that is relatively
497 unaffected by atmospheric stability. This approach is based the trajectory simulation model (Wilson
498 et al., 1981) to calculate the sensor height and a flux correction factor (ratio of horizontal to vertical
499 flux), so uncertainty would be introduced whenever the simulated atmospheric conditions deviate
500 from actual conditions. The IHF method has relatively few model assumptions (i.e., uniform source
501 strength and known upwind fetch distance), but is dependent on the accuracy of the concentration-
502 height profile at the measurement site. For complex, expensive, and large-scale field experiments,
503 especially those involving multiple simultaneous experiments, it is often cost-prohibitive to collect
504 highly detailed concentration-height measurements, which can introduce uncertainty.

505 The ISCST3 is a steady-state atmospheric dispersion model, so uncertainty would be
506 introduced for variable source strengths or when wind conditions are variable during an hourly time
507 step. CALPUFF is a non-steady-state Lagrangian puff model that tracks a fumigant in the
508 atmosphere in a more natural manner, likely performing better than ISCST3, but the results depend
509 on the gridding system employed and the representativeness of the meteorological data.

510 It is clear that further research is needed to better understand the accuracy and performance
511 of these methods for calculating fumigant emissions.

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LIST OF FIGURES

Figure 1. Site layout and positioning of fields. The experiment conducted at Standard Injection field is described by *Yates et al.* (2015).

Figure 2. The net radiation (W m^{-2}) as a function of hour of day at the field site (solid bars). The values are averages over the entire experiment of the hourly net radiation and the error bars are the standard deviations. Crosshatched bars are net radiation measurements simultaneously taken at a nearby field site and reported by *Yates et al.* (2015). The low standard deviations reflect relatively uniform cloudless conditions throughout the experiment.

Figure 3. Wind rose diagrams showing the wind direction, wind speed and frequency that the wind will occur in a specific direction. In A, wind measurements at 10 m are shown. In B, wind measurement at 1.6 m and at field center are shown.

Figure 4. (A) Temperature difference (A), gradient Richardson's number (B), and atmospheric stability parameter for momentum (C).

Figure 5. Comparison of Ω_f (Equation 1) for standard-injection and deep-injection fields for each sampling period. The slope of the regression line (solid) is close to the 1:1 line (dashed) indicating similar behavior in both fields.

Figure 6. Comparison of measurements of the 1,3-D concentration at 40 cm height at the center of the field (Center). In Figure S1 (B–D), concentrations at 1.5 m height are averages of the air

676 monitoring stations surrounding the field site and located at 30 m, 90 m, and 120 m from the edge
677 of the field.

678

679 Figure 7. Volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application for the
680 aerodynamic, integrated horizontal flux, and theoretical profile shape methods. Shaded areas are the
681 24 h average flux values for the ADM (gray) and TPS (stippled) methods. The results are for the DI
682 field.

683

684 Figure 8. Average 1,3-D volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application
685 for the DI field experiment. Values were calculated by averaging the aerodynamic, integrated
686 horizontal flux, and theoretical profile shape methods at each time point.

687

688 Figure 9. Volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application for the ISCST3
689 and CALPUFF method. Shaded areas are the 24 h average flux values for the CALPUFF (gray)
690 and ISCST3 (stippled) methods. The results are for the DI field.

691

692 Figure 10. (A) Telone II (1,3-D cis + trans) soil gas phase concentration ($\mu\text{g cm}^{-3}$) with depth in
693 soil. (B) Chloropicrin soil gas phase concentration ($\mu\text{g cm}^{-3}$) with depth in soil. Each line represents
694 the concentration distribution at a particular time after application. In (C), the initial and final soil
695 water content ($\text{cm}^3 \text{cm}^{-3}$) with depth are presented. The results are for the DI field.

696

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 [§]	Milham sl	237	237	222	2.89	162	178

[§] - Yates *et al.* (2015)

Table 2. Total emissions of 1,3-D and chloropicrin from the deep-injection plot (DI). The total 1,3-D and chloropicrin mass applied was 430 kg and 242 kg, respectively. For standard-injection plot (SI), the total 1,3-D and chloropicrin mass applied was 474 kg and 222 kg, respectively (Yates *et al.*, 2015).

Fumigant	ADM [§]		IHF [§]	TPS [§]	ISCST3		CALPUFF	
	SI	DI	DI	DI	SI	DI	SI	DI
Total emissions (%)								
1,3-D (cis)	42%	32%	22%	17%	19%	18%	32%	30%
1,3-D (trans)	28%	22%	15%	13%	13%	13%	23%	22%
chloropicrin	1%	0%	0.5%	0.3%	1%	0.4%	2%	1%
Telone	35%	27%	19%	15%	16%	16%	28%	26%
Maximum flux rate ($\mu\text{g m}^{-2} \text{s}^{-1}$)								
1,3-D (cis)	17.6	18.5	8.6	8.8	7.2	8.2	18.0	19.0
1,3-D (trans)	9.3	13.8	6.3	8.7	4.7	5.3	11.9	14.4
chloropicrin	0.7	0.2	0.4	1.3	0.6	0.6	3.9	3.2
Telone	25.0	32.3	14.9	17.5	11.7	13.2	29.9	33.4

[§] - ADM: Aerodynamic method; IHF: Integrated horizontal flux method; TPS: theoretical profile shape method

Figure 1. Site layout and positioning of fields. The experiment conducted at Standard Injection field is described by *Yates et al. (2015)*.

Figure 2. The net radiation (W m^{-2}) as a function of hour of day at the field site (solid bars). The values are averages over the entire experiment of the hourly net radiation and the error bars are the standard deviations. Crosshatched bars are net radiation measurements simultaneously taken at a nearby field site and reported by *Yates et al.* (2015). The low standard deviations reflect relatively uniform cloudless conditions throughout the experiment.

Figure 3. Wind rose diagrams showing the wind direction, wind speed and frequency that the wind will occur in a specific direction. In A, wind measurements at 10 m are shown. In B, wind measurement at 1.6 m and at field center are shown.

Figure 4. (A) Temperature difference (A), gradient Richardson's number (B), and atmospheric stability parameter for momentum (C).

Figure 5. Comparison of Ω_f (Equation 1) for standard-injection and deep-injection fields for each sampling period. The slope of the regression line (solid) is close to the 1:1 line (dashed) indicating similar behavior in both fields.

Figure 6. Comparison of measurements of the 1,3-D concentration at 40 cm height at the center of the field (Center). In Figure S1 (B–D), concentrations at 1.5 m height are averages of the air monitoring stations surrounding the field site and located at 30 m, 90 m, and 120 m from the edge of the field.

Figure 7. Volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application for the aerodynamic, integrated horizontal flux, and theoretical profile shape methods. Shaded areas are the 24 h average flux values for the ADM (gray) and TPS (stippled) methods. The results are for the DI field.

Figure 8. Average 1,3-D volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application for the DI field experiment. Values were calculated by averaging the aerodynamic, integrated horizontal flux, and theoretical profile shape methods at each time point.

Figure 9. Volatilization rate ($\mu\text{g m}^{-2} \text{s}^{-1}$) as a function of time (day) after application for the ISCST3 and CALPUFF method. Shaded areas are the 24 h average flux values for the CALPUFF (gray) and ISCST3 (stippled) methods. The results are for the DI field.

Figure 10. (A) Telone II (1,3-D cis + trans) soil gas phase concentration ($\mu\text{g cm}^{-3}$) with depth in soil. (B) Chloropicrin soil gas phase concentration ($\mu\text{g cm}^{-3}$) with depth in soil. Each line represents the concentration distribution at a particular time after application. In (C), the initial and final soil water content ($\text{cm}^3 \text{cm}^{-3}$) with depth are presented. The results are for the DI field.