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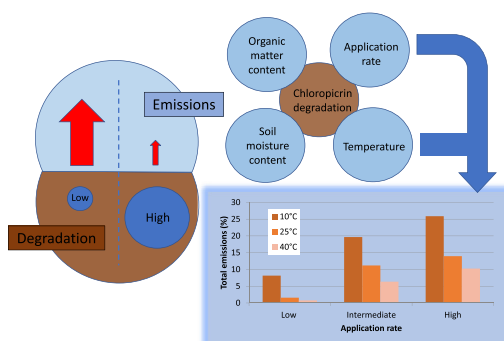
# Effect of application rate on chloropicrin half-life and simulated emissions across a range of soil conditions☆

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## HIGHLIGHTS

- Batch studies were used to study chloropicrin degradation in soil.
- Chloropicrin application rate was positively related to its degradation half-life.
- This relationship generally held across a range of soil conditions.
- Predicted emissions to air varied greatly in response to changes in half-life.
- Results will be of use to regulators in better estimating chloropicrin emissions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The volatile release of agricultural fumigants from soil to air is a critical concern in terms of human and environmental health. A major control on the release of fumigants from soil to air is their degradation rate within the soil; however, this is a function of human/soil/environmental conditions and their inter-relationships. For the common fumigant chloropicrin (CP), it is known that application rate has a marked effect on degradation rate, with a potential further influence on CP emissions. We conducted batch degradation studies to better understand how CP degradation rate changes in response to application rate (56, 224, 392 kg ha<sup>-1</sup>) under gradients of soil temperature (10, 25, and 40 °C), soil moisture content (1, 8, and 15%), and organic matter content (1, 2, and 3%). A general trend of degradation rate decreasing with increasing application rate was observed across almost all such gradients, which is likely attributable to decreased microbial numbers and activity (i.e., degradation) at high (toxic) application rates. The effects of these ranges in degradation rate on emissions from soil to air were predicted using an analytical solution model, indicating that between the low and high application rates, total emissions percentage increased markedly (increases ranging from 69 to 99.8 percentage points, depending on prevalent conditions). The work will be useful to state and federal regulators in assessing the likely impact of CP use on air quality and human health.

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## 1. Introduction

Soil fumigants such as chloropicrin (CP) are an important component of U.S. agriculture given their effectiveness in pre-plant pest control when growing high value crops such as strawberries (Yan et al., 2012), peppers (Gilreath et al., 2005), and almonds (Browne et al., 2013). Diffusing through the soil pore space as a gas, CP has been shown to be effective in the control of plant pests such as nematodes and fungi (United States Environmental Protection Agency [USEPA], 2008). Typically, CP is applied by either shank injection or drip application, either with or without tarping (USEPA, 2008). Owing to the ban on the use of methyl bromide, CP use in areas such as California and Florida has increased markedly in recent years; for example, in California between 2007 and 2015, the use of CP increased from 2.5 million kg to 3.9 million kg (56% increase) (California Department of Pesticide Regulations [CDPR], 2017). However, although critical to the continued success of high value crop production in such areas, the use of fumigants such as CP is strictly controlled owing to their potential to damage air quality and thus pose an inhalation risk to the general population living and working near applied areas (bystander exposure). As a volatile organic compound, CP (and other fumigants) is also implicated in the formation of near-surface ozone (smog) in certain regions (CDPR, 2009, 2010). Methods to minimize CP release from soil to the atmosphere and thereby protect air quality, e.g., covering soil with plastic tarps (Ou et al., 2007; Qin et al., 2008), surface sealing with water (Gao and Trout, 2007) or ammonium thiosulfate solution (Qin et al., 2008), deep injection (Ashworth et al., 2009), and surface biochar application (Wang et al., 2015) have therefore been developed over recent decades. Although tarping post-fumigation is not mandated by regulations for CP, buffer zones (non-treated areas around each applied field) are required as a protection against potential bystander exposure (USEPA, 2008).

As organic chemicals, fumigants degrade in soil via both chemical and biological (microbial) processes. In turn, the fumigant degradation rate is a very important factor controlling emissions, as rapidly degrading fumigants tend to show lower emissions. Therefore, understanding the factors controlling degradation rate in soil is a critical element in assessing fumigant fate and transport, e.g., in assessing emissions losses to the atmosphere. In previous work (Ashworth et al., 2015) we found that CP emissions percentage was strongly and positively related to CP percentage in co-formulations with 1,3-dichloropropene (1,3-D), i.e., we reported 0.018, 1.5, 8.6, 11.2, and 14.5% total emissions for C-17 (17% CP), C-35 (35% CP), PC-60 (60% CP), PC-80 (80% CP) and TriClor (100% CP), respectively, when these products were applied at a uniform product application rate (156 kg CP + 1,3-D ha<sup>-1</sup>). In that study, we hypothesized that the mass of CP applied, and its subsequent rate of degradation, controlled the emission rate. Indeed, degradation studies performed as part of that work showed that the half-life of CP decreased with decreasing application mass/rate. The observed relationship between CP application rate and its emissions concurred with a meta-analysis that we also performed for a relatively large number of field studies, which indicated that CP emissions were relatively low when it was co-applied with 1,3-D but relatively high when it was applied alone (in non-tarped situations (bare soil), i.e., emissions of CP averaged 57% when applied alone but only 10% when co-applied with 1,3-D) (Ashworth et al., 2015 and references therein). It was considered that the low emissions of CP when co-applied with 1,3-D are likely a result of the application of co-formulations such as C-17 and C-35, where the low proportion/mass of CP would likely have been rapidly degraded in the soil.

Subsequent work (Qin et al., 2016) further highlighted the relationship between fumigant application rate and degradation rate. These workers showed that the half-lives of the fumigants CP, dimethyl disulfide, and methyl iodide increased markedly with increasing application rate. For example, between application rates of 10 and 100 mg kg<sup>-1</sup>, CP half-life increased 12-fold. The potential importance of microbial CP

degradation was also indicated by this work, suggesting that at high application rates, CP-degrading microbes were killed off. Other research has also noted a relationship between fumigant application mass and degradation rate (Ma et al., 2001; Dungan and Yates, 2003; Guo and Gao, 2009). Zheng et al. (2004) found that CP degradation half-life increased from 0.4 days at an application rate of 16 mg kg<sup>-1</sup> to 15.8 days at 295 mg kg<sup>-1</sup>. We have further shown this effect for a range of CP application rates (Ashworth et al., 2018), looking at both degradation rate (across an application rate range of 38–612 kg ha<sup>-1</sup>; 2.5–40 mg kg<sup>-1</sup>) and emissions (across an application range of 56–392 mg kg<sup>-1</sup>). Based on this work, we identified that the relationship between application rate and emissions was not linear; rather, it was fitted well by a second-order polynomial equation ( $y = -0.0002x^2 + 0.1917x - 6.1371$ ;  $r^2 = 0.92$ ,  $n = 12$ ), indicating that at low application rates CP is degraded disproportionately faster than at higher application rates, leading to very low emissions. Understanding the effect of CP application rate on its emissions may have important implications for balancing agricultural production and air quality protection in areas of CP use. For example, from a regulatory perspective, CP emissions are currently assumed to scale linearly with application rate; if this is not the case (as suggested by our previous study described above), relatively low CP application rates (e.g., for formulations such as C-17 and C-35) may have a lower impact on air quality than previously thought. This could, for example, impact the required size of buffer zones surrounding CP-fumigated fields, which are intended to reduce bystander risk exposure.

These previous studies have shown that chloropicrin application rate strongly impacts its emissions from soil via an effect on degradation rate. However, these studies were not performed under wide ranges of controlled soil/environmental conditions to explicitly quantify the impacts of such conditions on the application rate–degradation rate relationship. Moreover, apart from our own work, these studies did not include an assessment of the impact of this relationship on CP emissions. In the present work, we aimed to elucidate the relationship between CP application rate and its degradation rate across a wide range of carefully controlled soil conditions that may be prevalent during fumigation events (i.e., gradients of moisture content, organic matter content, and temperature). Since experimentally studying the effect of a wide range of conditions on soil–air emissions would be extremely time consuming, we employed an analytical solution to predict emission losses using the measured degradation half-lives; this solution was initially verified against a CP emissions column study undertaken as part of this study.

## 2. Materials and methods

### 2.1. Materials

The CP used in this study was provided by TriCal Inc. (Hollister, CA) and had a purity of 99.78%. Sodium sulfate (anhydrous), n-hexane, and ethyl acetate were obtained from Fisher Scientific (Fairlawn, NJ). XAD-4 tubes (two-section; 400/200 mg) were purchased from SKC Inc. (Eighty Four, PA). Sandy loam soil (75% sand, 18% silt, 7% clay; 0.92% organic matter; Arlington soil series) was collected from the plowed, upper 30 cm of Field 2B of the University of California Riverside Agricultural Station. The soil was sieved to 5 mm and stored in sealed plastic bags at 4 °C until use.

### 2.2. Degradation study

The degradation rate of chloropicrin was assessed under a range of conditions according to standard procedures, as follows. Soil was sieved to <2 mm and weighed (10 g dry weight equivalent) into a 20-mL glass vial and CP added to result in an application equivalent to either 56, 224, or 392 kg ha<sup>-1</sup> by assuming (i) a soil bulk density of 1.5 g cm<sup>-3</sup> and (ii) that CP acts over a depth of 1 m under field conditions (based on

previous observation in our laboratory). The value of 392 kg ha<sup>-1</sup> represents the maximum permissible application rate for CP under federal guidelines; we then took low and intermediate values in relation to this maximum. The CP was added as a 5- $\mu$ L spike of aqueous solution, after which the vial was immediately capped with a leak-proof, Teflon-faced septum. Vials were then incubated at constant temperature, with triplicate vials moved to a -19- $^{\circ}$ C freezer at 0 (immediately after spiking), 0.25, 1, 2, 4, 7, and 10 days. At the end of the experiment, the frozen soil samples were extracted by de-capping, rapid addition of ~10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate, immediate re-capping, and shaking for 1 h. After shaking and settling, ~1 mL of supernatant was transferred to an amber vial for analysis.

For each application rate, a number of treatments were used to determine the effects of temperature, moisture content, and organic matter on the relationship between CP application rate and degradation rate. In addition, the importance of microorganisms in the relationship between CP application rate and degradation was assessed by comparing sterilized and non-sterilized soils. The various treatments are described in Table 1.

### 2.3. Emissions simulations

#### 2.3.1. Column study

In order to determine the potential effect of application rate-induced changes in degradation rate on CP emissions from soil to air, an analytical solution (Yates, 2009) was utilized. To first validate the model against experimental soil-air CP emissions data, a laboratory soil column study, in which a shank injection of CP was emulated, was performed as follows. Stainless steel soil columns (150-cm length, 12-cm diameter) were packed with Arlington-series soil (gravimetric moisture content of 4%) to an equivalent dry bulk density of 1.5 g cm<sup>-3</sup>. The system was sealed with a 5-cm long volatilization chamber placed over the soil surface. The CP was applied at a rate equivalent to 156 kg ha<sup>-1</sup> (139 lb acre<sup>-1</sup>). Immediately after injection of CP at a depth of 46 cm below the soil surface, clean air was pulled across the soil surface through the volatilization chamber. Thus, CP emitted from the soil was swept, via Teflon tubing, through XAD-4 sorbent tubes, which trapped the CP. An XAD-4 tube was used in this way for 4 h before being replaced with a new tube. Used tubes were stored at -19  $^{\circ}$ C. The experiment was conducted in triplicate for a total of 184 h. The XAD-4 tubes were extracted by removing the resin contents into 10-mL glass vials, adding 4 mL of n-hexane, capping with a Teflon-faced septum, and shaking for 30 min. After settling, ~1 mL of supernatant was transferred to an amber vial for analysis. Preliminary studies showed that the recovery of this procedure was 85.2  $\pm$  3.2%. The total loss of CP from soil to air (expressed as a percentage of that added) was then determined. Further

details of the soil column procedures can be found in Ashworth et al. (2018). An additional degradation study (performed as described above) was carried out for the particular conditions under which the column study was performed (i.e., 4% gravimetric moisture content, 25  $^{\circ}$ C, equivalent application rate of 156 kg ha<sup>-1</sup>). The resulting degradation rate constant was used in the simulation of CP emissions from the column using the analytical solution model.

#### 2.3.2. Analysis

Soil and XAD-4 extracts were analyzed using an Agilent Technologies 7890C gas chromatograph (GC), equipped with a microelectron capture detector. The column was a DB-VRX 122-1534 with dimensions of 30 m  $\times$  0.25 mm  $\times$  1.4  $\mu$ m (Agilent Technologies) running at a flow rate of 1.4 mL min<sup>-1</sup> and with helium as the carrier gas. The inlet temperature was 240  $^{\circ}$ C and the detector temperature was 290  $^{\circ}$ C. The GC oven temperature was maintained at 45  $^{\circ}$ C for 1 min after sample injection, increasing to 80  $^{\circ}$ C at a rate of 2.5  $^{\circ}$ C min<sup>-1</sup>, and then to 120  $^{\circ}$ C at a rate of 30  $^{\circ}$ C min<sup>-1</sup> before being held at this temperature for 2 min. Under these conditions, the retention time of CP was 8.1 min. Sets of eight standards encompassing the range of concentrations in the samples were prepared from the standard CP solution. Standards were prepared in hexane for the XAD-4 extracts and ethyl acetate for the soil extracts (i.e., the same as the samples).

#### 2.3.3. Analytical solution model

Yates (2009) presented analytical solutions describing the fate and transport of pesticides applied to soil. For fumigants, the solutions allow effective determination of total emission losses and can be used to characterize differences in emissions relative to changes in factors such as soil degradation rate, surface barrier conditions, application depth, and soil packing (bulk density). A full description of the derivation of the fate and transport model is given by Yates (2009). The aspects of the model relevant to the present work are described as follows:

The mass transfer coefficient  $h$  is defined as

$$h = D_G^{air} / b \quad (1)$$

where  $D_G^{air}$  is the binary diffusion coefficient for the chemical in pure air (cm<sup>2</sup> h<sup>-1</sup>) and  $b$  is the thickness (cm) of a stagnant boundary layer at the soil surface.

The effective mass transfer coefficient  $H_E$  is then defined as

$$H_E = h / R_G \quad (2)$$

where  $R_G$  is the gas retardation coefficient, defined as

$$R_G = R_L / K_H \quad (3)$$

where  $K_H$  is the Henry's Law constant and  $R_L$  is the liquid phase retardation coefficient, defined as

$$R_L = \theta + \rho_b K_D + \eta K_H \quad (4)$$

where  $\theta$  is the water content (cm<sup>3</sup> cm<sup>-3</sup>),  $\rho_b$  is the soil bulk density (g cm<sup>-3</sup>),  $K_D$  is the solid/liquid partition coefficient, and  $\eta$  is the air content cm<sup>3</sup> cm<sup>-3</sup> (=total porosity  $\phi$  -  $\theta$ ).

Total volatilization is given by

$$C_0 H_E e^{\frac{-z_0 \sqrt{\mu}}{\sqrt{D_E}}} \quad (5)$$

where

$C_0$  is the applied mass (mg cm<sup>-1</sup> or 100%),  $z_0$  is the application depth (cm),  $\mu$  is the first-order degradation coefficient (h<sup>-1</sup>), and  $D_E$  is the

**Table 1**

Treatments used to study CP degradation rate at various application rates.

Treatment	Temperature ( $^{\circ}$ C)	Moisture content (%) <sup>a</sup>	Organic matter content (%) <sup>b</sup>	Sterilized (yes/no) <sup>c</sup>
A	10	8	1	No
B	25	8	1	No
C	40	8	1	No
D	25	1	1	No
E	25	15	1	No
F	25	8	2	No
G	25	8	3	No
H	25	8	1	Yes

<sup>a</sup> Soil moisture was adjusted either by air drying or by the addition of deionized water. A value of 1% indicates air-dry soil; a value of 15% is approximately field capacity.

<sup>b</sup> An organic matter content of 1% is that of the natural soil. Organic matter was increased to 2% and 3% using dried and ground (<2 mm) composted cow manure (Black Kow, Oxford, FL).

<sup>c</sup> Two 1-h autoclaving periods conducted 24 h apart, each at 121  $^{\circ}$ C, were used to sterilize the soil and thus allow an assessment of the contribution of microorganisms to CP degradation.

effective dispersion coefficient ( $\text{cm}^2 \text{h}^{-1}$ ), defined as

$$D_E = D_G/R_G \quad (6)$$

where  $D_G$  is the soil gas diffusion coefficient ( $\text{cm}^2 \text{h}^{-1}$ ).

For the soil column experiment described above, the values for each of these parameters are shown in Table 2.

### 3. Results and discussion

#### 3.1. Degradation study

##### 3.1.1. Effects of environmental variables

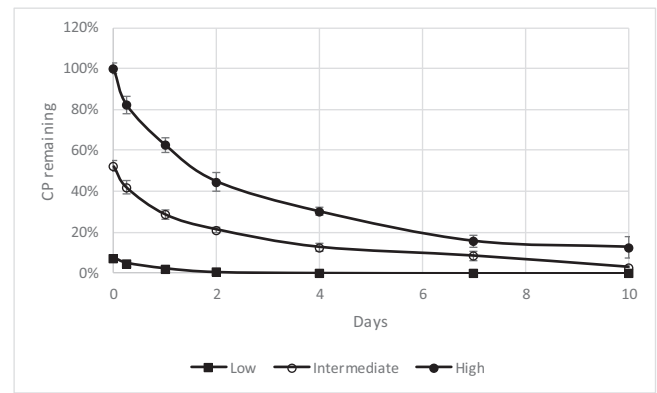
The loss of CP over time (Fig. 1 shows an example for the 25 °C, 8% moisture content, 1% organic matter content treatment) under each experimental condition was fitted with first-order kinetics, yielding correlation coefficients ranging from 0.84 to 1.00 (average =  $0.94 \pm 0.05$ ;  $n = 24$ ). Fig. 2 shows the effects of soil temperature (a), moisture content (b), and organic matter content (c) on the degradation half-life of CP. As expected based on previous research, increases in temperature and organic matter content led to faster degradation of CP, with decreases in half-life between 10 °C and 25 °C and between 25 °C and 40 °C, as well as between 1% and 2% organic matter and between 2% and 3% organic matter. The effect of moisture content was slightly different: the higher moisture contents (8% and 15%) showed similar half-lives, whereas the 1% level yielded much greater half-lives. Overall, these findings demonstrate that the ranges in environmental conditions potentially experienced during fumigation under field conditions likely have marked impacts on the degradation, and hence fate, of CP. In each case, the potential role of microorganisms in CP degradation helps to explain the observed effects. The importance of microorganisms in CP degradation in this soil is shown in Fig. 3, wherein sterile and non-sterile soils are compared. It is evident that sterilization of the soil led to a significantly longer CP half-life at each application rate, suggesting that microorganisms play a predominant role (as compared with chemical processes) in CP degradation. As such, increasing soil temperature and organic matter content probably enhanced microbially-mediated processes including CP degradation. In terms of soil moisture, microorganisms can become inactive in very dry soil (Barros et al., 1995), as suggested by the long half-lives observed in the 1% moisture content soil. Although the effect of microorganisms was likely predominant overall, chemical degradation processes were likely also enhanced by increasing soil temperature and organic matter content; thus, further enhancing CP degradation under these

**Table 2**

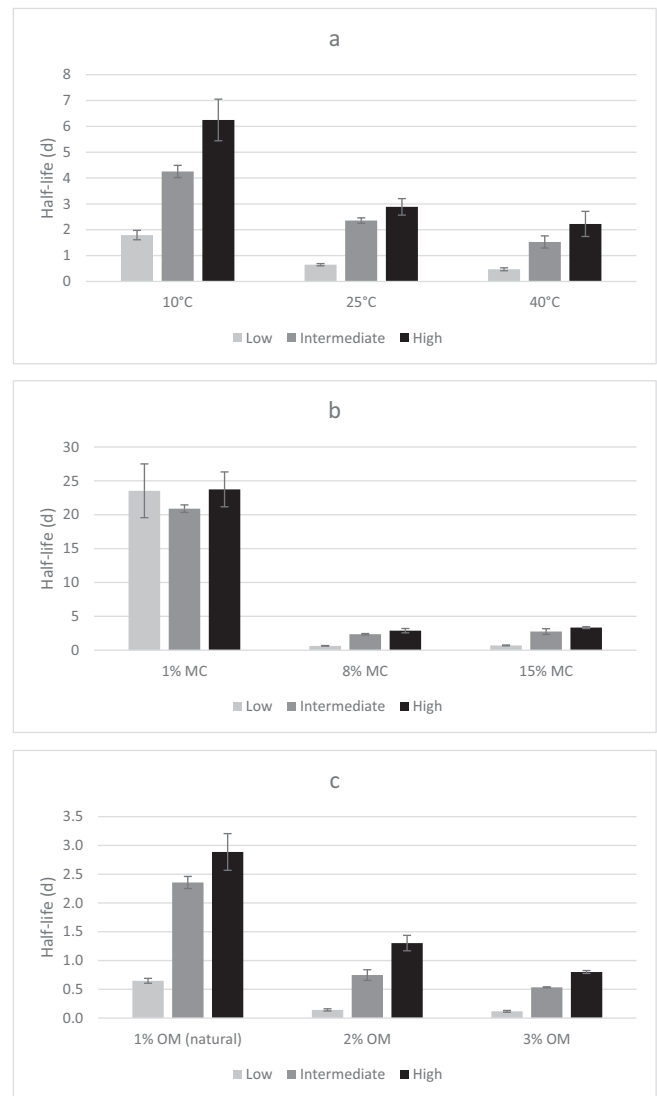
Parameter values used in the analytical solution model of Yates (2009) to predict CP emission losses from soil columns.

Parameter	Value
Gravimetric moisture content	$0.04 \text{ cm}^3 \text{ cm}^{-3}$
Bulk density, $\rho_b$	$1.5 \text{ g cm}^{-3}$
Volumetric moisture content, $\theta$	$0.06 \text{ cm}^3 \text{ cm}^{-3}$
Porosity, $\phi$	$0.43 \text{ cm}^3 \text{ cm}^{-3}$
Air content, $\eta$	$0.37 \text{ cm}^3 \text{ cm}^{-3}$
Application depth, $z_0$	–46 cm
Application mass, $C_0$	100% ( $156 \text{ kg ha}^{-1}$ ; $139 \text{ lb ac}^{-1}$ )
Henry's constant, $K_H$	0.103
Solid/liquid partition coefficient, $K_D$	0.175
Degradation rate constant, $\mu$	$0.01 \text{ h}^{-1a}$
Binary gas diffusion coefficient, $D_G^{air}$	$296.4 \text{ cm}^2 \text{ h}^{-1}$
Boundary layer thickness, $b$	0.5 cm
Soil gas diffusion coefficient, $D_G$	$19 \text{ cm}^2 \text{ h}^{-1}$
Mass transfer coefficient, $h$	$592.8 \text{ cm h}^{-1}$
Effective mass transfer coefficient, $H_E$	$169.1 \text{ cm h}^{-1}$
Liquid retardation coefficient, $R_L$	0.361
Gas retardation coefficient, $R_G$	3.505
Effective soil diffusive coefficient, $D_E$	$5.706 \text{ cm}^2 \text{ h}^{-1}$

<sup>a</sup> As measured in the degradation study performed under the conditions prevalent in the column study.



**Fig. 1.** Loss of CP over time at 25 °C, 8% moisture content, and 1% organic matter for low, intermediate, and high application rates. Error bars represent standard deviation of three replicates. Error bars for the low application rate are obscured by the data markers.



**Fig. 2.** Measured half-life of CP at low, intermediate, and high application rates under differing temperature (a), moisture content (MC) (b), and organic matter content (OM) (c) treatments. Unless stated otherwise, the temperature, moisture content, and organic matter content were 25 °C, 8%, and 1%, respectively (see Table 1). Note differing y-axis scales. Error bars represent the standard deviation of three replicates.

conditions. In contrast, the low rate of degradation in the 1% moisture content soil may be partly attributable to a reduction in hydrolysis under such dry conditions.

### 3.1.2. Effects of application rate

The main focus of this work was to study the effect of application rate on CP degradation across a range of carefully controlled environmental conditions; this has not been previously studied. Within each of the various temperature, moisture content, and organic matter content treatments (except the 1% moisture content treatment), application rate had the same effect on CP degradation, i.e., increasing the application rate increased the measured half-life, with an average half-life increase between the low and high application rates of 462% (range 244–842%). One-way analysis of variance (ANOVA) demonstrated that the effect of application rate was highly statistically significant ( $P$  values  $< 0.0014$ ) within each temperature, moisture content, and organic matter treatment (except for the 1% moisture content treatment;  $P > 0.05$ ). Our previous work (Ashworth et al., 2015; Ashworth et al., 2018) found that CP degradation rate is strongly affected by its initial concentration, likely owing to a reduction in microorganism numbers and activity at high (toxic) CP concentrations. The present work confirms that this trend is evident across a wide range of environmental conditions and not confined to the relatively “standard” conditions considered previously (i.e., intermediate temperature and moisture content and low organic matter content). As such, its impact on the fate of CP should be considered important when assessing the risks associated with field CP fumigation.

### 3.2. Laboratory soil columns and simulation of soil–air emissions

In the laboratory soil columns conducted for this study, total CP emissions from soil to air were 14.5 ( $\pm 4$ )% ( $n = 3$ ). Using the parameters listed in Table 1, the simulation model gave total emissions of 14%, showing very good agreement with the experimental results. This model has previously shown very good agreement with experimental data for MeBr emissions under field conditions (Yates, 2009) and MeI in soil columns (Luo et al., 2011). Taken in conjunction with the present findings, we therefore consider the model to be a potentially useful tool for simulating fumigant emissions under a range of conditions. As such, we believe that it can be reasonably used to predict emissions for the differing degradation rates measured in the present study. For simplicity, only the degradation rate parameter (Table 2) was adjusted in the model in order to examine its explicit effect on total emissions. Measured rate constants ( $= \ln(2) / \text{half-life [h]}$ ) for each treatment and application rate were used in the simulation model (Eq. (5)). Fig. 4 shows the resulting outputs (total emission values) from the model for each

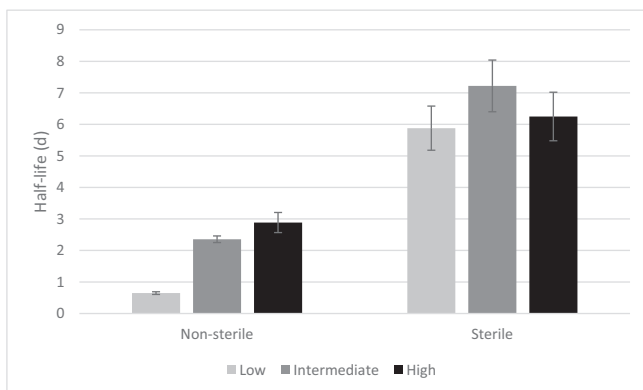
application rate under the temperature (a), moisture content (b), and organic matter content (c) treatments.

In general, degradation rate had a marked effect on predicted emission loss, with total emissions ranging from 0.005% (low application rate at 3% organic matter, 8% moisture content, and 25 °C) to 50.2% (high application rate at 1% moisture content, 1% organic matter content, and 25 °C) across all environmental treatments and application rates. The environmental treatments had a marked impact on emission losses. For example, within each application rate, increasing temperature reduced emissions, with emission decreases of between 60 percentage points (pp) (high application rate) and 91 pp (low application rate) between the 10 and 40 °C treatments. Similarly, increasing organic matter content decreased emissions by between 83 pp (high application rate) and 99 pp (low application rate) between the 1 and 3% organic matter content treatments. Moreover, increasing the soil moisture content from 1 to 15% decreased emissions by between 68 pp (high application rate) and 97 pp (low application rate). The potential importance of microorganisms and microbial processes in relation to CP emissions can be seen by comparing the sterilized and non-sterilized soils (Fig. 5); with sterilization, emissions increased by between 87 pp (high application rate) and a dramatic 1497 pp (low application rate).

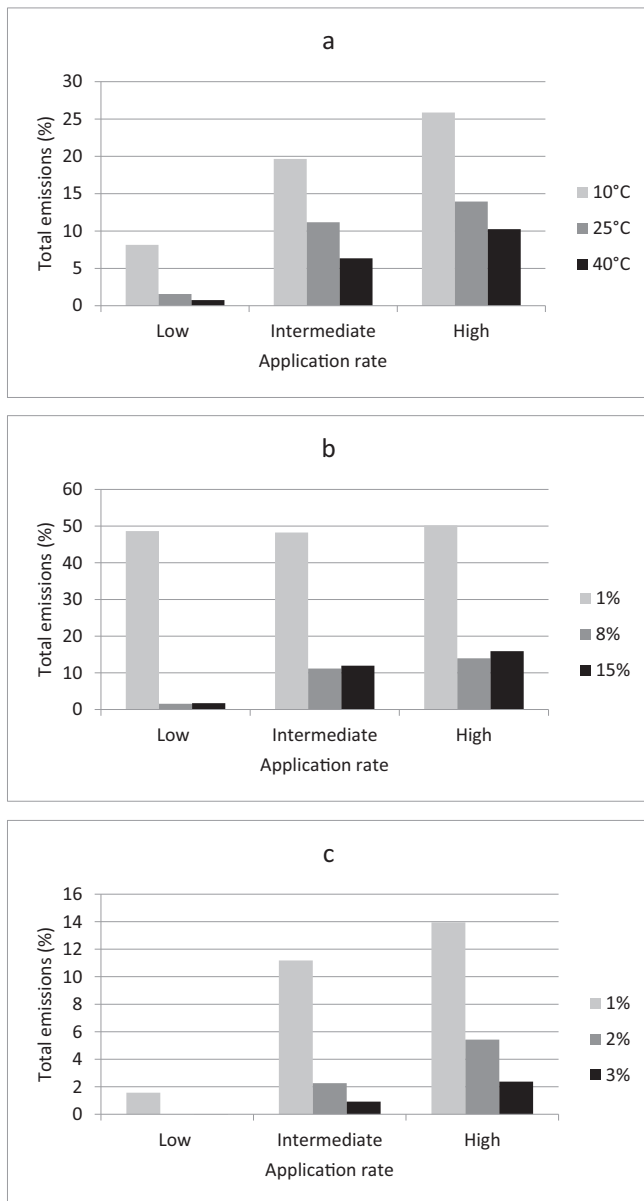
Application rate also had a marked impact on emission losses. Within each of the various temperature, moisture content, and organic matter content treatments (except the 1% moisture content treatment), a lower application rate led to markedly lower emissions, with emission reductions between the low and high application rates ranging from 69 to 99.8 pp (average 90 pp). Clearly, therefore, application rate strongly affected emission loss across a wide range of environmental conditions likely to be encountered in fumigated fields. Previously, the only published information related to this phenomenon was relevant only to a particular set of environmental conditions and had also not been used to assess the impact of application rate on emissions. The present work improves our understanding of this phenomenon by presenting a quantitative analysis of this relationship. Although the mechanism underpinning this relationship is not certain (i.e., why a lower CP application rate leads to its faster degradation), the comparison of sterilized and non-sterilized soils in this study suggests that microorganisms likely play a key role. As suggested previously (Ashworth et al., 2015; Qin et al., 2016; Ashworth et al., 2018), higher application rates likely result in a greater kill-off of microorganisms, leading to a potentially depleted ability of the remaining microbial population to degrade the added CP. The lack of an application rate effect in the sterilized soil (Fig. 3; ANOVA  $P > 0.05$ ) indicates that microbes do indeed play an important role in this relationship. Quantification of the significance of microbes in CP degradation has been reported by others (Gan et al., 2000; Zheng et al., 2003; Ibekwe et al., 2004; Zhang et al., 2005) and can also be undertaken using the present data. Comparing the sterilized and non-sterilized soils (both at 25 °C, 8% moisture content, 1% organic matter content; Fig. 3), it can be calculated that microbial degradation accounted for approximately 89, 67, and 53% of the total CP degradation for the low, intermediate, and high application rates, respectively. Therefore, at high application rates, almost half of the ability of the soil to degrade CP is lost if microbes are killed off due to toxicity. Having said that, if we assume that autoclaving completely sterilized the soil (i.e., that all degradation in the sterilized soil was a result of chemical degradation processes), then the approximate doubling of half-life under these conditions as compared with the highest application rate (6.25 d vs. 2.89 d, respectively) suggests that the highest CP application rate did not completely sterilize the soil. Nevertheless, the decline in microbe numbers at high application rates has a strong potential to reduce CP degradation potential and thereby lead to a reduction in soil–air emissions.

## 4. Conclusions

Studying the degradation of fumigants under a range of soil conditions is critical to better understanding their fate and transport under

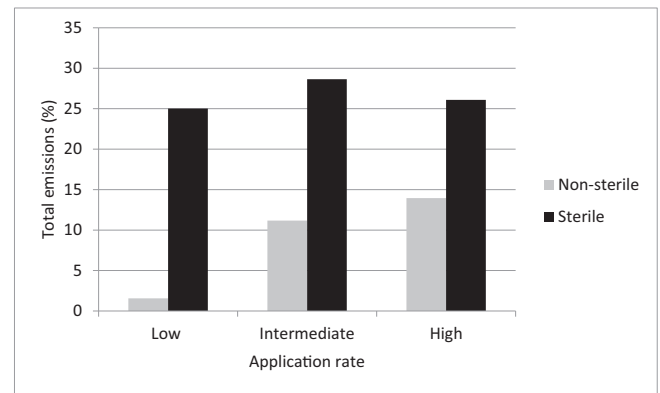


**Fig. 3.** Measured half-life of CP at low, intermediate, and high application rates under non-sterile and sterile soil conditions (25 °C, 8% moisture content, 1% organic matter content). Error bars represent the standard deviation of three replicates.



**Fig. 4.** Predicted CP emissions at low, intermediate, and high application rates under differing temperature (a), moisture content (b), and organic matter content (c) treatments. Unless stated otherwise, the temperature, moisture content, and organic matter content were 25 °C, 8%, and 1%, respectively (see Table 1). Note differing y-axis scales. For the low application rate, emission losses at 2 and 3% organic matter were each 0.01%.

field conditions. This has clear implications for helping safeguard human and environmental health. The role of application rate in impacting the degradation and emissions of CP (and potentially other fumigants) has not been well studied but could be an important factor in assessing the risks associated with CP field applications across different application rates. This work furthers our understanding of CP fate and transport in relation to application rate by considering the relationship across a range of environmental gradients. In general, the strong negative relationship between application rate and degradation rate held across the various gradients, leading to relatively very low predicted emissions at low application rates, especially under conditions of relatively high temperature, low organic matter content, and high moisture content. The effects could be strongly related to microbial activity in the soil, both by the impacts of the environmental variables (e.g., via low organic matter content, high temperature, and high soil moisture content increasing microbial activity, leading to enhanced CP



**Fig. 5.** Predicted CP emissions at low, intermediate, and high application rates under non-sterile and sterile soil conditions (25 °C, 8% moisture content, 1% organic matter content).

degradation) and by the higher CP application rate killing off CP-degrading microbes, leading to reduced CP degradation. Such effects should be taken into account when assessing the risks associated with CP use under field conditions.

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