# Application rate affects the degradation rate and hence emissions of chloropicrin in soil

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## HIGHLIGHTS

- Widespread use of agricultural fumigants is a concern in relation to air quality.
- Soil columns were used to measure fluxes of chloropicrin from soil to air.
- Emissions percentage of chloropicrin was positively related to application rate.
- Chloropicrin was more rapidly degraded at low application rates.
- The results may have implications for the setting of farm buffer zone sizes.

## GRAPHICAL ABSTRACT
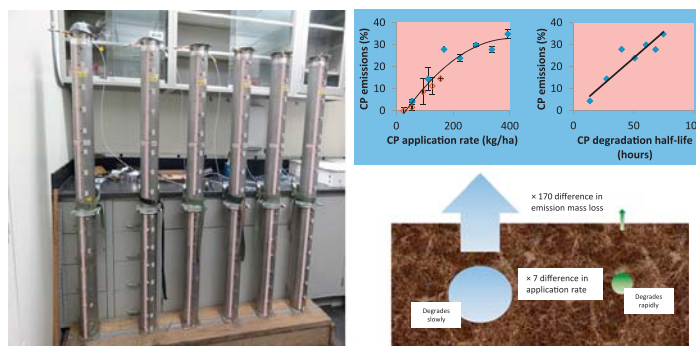


## ARTICLE INFO

## ABSTRACT

Increasingly stringent regulations to control soil-air emissions of soil fumigants has led to much research effort aimed at reducing emission potential. Using laboratory soil columns, we aimed to investigate the relationship between chloropicrin (CP) application rate and its emissions from soil across a wide range of CP applications (equivalent to 56–392 kg ha$^{-1}$). In contrast to the known behavior of other fumigants, total emission percentages were strongly and positively related to application rate (i.e., initial mass), ranging from 4 to 34% across the application rate range. When combined, data from a previous study and the present study showed good overall comparability in terms of CP application rate vs. emission percentage, yielding a second-order polynomial relationship with an $R^2$ value of 0.93 (n = 12). The study revealed that mass losses of CP were strongly disproportional to application rate, also showing a polynomial relationship. Based on degradation studies, we consider that a shorter half-life (faster degradation) at lower application rates limited the amount of CP available for emission. The non-linear relationship between CP application rate and CP emissions (both as % of that applied and as total mass) suggests that low application rates likely lead to disproportionally low emission losses compared with higher application rates; such a relationship could be taken into account when assessing/mitigating risk, e.g., in the setting of buffer zone distances.

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## 1. Introduction

The agricultural use of chemical fumigants is a critical and effective component of crop production in areas such as California and Florida

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where high-value cash crops are grown. In California, the use of fumigants increased 24% from 17 million kg in 2007 to 21 million kg in 2015 (California Department of Pesticide Regulations [CDPR], 2017). However, the use of fumigants is highly regulated due to their high volatility and emissions from soil to air, where they are both an inhalation risk in their own right and are implicated in the formation of near surface ozone (smog) (CDPR, 2009; CDPR, 2010). The soil fumigant chloropicrin (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). As a preplant fumigant for a range of crops including strawberries (Yan et al., 2012), peppers (Gilreath et al., 2005), and almonds (Browne et al., 2013), it is applied by either shank injection or drip application with or without tarps (USEPA, 2008). Its use is increasing due to restrictions on the use of methyl bromide and other fumigants; in California between 2007 and 2015, use of CP increased from 2.5 million kg to 3.9 million kg (56% increase) (CDPR, 2017). Efforts, such as refined application methodologies, are constantly being developed 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).

In a recent study using laboratory soil columns (Ashworth et al., 2015), we studied the co-application of CP with 1,3-dichloropropene (1,3-D) to determine whether the presence of 1,3-D affected CP emissions. This research objective arose from a meta-analysis of field data relating to CP applications, in which low CP emissions were observed across a relatively large number of studies when it was co-applied with 1,3-D but relatively high when it was applied alone. Overall, in non-tarped situations (bare soil), 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). In the experimental work described in that study, we found that emissions percentage was strongly and positively related to CP percentage in the formulation: 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$^{-1}$). Degradation studies, conducted at the same initial mass of total fumigant (1,3-D + CP) as in the soil columns, showed that the half-life of CP in each co-formulated product decreased with decreasing percentage of CP in the formulation (i.e., its degradation rate was dependent upon initial mass). A second degradation study confirmed that these CP half-lives were similar in the absence of 1,3-D. Based on this study, it was considered that 1,3-D had little influence on CP emissions; rather, the mass of CP applied, and its subsequent rate of degradation, controlled the emission rate. Thus, as observed in our previous meta-analysis of field data (Ashworth et al., 2015), low emissions of CP when co-applied with 1,3-D are likely due to 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.

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, fumigant emissions are 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 may have a lower impact on air quality than previously considered. However, our previous study was limited in its range of CP application rates, with five application rates covering the equivalent of 26–156 kg ha$^{-1}$, which fall well below the maximum recommended rate on the product label. Moreover, it was considered that the effect of application rate on CP emission percentage should be studied entirely in the absence of 1,3-D to limit any confounding influence of co-application. Therefore, in the present study, we aimed to further investigate the relationship between CP application rate and CP emissions across a wider range of CP applications, i.e., seven application rates covering the equivalent of 56–392 kg ha$^{-1}$ (50–350 lbs acre$^{-1}$; note that 350 lbs acre$^{-1}$ is the maximum allowable application rate under USA regulations). We also aimed to better understand the mechanism by which CP degradation rate affected the percentage of total emissions from the soil columns.

## 2. Materials and methods

### 2.1. Chemicals, sampling tubes, and soil

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 in a cool environment. The gravimetric moisture content of the soil was 4%.

### 2.2. Soil column study

Stainless steel soil columns (12 cm diameter × 150 cm length) were used to study the surface emissions of CP, following a simulated shank injection at 46 cm soil depth. The design and set-up of the columns has been described previously (Ashworth and Yates, 2007; Ashworth et al., 2009). Soil (4% gravimetric moisture content) was packed into the columns in 5 cm intervals to an equivalent dry bulk density of 1.5 g cm$^{-3}$. The top of each column was sealed with a stainless steel flux chamber to trap headspace gas. The columns were housed in a controlled temperature room where the ambient temperature was maintained at 25 °C.

At Time-0, the relevant masses of fumigant for equivalent application rates of 56, 112, 168, 224, 280, 336, and 392 kg ha$^{-1}$ (50, 100, 150, 200, 250, 300, and 350 lbs acre$^{-1}$, respectively) were injected into the center of each soil column at 46-cm depth. Each application rate treatment was performed in triplicate. For each column, a vacuum (100 mL min$^{-1}$) was immediately applied to the flux chamber to sweep headspace gas vapors through an in-line sorbent tube (XAD-4 filter media) that was replaced every 4 h throughout the experiment, which lasted for a total of 184 h. Backup XAD-4 tubes were used to check for fumigant breakthrough. After the 4 h of sampling, tubes were capped on both ends and stored in a freezer at −19 °C. Background air within the controlled column environment was sampled daily by pulling the air through an XAD-4 sorbent tube for 24 h periods. In addition, at the start of the experiment, blank XAD-4 tubes were placed in the sample storage freezer (i.e., storage blanks). Analysis of all storage blank and background air sampling tubes yielded non-detectable levels of CP and so no correction was required for potential sources of contamination.

At the end of the experiment, XAD-4 tubes were cut into their two sections and each placed into separate glass vials. After the addition of 4 mL n-hexane, the vials were immediately capped, shaken for 30 min, and then 1 mL of supernatant solvent was removed to an amber vial for gas chromatography analysis.

### 2.3. Degradation study

The degradation kinetics of CP at each of the application rates were determined. Moist soil (10.4 g at 4% gravimetric moisture content, equaling 10 g soil dry weight equivalent) was weighed into 20 mL glass vials and spiked with differing amounts of CP to simulate a wide range of application rates. Application rates were converted to soil concentrations based on the assumption that CP added in the field (or a column) acts over a depth of about 1 m (this was based on previous soil gas