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

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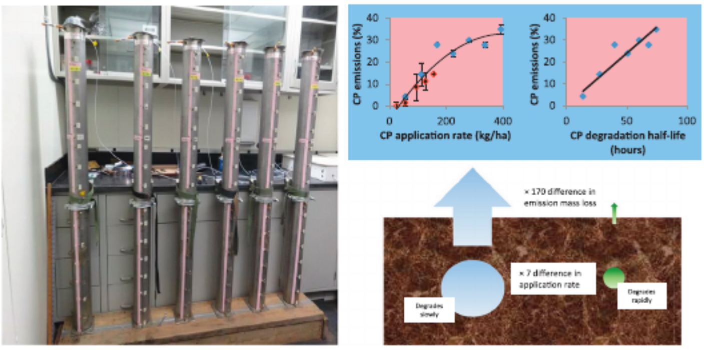
HIGHLIGHTS

- 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



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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.

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 measurements in soil columns). As such, we used soil concentrations of 2.5, 5, 10, 15, 20, 30, and 40 μg g^{-1} for the degradation study. According to the above conversion approach, these concentrations are equivalent to application rates of approximately 38, 76, 152, 228, 306, 459, and 612 kg ha^{-1}; thus encompassing (and extending) the range of application rates used in the columns.

The CP-spiked vials were immediately capped (Teflon faced butyl caps) and placed at 25 °C. At Time- 0 (immediately after adding fumigant), 1, 2, 4, 8, 24, 48, 72, 144 and 240 h, triplicate vials were removed and placed at −19 °C. At the end of the experiment, 10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate were quickly added to each frozen vial before immediate re-capping, shaking for 1 h, and subsequent removal of 1 mL of supernatant to an amber vial for gas chromatography analysis. Degradation loss of CP from the soil was fitted with a first order kinetic model to calculate the degradation rate constant and half-life at each application rate. The effect of microbes on CP degradation was determined by autoclaving (two 1 h autoclaving periods conducted 24 h apart, each at 121 °C) additional soil prior to conducting the degradation study.

2.4. Analysis

Analysis of XAD-4 tube solvent extracts was carried out 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 × 0.25 mm × 1.4 μm (Agilent Technologies) running at a flow rate of 1.4 mL min^{-1} and with helium as the carrier gas. The inlet temperature was 240 °C and the detector temperature was 290 °C. The GC oven temperature was maintained at 45 °C for 1 min after sample injection, increasing to 80 °C at a rate of 2.5 °C min^{-1}, and then to 120 °C at a rate of 30 °C min^{-1} before being held at this temperature for 2 min. Under these conditions, retention time of CP was 8.1 min. Sets of eight standards encompassing the range of concentrations of 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).

3. Results and discussion

3.1. Total emission losses

Average total emission losses for each of the seven treatments are shown in Fig. 1 (closed symbols) in relation to application rate. Total emissions ranged from 4.3 to 34.8% of the amount added and showed a relatively strong ($R^2 = 0.88$) second-order polynomial relationship with application rate (not shown). Theoretically, when expressed as a percentage of the amount added, emissions should be approximately equal regardless of application rate. Indeed, such behavior was observed for 1,3-D in our previous work, for which emissions ranged from 30 to 35% regardless of application rate (Ashworth et al., 2015). However, the results we obtained for CP in the present study are in concurrence with those for CP in that previous study and again suggest that emissions percentage is related to a soil process controlled by application rate. This is not observed for other fumigants and is discussed in more detail below.

Shown in Fig. 1 is the relationship obtained when combining the dataset from the current study (closed symbols) with that obtained by Ashworth et al. (2015) (open symbols). When considering both sets of data, a strong ($R^2 = 0.93$) second-order polynomial relationship is observed between emissions and application rate (Fig. 1). In the previous study, the range of CP application rates was 26–156 kg ha^{-1} and the relationship between application rate and emissions percentage was very well described with a third-order polynomial equation ($R^2 = 0.99$) (not shown), which suggested the beginning of a plateau in emissions as application rate increased. By extending the range of application rates up to 392 kg ha^{-1} in the present study, the full development of this plateau is apparent at the highest application rates and corresponds to a total emissions percentage of ~32%. These findings suggest that increased CP application rates (above 392 kg ha^{-1}) would not yield increases in emissions percentage (although clearly the total mass of emissions would increase).

Fig. 2 shows the CP equivalent mass lost per ha via emissions at each application rate for data from the present study and those from Ashworth et al. (2015). This relationship is also curvilinear and indicates that relatively very low masses are lost via emission at low application rates due to a combination of the low added mass and a low emissions percentage (Fig. 1). The straight line in Fig. 2 represents the linear relationship between the two variables scaled according to the maximum emission loss at the highest application rate, i.e., the theoretically-expected values (the approach generally used to determine fumigant fluxes from a regulatory standpoint). It is evident that the measured curvilinear relationship results in markedly lower emission losses compared with the linearly-scaled approach, particularly at low application rates. Most notably, between the lowest and highest application rates in the present study, which differ by seven times, the emission mass loss differs by 170 times.

3.2. Emission fluxes

Average emission fluxes over the course of the experiment are shown in Fig. 3. All application rates yielded a similar flux profile, with

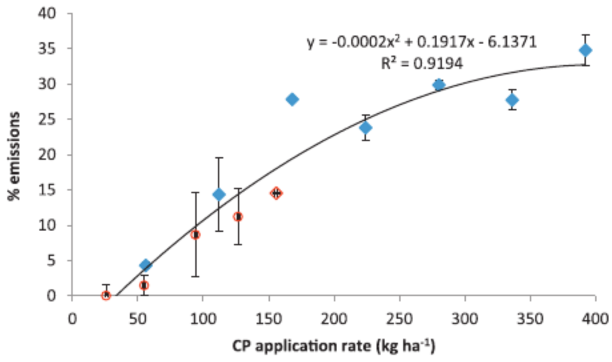

Fig. 1. Relation between total CP emissions (as a percentage of the amount added) and application rate for both the present study (closed symbols) and our previous study (open symbols; Ashworth et al., 2015). Data points show the averages ±1 standard deviation. Circular symbols denote co-application of CP with 1,3-D; diamond symbols denote single CP application. The curve shows the second-order polynomial relationship.

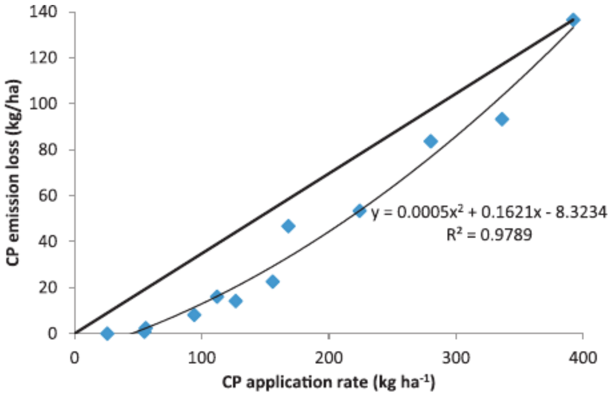

Fig. 2. Relation between application rate and CP emissions on a mass basis. The curve shows the second-order polynomial relationship of the data points. The straight line shows a linear scaling of the emission loss at each application rate relative to the maximum value.

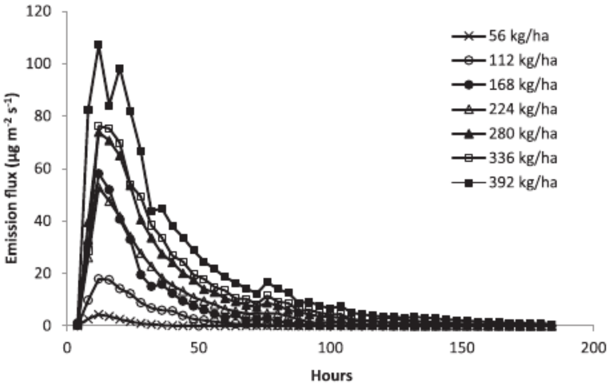

Fig. 3. Average CP emission fluxes for each application rate during the experiment.

a rapid increase in emissions followed by a relatively slow general decline. In general, the magnitude of the flux at any given time reflected the magnitude of the application rate, as would be expected. However, there were only small differences between the 168 and 224 kg ha^{-1} curves and the 280 and 336 kg ha^{-1} curves; the reason for the small differences is unclear but may be due to experimental uncertainty between the triplicate columns.

Maximum fluxes occurred at 12 h after application in all treatments, which is considerably earlier than that observed in CP field flux data, where peak flux timing under field conditions from deep injections (such as used in this study; 46 cm) typically occurs 24 h after application or later (Gao and Trout, 2007; Yates et al., 2016). However, the timing of the peak flux rates in this study was not the focus; rather, this study was concerned with the relative magnitude of the peak flux rates and their association with application rate (initial mass). This relationship is given in Fig. 4, together with data from Ashworth et al. (2015) (open symbols). Across both datasets, a third-order polynomial curve fit the data very well ($R^2 = 0.94$). The non-linear relationship suggests that at low application rates, the emission peak becomes very low. It also indicates that, as expected, increasing the application rate results in increasing peak emissions; however, a doubling of the application rate leads to a greater than doubling of the peak emission flux. These observations again suggest that emissions were controlled by a soil process related to application rate. The possible reasons for this are discussed below.

3.3. Degradation

In addition to atmospheric emissions, degradation is considered a dominant factor in fumigant fate within the column system. In common with other fumigants, degradation rates for CP are known to be dependent on soil factors such as microbial activity, organic matter content, and temperature. Since determining in-situ degradation rates within the column was not possible, separate degradation studies were performed to quantify this parameter across a range of CP application rates. To allow for comparison with the column system, the same experimental conditions imposed on the columns were applied in the degradation studies. As seen in Fig. 5, CP half-life was strongly affected by application rate, with a strong second-order polynomial relationship observed between the two variables ($R^2 = 0.98$). This is consistent with the third-order polynomial relationship observed between these two variables in the previous study. Across the range of application rates used in the soil columns (56–392 kg ha^{-1}), the half-life of CP ranged from approximately 10–75 h, indicating that a differing half-life at each application rate (initial mass) likely affected the fate of the CP within the columns. A strong dependency of CP degradation rate on initial mass has been previously demonstrated (Ashworth et al., 2015; Qin et al., 2016); similar results have been obtained for other soil fumigants, i.e., 1,3-D and methyl isothiocyanate (Ma et al., 2001; Qin et al., 2016) and dimethyl disulfide (Qin et al., 2016).

In order to further elucidate the CP degradation mechanism, we determined the half-life of CP (1) at increased application rates (up to 612 kg ha^{-1}) and (2) in autoclaved soil. At increased application rates, the degradation curve showed evidence of a plateau at a half-life of around 90 h (Fig. 5). By determining CP half-life in autoclaved soil, the contributions of chemical and biological processes to its degradation could be distinguished. For the autoclaved soil, it was found that CP half-life ranged from 140 to 190 h and showed no correlation with application rate ($R^2 = 0.0018$; data not shown). The much greater half-life in the absence of microbes indicates that microbial processes are very important in CP degradation. This comports with work by Wilhelm et al. (1997), Gan et al. (2000), Zheng et al. (2003), Zhang et al. (2005), and Qin et al. (2016). Indeed, Gan et al. (2000) estimated microbial degradation accounted for 68 to 92% of CP degradation, and a similar finding (84%) was reported by Zheng et al. (2003). Castro et al. (1983) reported that certain *Pseudomonas* species possessed the ability to degrade CP and that the main pathway for CP degradation was via sequential dechlorination to dichloromethane, chloronitromethane, and nitromethane. The disappearance of CP was accompanied by increasing dichloronitromethane, which subsequently decreased slowly over time.

The importance of microbes in the degradation of CP may help to explain the relationship between half-life and application rate. We hypothesize that as application rate increased, CP-degrading microorganisms were increasingly suppressed, reducing the ability of the soil to degrade CP. With such a process, the application rate should reach a level where all of the microbes have been effectively suppressed and no further effect on degradation rate is observed, i.e., would present itself as an apparent plateau observed at high application rates in Fig. 5.

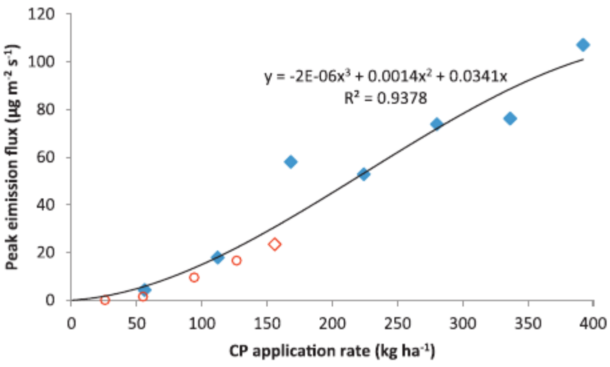

Fig. 4. Relation between peak (maximum) CP emission flux and application rate for the present study (closed symbols) and our previous study (open symbols; Ashworth et al., 2015). Circular symbols denote co-application of CP with 1,3-D; diamond symbols denote single CP application.

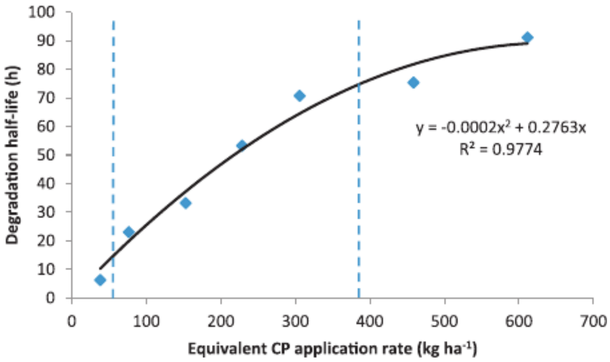

Fig. 5. Second-order polynomial relationship between CP application rate and half-life. The region between the vertical dotted lines represents the application rate range used in the soil columns.

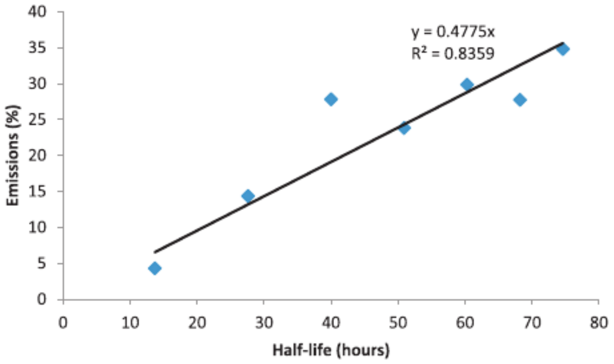

Fig. 6. Relation between CP half-life and column emissions (as a percentage of the amount added).

3.4. Relation between degradation rate and emissions

Based on the above, it is hypothesized that the relationship between CP application rate and degradation rate (Fig. 5) provides an explanation for the observed relationships between application rate and (i) total emission percentages (Fig. 1) and (ii) peak emission flux (Fig. 4). The proposed process can be summarized as follows:

1. As CP application rate increases, degradation rate decreases due to the suppression of CP-degrading microbes;
2. The decreasing degradation rate causes a greater percentage (and much greater mass) of the applied CP to remain within the soil;
3. The CP remaining in the soil is subject to emission to the air.

The positive linear relationship between CP half-life and emissions percentage at the varying application rates is shown in Fig. 6. The strength ($R^2 = 0.84$) of this relationship provides further evidence for the proposed process outlined above. It is evident from Fig. 6 that at the highest application rate, the plateau in the curve is beginning to form. Indeed, the CP half-life at 392 kg ha^{-1} (75 h) was close the plateau value of ~90 h. This provides an explanation for why further increases in CP application rate would not lead to continued increases in emissions (i.e., why a plateau is observed in Fig. 1).

4. Conclusions

In the present study, a clear positive relationship between emissions of CP (expressed as a percentage of the total CP applied) and application rate (between 56 and 392 kg ha^{-1}) was observed ($R^2 = 0.88$; $n = 7$). When these data were combined with those from a previous study (Ashworth et al., 2015), the relationship was further improved ($R^2 = 0.93$; $n = 12$). A further strong positive (second-order polynomial) relationship between CP half-life and CP application rate was also observed ($R^2 = 0.98$). It is hypothesized that as application rate increased, CP-degrading microbes were suppressed by the fumigant, resulting in a lower ability of the soil to further degrade CP. The significance of microbes in the degradation of CP was confirmed using autoclaved (sterile) soils. This finding, in turn, provides an explanation for the increasing total emission percentage losses with increasing application rate. Indeed, CP half-life was positively correlated with total emission losses ($R^2 = 0.84$). Therefore, it appears that a decrease in degradation rate as application rate increases leads to a greater percentage of the CP being available for emission to the air. Overall, this work has identified and quantified the phenomenon of CP percentage emission losses increasing with application rate. By relating this to the observation that the CP degradation rate decreases at higher application rates, a plausible explanation for this phenomenon is provided. This work has significance to the risk assessment of CP use. 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. However, it should be borne in mind that this study was conducted using laboratory soil columns, in which it is impossible to fully simulate realistic field conditions. As such, performing experiments to determine the effect of application rate on chloropicrin emissions under field conditions would be of great benefit to better assess the processes highlighted in this study.

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