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Assessing influences of farmyard manure addition, elevated CO_2, soil sterilization, soil types, and soil moisture on clothianidin dissipation kinetics

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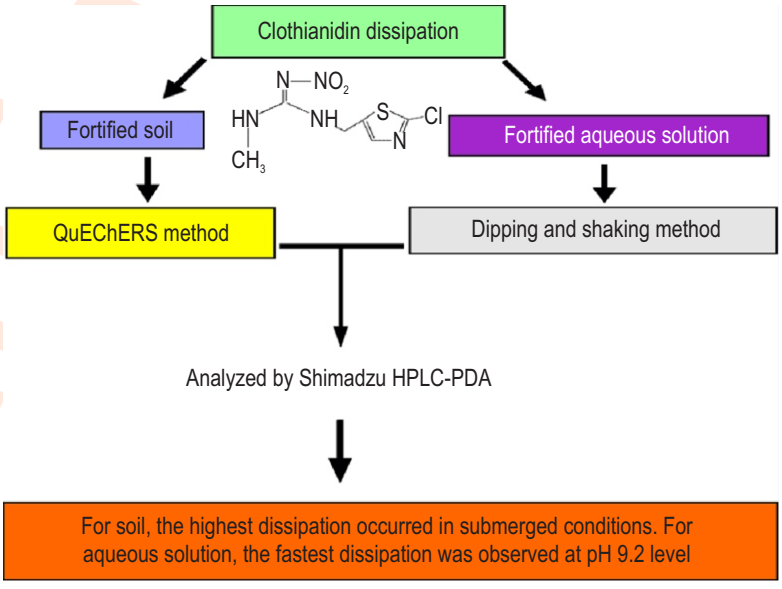
Abstract

Aim: To investigate the effects of farmyard manure addition, elevated CO_2, soil sterilization, dry conditions, field-capacity conditions, and submerged conditions on clothianidin dissipation from the soil, as well as the effects of different pH levels, namely, pH 4.0, 7.0, and 9.2, on its dissipation from the aqueous solutions.

Methodology: Samples were processed by the QuEChERS method from the soil and the dipping and shaking method from the aqueous solution, and then analyzed by Shimadzu HPLC-PDA.

Results: The results revealed that clothianidin dissipation from soil and aqueous solution best fit first-order kinetics, with the coefficient of determination r^2 value < 0.90. In the soil, varying clothianidin dissipation was recorded with significant impact and their decreasing dissipation rate was as follows: submerged conditions ($t_{1/2}$103.7–107.5 days) > elevated CO_2 ($t_{1/2}$115.7–143.3 days) > farmyard manure addition ($t_{1/2}$130.8–150.5 days) > field-capacity conditions ($t_{1/2}$158.4–215.0 days) > dry conditions ($t_{1/2}$250.8–334.4 days) > soil sterilization ($t_{1/2}$342.0–376.2 days). In the aqueous solution, clothianidin dissipation was slow at pH 4.0 ($t_{1/2}$430 days) but fast at pH 9.2 ($t_{1/2}$273.6 d days).



Interpretation: The findings suggest that clothianidin dissipation could be positively affected by FYM addition, elevated CO_2, soil sterilization, dry conditions, field-capacity conditions, submerged conditions, and aqueous pH level in all the treatments. This information would help gain a better understanding of clothianidin dissipation in the environment for good agricultural practices,proper risk assessment, and monitoring guidelines.

Key words: Aerobic-anaerobic degradation, Microbial activity, Organic carbon content, Persistence half-life period

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Introduction

Clothianidin is a member of neonicotinoid insecticides, which acts on the central nervous system of insects as acetylcholine receptor agonists (Pang *et al.,* 2020). It is highly effective against pests belonging to the orders Hemiptera, Coleoptera, Thysanoptera, Diptera, and Lepidoptera (CIBRC 2009; Jeschke *et al.,* 2010; Uneme *et al.,* 2006). Globally, clothianidin is commonly used as soil, seed, and foliage treatment to protect plants (Jeschke *et al.,* 2003; Li *et al.,* 2018). Extensive usage of clothianidin results in its detection in different environmental matrices over the past decades (Hladik *et al*., 2018), For example, Prairie wetland, Canada (Main *et al.*, 2014); the Midwestern United States (Hladik et al., 2014); Southern Ontario, Canada (Schaafsma *et al*., 2015; Struger *et al*., 2017); and Belize (Bonmatin *et al.,* 2019). Clothianidin contamination in the surrounding environment is facilitated by surface runoff and subsurface tile drains (Chrétien *et al.,* 2017; Mulligan *et al.,* 2015). Clothianidin exhibits longer persistence with estimated half-lives of 43–1328 days and medium leaching-potential with organic partition coefficient of 84–345 ml g^{-1} in soil (Stupp and Fahl, 2003). The author also stated that clothianidin residues in soil degrade within 50% dissipation time (DT_{50}) of 143–1001 days.

Another study by Zhang *et al.* (2016a) found that clothianidin in residues dissipate with half-life ranging from 35.73 to 36.10 days in soil alone. Due to high temperature and high precipitation, the half-life of clothianidin residue is shortened to 3.5–10.4 days in soil (Zhang *et al.,* 2016b), wherein investigating clothianidin degradation in soil shows medium persistence with a half-life period of 15.18 days (Bansal *et al.,* 2019). Numerous studies have also reported that data on the half-lives value of clothianidin in soil vary greatly ranging from 17 to 6931 days (Bonmatin *et al.,* 2015; Li *et al.,* 2019; Zhang *et al.,* 2018). At 125 and 250 g a.i./ha clothianidin application rate in sugarcane field, the residue can be only detected up to 90 days after treatment with LOQ of 0.01 mg kg^{-1} in soil (Bansal *et al.,* 2019). Reduced clothianidin dissipation in Sacramento River and rice field water samples are reported with derived DT_{50} values of 16.6 and 18.0 days (Mulligan *et al.,* 2016a). Clothianidin residue in water has been reported to be hydrolytically stable (European Commission Health and Consumer Protection Directorate-General, 2005). Thus, it may eventually cause a great concern worldwide (Pietrzak *et al.,* 2020).

Several factors are considered to play an essential roles in modulating pesticide dissipation; for instance, moisture, pH, organic carbon, and microbes (Anderson *et al.,* 2015; Chatterjee *et al.,* 2013; Kumar and Gupta, 2020; Tiryaki and Temur, 2010). Similarly, previous studies have also reported that pesticide dissipation is dependent on soil sterilization, soil types, carbon dioxide, and organic matter (Ali *et al.,* 2014; Khandelwal *et al.,* 2014; Kumar *et al.,* 2017; Li *et al.,* 2012). However, farmyard manure has attainted interest as a potential organic amendment due to its cost-effectiveness, convenience, and easy accessibility (Mate *et al.,* 2014). FYM can improve soil fertility and soil quality, leading to substantial gains in crop production (Liang *et al.,* 2012; Liu *et al.,* 2010; Mandal *et al.,* 2007; Tadesse *et al.,* 2013); and the use of FYM is reported to greatly affect the dissipation rate of pesticides (Ramasubramanian 2020; Suyal *et al.,* 2018). Clothianidin persistence in sandy clay loam soil under tropical sugarcane ecosystem recorded a positive effect as a result of organic manuring (Ramasubramanian 2021). In fact, there has been mounting concern about global warming because of the rising green house gases in the atmosphere, such as CO_2, that could potentially alter the fate of pesticide dissipation in the environment (Kumar *et al.,* 2017; Mukherjee *et al.,* 2016).

Elevated CO_2 concentration in soil may increase pesticide dissipation such as cyantraniliprole by 47.7%–98.8% in the open-top chamber (Kumar and Gupta, 2020). However, to the best of our knowledge, there is limited information available from the scientific literature survey considering clothianidin dissipation behavior with FYM addition, elevated CO_2, soil sterilization, and moisture content in soil; and pH in aqueous solution. Accordingly, the present study aimed at evaluating clothianidin dissipation from two soil types (namely Alfisolsoil and Inceptisol soil) under the influence of FYM addition, elevated CO_2, soil sterilization, dry conditions, field-capacity conditions, and submerged conditions over a period of 120 days. The study also explored clothianidin dissipation from aqueous solution under the effects of three different pH levels, *i.e.,* pH 4.0, 7.0 and 9.2 for 120 days. The uniqueness of this study lies in the fact that the data generated can expand knowledge on the long-term environmental impacts of clothianidin usage, especially in tropical regions.

Materials and Methods

Soil: Two different geographical locations were selected as soil sampling sites. The two geographic locations were agricultural fields at Tairenpokpi, Manipur with a sub-tropical humid climate belonging to the Eastern Himalayan region (Latitude 24°38'35.412" N; Longitude 93°40'13.008"E) and the ICAR-Indian Agricultural Research Institute (ICAR-IARI), New Delhi, with a tropical and sub-tropical steppe climate belonging to the Trans-Ganga Plains Region (Latitude: 28°38'23"N, Longitude: 77°09'27"E), India, according to India's classification of Agro-climatic zones (Balasubramanian, 2017). Soil samples with no previous record of clothianidin application were manually collected from the sites (0–15 cm soil depth). These soil samples were air-dried in shade, ground to pass through a 2 mm sieve, and stored in a plastic bag at room temperature (24±2°C). The physical and chemical properties of the soils were determined using the standard protocol for soil characterization: soil pH following the without of Jackson (Jackson 1958); organic carbon adopting the Walkley and Black methods (Black 1965); and soil texture employing the Bouyoucos hygrometer method (Jackson, 1958) (Table 1).

Farmyard manure: Farmyard manure (FYM) was prepared using cattle manures from the Division of Agronomy, ICAR-Indian Agricultural Research Institute (ICAR-IARI), New Delhi. The

physico-chemical properties of FYM were determined following Kjeldahl method (Kjeldahl, 1883) (Table 2).

Instrumentation: Clothianidin residue analysis was performed using Shimadzu HPLC system equipped with a PDA detector and RP-18 column (250 × 4.6 mm, 5 µm). The HPLC was operated with 10 µl injection volume at 270 nm wavelength. The mobile phase employed was acetonitrile: water solvent system (70:30, v/v) at 1 ml min^{-1} flow rate. The retention time of clothianidin was 2.95 min.

Chemicals: Clothianidin (Dantotsu® 50% Water dispersible granules, WDG) was obtained as a gift from Sumitomo Chemicals India Pvt. Ltd. Primary-secondary amine (PSA) sorbent, $MgSO_4$ (anhydrous), and $NaSO_4$ (anhydrous) were procured from Merck Life Science Pvt. Ltd., India. HPLC analytical grade solvents, such as acetone, hexane, dichloromethane, methanol, and acetonitrile were purchased from Merck Life Science Pvt. Ltd., India. Doubled-distilled Millipore water was used.

Extraction of clothianidin from soil: Clothianidin in was extracted following standard QuChERS AOAC official method 2007.01 with minor modifications (in triplicate). To the clothianidin-fortified soil, acetonitrile, anhydrous $MgSO_4$, and anhydrous NaCl were added; and thereafter the obtained solution was centrifuged at 5000 rpm for 12 min. The supernatant solution thus obtained was extracted and then transferred to a PTEF centrifuge tube containing PSA sorbent and anhydrous $MgSO_4$. The resultant content was mixed by vortexing for 1 min and centrifuged for 12 min at 5000 rpm. Finally, the supernatant was filtered and analyzed using HPLC.

Extraction of clothianidin from aqueous solutions: Clothianidin extraction was performed following the dipping and shaking method. For this purpose, the aqueous solution containing clothianidin was extracted three times using an equivalent amount of fresh dichloromethane (3 × 30 ml) after diluting with 2% aqueous NaCl solution. Next, the aqueous solution was shaken (3 min) and kept undisturbed (4 min) to separate the layers. After the layer separation, the organic-solvent phase was collected and passed through anhydrous Na_2SO_4 to remove any traces of moisture. Subsequently, the resulting organic solvent was concentrated using a rotary vacuum evaporator (34±2°C), re-dissolved in HPLC grade acetonitrile (5 ml),and analyzed using HPLC.

Effect of farmyard manure addition: The experiment was designed to study clothianidin dissipation from soil under the effects of FYM addition over 120 days. For this purpose, 0.05 g of FYM was thoroughly mixed with 1.95 g soil. The mixed soil was spiked with clothianidin @10 µg g^{-1} level and transferred to beakers. Field capacity moisture treatment without FYM addition served as a control.

Effect of elevated CO_2 conditions: The study was conducted to assess the effect of elevated CO_2 on clothianidin dissipation in soil for 120 days. To examine the effect of elevated CO_2, the soil samples were kept inside Open Top Chambers maintained at 750±20 µl l^{-1} elevated CO_2 level, 25±3°C temperature, and 70±3% relative humidity. The soil was then treated with clothianidin @ 10 µg g^{-1}. Field-capacity moisture treatment without elevated CO_2 served as a control.

Effect of soil sterilization: Clothianidin dissipation under the influence of soil sterilization was investigated in Inceptisol and Alfisol soils under field-capacity moisture conditions for 120 days. For evaluating the effect of soil sterilization, Alfisol and Inceptisol were sterilized at 120±2°C and ~1.036×105 Pa pressure. After sterilization, the soil was treated aseptically with clothianidin @10 µg g^{-1} in a laminar flow chamber. Field-capacity moisture treatment without sterilization served as a control.

Effect of soil moisture content: The effect of dry conditions, field-capacity conditions, and submerged conditions onclothianidin dissipation was studied inInceptisol soil and Alfisol soil for 120 days. The soil (20 g, d.wt.) was treated with clothianidin at 10 µg g^{-1} level in beakers (200 ml). In field-capacity treatments, calculated amount of doubled-distilled water was added to soil in order to produce field-capacity moisture levels.

Table 1: Physical and chemical properties of soil collected from agricultural fields in Delhi and Manipur state, India

Regions	Soil type	pH	Organic carbon (%)	Textural class	Sand (%)	Silt (%)	Clay (%)
Delhi	Inceptisol	7.8±0.5	0.2±0.1	Sandy loam	71.4±2.1	18.1±0.8	10.4±0.7
Manipur	Alfisol	5.0±0.3	0.9±01	Clay loam	33.1±2.2	36.5±0.7	30.4±0.6

Data are mean of three replicates ±SD

Table 2: Physical and chemical properties of farmyard manure

Parameters	pH	Organic carbon (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Farmyard manure (FYM)	6.4±0.2	24.2±0.1	26.2±0.1	2.8±0.1	9.8±0.1

Data are mean of three replicates ±SD

Table 3: Bartlett Chi-square test of clothianidin dissipation from soil under treatment of dry conditions, field-capacity conditions, submerged conditions, FYM addition, soil sterilization, and elevated CO_2; and from aqueous solution under treatment of pH 4.0, pH 7.0, and pH 9.2 over 120 days

Factors	Bartlett's test	Chi-square value	DF	Prob.
Days (Dissipation)	Before transformation	130.20	21	<0.001
	After transformation	4.821	21	0.9999
Days (pH)	Before transformation	41.39	11	<0.001
	After transformation	0.50	11	0.9999

For submerged treatments, sufficient amount of doubled-distilled water was added to soil to raise the water level to ~3 cm above the soil surface. In dry treatments, no water was added to the soil, thereafter the samples were covered with perforated aluminium foil and maintained at constant weight by replenishing the lost water on every alternate day.

Effect of pH levels: To explore the pH effect in aqueous solution, different pH levels, viz pH 4.0, 7.0, and 9.2 were established using buffer tablets of pH 4.0, 7.0, and 9.2 in double-deionized Millipore water, respectively. The aqueous solutions were then treated with clothianidin @10 µg ml^{-1}. The pH levels of the aqueous solutions were maintained throughout the experimental period.

All the fortified samples (soil and aqueous solution), except for the elevated CO_2 treatment, were placed in a BOD incubator maintained at 25±3°C and 70±3% relative humidity. Samples were randomly withdrawn in triplicate at different time intervals: 0, 1, 3, 5, 7, 10, 15, 30, 60, 90, and 120 days. Thereafter, the samples were processed and analyzed, as described under the Methods and Materials section in the extraction of clothianidin from soil and aqueous solutions. The dissipation of clothianidin was monitored using first-order kinetics, $\partial C/C = -k\partial t$, where 'C' is the concentration and 't' is the time for 120 days. The half-life ($t_{1/2}$) of dissipation was estimated by the formula, $t_{1/2} = 0.693/k$.

Statistical analyses: The experimental data on clothianidin dissipation from soil were taken under FYM addition, elevated CO_2, soil sterilization, dry conditions, field-capacity conditions, and submerged conditions; and factors taken were two soil types (namely, Inceptisol and Alfisol soil), and time (days) (namely, 0, 3, 5, 7, 10, 15, 30, 50, 60, 90 and 120 days) as the three sources of variability. Data pertaining to experiments on clothianidin dissipation from aqueous solution were taken under different pH levels (namely, pH 4.0, pH 7.0, and pH 9.2) and time (days) (0, 3, 5, 7, 10, 15, 30, 50, 60, 90 and 120 days) as two sources of variability. All the experiments were performed in triplicate. Both the data sets were initially analyzed using PROC UNIVARIATE of SAS for performing the Shapiro-Wilk test to assess the normality of data and Bartlett chi-square tests using PROC IML of SAS to assess the heterogeneity of variances over days to confirm that the assumptions of ANOVA are met. The results showed significance of normality tests, which implies non-normality of data and also the variances were found to be heterogeneous at 5% level of significance. Since variability was found high over time, an Aitkens transformation was used to normalize the data which consists of dividing each observation with its root mean square error (RMSE) calculated for each day.

Further, the transformed data on clothianidin dissipation from soil were subjected to three-way ANOVA and the transformed data pertaining to experiments on clothianidin dissipation from aqueous solution were subjected to two-way ANOVA using PROC GLM of the SAS software package, version 9.4 (SAS Institute, Cary, North Carolina, USA) after confirming the homogeneity of error variance by Bartlett's chi-square (Table 3). It was found that all the effects and their interactions were significant. Hence, the results were further examined with Tukey's Honest Significant Difference (HSD) test to identify the pair-wise significant differences among various effects and interactions. The effect pairs designated with same letter are at par, while the effect pairs with different letters are significantly different at $P<0.05$. All the data are represented in terms of the original means as (mean±SE) with lowercase superscript letters expressing the homogeneous groups of treatments.

Results and Discussion

In soil, the QuChERS method gave a mean-recovery percentage of 95±1.0%; and, in aqueous solution, the mean-recovery percentage of dipping and shaking method was 84.3±0.5%. Clothianidin dissipation was investigated in two different soil types with FYM addition. The results revealed that addition of FYM in Inceptisol soil declined total clothianidin in residue by only 44% after 120 days (Fig. 1A).It was also observed that more than 50% of parent clothianidin residues in Alfisol soil dissipated at the end of the study period (Fig. 1B). Higher half-life value of clothianidin ($t_{1/2}$) was recorded in Inceptisol soil (150.5 days) compared to Alfisol soil (130.8 days), using first-order dissipation kinetics. It was observed that increase in half-life period of clothianidin was strongly related to longer the dissipation time in soil. One plausible explanation is that increased clothianidin dissipation seems to be linked to higher microbial activity in FYM-added soils, which indicates possible impact of FYM addition. In a previous study, Suyal *et al.* (2018) reported that the percent dissipation of neonicotinoid pesticide on fifth day declined by ~70.1% in FYM added soil compared to ~41.2% observed value in control soil, suggesting the availability of decomposable organic matter. Documented half-life of clothianidin in chicken manure (3.50 days) was lower than

inorganic fertilizer (5.27 days), urea (10.44 days), and granule alone (3.53 days) because of direct sunlight-irradiation and high dissipation rate (Zhang *et al.,* 2016 b). With the FYM amendment, the pesticide dissipation increase as much as 26.2% of the control treatment after 60 days (Mukherjee, 2009), and enhance the effectiveness of pesticide dissipation in soil by more than 22.07% after 21 days (Kadian *et al.,* 2008). On the contrary, the addition of FYM in soil only results in a slight decrease of neonicotinoid dissipation against non-manurial soil, indicative of the adsorption process (Ramasubramanian, 2020). Organic manuring of clothianidin in sandy clay loam soil reduces dissipation in manurial soils (21 days) compared to non-manurial soil (22.4–24.8 days), resulting in an insignificant effect of organic manures on clothianidin persistence that lasts only up to 90 days after treatment (Ramasubramanian, 2021).

Experiment on clothianidin dissipation subjected to elevated CO_2 at 750±20 µl l^{-1} was conducted in soil. Based on the results, the elevated CO_2 treatment increased clothianidin dissipation by nearly 46% in Inceptisol soil and 52% in Alfisol soil within 120 days (Fig. 1A, B). This rapid clothianidin dissipation in Alfisol soil (115.7 d) compared to Inceptisol soil (143.3 d) suggest that elevated CO_2 treatment may tend to stimulate dissipation from the soil. Previous studies have shown faster dissipation in elevated CO_2 conditions than that of ambient CO_2 conditions (Khandelwal *et al.,* 2014; Kumar *et al.,* 2017; Manna *et al.,* 2013), which is comparable with the results of this study. This elevated CO_2 condition in soil is likely to associate with higher degradation of pesticides (Chatterjee *et al.,* 2013; Kumar and Gupta 2020; Mukherjee *et al.,* 2018). Similar observation stated the existence of a positive correlation between pesticide dissipation and soil microbial activity (Kumar and Gupta, 2020).

Effect of soil sterilization on clothianidin dissipation was assessed in fortified soil. The data showed that clothianidin residue in Inceptisol soil was reduced slightly by ~20 % after 120 days (Fig. 1A). On the other hand, clothianidin residue in Alfisol soil dropped moderately by ~21 % over the experimental period (Fig. 1B). However, there was no significant difference in clothianidin dissipation rate between sterilized Alfisol soil (342.0 days) and sterilized Inceptisol soil (376.2 days) at P<0.05. Possibly, the low dissipation of clothianidin from sterilized soil may be partly associated with the loss of microbial communities due to sterilization process. White-rot fungus (*Phanerochaetes ordida*) can rapidly dissipate clothianidin residue up to 37% in a nitrogen-limited medium after 20 days of incubation period at 30°C (Mori *et al.,* 2017). With *Pseudomonas stutzerismk* treatment, only 62% of clothianidin residue is aerobically degraded to 2-chloro-methyl thiazole and methyl 3-(thiazolyl) methyl guanidine within 14 days at 30°C (Parte and Kharat, 2019). Clothianidin can dissipate more rapidly in non-sterilized conditions (25.7–86.7 days) than in sterilized conditions (54.1–130 days) because of microbial activity by proteobacteria and actinobacteria (Zhang *et al.,* 2018). Concurrently, rapid pesticide degradation in non-sterile soil is linked to microbial intervention (Chatterjee *et al.,* 2013; Khandelwal *et al.,* 2014; Reddy *et al.,* 2013), as a result of microbiome process (Liu *et al.,* 2020). Degrading rate of clothianidin in consortia treatment was much higher than that of natural attenuation and biostimulation, which transforms nitroimino moiety of clothianidin to urea compound by cleavage of different bonds (Wang *et al.,* 2019). Recently, Zhang *et al.* (2020) found that degradation of clothianidin in soil may be associated with biotic and abiotic processes. More specifically, the microbial degradation of neonicotinoids could be greatly influenced by the concentration of insecticides, soil temperature, moisture content, and microorganism adaptability (Pietrzak *et al.,* 2020).

Study on clothianidin dissipation under the influence of dry conditions, field-capacity conditions, and submerged conditions were conducted in soil. Statistical analysis revealed that, under dry conditions, clothianidin residues from Inceptisol soil ($t_{1/2}$ 334.4 d) were depleted slowly by ~21% (Fig. 1A); whereas clothianidin from Alfisol soil ($t_{1/2}$ 250.8 d) dropped moderately by ~29% (Fig. 1B). It was also observed that the percent dissipation of clothianidin with field-capacity conditions was up to ~32 percent in Inceptisol soil ($t_{1/2}$ 215.0 days) and ~40 percent in Alfisol soil ($t_{1/2}$ 158.4 days) after 120 days. In submerged conditions, the parent clothianidin residue declined steadily by~51% in Inceptisol soil (107.5 days) and fell rapidly by ~56 % in Alfisol soil (103.7 days) during the study period. There was a significant effect of dry conditions (9.10^{b}±0.001), field-capacity conditions (8.72^{c}±0.001), and submerged conditions on clothianidin dissipation from the soil at *P*<0.05. The data analysis suggests that faster dissipation of clothianidin in Alfisol soil than in Inceptisolsoil across all the treatments might be attributed due to higher organic matter content and microbial activity. Li *et al.* (2018) and Stupp and Fahl (2003) demonstrated that dissipation of clothianidin largely depends on microbial activity, moisture content, and soil organic content in the soil, which is in good agreement with the findings of the present study. Higher clothianidin dissipation in soil corresponds to higher organic carbon content (Zhang *et al.,* 2018) and microbial growth (Kah *et al.,* 2007). Moreover, the presence of clay content in the soil promotes the sorption of pesticides, rendering slow degradation of pesticides (Sahu *et al.,* 2019).

Li *et al.* (2012) also pointed out that clothianidin dissipation could be affected by various environmental conditions, such as temperature and humidity. In the present study, the dissipation rate of clothianidin residue from soil was highest in submerged conditions (51.87–56.85%), followed by field-capacity conditions (32.31–40.83%) and dry conditions (21.69–29.09%) after 120 days. It is plausible that the fastest clothianidin dissipation rate in submerged conditions may be associated with partially anaerobic environment, while the slowest clothianidin dissipation rate in dry conditions may be related to low microbial activity in soils lacking moisture. Similarly, Mulligan *et al.* (2016b) found that clothianidin residues achieve rapid dissipation in anaerobic environment but not in aerobic environment due to lack of microbial population. Physiological stress induces slow microbial activity is also reported in dry conditions (Kumar and Gupta, 2020). The dissipation half-life of clothianidin was 143–10001 days in aerobic conditions and 21

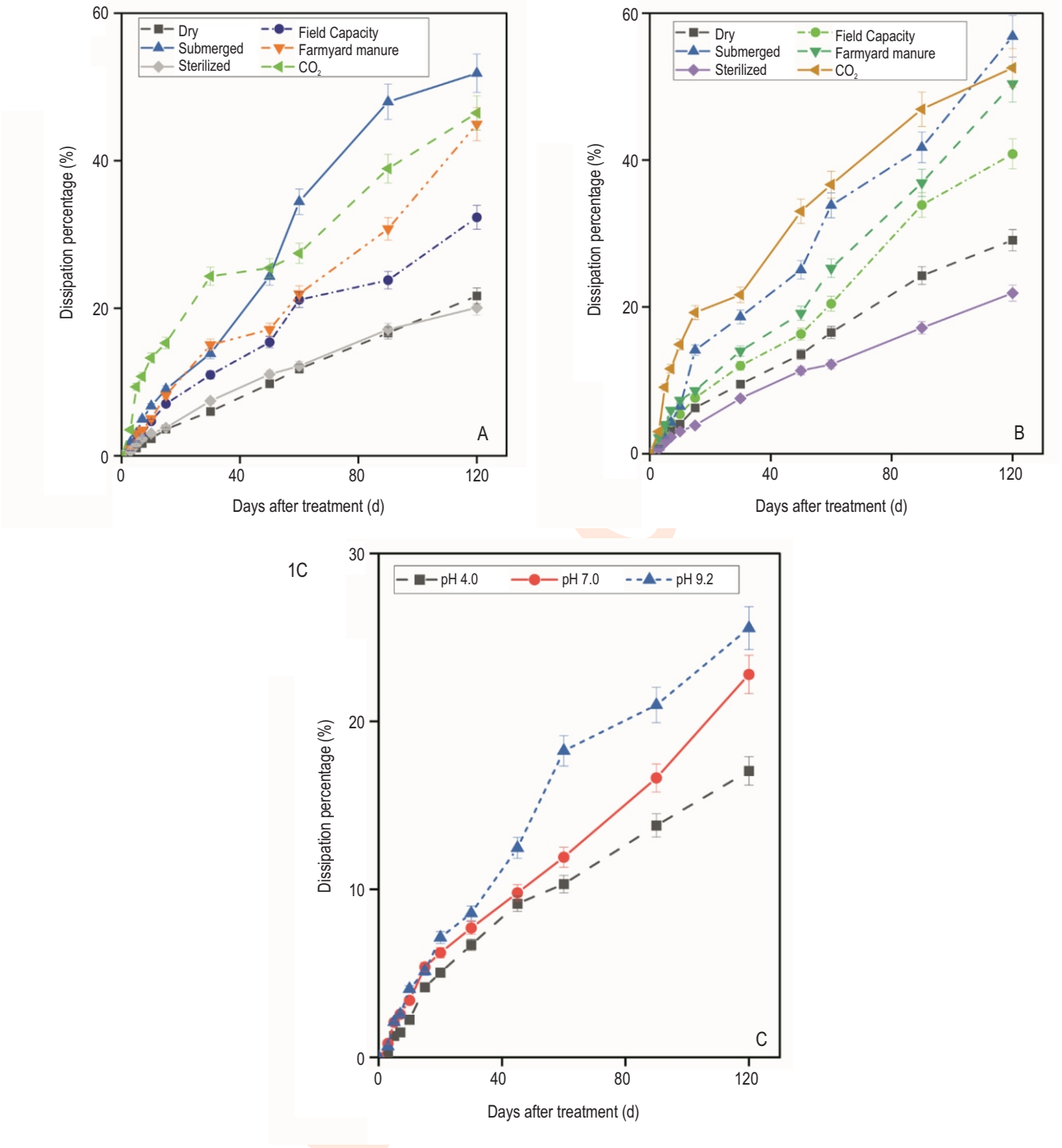

Fig. 1: Temporal variation of clothianidin dissipationin Inceptisol soil(1A) and Alfisol soil (1B)under the influenceof dry conditions, field-capacity conditions, and submerged conditions), soil sterilization, FYM addition, and elevated CO_2; andaqueous solution (1C) at pH 4.0, 7.0, and 9.2.Error bars indicate standard error of mean (n=3).

days in anaerobic conditions in nine different soil types under laboratory conditions (European Commission Health and Consumer Protection Directorate-General, 2005). However, Stupp and Fahl (2003) underlined that clothianidin residues exhibit slow degradation, with half-life values of 143–1328 days. Clothianidin dissipation under harsh climatic environments manifests a half-life value of 10.4 days in soil (Zhang *et al.,* 2016 b), and its response is largely governed by physical, chemical, and biological processes (Bansal *et al.,* 2019). We examined the effect of different pH levels, namely, pH 4.0, pH 7.0, and pH 9.2,

on clothianidin dissipation from aqueous solutions over 120 days under laboratory conditions. It was noticed that the maximum dissipation percentage of clothianidin residues in aqueous solution was recorded in alkaline pH 9.2 (25%), followed by neutral pH 7.0 (22%) and acidic pH 4.0 (~20%) (Fig. 1C), indicating the presence of rapid hydrolytic degradation. In all the treatments, clothianidin residues persisted beyond the study period of 120 days in the aqueous solution. Another researcher (Stupp and Fahl 2003) have demonstrated that clothianidin residue did not degrade effectively in the pH range of 5–7 at 25–50°C, which is in line with the present result. Clothianidin is hydrolytically stable at pH 4.0 and pH 7.0 but not at pH 9.0, as a result of close dependency on pH (Uneme *et al.,* 2006).

The findings of this study suggest that in general, the ultimate fate of clothianidin dissipation from soil could be markedly affected by FYM addition, elevated CO_2, soil sterilization, dry conditions, field-capacity conditions, and submerged conditions in all the treatments. Clothianidin dissipation from soil was fastest in submerged conditions, followed by elevated CO_2, FYM addition, field-capacity conditions, dry conditions, and soil sterilization across all the treatments. Clothianidin dissipation from aqueous solution was highest at pH 9.2 but lowest at pH 4.0. These observations will be valuable for determining the proper and safe use of clothianidinas part of good agricultural practices (GAP), proper risk assessment, and monitoring guidelines. Additionally, the use of farmyard manure in field soil could represent a feasible strategy to reduce dissipation as a step toward sustainable agriculture. Future studies should focus on comprehensive deciphering of the complex mechanisms and underlying interplay of factors behind the dissipation process in field conditions.

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