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Clothianidin decomposition in Missouri wetland soils

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Abstract

Neonicotinoid pesticides can persist in soils for extended time periods; however, they also have a high potential to contaminate ground and surface waters. Studies have reported negative effects associated with neonicotinoids and nontarget taxa, including aquatic invertebrates, pollinating insect species, and insectivorous birds. This study evaluated factors associated with clothianidin (CTN) degradation and sorption in Missouri wetland soils to assess the potential for wetland soils to mitigate potential environmental risks associated with neonicotinoids. Solid-to-solution partition coefficients (K_d) for CTN sorption to eight wetland soils were determined via single-point sorption experiments, and sorption isotherm experiments were conducted using the two most contrasting soils. Clothianidin degradation was determined under oxic and anoxic conditions over 60 d. Degradation data were fit to zero- and first-order kinetic decay models to determine CTN half-life ($t_{0.5}$). Sorption results indicated CTN sorption to wetland soil was relatively weak (average K_d, 3.58 L kg^{-1}); thus, CTN has the potential to be mobile and bioavailable within wetland soils. However, incubation results showed anoxic conditions significantly increased CTN degradation rates in wetland soils (anoxic average $t_{0.5}$, 27.2 d; oxic average $t_{0.5}$, 149.1 d). A significant negative correlation was observed between anoxic half-life values and soil organic C content ($r^2 = .782$; $p = .046$). Greater CTN degradation rates in wetland soils under anoxic conditions suggest that managing wetlands to facilitate anoxic conditions could mitigate CTN presence in the environment and reduce exposure to nontarget organisms.

1 | INTRODUCTION

Neonicotinoids, such as clothianidin (1-[(2-chloro-1,3-thiazol-5-yl) methyl]−3-methyl-2-nitroguanidine [CTN]) and imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine [ICD]), are a class of pesticides used in agriculture since the 1990s whose use has substantially increased since the mid-2000s. Neonicotinoids can persist in agricultural soils and have great potential to contaminate

Abbreviations: BK, B.K. Leach Memorial; CA, conservation area; CEC, cation exchange capacity; CTN, clothianidin; EB, Eagle Bluffs; FR, Four Rivers; HPLC, high-performance liquid chromatography; ICD, imidacloprid; MDC, Missouri Department of Conservation; nAChR, nicotinic acetylcholine receptor; ORP, oxidation-reduction potential; OS, Otter Slough; SOC, soil organic carbon; SPE, solid-phase extraction; TS, Ted Shanks.

ground and surface waters (Bonmatin et al., 2005; Chagnon et al., 2015; Jones, Harrington, & Turnbull, 2014; Main et al., 2014). Residual neonicotinoids in the environment can potentially have negative impacts on nontarget organisms (Anderson, Dubetz, & Palace, 2015; Henry et al., 2012; Main, Webb, Goyne, & Mengel, 2018; Morrissey et al., 2014; Pisa et al., 2015; Van Dijk, Van Staalduinen, & Van der Sluijs, 2013). Furthering our understanding of neonicotinoid environmental fate and transport is important to mitigate possible negative effects of residual neonicotinoids on nontarget taxa.

Neonicotinoids are water-soluble compounds that provide systemic protection from a wide range of biting and root-boring insects. Neonicotinoid compounds mimic nicotine's mode of action and act on the central nervous system of insects by irreversibly binding to the nicotinic acetylcholine receptor (nAChR), resulting in paralysis and death when ingested at high concentrations (Bonmatin et al., 2015). Neonicotinoids are generally more toxic to invertebrates than vertebrates due to a limited ability to cross the blood–brain barrier in vertebrates, a greater affinity to invertebrate nAChRs (Chao & Casida, 1997; Tomizawa & Casida, 1999, 2003, 2005), and a greater abundance of nAChRs in invertebrate central nervous systems (Van Dijk et al., 2013). For these reasons, neonicotinoids have become an effective tool for agricultural insect management.

Neonicotinoids are regularly applied in row-cropping agricultural operations, vegetable production, and orchard operations. Neonicotinoids can be applied via seed coating, foliar spray, soil drench, and stem application (Jeschke, Nauren, Schindler, & Elbert, 2011). Seed treatments were introduced in the early 2000s as a cost-effective preventative approach that could potentially decrease the negative effects on pollinating species associated with spraying methods. However, the use of seed treatment coincided with a major increase in neonicotinoid use, and by 2011 34–44% of soybean [*Glycine max* (L.) Merr.] and 79–100% of maize (*Zea mays* L.) hectares planted in the United States received a neonicotinoid seed treatment (Douglas & Tooker, 2015). Globally, most neonicotinoids (~60%) applied are delivered via seed or soil treatment (Jeschke et al., 2011). However, studies have shown that ~5% of the neonicotinoid coating is taken up by the plant while ~95% remains in the soil or becomes drift (<1%) (Goulson, 2014; Sur & Stork, 2003). Remnant neonicotinoid residues in soils can leach into ground and surface waters (Main et al., 2014), sorb to soil (Goulson, 2013; Satkowski et al., 2018), or ascend into nontarget plants (Botas, David, Hill, & Goulson, 2016). Many studies have found negative effects associated with neonicotinoids and nontarget taxa, including aquatic invertebrates (Anderson et al., 2015; Morrissey et al., 2014; Pisa et al., 2015; Schepker, Webb, Tillitt, & LaGrange, 2020; Van Dijk et al., 2013), pollinating species (Henry et al., 2012; Main et al., 2018; Whitehorn, O'Connor, Wackers, & Goulson, 2012), insectivorous birds (Hallmann, Foppen, Van Turnhout, De Kroon, & Jongejans, 2014), and female and fawn white-tailed deer (Berheim et al., 2019). A comprehensive understanding of neonicotinoid fate in the environment and effects on nontarget taxa is important due to their extensive use in landscaping and agricultural operations.

Core Ideas

- Clothianidin degradation is more rapid under anoxic conditions in Missouri wetland soils.
- SOC negatively correlated with CTN half-life values under anoxic conditions.
- Clothianidin has a weak sorption affinity for the Missouri wetland soils studied.
- Anoxic conditions may be a viable strategy to mitigate Clothianidin presence in wetland soils.

The potential of CTN leaching into ground and surface waters is governed by soil sorption processes. Previous studies have found that soil organic matter and soil organic C (SOC) influence CTN sorption to soil (Li et al., 2018; Liu, Zheng, Ma, & Liu, 2006; Mulligan, Parikh, & Tjeerdema, 2015). Clothianidin appears to be a more weakly sorbed neonicotinoid based on reported *K*d values. Mulligan et al. (2015) reported CTN *K*d values in California rice paddy soils ranging from 5.1 to 10.8 L kg^{-1}, and Li et al. (2018) reported CTN *K*d values in three Mississippi agricultural soils with minimal SOC content (0.8–6.4 g $kg^{-}1$) ranging from 0.62 to 1.94 L kg^{-1}. Zhang, Ren, Sun, and Min (2018) found CTN *K*d values in four China agricultural soils ranging from 1.02 to 5.25 L kg^{-1}.

Clothianidin is moderately soluble and has a high leaching potential in soil; however, the compound can also persist in soil (PPDB, 2015). Clothianidin has been found to persist in soil and in water for extended periods of time (Jones et al., 2014; Whiting, Strain, Campbell, Young, & Lydy, 2014). Field studies have reported CTN oxic soil half-life values ranging from 277 to 1,386 d (Goulson, 2013). Some studies found the presence of soil microbes to be important in neonicotinoid degradation (Herner, Bazok, & Briski, 2014; Liu et al., 2010; Pandey, Dorrian, Russell, & Oakeshott, 2009). In addition, the presence of flooded, anoxic conditions has been suggested to be an important factor affecting CTN half-life in certain soils (Herner et al., 2014; Liu et al., 2015; Mulligan et al., 2016). Understanding the effect that oxic and anoxic conditions have on CTN degradation in wetland soils is valuable information for conservation area managers due to the wetting and drying cycles in wetlands characterized by seasonal or temporary hydrology.

Few studies have investigated sorption and anoxic degradation of CTN in soil, and, to our knowledge, no studies have investigated CTN sorption and anoxic degradation in wetland soils. Thus, the objectives of this study were (a) to determine CTN half-life values under oxic and anoxic conditions, (b) to quantify CTN *K*d values for Missouri wetland soils, (c) to elucidate the effect of wetland soil anoxic conditions on CTN degradation as a function of time, and (d) to examine the influence of physical and chemical properties of wetland soil on sorption and half-life values.

2 | MATERIALS AND METHODS

2.1 | Wetlands sampled, soil sampling, and soil characterization

In collaboration with the Missouri Department of Conservation (MDC) Geographic Information Systems specialists, a list of all MDC intensively managed wetland conservation areas (CAs) was compiled. To meet the definition of a MDC intensively managed wetland CA, the area must have a reliable water source and contain an infrastructure that permits control of water level/distribution. All possible wetland pools within each intensively managed CA that met these criteria were identified. To reduce edge effects in small wetlands and to reduce the number of potential sites, only wetland pools containing hydric soil with an area greater than 0.78 ha were selected. Soils were identified as hydric using the 2015 Natural Resources Conservation Service national hydric soils list. From the list of 1,265 possible study sites, five wetland pools were randomly selected to be used in the anoxic and oxic incubations. The five CA wetland pools sampled were: B.K. Leach Memorial (BK), wetland 8; Eagle Bluffs (EB); Four Rivers (FR); Otter Slough (OS); and Ted Shanks (TS). Three more wetland pools were randomly selected for soils from a total of eight wetlands to be used in the single-point batch sorption experiment. The three additional CA wetland pools sampled were: BK, Wetland 3; Marais Temps Clair (MTC), and Nodaway Valley (NV). Soil samples were collected from study wetlands between mid-August and mid-October 2016. Within each study wetland, soil samples were collected at a depth of 0–10 cm in locations that contained characteristic wetland vegetation (e.g., *Polygonum* spp., *Cyperaceae* spp., *Juncaceae* spp., *Typha* spp.) in Missouri. If a selected wetland was determined unsuitable (i.e., majority of the site planted in crops), then an alternate wetland within the same CA containing the same soil series and soil textural classification was sampled. Wetland pools that contained a small portion of the area planted to crops were sampled if the uncropped portion of the pool exhibited wetland characteristics and was greater than 0.78 ha; however, no soil samples were collected under cropped areas. Details of the sample processing and soil characterization and background pesticide analyses are described in Supplemental Tables S1 and S2.

2.2 | Batch sorption experiments

Single-point batch sorption experiments were conducted to determine solid-to-solution partition coefficient (K_d) values. Five grams of air-dried soil was placed in 50-ml fluorinated ethylene propylene centrifuge tubes and suspended in 14.4 ml of 0.01 M $CaCl_2$ (I = 0.03 M) background electrolyte solution. To inhibit microbial degradation, 0.5 ml of NaN_3 solution (30.9 mM) was added to each reaction vessel to achieve a final concentration of 1.03 mM (Wolf, Dao, Scott, & Lavy, 1989). Each tube was spiked with 0.1 ml of 0.105 mM CTN to achieve a final CTN solution concentration of 175 μg L^{-1} (~500 μg kg^{-1}) (Donnarumma et al., 2011), resulting in a total solution volume of 15 ml and a 1:3 (w/v) soil/solution ratio. Reaction vessels were wrapped in aluminum foil to prevent photodegradation. Duplicate controls (no CTN), triplicate adsorbent-free controls (i.e., no soil), and triplicate sorption samples were agitated in the dark at 25 ˚C on an end-over-end shaker (7 rpm) (E6000, Eberbach) for 24 h, based on preliminary experiments to determine sorption equilibrium time. After reaction, samples were centrifuged at 3,500 rpm for 15 min (J2-21 M/E, Beckman) to separate solids and solutions. The supernatant was decanted and filtered through a 0.45-μm nominal pore size polytetrafluoroethylene hydrophilic membrane filter. The entire supernatant associated with each sample was evaporated to dryness under N_2(g), reconstituted in 1 ml of methanol, and stored at 4 ˚C for analysis of CTN concentration remaining in solution.

Sorption isotherms were developed for two soils with contrasting K_d values (NV and OS). Experimental conditions were identical to the single-point batch sorption experiments described previously, with the exception of CTN concentration (0; 200; 500; 1,000; 2,500 μg L^{-1}). Adsorbent-free controls (no soil) were reacted in triplicate. Samples and controls were processed after reaction as described previously.

For the batch equilibrium and isotherm sorption experiments, the amount of CTN sorbed to the soil after the reaction was calculated using Equation 1.

$$q = \frac{V\left(C_B - C_S\right)}{m_s} \tag{1}$$

where q is the surface excess of CTN (i.e., amount sorbed) after the reaction period (μg kg^{-1}); C_B and C_S are equilibrium CTN concentrations (μg L^{-1}) in blanks and samples, respectively, after reaction; V is the volume of solution (L) added to individual reaction vessels; and m_s is mass of soil (kg) within each reaction vessel (Essington, 2015). The K_d values were calculated by dividing q by C_S.

2.3 | Wetland soil incubation

Soils collected at five randomly selected sites (BK, EB, FR, OS, TS) were spiked with CTN and incubated under oxic and anoxic conditions. Triplicate samples of wetland soils and three soil-free controls for both anoxic and oxic incubations were destructively sampled on Days 0, 2, 5, 10, 30, and 60. Anoxic experiments were conducted in an oxygen-free (<1 ppm) anaerobic chamber (Coy) with a 95% N_2 (g)/5% H_2(g) atmosphere. All supplies (i.e., plastic bottles, water, etc.) were stored in the anaerobic chamber for 1 wk prior to anoxic incubation to allow degassing of O_2(g). Sample polypropylene bottles (250 ml, screw cap; Fisher Scientific) were packed with moist soil (50 g oven-dry equivalent) to a bulk density of 1.1 g cm^{-3}. Soil-packed bottles were left in the anaerobic chamber for 12 h to allow diffusion of O_2 out of soil. Soil samples were then spiked with CTN solution to achieve an initial concentration of 500 μg kg^{-1} (Donnarumma et al., 2011), and sufficient deoxygenated water was added to fully saturate the samples (i.e., 100% water-filled pore space) and achieve a 4-cm layer of standing water above the soil surface. This depth of standing water was maintained throughout the incubation experiment and is referred to as the flood layer. Incubation vessels were wrapped in aluminum foil to prevent photodegradation, and samples were incubated in the anaerobic chamber at 25 ˚C. After incubation for a specified length of time, anoxic samples were centrifuged (3,500 rpm, 15 min, 12 ˚C) (J2-21 M/E, Beckman), and the supernatant (standing water plus soil water) was decanted into a separate bottle, sealed, and stored at −18 ˚C until further analysis. Duplicate bottles of each wetland soil with 4 cm of standing water were included in the anoxic incubation and used to measure the oxidation-reduction potential (ORP) and pH on a weekly basis. An ORP/pH probe (5565, YSI) attached to a meter (556 MPS, YSI) was used to collect measurements at a depth of 4 cm.

The oxic incubation experiment was similar to anoxic incubation; however, soil samples were maintained at 60% water-filled pore space, and all experiments were conducted under ambient atmospheric conditions. Oxic incubation bottles were wrapped in aluminum foil and stored in a dark room at constant temperature (25 ˚C). The bottles were opened weekly to introduce oxygen into the 70 cm^3 of headspace. Study soils used for the oxic and anoxic incubations were not sterilized, thereby permitting the indigenous soil microbial community to function. Following incubation, soil samples from oxic and anoxic experiments were stored at −18 ˚C until CTN was extracted from the soil. The CTN concentration was quantified as described in subsequent sections.

Clothianidin data were fit to zero- and first-order kinetic decay models (Snoeyink & Jenkins, 1980). For zero-order kinetics, [CTN] versus t (time) was plotted, and the rate constant (k) was determined. Half-life ($t_{0.5}$) values were calculated using Equation 2:

$$t_{0.5} = \frac{[\mathrm{CTN}]}{2k} \tag{2}$$

where [CTN] is the mean initial CTN concentration. For first-order kinetics, the natural log of [CTN] versus time was plotted, and k was determined. The half-life ($t_{0.5}$) was calculated using Equation 3.

$$t_{0.5} = \frac{\ln 2}{k} \tag{3}$$

2.4 | Soil extraction and analysis of CTN

Included here is a brief description of the methodology; details of the soil extraction, clean-up procedure, and high-performance liquid chromatography (HPLC) analysis of CTN are provided in the Supplemental Materials. The soil phase of oxic and anoxic samples was analyzed for CTN by extracting twice with 90% acetonitrile followed by evaporating to remove the acetonitrile and then diluting to 50 ml with ultra-pure water. Diluted samples were spiked with ICD as a surrogate and extracted with C18 solid-phase extraction (SPE). Samples were eluted from the SPE cartridges with ethyl acetate, concentrated to dryness, and reconstituted in methanol for HPLC analysis. Analysis of CTN was performed using reverse-phase HPLC with a diode array detector (NexeraXR SIL-20AC, Shimadzu) and a gradient method with mobile phases of acetonitrile and formic acid. The aqueous phase from anoxic samples was analyzed for CTN by spiking with an ICD surrogate and extracted via SPE; elution of the chemicals from SPE cartridges and other steps were the same as detailed above.

2.5 | Statistical analysis

Extraction efficiencies for soil and water phase samples were determined through preliminary experiments (mean soil phase extraction efficiency, 72.2%; mean water phase extraction efficiency, 90.8%). Due to incomplete extraction, CTN data from incubation studies were corrected using a correction factor that incorporated the entire extraction and sample cleanup process (see Supplemental Materials). A correction factor was not applied to data from sorption studies. Diagnostic plots of each data set were analyzed to detect and remove outliers. Data were analyzed using Origin 2018 (OriginLab Corp.) and R (version 3.4.3; R Core Team, 2017) software packages. Coefficients of determination (r^2), p values, and SEs were determined using linear regression analysis of raw and log-transformed degradation data. A one-way ANOVA

TABLE 1 Clothianidin solid-to-solution (K_d) and organic carbon-to-solution (K_{oc}) partition coefficients for wetland soils collected from eight Missouri Conservation Areas: B.K. Leach (BK); Eagle Bluffs (EB); Four Rivers (FR); Marias Temps Claire (MTC); Nodaway Valley (NV); Otter Slough (OS); and Ted Shanks (TS)

Site name	Wetland no.	K_d	K_{oc}
		L kg^{-1}	L kg$_{oc}$$^{-1}$
BK	3	4.70 ± 0.22[a]	207 ± 9.73
BK	8	2.08 ± 0.17	97.3 ± 8.08
EB	88	4.16 ± 0.56	283 ± 38.3
FR	175	2.12 ± 0.22	100 ± 10.3
MTC	300	3.33 ± 0.17	93.1 ± 4.62
NV	334	5.87 ± 1.14	214 ± 41.6
OS	360	1.76 ± 0.09	103 ± 5.53
TS	448	4.63 ± 1.55	147 ± 49.4
Mean		3.58 ± 0.52	156 ± 21.0

[a]Means and 95% CI are provided.

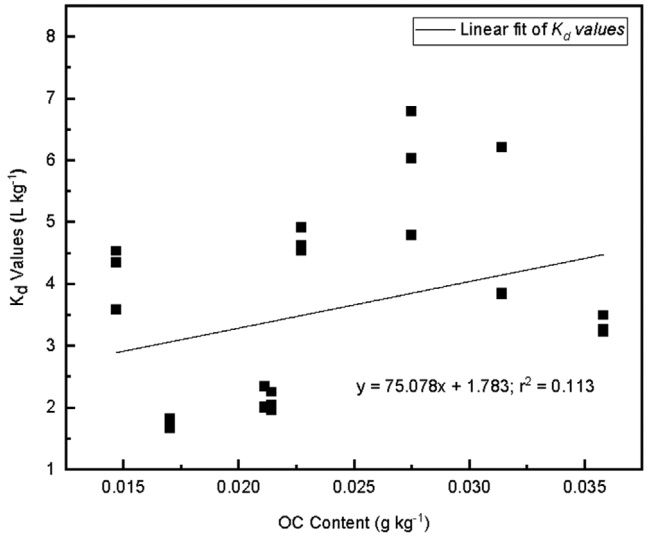

FIGURE 1 Solid-to-solution coefficients (K_d) plotted as a function of soil organic carbon content (OC) for wetland soils collected at eight Missouri Conservation Areas: B.K. Leach (Wetlands 3 and 8); Eagle Bluffs; Four Rivers; Marias Temps; Nodaway Valley; Otter Slough; and Ted Shanks. Linear fit and regression equation of data are shown (p = .108)

and post hoc comparison (Tukey HSD) were performed to compare average half-life values and obtain test statistics. Significance was determined at α = .05 confidence level for all analyses. Clothianidin decomposition in anoxic incubation studies was analyzed by considering soil phase independently and in combination with the flood layer.

3 | RESULTS AND DISCUSSION

3.1 | CTN sorption to wetland soils

Single-point solid/solution partition coefficients (K_d) and organic carbon/solution (K_{oc}) partition coefficients were calculated for the eight Missouri wetland soils (Table 1). Mean K_d values for CTN sorption were 4.70, 2.08, 4.16, 2.12, 3.33, 5.87, 1.76, and 4.63 L kg^{-1} for wetland soils collected from BK (Wetland 3), BK (wetland 8), EB, FR, MTC, NV, OS, and TS, respectively; the overall mean (± 95% CI) for all soils studied was 3.58 ± 0.52 L kg^{-1}. These values are similar to CTN K_d values found in the literature (Li et al., 2018; Mulligan et al., 2016; Zhang et al., 2018). Linear regression analysis was performed to evaluate the relationship between K_d values and soil organic C content, and no significant linear relationship between the two variables was observed (r^2 = .113; p = .108) (Figure 1). We included K_{oc} values (Table 1) for comparison to other studies presenting such information (Mulligan et al., 2016); however, the lack of a linear correlation suggests K_{oc} values are not a useful parameter for predicting CTN sorption in Missouri wetland soils. Correlations between soil properties reported in Supplemental Table S1 (i.e., clay content, total nitrogen, cation exchange capacity [CEC], and pH) and K_d values were evaluated via linear regression analysis. None of the soil characteristics measured were significantly correlated to K_d values, which contradicts relationships reported in previous studies. For example, studies have found significant positive correlations between CTN K_d values and SOC content (Li et al., 2018; Mulligan et al., 2015; Zhang et al., 2018). Li et al. (2018) found a positive correlation between CTN K_d values and pH, whereas Mulligan et al. (2015) did not find a significant correlation with pH or CEC. These conflicting results suggest that the soil properties influencing CTN sorption remain poorly understood. However, the wetland soils in this study may not have incorporated sufficient variability to capture correlations between soil properties and CTN sorption.

Sorption isotherms (Figure 2) show CTN sorbed (q) to soils collected from NV and OS as a function of equilibrium concentration (C_{eq}) remaining in solution after reaction. Both sorption isotherms were linear (NV, r^2 = .971; OS, r^2 = .998), indicating partitioning between the aqueous and solid phase, with NV soil displaying a greater affinity for CTN. Based on the isotherm slopes (Figure 2), the K_d values for NV and OS soil are approximately 6.66 and 4.17 L kg^{-1}, respectively. The isotherm-calculated K_d value for OS contrasts with the K_d value calculated in our single-point batch experiment (1.76 L kg^{-1}) (Table 1). Although these values differ, they are within the same order of magnitude, and both values indicate weak CTN sorption to OS soil. Sorption isotherms of CTN presented in Li et al. (2018) also fit the linear sorption model; however, isotherms in the studies by Mulligan et al. (2016)

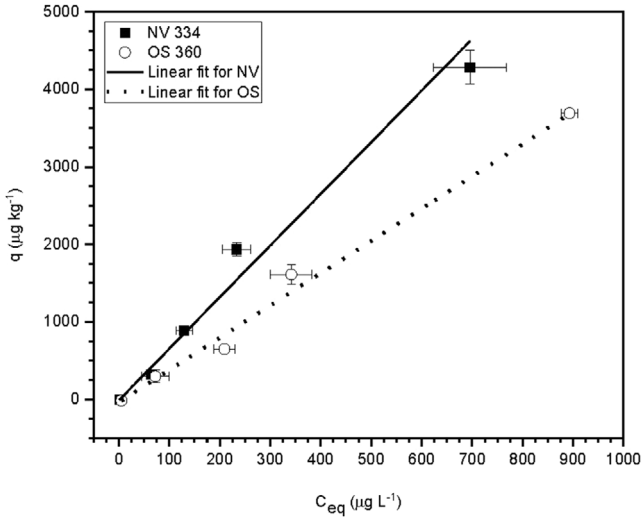

FIGURE 2 Clothianidin sorbed (q) to wetland soils collected from the Nodaway Valley (NV) and Otter Slough (OS) Conservation Areas as a function of equilibrium concentration (C_{eq}). Error bars, where visible, represent the 95% CI. Linear fits of sorption data are shown, and regression equations for each soil are as follows: NV, $y = 6.66x - 14.9$, $r^2 = .971$; OS, $y = 4.17x - 39.6$, $r^2 = .998$

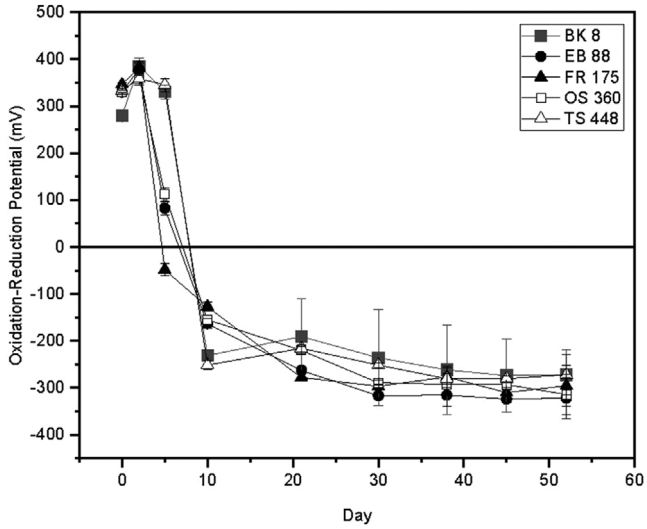

FIGURE 3 Mean oxidation-reduction potential measured in flood layer throughout 60-d anoxic incubation of wetland soils collected from five Missouri Conservation Areas: B.K. Leach (BK), wetland 8; Eagle Bluffs (EB); Four Rivers (FR); Otter Slough (OS); and Ted Shanks (TS 448). Error bars represent the 95% CI

and Zhang et al. (2018) were nonlinear and fit a Freundlich model with an exponential factor (n) < 1.

Solid-to-solution partition coefficients indicate CTN has a weak affinity for the soils studied; thus, there is potential for dissolved CTN to transport to water resources (Kuechle, Webb, Mengel, & Main, 2019). Additional research is required to understand soil properties influencing CTN sorption to wetland soils. Based on our sorption isotherms (Figure 2), the soils studied were not limited in their capacity to sorb CTN within the range of concentrations studied (i.e., up to 2,500 µg L^{-1}). This result contrasts with Mulligan et al. (2015) and Zhang et al. (2018), in which the nonlinear fit implied a saturation point for CTN sorption would be reached with increasing C_{eq}.

3.2 | CTN degradation in wetland soils

To evaluate CTN degradation in wetland soils under oxic and anoxic conditions, a set of incubation studies were conducted. All soils exhibited a similar trend, reaching anoxic conditions at approximately Day 10 of the study (Figure 3), which was consistent with the ORP profiles reported by Mulligan et al. (2016). Because materials and supplies used in the anoxic incubations were placed in the anaerobic chamber 7 d prior to the start of the experiment, the time lapse for inundated wetland soil in a field environment to reach anoxic conditions would not be analogous to that shown in this laboratory study due to a variety of factors (e.g., water depths, pool sizes, vegetative community). The average (± 95% CI) flood layer pH of all flooded microcosms was 7.25 ± 0.51 over the 60-d incubation.

Plots of mean CTN and ln(CTN)-transformed concentrations in oxic soil, anoxic soil, and anoxic soil plus flood layer samples showed significant exponential or linear decreases in CTN concentration with time at all five sites (Figure 4; Supplemental Figure S1a–e). Clothianidin degradation in all three treatments was modeled using zero-, first-, and second-order kinetic models, but only linear fits for zero- and first-order kinetic models were significant (Table 2). The r^2 values were very similar between zero- and first-order CTN degradation models at all sites; therefore, $t_{0.5}$ values were calculated for both models (Table 3). It is important to note that CTN initial concentrations for the oxic incubation were less than the anoxic incubation, potentially due to an analytical error, pipetting error, or stock solution degradation; however, the initial concentrations were consistent for all five oxic soils.

Clothianidin degradation under anoxic conditions was relatively rapid, with $t_{0.5}$ values ranging from 14.8 to 44.1 d for the total anoxic (soil + flood layer) data and from 15.8 to 50.5 d for the anoxic soil only (Table 3). Although zero- and first-order degradation models showed similar correlations to the CTN degradation data, zero-order models consistently estimated longer $t_{0.5}$ values than first-order models for the anoxic and total anoxic data, with the greatest disparity occurring in the total anoxic soil data for the TS site (29.4 vs. 14.8 d; Table 3). Degradation of CTN was most rapid at TS and slowest at EB (39.6–44.1 d), and $t_{0.5}$ values were shown to be inversely related to SOC content across sites (Figure 5).

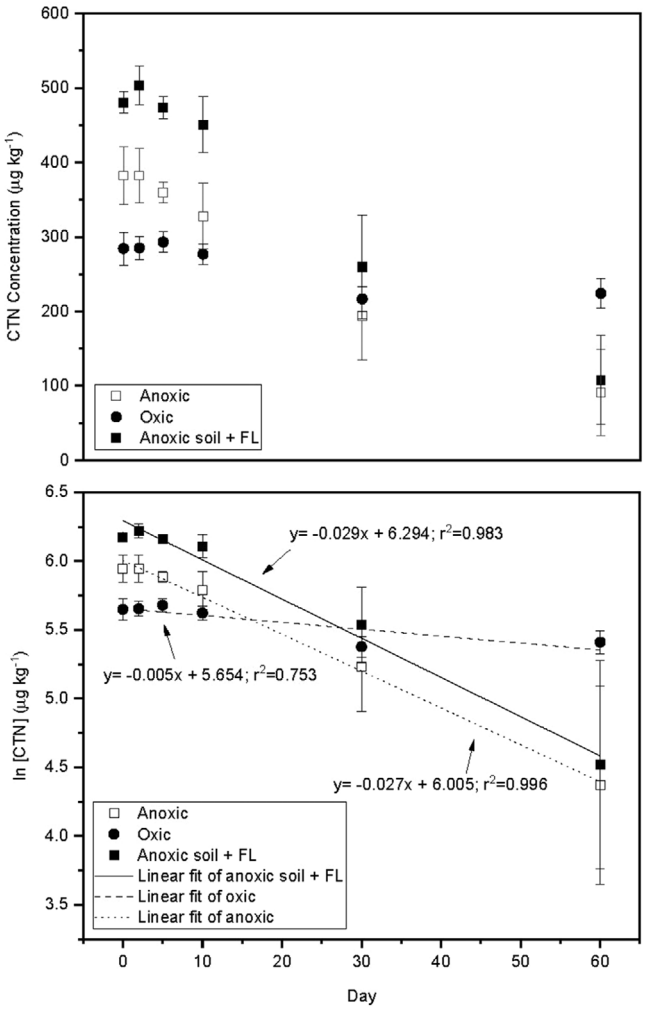

FIGURE 4 Mean degradation of clothianidin (CTN) and first-order linear regression analysis as a function of time under anoxic and oxic conditions in wetland soils collected from five Conservation Areas: B.K. Leach (BK), wetland 8; Eagle Bluffs (EB); Four Rivers (FR): Otter Slough (OS): and Ted Shanks (TS). Clothianidin analyzed from anoxic incubation soil (Anoxic), oxic incubation soil (Oxic), and anoxic incubation soil combined with the flood layer (anoxic soil + FL) are shown. Error bars, where visible, represent the 95% CI. Regression equations and r^2 values are shown

These results were consistent with Mulligan et al. (2016), where mean anoxic half-life at 25 °C was 28.3 d. The significant negative relationship between SOC and CTN degradation was also consistent with other studies (Li et al., 2018; Zhang et al., 2018) because SOC is a prevalent electron donor, leading to more rapid reduction of CTN in soils (Sutton-Grier, Keller, Koch, Gilmour, & Megonigal, 2011). Greater electron donor presence and anoxic conditions can lead to biotic and abiotic reduction of the nitroimine functional group (Pandey et al., 2009). Mulligan et al. (2016) analyzed anaerobic soil and aqueous phase for methyl-nitroguanidine and nitroguanidine metabolites, and neither were observed, suggesting these compounds may transform rapidly. Rapid reduction of nitro groups under anoxic soil conditions has been reported for dinitroaniline herbicides (Golab et al. 1979), and the explosives TNT and RDX were reduced in the presence of iron-bearing soil minerals (Cho, Bae, & Lee, 2012) and enzymatically by soil enterobacteria (Kitts, Green, Otley, Alvarez, & Unkefer, 2000). Anoxic conditions, greater SOC content, and increased temperatures (Mulligan et al., 2016) appear to affect CTN degradation and should be important considerations in wetland management decisions.

Oxic $t_{0.5}$ values ranged from 89.2 to 204 d, and, conversely to the anoxic treatments, zero-order models consistently estimated shorter $t_{0.5}$ values than first-order models (Table 3). Based on these $t_{0.5}$ values, annual carryover of CTN concentrations is likely and could be problematic in some crop management systems. Reported oxic $t_{0.5}$ values for this study were similar to Li et al. (2018), who reported CTN $t_{0.5}$ values ranging from 90 to 280 d. Zhang et al. (2018) reported $t_{0.5}$ values for CTN that were substantially shorter than those reported here, ranging from 47 to 79 d for CTN degradation in agricultural fields of China. Mulligan et al. (2016) reported a mean CTN $t_{0.5}$ of 3,100 d, which is substantially longer than other studies. Regarding the differences in $t_{0.5}$ values between the kinetic degradation models for oxic and anoxic treatments, residual plots indicated overall better fits (i.e., more random residual plots) to the first-order models than the zero-order models. Relative to the first-order estimates, zero-order models resulted in $t_{0.5}$ estimates that were an average of 23% shorter for the oxic treatments and 33–36% longer for the anoxic treatments (Table 3).

3.3 | Management implications

Based on the results of this study and those of Mulligan et al. (2016), the following conditions and management practices could reduce CTN and possibly other neonicotinoid concentrations in Missouri wetland soils: (a) facilitation of anoxic soil conditions, especially during warmer months, and (b) implementation of management strategies that will retain or accumulate SOC to minimize mobility of CTN in runoff or by leaching, such as the use of cover crops, addition of C-based amendments (e.g., compost, manure, or biosolids), and use of minimum-till or no-till. Our work indicates that CTN degrades more rapidly under anoxic conditions. Various factors affect the amount of time required to reach reducing conditions in a wetland setting (e.g., water depth, wetland vegetation; Mitsch & Gosselink, 2015). Surface oxygen diffusion and micro-oxic environments around vegetation affect the occurrence of anoxic conditions and should be

TABLE 2 Clothianidin (CTN) degradation kinetic models for wetland soils under anoxic and oxic conditions

Site name	Wetland no.	Anoxic soil				Total anoxic (soil + flood layer)				Oxic soil			
		Zero-order		First-order		Zero-order		First-order		Zero-order		First-order	
		r^2	*p* value	r^2	*p* value	r^2	*p* value	r^2	*p* value	r^2	*p* value	r^2	*p* value
BK	8	.927	6.41×10^{-10}	.966	1.84×10^{-12}	.957	1.23×10^{-11}	.968	1.20×10^{-12}	.648	5.61×10^{-5}	.663	3.93×10^{-5}
EB	88	.923	9.17×10^{-10}	.947	5.64×10^{-11}	.935	1.11×10^{-9}	.941	5.30×10^{-10}	.562	3.40×10^{-4}	.580	2.39×10^{-4}
FR	175	.973	6.10×10^{-14}	.960	7.04×10^{-12}	.967	9.11×10^{-12}	.960	3.67×10^{-11}	.426	0.003	.482	1.98×10^{-3}
OS	360	.938	1.79×10^{-10}	.980	3.40×10^{-14}	.955	1.57×10^{-11}	.973	3.35×10^{-13}	.559	3.63×10^{-4}	.681	4.51×10^{-5}
TS	448	.897	8.36×10^{-9}	.931	4.19×10^{-10}	.953	1.06×10^{-10}	.927	2.32×10^{-9}	.758	2.59×10^{-6}	.783	1.07×10^{-6}

Note. Results from linear regression analysis of untransformed (zero-order) and natural log transformed (first-order) data. Wetland soils were collected from five conservation areas: B.K. Leach (BK); Eagle Bluffs (EB); Four Rivers (FR); Otter Slough (OS); and Ted Shanks (TS).

TABLE 3 Half-life ($t_{0.5}$) values and zero- and first-order rate constants (k) for clothianidin degradation in wetland soils under anoxic and oxic conditions

Site name	Wetland no.	Anoxic soil				Total anoxic (soil + flood layer)				Oxic soil			
		Zero-order		First-order		Zero-order		First-order		Zero-order		First-order	
		k	$t_{0.5}$	k	$t_{0.5}$	k	$t_{0.5}$	k	$t_{0.5}$	k	$t_{0.5}$	k	$t_{0.5}$
		μg kg^{-1} d^{-1}	d	d^{-1}	d	μg kg^{-1} d^{-1}	d	d^{-1}	d	μg kg^{-1} d^{-1}	d	d^{-1}	d
BK	8	4.94 ± 0.36	36.5	0.024 ± 0.001	28.7	6.20 ± 0.34	38.1	0.023 ± 0.001	30.8	1.42 ± 0.26	107	0.006 ± 0.001	121
EB	88	4.31 ± 0.32	50.5	0.016 ± 0.001	44.5	5.66 ± 0.40	44.1	0.018 ± 0.001	39.6	1.06 ± 0.23	141	0.004 ± 0.001	177
FR	175	5.08 ± 0.21	38.8	0.027 ± 0.001	25.9	7.46 ± 0.37	32.4	0.031 ± 0.002	22.0	1.00 ± 0.29	146	0.003 ± 0.001	204
OS	360	5.11 ± 0.34	36.7	0.025 ± 0.001	27.4	6.56 ± 0.37	36.7	0.024 ± 0.001	28.6	1.42 ± 0.32	89.2	0.005 ± 0.001	128
TS	448	5.60 ± 0.49	30.9	0.044 ± 0.003	15.8	7.93 ± 0.47	29.4	0.047 ± 0.004	14.8	1.50 ± 0.21	90.5	0.006 ± 0.001	116
Average		5.01	38.7	0.027	28.5	6.76	36.1	0.029	27.2	1.28	115	0.005	149

Note. Wetland soils were collected from five Missouri Conservation Areas: B.K. Leach (BK), Eagle Bluffs (EB), Four Rivers (FR), Otter Slough (OS), and Ted Shanks (TS).

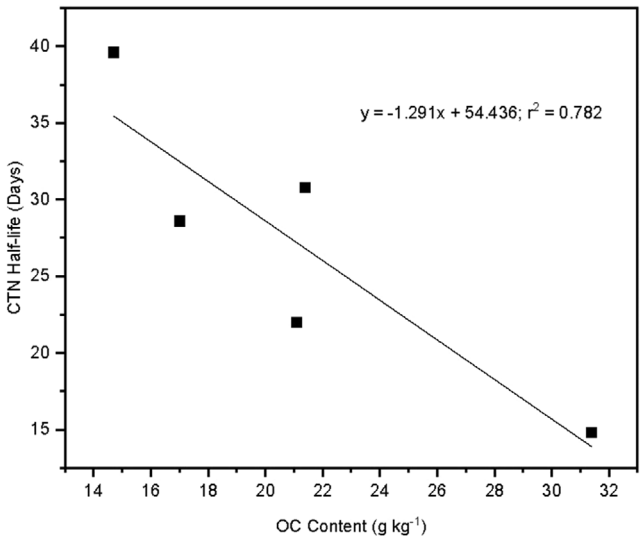

FIGURE 5 Mean first-order total anoxic half-life ($t_{0.5}$) values plotted as a function of soil organic carbon (OC) content for wetland soils collected from five Missouri Conservation Areas: B.K. Leach, wetland 8; Eagle Bluffs; Four Rivers; Otter Slough; and Ted Shanks. Linear fit is shown ($p = .046$)

considered. Neonicotinoids are less prevalent in Missouri wetlands with water depths ≥25 cm (Kuechle et al., 2019), thereby providing management guidance for water depths that promote degradation.

This study also showed that greater SOC content increases CTN degradation rate. For example, the TS wetland soil contained the greatest SOC content (31.4 g kg^{-1}) and had the shortest anoxic $t_{0.5}$ values (14.8–30.9 d), whereas the EB soil contained the least SOC content (14.7 g kg^{-1}) and had the greatest anoxic $t_{0.5}$ values (39.6–50.5 d). Wetland inundation and the formation of anoxic conditions can slow microbial decomposition of organic matter, thereby increasing SOC and building a greater electron donor source (Mitsch & Gosselink, 2015). Additionally, no-till planting could be another management strategy to retain SOC (Reeves, 1997; Shrestha, Singh, Forte, & Certini, 2015). A key challenge in Missouri is that managed wetlands are often drawn down (i.e., water levels lowered) in spring to facilitate crop production and soil disturbance or to promote plant germination. Managed wetlands are then typically reflooded in autumn to ensure available habitat for migratory birds (Fredrickson & Taylor, 1982). Water is maintained in these wetlands throughout winter for habitat and recreational purposes when microbial activity and CTN degradation would be low. Creating anoxic conditions for 30–60 d at a depth ≥25 cm (Kuechle et al., 2019), especially when temperatures are sufficient to enhance microbial activity (Mulligan et al., 2016), may be an effective wetland management strategy to promote neonicotinoid degradation.

4 | CONCLUSIONS

Results from the CTN sorption study demonstrated that CTN has a weak affinity for the wetland soils studied. Sorption isotherms for two contrasting soils (OS and NV) indicated that CTN sorption was linear over the range of concentrations studied (0–2,500 μg L^{-1}). Soil properties such as SOC, clay content, CEC, and pH were not significantly correlated to CTN sorption, suggesting that the wetland soils studied may not have represented a broad enough range in properties to discern relationships and that complex relationships may exist between CTN sorption and multiple soil properties. Results from anoxic and oxic incubations demonstrated that CTN degradation was significantly more rapid under anoxic conditions. The average $t_{0.5}$ value for the five soils under anoxic conditions was 27.2 d, compared with 149 d for soils under oxic conditions. Soil organic C content was negatively correlated with anoxic $t_{0.5}$ values, indicating that flooded, anoxic conditions combined with practices that sequester SOC will facilitate greater CTN degradation in Missouri wetland soils. Extending the period of anoxic conditions to facilitate CTN degradation in managed wetland soils will require careful consideration of the impacts associated with this management strategy on other management objectives such as promoting waterfowl habitat conditions and additional ecosystem services.

DATA AVAILABILITY STATEMENT

Datasets used to support this work are available at https://doi.org/10.5061/dryad.xpnvx0kd8.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Chelsey J. Beringer: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Writing-original draft; Writing-review & editing. Keith W. Goyne: Conceptualization; Methodology; Funding acquisition; Project admininstration; Writing-review & editing. Robert N. Lerch: Conceptualization; Methodology; Resources; Writing-review & editing. Elisabeth B. Webb: Conceptualization; Funding acquisition; Investigation; Methodology; Writing-review & editing. Doreen Mengel: Funding acquisition; Project administration; Resources; Writing-review & editing.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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