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Impact of Soil Aeration on the Environmental Fate of Pre-Emergent Herbicide Metolachlor

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Featured Application: The use of pre-emergent (or residual) herbicides like metolachlor has increased dramatically worldwide as an option to manage herbicide-resistant biotypes, as they suppress weed seed emergence from the soil. Hence, there is an emerging interest in comprehending its persistence and fate in cropping systems. Recurring flooding events and the consequent anoxic conditions in agro-ecosystems are ubiquitously present and inevitable. However, much less is known about the environmental fate of a popular herbicide like metolachlor in such soil environmental conditions. Hence, in this paper, we explored the impacts of the aerobic and anaerobic soil conditions of the environmental fate of ^{14}C-labeled metolachlor by using radioactive analytical techniques. This article contributes to better understanding the behavior of a globally utilized plant protection chemical like metolachlor in soils. The information generated could be applied for the efficacious and judicious use of metolachlor or similar herbicides in crop production systems.

Abstract: The impact of the aeration status of soils on the environmental fate of the soil-applied pre-emergent herbicide metolachlor is of significance to sustainable agriculture practices and has not been investigated thoroughly by existing research works. To address this knowledge gap, we examined the adsorption, desorption, degradation, and mineralization of radioactively labeled [^{14}C] metolachlor in Catlin, Flanagan, and Drummer soils under aerobic and anaerobic conditions. Based on our findings, anaerobic conditions in the soil significantly reduced the adsorption of ^{14}C-metolachlor while also promoting its desorption, thereby potentially releasing a greater amount of herbicide from the soil after a field application. The first-order degradation and mineralization kinetics of ^{14}C-metolachlor were distinctively enhanced by anaerobic conditions in all the soils tested. Furthermore, the degradation and mineralization rates of ^{14}C-metolachlor in non-sterilized versus sterilized soil microcosms clearly indicated microbial activity in the degradation of metolachlor in soil. The results from this study suggest that soil redox conditions could impact the bioavailability and environmental fate of herbicide metolachlor and should be taken into consideration as part of sustainable weed management programs.

Keywords: herbicide; bioavailability; adsorption; desorption; biodegradation; mineralization; aerobic soil; anaerobic soil

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1. Introduction

Metolachlor [2-chloro-N-(2-ethyl 6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide] (Figure 1) is a soil-applied herbicide widely used for pre-emergent weed control in a variety of crops like corn, soybean, peanuts, potatoes, tobacco, and vegetables [1]. Fernandez-Cornejo et al. [2] reported metolachlor as one of the top five most-used herbicides, based on the amount of active ingredient applied. Additionally, as more weed

species are reported to have developed resistance to post-emergence herbicides including glyphosate, the use of pre-emergent or residual herbicides like metolachlor is encouraged to promote the management of resistant biotypes. Unlike post-emergence herbicides, residual herbicides must remain active in the soil to stop weed populations from emergence. Metolachlor is used widely for weed control in the humid regions of the United States, primarily in the midwestern states [3], much of which are prone to flooding, which consequentially leads to transient anaerobic situations within the soil profile. While terrestrial soil environments are typically considered to be dominated by aerobic conditions, there are also situations where anaerobiosis prevails, such as high soil moisture resulting from a high water table or heavy rain [4]. Such variances in soil conditions are also expected to affect herbicide degradation [5], and thus it is essential to understand the fate and transformation of a soil-applied herbicide such as metolachlor in aerobic and anaerobic soil environmental conditions.

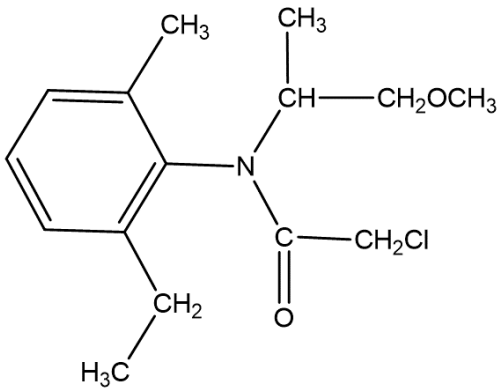

Figure 1. Chemical structure of metolachlor.

Metolachlor is a neutral non-ionizable herbicide dominated by apolar groups, and the adsorption mechanism has been frequently described by the herbicide interactions with soil organic matter [6]. The relatively high soil persistence, high water solubility, and significant toxicological implications of this universally used herbicide have attracted the interest of researchers from various fields [7]. However, existing works on the environmental behavior of metolachlor have primarily focused on its fate and degradation in an aerobic soil environment [8]. Like several other homocyclic herbicides containing halogens, metolachlor tends to undergo slower degradation kinetics under aerobic conditions than anaerobic conditions [9,10]. Although many studies have been published on the adsorption of metolachlor to soils [11–13], few attempts have been made to elucidate the models to predict this herbicide's soil binding affinities in an anaerobic environment.

Treatment of different soil types under anaerobic and aerobic conditions would allow further exploration of the bioavailability and metabolism of a popular herbicide like metolachlor. This knowledge could be applied to enforce more efficient and judicious usage of this herbicide in cropping systems. The present study was undertaken to investigate the environmental fate determinant factors like the adsorption, desorption, degradation, and mineralization of metolachlor in different soils treated under aerobic and anaerobic conditions.

2. Materials and Methods

2.1. Chemicals and Reagents

Uniformly ring-labeled ^{14}C-metolachlor (specific activity: 2.04 × 109 Bq mmol^{-1}) was obtained (Moravek Biochemicals and Radiochemicals, Brea, CA, USA). Unlabeled metolachlor (chemical purity: 99%) was also procured (Sigma Chemical Company, St. Louis, MO, USA). Organic solvents and water, which were of Optima Grade (Fisher Scientific, Pittsburgh, PA, USA), were used without further purification.

2.2. Soils

The three types of soil (Catlin, Flanagan, and Drummer) utilized in this study were collected (15 cm depth) from a field with no prior metolachlor application history at the University of Illinois Crop Sciences Research and Education Center in Urbana, Illinois. Although these soils have similar parent materials, they differ in their organic matter contents and drainage properties. Catlin (fine-silty, mixed, superactive, mesic Oxyaquic Argiudolls) is moderately well-drained, Flanagan (fine, smectitic, mesic Aquic Argiudolls) is somewhat poorly drained, and Drummer soil (fine-silty, mixed, superactive, mesic Typic Endoaquolls) is poorly drained. These soil samples were sieved through a 2-mm screen and stored at 4 °C. All the experiments were initiated within ~4 weeks of storage. The relevant physical and chemical properties of the three soil types used in this study were analyzed at the A&L Great Lake Laboratories (Fort Wayne, IN, USA) and are listed in Table 1.

Table 1. Selected properties of the soils used in the experiment.

Soil	pH	Texture (%)			WHC (%)	CEC ($Cmol_c\ Kg^{-1}$)	Organic Matter (%)
		Sand	Silt	Clay			
Catlin	7.6	10	58	32	31.4	13.9	3.3
Flanagan	6.5	12	56	32	32.0	17.5	3.7
Drummer	7.1	14	46	40	33.0	23.8	4.9

WHC: water holding capacity at 1/3 bar. CEC: cation exchange capacity.

2.3. Adsorption-Desorption Study

The adsorption isotherms of ^{14}C-metolachlor were determined using the batch equilibrium method for the three soil types. The initial concentrations of ^{14}C-metolachlor (0.1, 1, 5, and 10 mg L^{-1}) were prepared in a 0.01 M aqueous $CaCl_2$ solution as recommended by the USEPA guidelines for adsorption study [14], and 2 g of air-dried soil was equilibrated with 10 mL of a ^{14}C-metolachlor solution in 20-mL Teflon centrifuge tubes in a horizontal shaker (150 rpm) for 24 h (equilibration time based on a preliminary study) at room temperature (25 ± 1 °C). Preliminary studies have shown that none of the metolachlor added was degraded during 24 h of contact with any of the soils used.

For anaerobic treatment, a similar 2 g soil sample contained in the Teflon centrifuge tubes was flooded with the sterile deoxygenated water. The tubes were flushed with N_2 gas (also containing ~5% CO_2(g) and <2% H_2(g)), sealed, and incubated in an anaerobic chamber (Coy Laboratory Products, Inc., Grasslake, MI, USA) at room temperature (25 °C) for 2 weeks to allow complete reduction. To study the adsorption, ^{14}C-metolachlor was added using a concentrated O_2 free stock solution to the reduced soil (anaerobic system) in order to attain final concentrations of 0.1, 1, 5, and 10 mg L^{-1}. The sealed tubes were equilibrated on a shaker inside the anaerobic chamber for 24 h, where the oxygen was maintained at a concentration of zero.

At the end of the equilibration period, the soil suspension was centrifuged (15 min, 12,000× *g*). The aliquots were removed from each tube for a radioactivity assay using a Packard Tri-Carb (1900TR) scintillation counter. A control (treatment without herbicide) was included for calibration and background correction purposes. The difference between the initial and final concentrations of herbicide in the solution were used to calculate the amount adsorbed. All the experiments were performed in triplicate.

After equilibration and removal of 5 mL of the initial 10 mL of supernatant, herbicide desorption from the soil was estimated by adding an equal amount of a fresh 0.01 M $CaCl_2$ solution to the centrifuge tubes, dispersing the soil aggregates by vibration and re-shaking for 24 h. Sampling from the anaerobic soil treatments was handled inside an anaerobic glove box chamber. The soil samples were centrifuged (15 min, 12,000× *g*), and an aliquot of the supernatant was removed and analyzed by the radioactivity assay. The desorption process in each tube was repeated four times. Desorption was estimated by determining the amount of herbicide in the soil solution following equilibration and calculated by subtracting the amount of herbicide remaining on the soil surface [12].

2.4. Degradation Study

Soil incubations in microcosms: Soil incubations were performed under reduced (anaerobic) or oxidized (aerobic) conditions using serum bottle microcosms to determine the degradation kinetics of ^{14}C-metolachlor.

Anaerobic incubations: Microcosms consisting of serum bottles (60 mL) were amended with soil (10 g) and spiked with ring-labeled ^{14}C-metolachlor (specific activity of 2.37×10^3 Bq μmol^{-1}, diluted with unlabeled metolachlor) in 50 μL of methanol to produce a final concentration of 5 mg kg^{-1} of soil. This concentration corresponded to the recommended agriculture application rate. The metolachlor-spiked soils were agitated on a reciprocating shaker for 24 h at room temperature to ensure thorough mixing and evaporate the solvent. The soil then had 20 mL of sterile (autoclaved) and deoxygenated water added to simulate the soil flooding and saturation resulting from rainfall situations. The microcosm headspace was flushed with N_2 gas and immediately crimp sealed with a butyl stopper fitted with a vial containing 1 mL of 0.5 M NaOH to trap the mineralized $^{14}CO_2$. These microcosms were incubated in a dark, temperature-controlled chamber at 25 °C. Sterilized soil microcosms were included as a control for each soil type. Sterilization was achieved by autoclaving the soils twice on consecutive days at 121 °C for 1 h.

Aerobic incubations: The soil microcosms were built from serum bottles as described above. Sterile distilled water was added to the metolachlor-spiked soils to adjust the moisture content to about 60% of the field water-holding capacity (WHC). The serum bottles were lightly capped with a butyl stopper fitted with a NaOH trap and stored in the dark at 25 °C. The soil microcosms were aerated every week by equilibrating the headspace with the atmosphere. The soil moisture content was adjusted by returning each vessel to its initial weight with sterile distilled water.

2.5. Soil Sampling and Analysis

Anaerobic and aerobic microcosms were destructively sampled at consecutive intervals by removing the NaOH trap, followed by agitating the microcosm for 1 min and transferring the contents to a 50-mL Teflon centrifuge tube. Quantification of $^{14}CO_2$ in the NaOH traps was accomplished by direct liquid scintillation spectrometry (LSS) using a Packard Tri-Carb (1900TR) scintillation counter. The solid and liquid phases of the soil slurry were then separated by centrifugation (15 min, 12,000× g). Aqueous samples were removed and filtered (0.2 μm), and the total aqueous radioactivity was estimated using LSS [7]. The soil was extracted with a 20-mL acetone/water mixture (90/10, v/v) in a Teflon centrifuge tube with horizontal shaking for 24 h. The extracts were centrifuged at 12,000 rpm for 15 min. An aliquot was removed for LSS (to quantify the extractable radioactivity), and the supernatant was retained for the analysis of metolachlor.

For all treatments, triplicate soil extracts from each sampling day were combined, evaporated, and resuspended in methanol for HPLC analysis. The soil extract samples containing ^{14}C-metolachlor were analyzed using HPLC equipped with a Hewlett-Packard 1050 series auto-sampler instrument using a flow scintillation detector (Packard Radiomatic Flo-one/beta). The separation was achieved with an isocratic elution of the mobile phase composed of acetonitrile: water (50:50, v/v) through a 4.6 × 150 mm, 5-μm particle size, C_{18} column (Prontosil, Chadds Ford, PA, USA). Metolachlor had a reproducible retention time of 13.4 min at a flow rate of 1 mL min^{-1} under these conditions.

2.6. Data Analysis

The adsorption and desorption parameters of metolachlor in aerobic and anaerobic conditions for each soil type were calculated using the transformed Freundlich equation $\log C_s = \log K + 1/n \log C_e$, where C_s is the amount of metolachlor adsorbed to the soil (mg Kg^{-1}), C_e is the equilibrium concentration in the soil solution (mg L^{-1}), and K and $1/n$ are empirical constants that reflect the affinity of the soil for the herbicide and the degree of linearity between the amount adsorbed and the solution concentration, respectively. Regression analysis was performed on the adsorption and desorption isotherms to calculate

the K (intercept) and $1/n$ (slope) values of metolachlor in aerobic and anaerobic soils. Hereafter, K_{ads} and $1/n_{ads}$ will indicate the Freundlich parameters for adsorption, and K_{des} and $1/n_{des}$ will refer to the desorption parameters.

The degradation data of metolachlor in soil were fitted into the first-order kinetics model $C_t = C_0\ e^{-kt}$, where C_0 is the initial concentration (mg Kg^{-1} soil) of the herbicide in the soil, C_t is the herbicide concentration (mg Kg^{-1} soil) detected in the soil at time t, and k is the first-order rate constant. The degradation rate constants were calculated by the linear regression of the natural logarithm of the percentage of herbicide remaining against the time. The aerobic and anaerobic degradation half-life ($T_{1/2}$) for each soil type was calculated using the equation $T_{1/2} = ln2/k$. The statistical program SAS (Statistical Analysis Systems, version 9.3; SAS Institute Inc., Cary, NC, USA) was used to calculate the treatment means and standard errors ($n = 3$). The differences between the treatments were evaluated using a one-way analysis of variance (ANOVA) followed by the least significant difference (LSD) test at $p < 0.05$.

3. Results

3.1. Adsorption-Desorption

The Freundlich adsorption coefficient (K_{ads}) and slope ($1/n_{ads}$) along with the corresponding coefficients of determination (R^2) are given in Table 2. The results from the experiment adequately fit into the Freundlich isotherm ($R^2 > 0.96$) for the range of herbicide concentrations from 0.1 to 10 mg L^{-1} in all the soil types under both aerobic and anaerobic soil conditions. The $1/n_{ads}$ values ranged from 0.69 to 0.91 among the treatments. The K_{ads} of the metolachlor in the soils kept under aerobic and anaerobic conditions ranged from 1.23 to 5.85 L Kg^{-1} and 1.04 to 4.54 L Kg^{-1}, respectively. The anaerobic soil environment had significantly lower ($p < 0.05$) K_{ads} values consistently across the studied soil types. Furthermore, the K_{ads} was the lowest in the Catlin soils and the highest for Drummer soils under aerobic and anaerobic conditions, respectively.

Table 2. Adsorption (Freundlich model) of ^{14}C-metolachlor in different soil types under aerobic (Aer) and anaerobic (An) environmental conditions.

Soil	K_{ads}		$1/n_{ads}$		R^2	
	Aer	An	Aer	An	Aer	An
Catlin	1.23 ^{e†} (±0.04) *	1.04 ^{f} (±0.02)	0.69 (±0.03)	0.91 (±0.02)	1.00	0.96
Flanagan	3.50 ^{c} (±0.05)	2.16 ^{d} (±0.03)	0.82 (±0.03)	0.89 (±0.01)	1.00	0.99
Drummer	5.85 ^{a} (±0.08)	4.54 ^{b} (±0.07)	0.78 (±0.03)	0.80 (±0.02)	1.00	1.00

K_{ads} = Freundlich adsorption coefficient, $1/n_{ads}$ = adsorption isotherm slope, R^2 = goodness of fit for the Freundlich model. † Mean values followed by the same letter superscripts are not significantly different ($p < 0.05$). * Values in the parentheses are the 95% confidence intervals.

The desorption isotherms for metolachlor in all three soils and two environmental conditions also fit well with the Freundlich equation ($R^2 > 0.80$). The calculated Freundlich coefficients for desorption (K_{des}) of metolachlor are presented in Table 3**.** The K_{des} values of metolachlor were lower ($p < 0.05$) in the anaerobic soils when compared with the aerobic soil treatments. Among the three soils tested, the K_{des} values of metolachlor were highest for the Drummer soil irrespective of the redox conditions.

Table 3. Desorption (Freundlich model) of ^{14}C-metolachlor in different soil types under aerobic (Aer) and anaerobic (An) environmental conditions.

Soil	K_{des}		$1/n_{des}$		R^2	
	Aer	An	Aer	An	Aer	An
Catlin	3.11 ^{e†} (±0.04) *	2.75 ^{f} (±0.03)	0.21 (±0.002)	0.30 (±0.004)	0.94	0.90
Flanagan	7.63 ^{c} (±0.03)	5.52 ^{d} (±0.03)	0.21 (±0.006)	0.16 (±0.011)	0.92	0.85
Drummer	11.13 ^{a} (±0.04)	9.95 ^{b} (±0.03)	0.16 (±0.002)	0.09 (±0.028)	0.92	0.80

K_{des} = Freundlich desorption coefficient, $1/n_{des}$ = desorption isotherm slope, R^2 = goodness of fit for Freundlich model. † Mean values followed by the same letter superscripts are not significantly different ($p < 0.05$). * Values in the parentheses are the 95% confidence intervals.

3.2. Degradation

The degradation parameters of ^{14}C-metolachlor in the Catlin, Flanagan, and Drummer soil microcosms incubated under aerobic and anaerobic conditions are summarized in Table 4. The coefficients of regression (R^2) of the natural logarithm of the percentage of the initial compound remaining in the soil against time ranged from 0.82 to 0.95. They were statistically significant ($p < 0.05$), demonstrating that metolachlor degradation followed the first-order reaction kinetics model. Generally, in all the soils studied, the half-life ($T_{1/2}$) for metolachlor was significantly lower in the anaerobic soil environment (65–79 days) than in the aerobic environment (117–154 days).

Table 4. Degradation (first-order kinetics) and mineralization of ^{14}C-metolachlor in different soil types under aerobic (Aer) and anaerobic (An) environmental conditions.

Soil	k (day^{-1})		$T_{1/2}$ (days)		R^2		Degradation ‡		Mineralization #	
	Aer	An	Aer	An	Aer	An	Aer	An	Aer	An
Catlin	0.0048 (0.0018) *	0.0093 (0.0017)	144 ^{b†} (388)	75 ^{d} (415)	0.88 (0.85)	0.89 (0.88)	42.19 (67.99)	20.20 (69.96)	8.8 (ND)	13.1 (ND)
Flanagan	0.0045 (0.0014)	0.0088 (0.0010)	154 ^{a} (487)	79 ^{d} (675)	0.92 (0.57)	0.93 (0.81)	43.05 (74.02)	22.14 (78.4)	9.1 (ND)	14.2 (ND)
Drummer	0.0059 (0.0022)	0.0107 (0.0024)	117 ^{c} (314)	65 ^{e} (288)	0.82 (0.86)	0.95 (0.88)	31.00 (66.30)	19.92 (62.01)	11.0 (ND)	16.5 (ND)

k = rate constant, $T_{1/2}$ = degradation half-life, R^2 = goodness of fit for first-order degradation model. ‡ Percent of applied herbicide remaining after 140 days of incubation. # Percent of applied herbicide evolved as $^{14}CO_2$ after 140 days of incubation. * Values in the parentheses in each column represent the corresponding values for sterilized soil control. † Mean values followed by the same letter superscripts are not significantly different ($p < 0.05$). ND = not detected.

Among the different soil types used in the experiment, Drummer had the lowest $T_{1/2}$ for metolachlor under aerobic and anaerobic soil conditions (Table 4). Although the $T_{1/2}$ of the herbicide in Catlin and Flanagan was comparable for anaerobic incubation, metolachlor disappearance was marginally faster in the Catlin soil under aerobic incubation. Altogether, the microcosms with non-sterilized soils exhibited substantially greater degradation of the metolachlor than the corresponding sterilized control microcosms, despite their dissimilarities in the soil type and redox conditions.

3.3. Microbial Mineralization

The degradation kinetics of ^{14}C-metolachlor in non-sterilized soils incubated under both aerobic and anaerobic conditions in Catlin, Flanagan, and Drummer soils are depicted in Figure 2a–c, while Figure 2d–f illustrates the microbial mineralization pattern of metolachlor, measured as the amount of $^{14}CO_2$ evolved. Under both soil incubation treatments, there was a lag phase of at least 8 weeks before the evolution of mineralized $^{14}CO_2$. About 8–11% of the applied herbicide was mineralized in the soils maintained under aerobic incubation, whereas 13–16% of the metolachlor was converted to $^{14}CO_2$ in the anaerobic microcosm after 140 days of incubation (Table 4). No significant evolution of $^{14}CO_2$ was

measured in any of the sterilized control soils. Among the three soil types, Drummer exhibited the highest mineralization rate under both aerobic and anaerobic conditions.

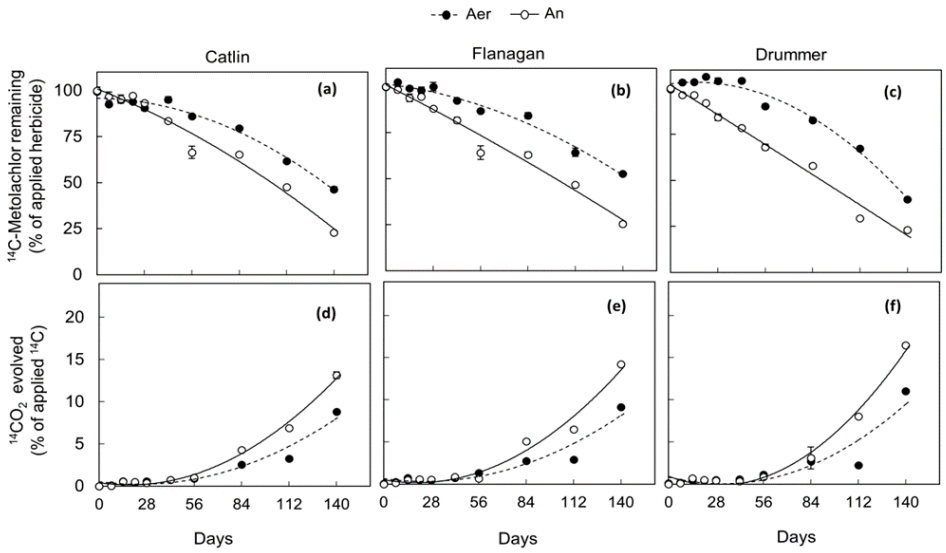

Figure 2. Degradation kinetics (**a**–**c**) and mineralization patterns (**d**–**f**) of ^{14}C-metolachlor in aerobic (Aer) and anaerobic (An) soil conditions in Catlin, Flanagan, and Drummer soils. Error bars, whenever visible, represent standard errors (n = 3).

4. Discussion

4.1. Adsorption-Desorption

The K_{ads} values of metolachlor from this study were within the range of the published metolachlor adsorption coefficients of 1.0–26.7 L Kg^{-1} [11,15–17]. A lower K_{ads} indicates less adsorption affinity of the herbicide for soils. The isotherm slopes ($1/n_{ads}$) were less than one for all the soils, implying a non-linear relationship between the amount of herbicide adsorbed and the concentration in the applied solution. This suggests the leaching potential of metolachlor leaching when accumulated at higher application rates within the soil profiles.

Under both aerobic and anaerobic soil conditions, metolachlor adsorption was highest in the Drummer soil, followed by Flanagan, and it was lowest in the Catlin soil. Such an adsorption increase corresponds to an increase in the soil organic matter content (Table 1) and emphasizes the involvement of organic matter in the adsorption process of metolachlor, which has already been communicated in previous studies [6,18]. Moreover, the difference in adsorption between the anaerobic and aerobic soils was more prominent in soils with high organic matter contents.

Another remarkable observation from the study is the noticeable reduction in the adsorption of ^{14}C-metolachlor in the anaerobic soils, as evident from their respective low K_{des} values compared with the aerobic incubations. There are some explanations proposed for reduced adsorption for herbicides in anaerobic soils. One theory suggests that modifications to functional groups on soil organic matter under anoxic soil conditions lead to reduced adsorption [19]. Another explanation proposed for relatively low herbicide adsorption is the decrease in the inorganic surface area caused by the reduction of ferric to ferrous ions [20]. However, the more significant decline in adsorption observed under anaerobic conditions in the soil with higher organic matter provides more support for the former theory.

The desorption coefficient (K_{des}) of metolachlor from the current study was in agreement with the previously reported values of 1.3–6.5 L kg^{-1} [15] and 5.9–51.6 L kg^{-1} [16]. Relatively low K_{des} values under anaerobic conditions for all three tested soils indicate that the desorption process was enhanced in the anaerobic or reduced soils. Such desorption patterns of the herbicide could improve its bioavailability and subsequently expedite the

degradation or bioactivity of the herbicide in soil. Furthermore, metolachlor desorption decreased with an increase in the organic matter content regardless of the soil environmental conditions, suggesting a role for soil organic matter in the desorption kinetics of metolachlor in soils.

The intriguing observation of the adsorption-desorption patterns of metolachlor in anaerobic soils suggests that soil redox is one of the governing factors for these processes in soil. The decreased adsorption of metolachlor under anaerobic conditions in different soil types may have significant implications for its bioavailability and environmental transport as an herbicide compound. For instance, weak adsorption suggests a high potential for metolachlor to lose herbicidal potency faster on sites where anaerobic conditions are predominant and a high risk for metolachlor to enter a lake or other water bodies along with soil sediments.

4.2. Degradation

The results from the present study suggest that the degradation of ^{14}C-metolachlor is enhanced by anaerobic conditions in all the soil types despite the differences in soil properties, as seen from the remaining fraction of the applied parent compound recovered from the soil at the end of the study, as well as their degradation half-life ($T_{1/2}$) values (Table 4). Chesters et al. [21] reported half-lives of metolachlor ranging from 36 to 182 days under aerobic soil conditions, and these are in agreement with the aerobic half-life for the herbicide in the current experiment. Seybold and McNamee [22] reported a 62-day half-life for metolachlor in anaerobic sediments, which is on par with the anaerobic $T_{1/2}$ values obtained from the present study. Other studies reported fluctuations estimated at 15–132 days in the degradation half-life of metolachlor, depending on the soil type and environmental conditions [23].

One of the earliest reports about the impact of soil aeration on the degradation of metolachlor was made by Walker and Brown, where a reduction in the half-life of the herbicide in soil was observed after an increase in soil saturation [24]. A similar trend was also reported by Rice et al. [8], where the first order $T_{1/2}$ of metolachlor degradation was substantially shorter for the saturated surface soils compared with that of unsaturated soils. Moreover, Accinelli et al. [25] reported a reduction in the half-life of metolachlor in flooded soil (24.1 days) when compared with non-flooded soils (32.2 days). In yet another study, faster degradation of metolachlor was observed in flooded soils with partial anaerobic conditions than in aerobic soils [26]. Conversely, there are also reports of a slight suppression of the degradation of metolachlor under anaerobic or reduced soil conditions [27].

Microbial degradation may contribute to the enhanced degradation of metolachlor observed from anaerobic or flooded microcosms, as flooding is characterized by strongly reduced conditions compatible with the activity of strictly anaerobic microorganisms [25]. Such an anoxic environment in the soil creates a conducive habitat for the microorganisms to perform specific reactions, which then leads to the active degradation of metolachlor. Stamper and Tuovinen [10] suggested anaerobic dehalogenation as one such viable microbial mechanism for transforming certain chloroacetanilide herbicides in soils incubated under anaerobic conditions. Additionally, the significant decrease in degradation rates observed in the autoclaved soils reiterates the importance of microbial pathways in the degradation and metabolism of metolachlor in soils of various properties and environmental conditions.

A negative correlation between the organic matter content of the soil and the degradation half-life of the herbicide was observed in both the aerobic and anaerobic microcosms, indicating metolachlor as being more persistent in soils with low organic matter content. This again emphasizes the importance of organic matter in determining the environmental fate of herbicides regardless of the soil conditions, a statement that has been made by previous studies [8]. This enhanced degradation can be attributed to larger populations of herbicide-degrading microbes, which can often be found in soils rich in organic matter.

4.3. Microbial Mineralization

In comparing its aerobic counterpart, the anaerobic soil conditions induced higher mineralization of ^{14}C-metolachlor irrespective of the soil type used, as evident from the increasing $^{14}CO_2$ measured from the soil microcosms. The mineralization level of the ^{14}C-metolachlor from the aerobic microcosms in the present study agreed with previous studies [28], where a $\leq$8% cumulative mineralization of ^{14}C-metolachlor was reported in cultivated soils. Krutz et al. [29] reported a higher level of cumulative mineralization at 17.6% for metolachlor in cultivated soils. Nevertheless, contrary to the observation made by this article, Rice et al. [8] noted that the mineralization of ^{14}C-metolachlor was minimal (<2%), regardless of the soil being saturated or not. Similarly, low levels of mineralization have also been reported for metolachlor herbicide in other studies [30].

Metolachlor is not readily mineralized in soil and requires a lag period before the initiation of this process [31,32]. It has also been agreed upon that the repeated application of herbicides could inhibit such lag periods from occurring during their mineralization [33]. Sites with long histories of herbicide usage could lead to better survival and acclimation of the herbicide degrading microbial populations in the soil, assuring faster mineralization following its application [34]. The observations on the evolution of $^{14}CO_2$ during the mineralization of ^{14}C-metolachlor confirmed the cleavage of the labeled phenyl ring in the metolachlor molecule.

5. Conclusions and Future Directions

Agricultural practices such as soil aeration can end up having a great impact on the microbial bioavailability of soil-applied herbicides such as metolachlor, and the findings of this study provided clear evidence for enhanced bioavailability and microbial biodegradation of metolachlor in the anaerobic soil systems. The respective Freundlich adsorption coefficients for anaerobic and aerobic soil conditions indicate that the adsorption of metolachlor in the soils was noticeably reduced under anaerobic conditions. Similarly, relatively low Freundlich desorption constants for metolachlor in the anaerobic soils, irrespective of their varying soil properties, suggest a greater release of adsorbed herbicide from the anaerobic soils. To the best of our knowledge, the current study is among the first attempts to evaluate the impacts of soil aeration on the binding and retention of metolachlor in soils from the upper midwestern United States that have been under corn-soybean crop rotations. Anaerobic soil incubations induced better degradation and mineralization of metolachlor in the range of soils evaluated, despite differences in the soil properties. Among the various soil types used in the experiment, Drummer soil with the highest organic matter content exhibited the highest rate of degradation and mineralization for metolachlor both under aerobic and anaerobic soil conditions. The non-sterilized soil microcosms showed substantial degradation and mineralization of metolachlor compared with the corresponding sterilized control microcosms despite the incubation conditions. These facts accentuate the major role of microbial activities in the degradation and metabolism of metolachlor within the soil profile, despite variances in the soil properties and aerobic conditions. These distinctive differences in the degradation and mineralization kinetics of metolachlor in aerobic and anaerobic soil environments suggest the need for a thorough investigation of microbial involvement in the fate of the herbicide when the soil undergoes changes in its redox status.

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