

Prediction of Adsorption Capacity, Degradation and Leaching Potential of Metolachlor in Selected Agricultural Soils of Ethiopia

Bereket Ayenew Alemu^{1*} and Endalkachew Getu²

¹Department of Chemistry, College of Natural and Computational Sciences, Madda Walabu University, Robe, Ethiopia

²Department of Environment and Climate Change, Ethiopian Civil Service University, Addis Ababa, Ethiopia

Abstract

The adsorption, degradation and leaching of metolachlor in soil samples from 10 locations, is covered in this paper. The batch equilibrium technique was used to conduct the adsorption experiments. Solid-phase extraction and HPLC chromatography were used to evaluate pesticides. The Langmuir and Freundlich models were used to analyze the equilibrium adsorption data. Adsorption and degradation rate are investigated employing kinetic models. According to the findings, the Freundlich ($R^2 \geq 0.99$) and pseudo second order ($R^2 \geq 0.99$) models offer the most accurate correlation between the experimental data. The investigated soils showed modest adsorption of metolachlor, with adsorption coefficients ranging from 2.27-6.75 $\mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$ and GUS index of 2.70-4.21. This suggests that the chemical may be able to travel downward with percolating water. Metolachlor had the maximum adsorption and persistence among the soils under study ($K_f=6.75 \mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$; DT_{50} 117.07 days) in SC1 soil, followed by SD10 ($K_f=2.27 \mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$; DT_{50} 33.25 days). Multiple linear regression analysis revealed that the GUS index depends on the combination of DT_{50} and K_f . The pesticide's poor adsorption on the 10 soils under study, as evidenced by KOC values in the range of 80.13-134.26, also indicates a high risk of contamination to the region's water sources.

Keywords: Degradation • Leaching • Adsorption • Metolachlor • Pesticides

Introduction

Pesticides have the ability to seep into groundwater and find their way into surface waters like rivers and lakes through runoff during rainstorm events. In addition to potentially endangering human health and aquatic environments, pesticides can disrupt regular biological processes, especially those of the endocrine system, which uses hormones to control physiological processes [1]. The identification and comprehension of the mechanisms governing the fate of pesticides, which pose a threat to non-target creatures and responsible for contaminating water resources, is becoming increasingly important. A pesticide molecule goes through a number of intricate, interconnected physical, chemical, and biological processes when it is sprayed to soil. According to Abdul Ghafoor, modelling is a potent method for gaining a thorough grasp of how pesticides affect the environment.

In order to promote prosperity while safeguarding the environment, the United Nations adopted the 2030 Agenda for Sustainable

Development in 2015, driven by the growing concern over ensuring that economic advancement is consistent with environmental protection [2]. Because of their potential for toxicity and the ability of some of their active ingredients to interact with the environment physico-chemically, resulting in high mobility and/or persistence, pesticides are regarded as having unique environmental importance. When the environmental quality criterion is not fulfilled, pesticides may become mobile through leaching caused by irrigation or rain [3]. This could result in contaminated water for human consumption and the prohibition of their use [4]. Three million tonnes of synthetic pesticides are used year on average worldwide to both agricultural and non-agricultural activities, which unintentionally contaminate non-target biota [5]. These agrochemicals are used excessively and improperly, which contaminates soil and water and poses serious risks to human health and the environment [6].

*Address for Correspondence: Bereket Ayenew Alemu, Department of Chemistry, College of Natural and Computational Sciences, Madda Walabu University, Robe, Ethiopia; E-mail: bersofsam12@gmail.com

Copyright: © 2026 Alemu BA, et al. This is an open-access article distributed under the terms of the creative commons attribution license which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

Received: 26 December, 2024, Manuscript No. POLLUTION-24-156728; **Editor assigned:** 30 December, 2024, PreQC No. POLLUTION-24-156728 (PQ); **Reviewed:** 14 January, 2025, QC No. POLLUTION-24-156728; **Revised:** 02 February 2026 Manuscript No. POLLUTION-24-156728 (R); **Published:** 26 February, 2026, DOI: 10.37421/2684-4958.2026.9.400

Ethiopia has an estimated population of 115 million, making it the second most populous nation in Africa. Pesticides are used in agriculture, which still employs the bulk of the population [7]. The agricultural sector employs around 85% of Ethiopia's labour force, mostly on large commercial farms and small farms that frequently use pesticides to increase agricultural yield. Ethiopia's ongoing agricultural transformation has brought pesticide effects on the environment and public health to the forefront of attention recently [8]. As with other nations in sub-Saharan Africa, reports have connected improper use of pesticides to environmental and health problems in Ethiopia [9].

The primary cause of pesticide diffuse contamination in groundwater is the application of pesticides in agricultural regions. Determining the quantity of herbicide needed for efficient weed control in soils and forecasting the amount of leaching and redistribution are made easier by an understanding of the mechanics of adsorption and desorption. The Degradation Half-Life (DT_{50}) and the adsorption coefficient (K_d) are two essential metrics for evaluating the mobility and polluting potential of pesticides. The degradation process changes the concentration of pesticide residues in soils, thereby controlling their persistence in soils, whereas the adsorption of pesticides onto soil particles limits their bioavailability to microorganisms and reduces their leaching potential to groundwater. Understanding the adsorption mechanisms that take place in the unsaturated zone's soil cover is crucial for researching the effects of pesticides on groundwater since they define the fate of pesticides in the environment. According to Olvera et al., the adsorption of the pesticide in the soil controls the pesticide's release rate, transportability, and availability of degrading microorganisms in the aqueous phase of the soil.

Metolachlor has been found in surface and ground water in numerous countries, has relatively high water solubility (488 mg L^{-1}) and the potential to leach into ground water. It also has low volatility (vapour pressure of $1.73 \times 10^{-3} \text{ Pa}$ at 20°C) and low K_{OC} (200 ml g^{-1}), which increase its potential for movement in the soil profile. The mechanisms of adsorption, degradation, and leaching mainly dictate an herbicide's fate in the soil environment. Clay and the amount of Organic Matter (OM) in the soil are two factors that affect metolachlor's fate. Currently, soil Organic Matter (OM) is the primary factor that promotes the mild adsorption of metolachlor. The risk of the herbicide's downward mobility and groundwater contamination is increased because this OM content is low in many agricultural soils and declines through the soil layers.

According to Sadegh-Zadeh et al., certain fractions of Organic Matter (OM) have an attraction for hydrophobic chemicals, which makes the OC content of the soil the primary factor responsible for herbicide adsorption. This is why it's usual practice to evaluate herbicide mobility through the soil using the soil organic adsorption coefficient (K_{OC}). For instance, a significant probability of pesticide leaching is indicated by a low sorption coefficient. Furthermore, a useful method for computing a mobility index is to ascertain the soil's Disappearance Half-Life Time (DT_{50}). Lengthy half-lives indicate strong

persistence. Degradation and sorption are therefore important components of the majority of the indices used to assess the risk of pesticide leaching, such the Groundwater Ubiquity Score (GUS), Relative Leaching Potential Index (RLPI), and/or Leachability Index (LIX).

How a system's adsorption characteristics change over time is the subject of adsorption kinetics? Surface covering thickness provides insight into a process's rate of operation. Adsorption is influenced by time, hence while constructing and renewing the adsorbent, it is essential to evaluate the rates of adsorption. So, in order to characterize metachlor's migration inside and onto the soil surface sites, it is imperative to understand adsorption kinetics and their kinetic parameters. According to Tykodi, kinetic adsorption studies offer details on the process of sorption, potential rate-limiting step. Kinetic models are used to validate the experimental isotherm results and look into the mechanism of the adsorption process. These kinds of kinetic studies reveal the rate at which the process happens and shed light on the adsorption mechanism's non-equilibrium stages. One crucial factor controlling the duration of an adsorption process is the contact time between the adsorbent and the adsorbate. This is because, for a given initial dosage of the adsorbent, it offers information on the sorption kinetics of the adsorbate.

The environment and public health have been impacted by large commercial farms and small farms that commonly use pesticides to boost agricultural productivity in Ethiopia in general the study area in particular. Pesticide contamination of groundwater is influenced by several environmental parameters. Furthermore, thoughtful characteristics of the soil, such as its organic carbon content, texture, pH, type of clay mineral, dissolved organic matter, and cation exchange capacity, have a significant impact on pesticide adsorption and leaching potential, which determine the fate of pesticides in the environment. Even though metolachlor's leaching potential and adsorption capacity have been studied in other environmental samples elsewhere, the study region has not yet been examined in relation to soil parameters. The purpose of the current study was to characterize metolachlor adsorption, degradation, and leaching in ten soils with varying characteristics.

Materials and Methods

Study area, and sampling locations

The enquiry was conducted in the southern Ethiopian highlands' Dinsho district in the Bale zone and Cheha district in the Gurage zone. The economy of the districts is primarily based on agriculture, which contributes significantly to the country's food supply. The Cheha district is situated between $8^\circ 32' 0''$ and $8^\circ 20' 0''$ N and $37^\circ 41' 20''$ and $38^\circ 2' 40''$ E, at an elevation of 900 to 2812 masl. The region was classified into three agro-ecological zones by EIAR (2011) based on the bimodal rainfall system: Lowlands (500–150 masl), midlands (1500–2300 masl), and highlands (2300–3200 masl). The district has received 1268 mm of annual rainfall on average over the

last ten years. 10.69°C is the average yearly low temperature and 24.97°C is the average high temperature. The three primary types of soil are nitisols, leptisols, and pellic vertisols.

The Dinsho district lies between 6° 58' 40" and 7° 20' 0" North and between 39° 44' 0" and 40° 26' 40" East. Physiography indicates that the bulk of the district's land area is situated at elevations greater than 2000 metres above sea level (masl). The district is divided into three agroclimatic zones: Lowlands (170-150 masl), midlands (1500-2300 masl), and highlands (2300-2600 masl). The district has a bimodal rainfall distribution, with an approximate annual mean rainfall of 1150 mm. The region experiences annual temperatures that typically vary from 17.5°C to 6°C. In the district, the four primary reference soil classifications are Pellic Vertisols, Eutric Cambisols, Nitisols, and Chromic Luvisols. Ten composite soil samples (0–15 cm) were collected for this investigation; Goha1 (SD10), Goha2 (SD11), Moche (SD8), Goha3 (SD9), Afir (SC5), Kechot (SC6) and Abret (SC4) were the seven from the Cheha district and the three samples, Doyomarufa

(SC7), Ketasire 2 (SC2), and Tulu (SC1), obtained from the Dinsho district.

Characteristics of the studied soils

The distribution of soil particle sizes was examined using the Bouyoucos hydrometer method. The pH of the soil was measured potentiometrically in H₂O and 1 M KCl solution at a ratio of 1:2.5 for the soil: water and soil: KCl solutions using a combination glass electrode pH meter. The Lavkulich method was applied in order to determine the Cation Exchange Capacity (CEC) of the soil. Organic carbon was estimated using the dichromate oxidation method, as described by Walkley and Black. Following the procedure described by Jamison et al., three undisturbed soil samples were collected using a core sampler, and the bulk density of the soil was ascertained from these samples. The moisture retention at Field Capacity (FC) of -0.33 bar and Permanent Wilting Point (PWP) of -15 bar was evaluated using the pressure plate apparatus method (Table 1).

Soil	Particle size distribution (%)			Bulk density	Water content (%)		pH	OM%	CEC	exAI
	Sand	Silt	Clay	(g cm ⁻³)	FC	AWHC (%)	H ₂ O	%	cmol _c kg ⁻¹	cmol _c kg ⁻¹
SD10	23.2	28.6	48.2	1.32	31	11.4	4.65	2.723	19.15	1.54
SD11	22.8	32.6	44.6	1.25	32.25	10	4.79	3.206	23.88	0.82
SD8	22	33	45	1.24	32.7	10.9	4.91	3.293	23.05	0.49
SD9	23.2	27	49.8	1.29	31	9.65	4.73	3.327	20.88	1.29
SC5	19.4	34	46.6	1.22	31.95	10.2	4.81	3.396	26.98	0.35
SC6	19.6	37	43.4	1.24	32.9	10.4	4.76	3.448	29.54	0.43
SC4	14.8	37.2	48	1.21	31.65	10.75	5.13	3.637	22.81	0.42
SC7	29.6	32.6	37.8	1.13	31.6	10	5.3	4.12	33.7	0.28
SC2	29.2	32.6	38.2	1.16	32.31	11.59	5.45	4.344	30.66	0.21
SC1	29	34.4	36.6	1.11	39.15	16.95	5.12	4.448	34.03	0.24

Table 1. Selected characteristics of the ten soils used in this study.

Reagent and materials

The HPLC measurement for metolachlor concentration was carried out using a Hewlett-Packard 1100 HPLC system (Agilent Technologies, Santa Clara, CA, USA) equipped with a UV variable wavelength detector set at 210 nm. The analytical standard for S-metolachlor with a purity of 99.5% was acquired from Dr. Ehrenstorfer GmbH located in Augsburg, Germany. Sodium chloride, which was purchased from Sigma-Aldrich in Zwijndrecht, The Netherlands, was utilized in the herbicide extraction process. Riedel de Haen (Seelze, Germany) provided HPLC-grade purity methanol, n-hexane, and ethyl acetate. Thermo Scientific TM, Vantaa, Finland, C18 cartridges (1000 mg, 6 mL) were used for Solid-Phase Extraction (SPE). Acetonitrile plus 0.1% phosphoric acid (pH 2.30) (70 + 30 by volume) was the mobile

phase, and it was injected at a volume of 70 µL at a flow rate of 1.0 mL min⁻¹. Wakosil reversed-phase column (C18, 4.6 mm ID × 250 mm; Wako Pure Chemical Industries, Ltd., Osaka, Japan) with a diameter of 5 µm was used. To evaluate recovery, soil samples devoid of herbicides were spiked at concentrations of 0.05, 0.5, and 5 µg g⁻¹. Recovery for soil samples exceeded 86% for all degrees of fortification. The lowest detection limit of metolachlor is 0.015 µg g⁻¹.

Sample preparation and extraction

Three independent, one-kilogram samples of each soil were collected using a soil auger. After all debris was removed, each soil sample was set to air dry and then homogenized and sieved using a 2 mm sieve. The soil samples were extracted using the QuEChERS technique

as described in Vera J, et al. After the quartering procedure, 200 g of the samples were collected, and 10 g of each soil sample were put as a representative quantity into a 50 mL centrifuge tube. The sample-containing vial was vortexed for one minute after being filled with 2 mL of deionized water and 10 mL of acetonitrile.

Method validation

Metolachlor at a concentration of 1 mg/mL in ethyl acetate were produced as separate mixed standard stock solutions. Using a serial dilution method, the calibration standard solutions were created from the secondary stock solutions. The calibration standard solutions were prepared in ethyl acetate at different concentration rates of 0.1, 0.2, 0.5, 1, 2, and 5 $\mu\text{g L}^{-1}$. To show the linearity of the matrix-matched calibration curve, standard solutions were applied in the range of 0.1–5 $\mu\text{g L}^{-1}$ to a blank soil matrix. The linearity of the calibration curve in ethyl acetate was also examined.

In order to reach the Limit of Detection (LOD) and Limit of Quantitation (LOQ), metolachlor was spiked with soil at the lowest concentration level that complied with the analytical method's criteria. This allowed for the evaluation of the method's sensitivity. The lowest spiking level concentration (LOQ) in samples that yielded consistent and reproducible results was determined by multiplying the signal-to-background-noise ratio (SBR) on each chromatogram by three. To conduct the recovery tests, blank (control) soil samples were spiked with standard metolachlor solutions at concentrations of 0.1, 0.5, and 1 $\mu\text{g g}^{-1}$.

Adsorption kinetics models

The batch equilibration approach was used to conduct kinetic studies in triplicate. This section examined the adsorption kinetics of metolachlor. For the kinetic trials, room temperature (25°C) and standard atmospheric pressure were employed. Using a constant temperature shaker, 10 mL of metolachlor solution at a concentration of 30 mg L^{-1} was mixed with a 2.0 g soil sample in a 50 mL bottle. Samples were obtained at predetermined intervals during each of the three treatments. After centrifuging at 8000 rpm for five minutes, the supernatant was filtered through a 0.45 μm micron filter to prepare it for future use. The absorption kinetics data were evaluated using the intra-particle diffusion model, the pseudo-first order kinetic model, the pseudo-second order model, and the Elovich equations.

Pseudo first order and pseudo second order models: The kinetic equation is written as follows in both models: Lagergren asserted that:

$$\log(Q_{\max} - Q_t) = \log Q_{\max} - 0.4342k_1t$$

where $Q_{\max}$ and Q_t are the amounts of pesticide adsorbed at equilibrium and at time t , respectively ($\mu\text{g g}^{-1}$), and t is the contact time (min). k_1 is the pseudo first order rate constant (min^{-1}). Finding the slope of the $\log(Q_{\max} - Q_t)$ plot with respect to t yields the pseudo first order rate constant.

According to Ho and McKay, the driving force in the pseudo second order model is proportionate to the active sites on the sorbent that are open to sorption.

$$t/Q_t = 1/k_2Q_{\max}^2 + t/Q_{\max}$$

where k_2 , calculated by plotting t/Q_t versus t , is the pseudo second order kinetic rate constant ($\text{g } \mu\text{g}^{-1} \text{ min}^{-1}$).

Elovich equation: This equation, which was first proposed by Roginsky and Zeldovich in 1934, suggests that adsorption proceeds in two phases: A fast initial reaction associated with the sorbate's movement to readily accessible external places, followed by a slower diffusion to the sorbent's micropores:

$$Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$$

When Q_t is plotted against $\ln t$, the intercept represents the amount sorbed during the first sorption phase, and α ($\mu\text{g g}^{-1} \text{ min}^{-1}$) represents the initial adsorption rate. The slope of the straight line can be used to calculate β ($\text{g } \mu\text{g}^{-1}$) is a desorption constant which describes the relationship between the activation energy and surface coverage for chemisorption.

Intra-particle diffusion model: First presented in the early 1960's, this model considers the effects of both diffusions in the sorbent and convective diffusion in the sorbate solution on sorption. The following is the linear formula:

$$Q_t = C + k_{\text{int}}t^{1/2}$$

where C ($\mu\text{g g}^{-1}$) is a quantity proportional to the extent of the boundary layer thickness. Where k_{int} ($\mu\text{g g}^{-1} \text{ min}^{-1/2}$) is the intra-particle diffusion rate constant.

Adsorption isotherms and models: The equilibrium periods and adsorption isotherms were calculated using the OECD Guide 106.5 g samples, each in duplicate, were weighed and placed into glass tubes. 10 mL of metolachlor solutions were then added, with the initial concentrations being 0, 3, 5, 15, 20, 25, and 30 $\mu\text{g mL}^{-1}$ in 0.01M CaCl_2 and ultra-pure water. 10 g of soil and 10 mL of each diluted pesticide were added to Corex centrifuge tubes and securely sealed with Teflon plugs for each batch adsorption system. Three trials for each type of soil and concentration level were conducted for each system. The tubes were set up on a shaker, and the suspensions were agitated for 24 hrs at 20 degrees Celsius in a thermostated chamber with sporadic shaking every 2 hrs and every 3 hrs. Each tube was then centrifuged for 15 minutes at 2500 rpm, after which the supernatant was filtered and decanted to get rid of any remaining contaminants. To find interference, duplicate control adsorption systems and blanks were created. For every soil sample, the equilibrium concentration of herbicide and the amount adsorbed were calculated.

The adsorption data were fitted to the Freundlich, and Langmuir equations. The Freundlich equation, which is associated with non-ideal, reversible, multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface, was then used to test the experimental results.

$$\log(q_e) = \log(K_f) + N_f \log(C_e)$$

Where K_f ($\mu\text{g}^{-1-n} \text{ mL}^n \text{ g}^{-1}$) is the adsorption coefficient characterizing the adsorption capacity, C_e is the equilibrium concentration of herbicide ($\mu\text{g mL}^{-1}$) and q_e is the quantity of herbicide adsorbed at equilibrium ($\mu\text{g g}^{-1}$) and N_f is the slope of an isotherm related to the adsorption intensity, which is employed as an indicator of the adsorption isotherm nonlinearity.

The Langmuir model has also been tested against the experimental results. According to Hans and Nicholas, the model holds true when adsorption entails the attachment of a single layer of molecules to the surface and the surface has a certain number of places where the solute molecules can be attached. Equation ten (the Langmuir model) is as follows:

$$1/Q = 1/Q_{\max} + 1/(K_L Q_{\max} C_e)$$

Where C_e is the equilibrium pesticide concentration ($\mu\text{g pesticide mL}^{-1}$), Q =amount of pesticide adsorbed ($\mu\text{g pesticide g}^{-1}$), $Q_{\max}$ =maximum amount of pesticides adsorbed ($\mu\text{g pesticide kg}^{-1}$ soil), and K_L is the affinity coefficient between the surface of soil particles and the pesticide residue, which is correlated with the bonding energy ($\text{mL } \mu\text{g}^{-1}$).

The soil OC-water partitioning coefficient (K_{OC}) was computed ($K_{OC}=100 K_f/(\%OC)$), which is regarded as the quantity of herbicide adsorbed per unit of OC. Additionally, K_f parameters were used to calculate the Groundwater Ubiquity Score (GUS) and organic carbon partition coefficient (K_{OC}), which give information on pesticide leachability and mobility, respectively. Therefore, Groundwater Ubiquity Scores (GUS) which is used to quantify the leaching potential of metolachlor in soils was computed as:

$$GUS = \log(DT_{50}) \times (4 - \log K_{OC})$$

Where K_{OC} is organic carbon partition coefficient (mL g^{-1}); DT_{50} is half-life in the soil (days).

For the assessment of GUS values, we have used net approach: Probability of pesticide leaching into groundwater is present (high leaching potential: $GUS > 2.8$); probability of pesticide leaching into groundwater is possible (low leaching: $GUS < 1.8$); pesticides possibly not leached into groundwater ($GUS = 1.8 - 2.8$).

Degradation experiments

Metabolachlor breakdown in soils was studied using laboratory incubation studies. A 50 mL flask containing 10 g of soil sample was aseptically spiked with 1 mL of the metolachlor stock standard solution in acetone. Furthermore, native soils were autoclaved at 120°C for one hour over the course of three days to create sterile soil samples. The chemical breakdown of the pesticide was confirmed using the sterile soil samples as controls. A sterile spatula was used to mix all of these soils, and a sterile cabinet was used for every step of the process. To guarantee complete mixing and acetone evaporation, the metolachlor-spiked soils were shaken for 48 hrs at room temperature in the dark using a reciprocating shaker. In order to maintain roughly 60% of the Water Holding Capacity (WHC), sterile distilled water was supplied. At 20°C , the soil samples were incubated. Weighing once a

week, the proper amount of sterile distilled water was added to maintain the soil moisture contents at a constant weight. To find out how much metolachlor was still present in the soil, samples were taken on days 0, 7, 14, 30, 60, and 80. At every sampling time interval, soil flasks in triplicate were taken out of each treatment. Following a 2 hour shaking on a reciprocating shaker, the soil samples were combined with 30 mL of acetone water (25:5, v/v), and ultrasonically extracted for 20 minutes at 20°C . Acetone in the filtrate was allowed to evaporate on a vacuum rotary evaporator following filtration. Prior to HPLC analysis, a 2 mL solution was collected and run through a $0.45 \mu\text{m}$ membrane filter.

First-order kinetics was used to compute the metolachlor dissipation rate constants: $C_t = C_0 e^{-kt}$, where C_t is the quantity of metolachlor in mg kg^{-1} soil at time t , C_0 is the amount at time 0 (mg kg^{-1} soil), and k is the rate constant (week^{-1}). The first-order rate equation $\log C_t = \log C_0 - kt$ was converted, and the dissipation rate constants were determined using linear regression.

According to pseudo first order kinetics, half-lives, or the amount of time needed for 50% of the herbicide to vanish from the soil, were computed as $t_{1/2} = \ln 2/k$. In this instance, $t_{1/2}$ is equal to DT_{50} , which is the amount of time required for 50% of the herbicide to be removed from the soil.

$$DT_{50} = 0.693/k$$

Statistical analysis

Using student tests, Pearson's linear correlations and multiple regressions between soil characteristics and factors related to herbicide adsorption, degradation, and leaching were examined. Using SAS software, an Analysis of Variance (ANOVA) was performed to determine the impact of soil physico-chemical parameters on adsorption capacity, degradation, and leaching potential.

Results and Discussion

Method validation

Over the used concentration range, a linear standard curve with a correlation coefficient (R^2) of 0.996 was produced. Metolachlor had LOD and LOQ mean values of 0.015 and $0.154 \mu\text{g g}^{-1}$, respectively. The range of its recoveries was 91.43–105.84%. Therefore, it seemed that the techniques used here to measure the herbicide adsorption in various agricultural soils were precise and dependable.

Evaluation of the equilibrium time

The amount of pesticide adsorbed in response to the soil-solution contact time was displayed on sorption kinetics plots. By fitting kinetic data to different mathematical models, sorbent kinetics can reveal details about the mechanisms engaged in the process, the rate and sequence of the adsorption response, and the amount of time needed to reach equilibrium. One crucial factor influencing how long an adsorption process lasts is the duration of contact between the

adsorbent and the adsorbate. This is because, according to Singh et al., it offers details on the sorption kinetics of the adsorbate for a specific initial dosage of the adsorbent. Based on differences in their organic matter contents only two soils (highest and lowest) were considered for adsorption kinetics study. In our instance, adsorption equilibria were reached for the pesticide-soil systems within the experimental time assessed (24 h), as shown in Figure 1. The limited reports that have been published about the behaviour of metolachlor (MC) in soil are consistent with this rather quick adsorption. For example, it was consistent with the findings published by Nkedi-Kizza et al., who noted that in batch adsorption investigations, a 24-hour period is regarded the equilibrium adsorption time. A divergent finding has been documented, indicating that equilibrium was established with in 72 hrs. In SC1 soil, metolachlor was quickly absorbed and reached $Q_{\max}$ after around 10 hours, whereas in SD2 soil, $Q_{\max}$ was attained after 24 hours. In the investigated soils, metolachlor adsorption equilibrium was attained in the range of 10–24 hrs, with an R^2 higher than 0.991–0.995. The variances in the soils' organic carbon contents (%OC) may be the cause of this variation in equilibrium periods between the soils.

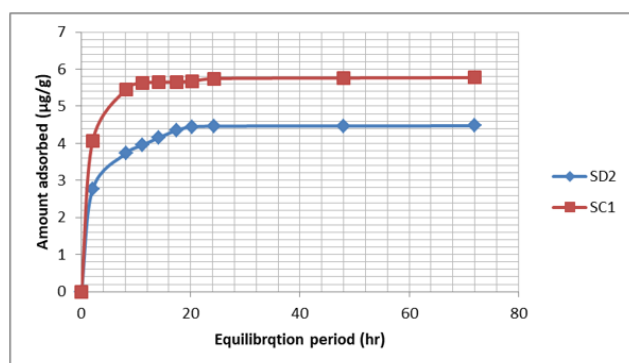


Figure 1. Isotherms of adsorption kinetics.

Fitting to kinetic models

Elovich model: Assuming that real solid surfaces are energetically heterogeneous, this model—which is well-known to depict chemisorption—is helpful in describing second order kinetics. Based on Table 2 and Figure 2C, it can be inferred that the Elovich equation adequately explains the kinetics of metolachlor sorption in SC1 and SD2 soils ($R^2 > 0.96$; $P < 0.05$) and $R^2 > 0.87$; $P < 0.05$, respectively, indicating a significant role for chemisorption. The amount adsorbed during the first fast phase of the equation's linear form is called the intercept. The conforming values of amount adsorbed during the initial stage, for SD2 and SC1 soils, were $2.6996 \mu\text{g g}^{-1}$ and $3.719 \mu\text{g g}^{-1}$, respectively. The slow phase's sorption rates ($\mu\text{g g}^{-1} \text{min}^{-1}$) were $0.5023 \mu\text{g g}^{-1} \text{min}^{-1}$, for SD2 and $0.5281 \mu\text{g g}^{-1} \text{min}^{-1}$ SC1 soils, according to the slope of the straight line. But still, compared to the errors noted (SC1=0.514; SD2=0.1921) from the evaluation of fitting the pseudo second order kinetic model, the Standard Errors (SE) seen during evaluation of the Elovich model for estimation of sorption kinetics parameters of metolachlor were higher 11.632 (SC1) and 13.148 (SD2). This might be as a result of the Elovich equation's ignoring of the effects of concurrent

desorption. According to Plazinski et al., the model's inadequate ability to describe the adsorption data is evident in their reports. They observed that the model is suitable only during the early stages of the sorption process, when the system is still relatively far from equilibrium. Consequently, despite the model appearing to fit well (Figure 2C), the model was rejected because of the significant standard error of the intercepts.

Intra-particle diffusion model: Pesticide adsorption onto soils from aqueous solutions is frequently assessed using the intra-particle diffusion model. Instantaneous adsorption occurs on the external surface during the first stage of the process. Gradual adsorption occurs during the second stage, where intra-particle diffusion acts as the rate-limiting mechanism. The final equilibrium step occurs during the third stage, where the solute shifts from larger pores to micropores, resulting in a slow adsorption rate. The multilinearity in the plots serves as evidence for this. It provides fitting plots and kinetic parameters. After being fitted to the model, the adsorption data showed poor regression and multilinearity ($R^2 > 0.56$ and 0.71). The model's application was denied due to the weak regression and high standard error of the parameters (Figure 2D and Table 2).

Pseudo first and pseudo second order models: Publicly available data indicates that pseudo first order kinetics work best at high initial concentrations and in the early stages of the sorption process when the system is not quite at equilibrium, that is, when there is little sorptive site coverage and it is reasonable to assume that the number of unoccupied sites will remain constant. Once the reaction proceeds and the system approaches equilibrium (Figure 1), adsorption becomes a pseudo second order reaction, where vacant sites and the concentration of metolachlor in solution constantly decrease.

For metolachlor in SD2 and SC1 soils, where data could not be fitted to the pseudo first order, Elovich, and intra-particle models, the fitting of the experimental data to the Pseudo First Order (PFO) and Pseudo Second Order (PSO), Elovich, and intra-particle kinetic models is shown in Figure 2 and Table 2. Table 2 displays $Q_{\max}$, the predicted rate constants (k_1 and k_2), and the matching determination coefficients R^2 . $Q_{\max}$, the experimental maximum amount of pesticide adsorbed, was taken into account for k_1 valuation. As the metolachlor adsorption equilibrium appeared to be reached within the experimental time, the current study showed that the second order kinetics model provided a more accurate match and $Q_{\max}$ prediction ($R^2 > 0.99$ ($P < 0.01$)) indicates that the data fit the pseudo second order kinetics effectively, indicating the role of chemisorption in the process. The entire data set was explained by this model, and its projected $Q_{\max}$ values coincided with the experimental values with the least amount of variation (0.192–0.514%). In support of the current investigation, numerous reports have demonstrated that the pseudo second order model can explain the sorption of organic pollutants from aqueous solutions. The sorption rates of metolachlor in the soils varied in the following order: SC1 > SD2 when K_2 values were considered. Put otherwise, the pesticide continued to bind most quickly in SC1 soil, but adsorption was slowest in SD2 soil.

Intra-particle diffusion model's parameters							
Soil (SD2)				Soil (SC1)			
k	C	SE	R ²	k	C	SE	R ²
0.2023	3.19	6.435	0.56	0.228	4.239	5.493	0.71
Pseudo-second-order kinetics model's parameter							
Soil (SD2)				Soil (SC1)			
k ₂	q _e	SE	R ²	k ₂	q _e	SE	R ²
0.17555	4.57456	0.1921	0.99	0.40352	5.81	0.514	0.99
Pseudo first order kinetics model's parameters							
Soil (SD2)				Soil (SC1)			
q _e	k ₁	SE	R ²	q _e	k ₁	SE	R ²
3.53729	0.0408	5.358	0.58	2.41767	0.0419	7.523	0.73
Elovich kinetics model's parameters							
Soil (SD2)				Soil (SC1)			
lnα	1/β	SE	R ²	lnα	1/β	SE	R ²
4.68579	0.5023	13.148	0.87	6.54093	0.5281	11.632	0.96

Note: Pinpoint the exact leaching risk of metolachlor.

Table 2. Coefficients of adsorption kinetic models.

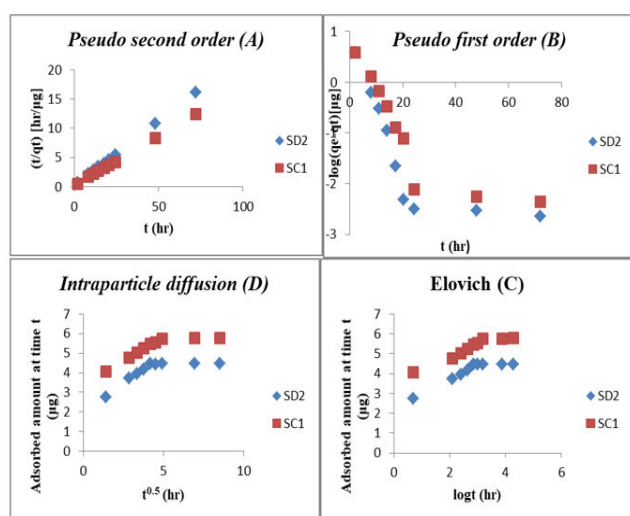


Figure 2. Models' curves of adsorption kinetics.

Adsorption isotherms

Figure 3A and B, displays the metolachlor adsorption isotherms for each of the ten tested soils. Classification of adsorption isotherms revealed that the metolachlor adsorption isotherm for each soil was L-type, indicating a slight competition between solute and solvent molecules for the surface adsorbing sites. These findings are consistent with earlier research published by Wu et al. The non-linear isotherms shown here could result from distinct adsorption mechanisms between the organic chemicals and various mineral and/or

organic soil components, or from aggregating certain interactions during soil metolachlor adsorption.

This study examined the two commonly used adsorption models, and the Freundlich equation, with a R^2 value >0.99 , gave a fair description of the sorption of metolachlor to soils covering the equilibrium values from 0 to 15 $\mu\text{g mL}^{-1}$ (Table 3). The adsorption isotherms for all soils had slopes of (N_f) less than 1, indicating the possibility of metolachlor leaching, particularly at higher application rates, and the fact that the amount of herbicide adsorbed by the soil decreased as solution concentration increased. For metolachlor, the K_f mean values fell between 2.27 and 6.75 ($\mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$). Most of the soils under study had K_f values higher than those reported by Baran and Gourcy. Additionally, it was more in line with the range reported by Kodesova et al., who discovered K_f values ranging from 0.3 to 6.1 after determining sorption isotherms for 11 different soils. With a value of $N_f=0.75$, SD11 soil had the maximum intensity of the herbicide's adsorption process on soil samples, while SC4 soil had the lowest intensity, with $N_f=0.426$ (Table 3). Of all the soils under investigation, Metolachlor has the highest adsorption in SC1 ($K_f=6.75 \mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$), followed by SC2 ($K_f=5.53 \mu\text{g}^{1-n}\text{mL}^n\text{g}^{-1}$). Table 3, shows that the greater K_f value of SC1 may be related to the soil's pH, CEC, or organic matter content. Metolachlor's poor binding to organic matter and clay minerals may have contributed to its lower K_f values in the examined soils. This could accelerate leaching into the subsurface soil, where it will dissipate more slowly and be more readily transported to groundwater. Despite the herbicide's low adsorption capacity, there were notable ($p<0.0001$) variations in the adsorption capacities of the soils to metolachlor (Table 3).

At a 2.11 mg L^{-1} starting concentration, the soils' metolachlor adsorption K_d values ranged from 1.13 mL g^{-1} to 3.25 mL g^{-1} (Table 3). At a given initial concentration, K_d values $<10 \text{ mL g}^{-1}$ (1.13 – 3.25 mL g^{-1}) were found in all of the examined soils (clay and clay loam), indicating that metolachlor is not tightly bound to the surface in these soils and that soil movement may be possible in certain environmental conditions. For the adsorption of metolachlor by vadose zone materials with a mean OC and clay content of 1.36% and 13.2%, respectively, Sidoli et al. observed similar higher K_d values (2.34 – 6.32 mL g^{-1}) related to the existing study (1.27 – $3.39 \mu\text{g mL}^{-1}$). In the same range as the current investigation, Marín-Benito et al. reported K_d values of 0.37 mL g^{-1} and 1.56 mL g^{-1} for two soil types with distinct textures (clay sandy loam and sandy), as well as medium and low OM contents. Comparable to the current investigation (1.27 – $3.39 \mu\text{g mL}^{-1}$), Alletto et al. and Vryzas et al., reported that higher K_d values (1.3 – $8.7 \mu\text{g mL}^{-1}$ or 0.27 – $2.85 \mu\text{g mL}^{-1}$) were found for the adsorption of metolachlor in agricultural soils with OC levels ranging from 0.8% to 3.8% or from 0.12% to 0.84%. Kodesova et al., also measured the sorption isotherms of soils and discovered alike K_f values varying from 0.3 to 6.1 L kg^{-1} , with the pH and organic matter content of the soils having a substantial correlation with the K_f constant. The high OM content of the soil might have promoted and enable more metolachlor molecule adsorption. In the examined soils, the K_d values for metolachlor fell between those of other findings, such as 0.51 – 3.40 mL g^{-1} , 0.76 – 16.67 mL g^{-1} , and 0.6 – 5.7 mL g^{-1} .

The physico-chemical properties of the soil as well as the herbicides themselves affect herbicide adsorption in the soil. Pesticides with high K_{OC} ($>1000 \text{ L kg}^{-1}$) show significant pesticide adsorption in soil and organic matter components. Metolachlor K_{OC} values in the investigated soils ranged from 80.13 to 134.26 L kg^{-1} (Table 3), which was less than what was stated in Zemolin et al. In this investigation, the K_d values of 1.13 to 3.25 mL g^{-1} , and a mean of 1.91 mL g^{-1} revealed that metolachlor adsorption in soil is low to moderate, according to similar research. Metolachlor was consequently predicted to partially adsorb in the soils. Furthermore, according to Copaja and Gatica all estimated K_{OC} values (a measure of sorption in soils) were less than 500, indicating a significant likelihood of chemical runoff or leaching and minimal chemical adsorption into the soil.

Pesticide half-life and K_{OC} are associated by an experimentally derived value termed the groundwater ubiquity score, or GUS. Hyun et al. applied the GUS to analyze which pesticides in the soil might contaminate groundwater, and they identified metolachlor as a groundwater pollutant if its GUS index was higher than 2.8. The primary factors influencing a pesticide's ability to leach into soil are usually persistence and adsorption. Thus, the leaching potential of metolachlor in the target soils was computed and displayed in Table 3. If a chemical's GUS is less than 1.8, it is considered to have a low leaching candidate; if it is larger than 2.8, it is considered to have a high leaching potential. If a chemical's GUS is between 1.8 and 2.8, it is considered to be in the "transition zone".

Based on measured K_{OC} and DT_{50} values, the present study's estimated GUS index ranged from 2.70 to 4.21 (Table 3). For example, fungicide metolachlor, which has a GUS value of 2.32, was projected to leach moderately based on estimates when pesticide leaching in Hawaii's soil was examined using GUS values. This indicates that significant leaching of the chemical is expected in soils similar to the one described. The current study's GUS index did not agree with Wu et al.'s findings in five soils with average percent organic matter contents ranging from 2.72% to 4.45%. GUS (2.70 to 4.21) for the herbicide metolachlor was significantly greater than 2.8, indicating a high-leacher chemical.

Given the agricultural soils in the research area's likely leachability of metholachlor, there may be a chance of groundwater pollution. Thus, it is possible to draw the conclusion that the agricultural soils under investigation are amenable to metolachlor leaching (Table 3). Preferential flow, which happens in dry soils when the wetting front is weakened by partially water-repellent layers, resulting in fingered flow, or when flow is concentrated in recently developed fissures, may be the cause of herbicide mobility in the soil profile. Furthermore, owing to the herbicide's poor soil particle adsorption capabilities, that favored flow, significantly affects herbicide leaching in the studied area. Nonetheless, the data presented in this study clearly show that there was heterogeneity in K_{OC} levels (Table 3). The reason for the variance in K_{OC} amongst soils could be attributed to the inorganic matrix's involvement in the sorption process. This could be by direct means such as sorbing the chemical or indirectly through altering the role of organic matter.

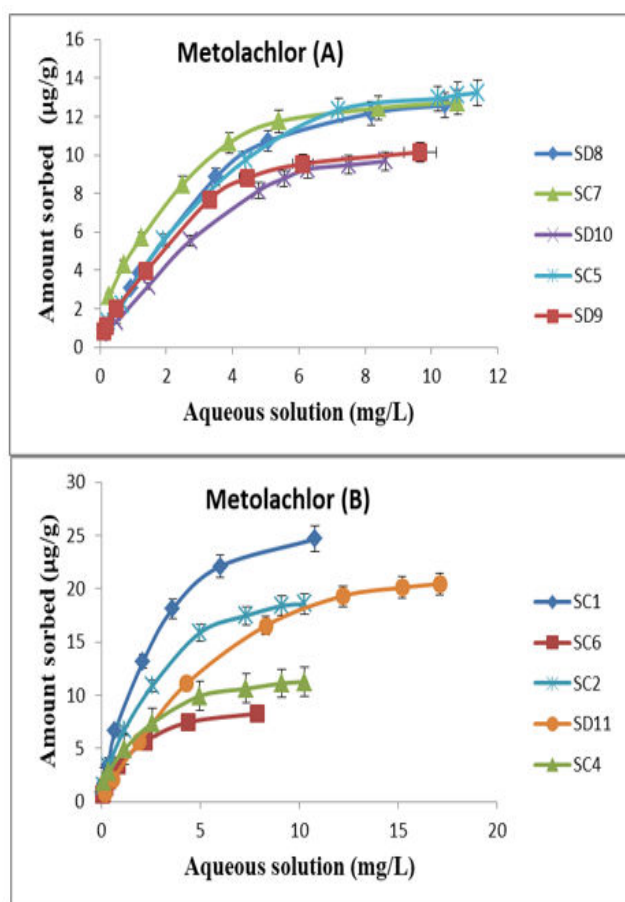


Figure 3. Adsorption isotherms of metolachlor (A and B).

Since the herbicide has a higher leaching potential in the soils under study, metolachlor immobilization or degradation methods must be developed in order to prevent water contamination. The sorption of hydrophobic pesticides by soils is facilitated by materials containing a high content of Organic Carbon (OC). The utilization of natural or synthetic materials with a high OC content is one of the strategies employed to achieve this. According to Gupta et al. and Marín-Benito

et al., this process usually results in the pesticides becoming immobile in the soil, which enhances their subsequent breakdown by reducing their mobility and so lowering water contamination. However, under field conditions, a number of factors could alter a pesticide's real dissipation rate. As a result, fieldwork is necessary to pinpoint the exact leaching risk of metolachlor.

Soil	K _f	N _i	R ²	K ₁	DT ₅₀	% Dissipated	f _{OC}	K _{OC}	K _d	GUS
SD10	2.27H	0.72	0.99	0.0058	33.25J	66.59	0.015777	80.13C	1.27F	2.70E
SD11	2.85G	0.75	0.99	0.0064	36.82I	65.93	0.018619	82.84C	1.55E	2.90ED
SD8	2.92FG	0.7	0.99	0.0077	44.09H	74.75	0.019084	84.03C	1.58E	3.09D
SD9	3.05EF	0.61	0.99	0.0084	52.16G	77.55	0.019316	85.68C	1.64E	3.22D
SC5	3.12E	0.62	0.99	0.0094	62.35F	83.67	0.019664	86.23C	1.67E	3.58C
SC6	3.15E	0.54	0.99	0.0107	71.31E	87.63	0.020012	86.86C	1.69E	3.70C
SC4	4.42D	0.426	0.991	0.0127	80.09D	91.9	0.021114	109.46B	2.29D	3.79BC
SC7	4.99C	0.447	0.994	0.0149	87.59C	94.91	0.023898	110.12B	2.56C	3.92BAC
SC2	5.53B	0.571	0.992	0.0178	105.87B	96.98	0.025174	114.50B	2.82B	4.07BA
SC1	6.75A	0.652	0.994	0.0196	117.07A	97.96	0.025812	134.26A	3.39A	4.21A
mean	3.91	-	-	-	69.06	-	-	97.41	2.05	3.52
CV	2.97	-	-	-	3.02	-	-	7.44	6.1	5.83
R ²	0.995	-	-	-	0.996	-	-	0.946	0.965	0.974
p	<0.0001	-	-	-	<0.0001	-	-	<0.0001	<0.0001	<0.0001

Note: Means with the same letter are not significantly.

Table 3. Parameters of adsorption, degradation, and bioavailability of metolachlor in soils.

In this investigation, the computed K_{OC} values for metolachlor were more than 50.87 to 56.41 mL g⁻¹ of the six soils with an OC content between 1.10% and 2.10%, and lesser than 173.70 to 195.90 mL g⁻¹ of the two soils with an OC concentration between 2.50% and 4.20%. Metolachlor adsorption in these agricultural soils was consistent with previous studies, who likewise discovered that metolachlor adsorption was often weak in soils and mostly depended on Organic Matter (OM). The adsorption coefficient per unit of organic carbon (K_{OC}) was used to express K_f values. The K_{OC} values can be used to assess or forecast the migration and behavior of organic compounds in the environment, as they show the hydrophobicity of pesticides. Based on K_{OC} values, McCall suggested a classification system for pesticide mobility. The pesticide in SC1 soil had the highest K_{OC} value (K_{OC}=134.26), while the pesticide in SD10 soil had the lowest K_{OC} value (K_{OC}=80.13). According to McCall's classification, soil with K_{OC} values ranging from 0 to 50 is considered to have "very high" mobility. K_{OC} values between 10 and 100 are categorized as having a weak adsorption capacity in soil by CEPIS OPS/OMS. With respect to the K_{OC} values found in the present investigation metolachlor in the 10 soils was categorized as having a high mobility capacity and weak soil adsorption.

Degradation experiment

Pesticide breakdown or transformation is strongly influenced by the soil's physicochemical properties and bioavailability. According to Purnomo et al. and Wang et al., some pesticides are permanently bonded to soil particles, meaning they cannot be degraded by biodegradation and stay in the soil for extended periods of time. A negative linear trend was observed in the dissipation of metolachlor on soils with time, indicating a reduction in the amount of herbicide in the soil with increasing time (Figure 4A and B).

Metolachlor dissipation kinetics in soil (0–20 cm) followed first-order kinetics, with half-lives of degradation in soils ranging from 33.25–117.07 days (Table 4). These findings fall between the 10.3–221 days' range described by the PPDB in laboratory conditions. These results are greater than those found in studies of Lewis et al.; Long et al., and Shaner et al., suggesting that the herbicide is more persistent in SC1 than SD10 soil. The herbicide metolachlor degraded at the fastest rate (0.0196 day⁻¹) in SD10 soil and the slowest rate (0.0058

day⁻¹) in SC1 soil. This finding also concur published data that indicates the rapid dissipation of metolachlor in soils with different organic matter concentrations (DT₅₀ values of 26.3-40.1 days) and 13–38 days. For metolachlor dissipation, the rate constant (k), was different from the findings of Parlakidis, et al., which is 0.032 day⁻¹. The half-life (DT₅₀) of metolachlor in the current study was longer (33.25-117.07 days) than the DT₅₀ value for metolachlor (21.66 days) in prior research of a similar kind. Despite the fact that the investigated soils' physiochemical characteristics aren't the same as those of soils from earlier metolachlor field dissipation studies, the half-life of 33.25 to 117.07 days falls between (or, in some cases, exceeds) the range of 13 to 142 days reported in earlier field studies. Table 3, indicated that soils with lower organic matter contents had longer half-live times. On the other hand, Long et al., discovered that metolachlor was more persistent in soils with lower OM content, and the degradation acceleration in soils with higher OM content was ascribed to the relatively large microbial population that breaks down metolachlor. Since metolachlor had the lowest DT₅₀ for SD10 (33.25 days), it is likely that diffusion played a significant role in lowering the pesticide's concentration in the solution and limiting its capacity to percolate into groundwater or lower soil layers. In contrast, metolachlor's DT₅₀ in SC1 was the greatest of the ten soils, which would mean that organic matter controls the pesticide's adsorption. Following the 80-day incubation period, Table 6 indicated that the soils had final metolachlor residual level of 66.6-97.96% of the initial concentration. In accordance with Gavrilescu, a pesticide is generally regarded as persistent if its half-life is greater than 100 days (non-persistent <30 days). Consequently, metolachlor herbicide in the present study could have been classified as a persistent compound in all the studied soils (Table 4). Table 3 demonstrated a statistically significant ($p < 0.0001$) variation in the metolachlor DT₅₀ value across the soils, suggesting a substantial influence of the physico-chemical characteristics of the soils on degradation. An increase in Organic Matter (OM) content among various soils resulted in a decrease in herbicide degradation and leaching and an increase in adsorption (Table 3). According to Table 4, the rate of metalochlor decomposition in soils declined as follows: SC1>SC2>SC7>SC4>SC6>SC5>SD9>SD8>SD11>SD10.

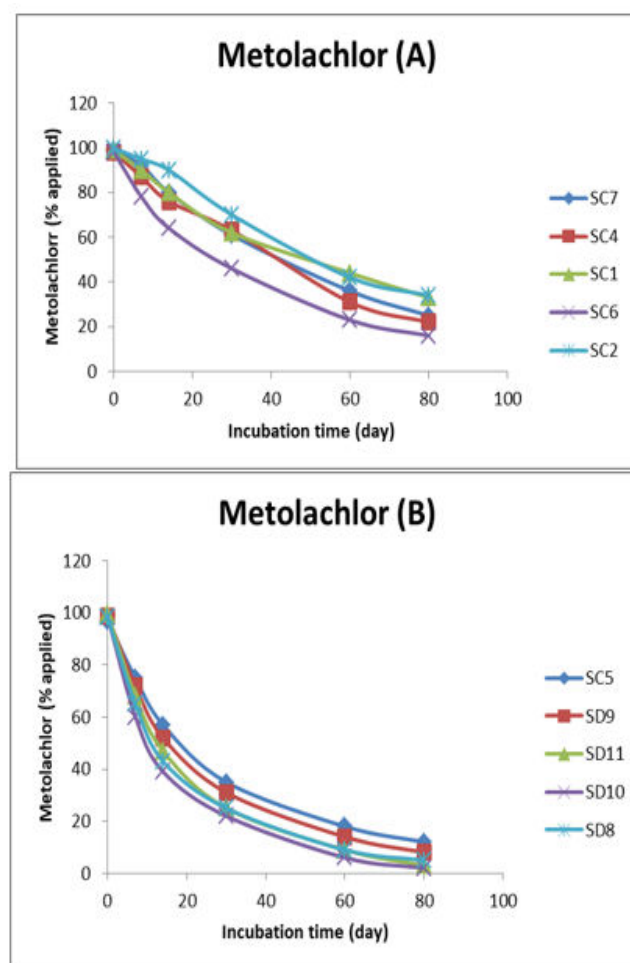


Figure 4. Degradation development of metolachlor (A and B).

Degradation	Soil									
Parameters	SD10	SD11	SD8	SD9	SC5	SC6	SC4	SC7	SC2	SC1
k (day ⁻¹)	0.0196	0.0178	0.0149	0.0127	0.0107	0.0094	0.0084	0.0077	0.0064	0.0058
DT ₅₀	33.25	36.82	44.09	52.16	62.35	71.31	80.09	87.59	105.87	117.07
R ²	0.995	0.997	0.996	0.997	0.991	0.992	0.994	0.988	0.996	0.994

Table 4. Half-lives and degradation rates of metolachlor.

Correlation and linear regression analyses results are presented in Tables 5, 6 and Figure 5. The organic matter content of the soils was positively and substantially ($r=0.96$, $p<0.001$) correlated with K_f (Table 5). The OM content of the soil significantly affected both the adsorption coefficient K_f and the degradation half-life DT_{50} of metolachlor (Table 6). As predicted, a linear regression analysis showed that K_f and DT_{50} had a positive connection ($r=0.96$, $p<0.0001$). The equivalent degradation or persistence for metachlor in soil appears to be quantifiable using the adsorption coefficient, as indicated by the regression equation (Table 6) $DT_{50}=19.028 K_f-5.1977$, ($p<0.0001$). A significant positive correlation ($r=0.96$, $p<0.01$) was found between the half-life and the soil organic matter content. This suggests that soil OM plays a major role in determining how long metolachlor persists in soils, even though clay content and other soil property parameters also affect how quickly metolachlor degrades in soils (Table 6). The reduction in metolachlor persistence in soils with OM content was consistent with earlier findings published by Wu et al., who ascribed the rise in metolachlor degradation rate in soils with a relatively high OM content to a relatively large microbial population that breaks down metolachlor.

Herbicide degradation rate constants were found to be between 0.0058 and 0.0198 day^{-1} , or half-lives of 117.07 and 33.25 days. Upon statistical analysis of the herbicide degradation results, it was discovered that there was a negative correlation ($r>-78$, $p<0.001$) between the degradation rate and clay content, and a positive correlation CEC ($r>0.83$, $p<0.001$), and pH ($r>0.81$, $p<0.001$) (Table 3).

Analogous to study published in Alletto et al., soil CEC was found to have a strong positive connection with metolachlor adsorption ($r=0.79$, $p<0.001$). While clay content had negative correlation ($r=-0.81$, $p<0.001$) with metolachlor sorption, in contrast to the previously shown relation in other researches, and there was a positive correlation (Table 5) between soil pH and metolachlor sorption ($r=0.83$, $P<0.001$). Similar results indicate that, there appears to be a significant positive correlation (significant at the 0.05 level) between the sorption of metolachlor and the organic carbon content, clay, and CEC.

Comparable to a prior study, the current study's Table 5, further shows that the distribution coefficient (K_d) of metolachlor and its leaching showed a strong negative connection ($r=-0.97$, $p<0.001$). The herbicide's leaching potential is substantially influenced by both adsorption capacity and persistence ($GUS=GUS=-0.08411K_f-0.01371DT_{50}+5.076$; $R^2>0.99$; $P<0.001$, $SE=0.0684$), as demonstrated by multiple regression analysis (Table 6), which can be used to predict the leaching potential of metolachlor in the research region. Moreover, the combined effect of K_f and OM is more significant than the individual contributions of the corresponding parameters.

	K_f	DT_{50}	GUS	K_d	Silt (%)	Clay (%)	OM (%)	pH	CEC (cmol _c kg ⁻¹)	K_{OC}	K (Rate)
K_f	1										
DT_{50}	-0.89**	1									
GUS	-0.97**	-0.99**	1								
K_d	1.00**	0.96**	-0.97**	1							
Sand (%)	0.57ns	0.46ns	-0.46ns	0.57ns							
Silt (%)	0.33ns	0.44ns	-0.43ns	0.33ns	1						
Clay (%)	-0.81**	-0.78**	0.76**	-0.81**	-0.31ns	1					
OM (%)	0.96**	0.96**	-0.97**	0.96**	0.36ns	-0.85**	1				
pH	0.83**	0.81**	-0.85**	0.83**	0.32ns	-0.74*	0.87**	1			
CEC (cmol _c kg ⁻¹)	0.79**	0.83**	-0.81**	0.79*	0.46ns	-0.92**	0.86**	0.67*	1		
K_{OC}	0.99**	0.93**	-0.95**	0.99**	0.34ns	-0.73*	0.91**	0.79*	0.71*	1	
K (Rate)	0.98**	-0.94**	-0.99**	0.98**	0.38ns	-0.82**	0.97**	0.84**	0.83**	0.95**	1

Note: ns: non-significant, * and ** represent $p<0.05$ and $p<0.01$, respectively.

Table 5. Correlation between K_f , K_d , k, DT_{50} , GUS of metolachlor and selected soil properties.

Additionally, it is evident that the combined impact of OM (%) and K_f was statistically significant ($R^2 > 0.97$, $p < 0.0001$) in determining the DT_{50} of metolachlor in the soil under investigation Table 6. Based on Table 6, it can be inferred that OM has a greater negative coefficient than K_f , suggesting that OM has a greater contribution to the DT_{50} prediction. The previous authors reported that the amount of clay and organic matter in the soils enhanced the amount of metolachlor that was adsorbed. In this investigation, K_d was discovered to have a significant negative link with clay ($r = -0.81$, $p < 0.01$) and a significant positive connection with soil OM content ($r = 0.96$, $p < 0.01$), CEC ($r = 0.79$, $p < 0.05$), and pH ($r = 0.83$, $p < 0.01$). Table 6, also illustrates how the pedotransfer function could have been used to predict the adsorption capacity (K_f) of metolachlor. It was discovered that the adsorption capacity of metolachlor increased with the soil's OM content

($p < 0.001$), pH ($p < 0.01$), and CEC ($p < 0.001$), suggesting that these soil parameters had a significant impact on the soils' ability to adsorb metolachlor. As an illustration, Alletto et al. found that the soil's organic matter (OC) concentration was the main factor influencing the adsorption of metolachlor by soils. Similar reports have stated that K_f is dependent on pH, clay content, and OC in the plough layers. A hydrophobic molecule has a higher chance of emerging from the aqueous phase and making strong hydrophobic interactions with OM in soil, which could explain the substantial positive correlation between K_f and OM content of soils. Adsorption was larger with pH than with the other soil variables across all agricultural soils, and multiple regressions of the adsorption constants against chosen soil properties showed that pH was best associated to metolachlor adsorption ($R^2 = 0.83$) with adsorption increasing as pH increased (Figure 5).

Equation	P value	R^2	SE
$K_f = 4.449pH - 18.069$	0.003	0.83	1.059
$K_f = 0.214CEC - 1.649$	0.0069	0.78	0.059
$K_f = 2.536OM - 5.091$	8.8E-06	0.96	0.255
$K_f = -0.24773clay + 14.882$	0.0043	0.81	0.063
$DT_{50} = 86.25pH - 356.868$	0.0047	0.8	22.26
$DT_{50} = 50.30OM\% - 109.414$	1.26E-05	0.96	5.303
$DT_{50} = 19.028K_f - 5.1977$	1.57E-05	0.96	2.067
$DT_{50} = -4.71(clay\%) + 277.78$	0.0082	0.78	1.352
$DT_{50} = -0.169K_f + -0.481OM + 6.171$	0.000017	0.97	0.596
$GUS = -0.911OM + 7.033$	4.02E-06	0.94	0.082
$GUS = -0.0830clay + 0.123$	0.01	0.76	0.025
$GUS = -0.3449K_f + 5.147$	0.00478	0.93	0.019
$GUS = -0.08411K_f - 0.01371DT_{50} + 5.076$	0.000018	0.99	0.068

Table 6. Functions showing k_f , DT_{50} and GUS prediction.

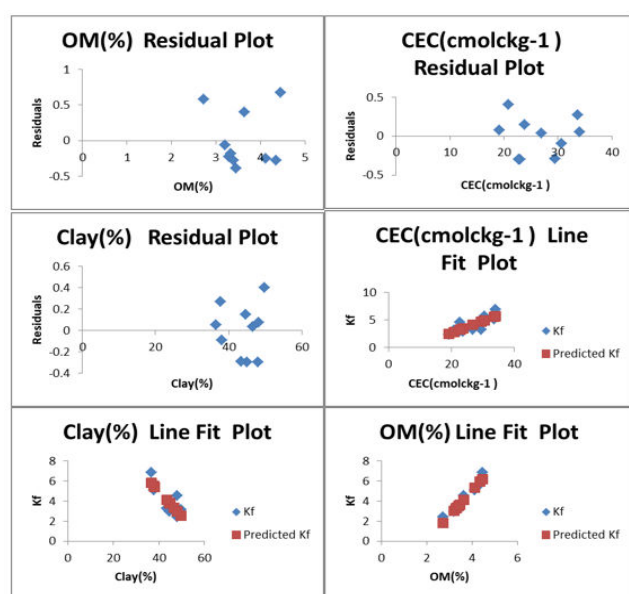


Figure 5. Regression analysis between soil properties and K_f .

Conclusion

The Freundlich isotherm was determined to best suit the experimental data out of the two isotherm models that were used, Langmuir and Freundlich, as shown by the high values of the correlation coefficients (R^2) and low standard error. The study's findings have shown that there are notable variations in the surface soils under investigation when it comes to metolachlor adsorption and degradation. Estimated K_f and K_{OC} values indicate that metolachlor has low adsorptivity in soils and will likely exhibit significant mobility. The quality of groundwater is at risk due to the low adsorption and consequently significant pesticide mobility. Metolachlor degradation was found to have a high connection with both K_f and DT_{50} when

combined. More persistence and extremely low pesticide adsorption capacity were probably the causes. In light of these findings, metolachlor may seep into the subsurface soil where it will dissolve more slowly and be more readily absorbed by groundwater. Metolachlor exhibits poor breakdown or binding to organic matter and clay minerals in the surface soil. In the examined soils, metolachlor has a strong leaching capability based on its mobility rating and GUS index. There was a correlation between the metolachlor GUS index and DT_{50} , OM, clay, and K_f . Furthermore, the results of the multiple linear regressions indicated that the GUS index depends on the combination of DT_{50} and K_f . To adopt control measures and restrict the use of metolachlor pesticide, on site research (field condition) is required in the research area's agricultural soils since the probability of pesticide contamination of groundwater may be influenced by numerous environmental conditions.

Acknowledgments

We express our gratitude to everyone who participated in the manuscript preparation review process.

Disclosure Statement

The authors assert that none of their financial or personal affiliations could have influenced the work presented in this study.

Data Availability Statement

Information will be provided upon request.

References

1. Barbieri, Maria Vittoria, Luis Simón Monllor-Alcaraz, Cristina Postigo, and Miren López de Alda. "Improved fully automated method for the determination of medium to highly polar pesticides in surface and groundwater and application in two distinct agriculture-impacted areas." *Sci Total Environ* 745 (2020): 140650.
2. Fernandes, Caroline Lopes Feijo, Lisiane Martins Volcão, Paula Florêncio Ramires, and Renata Rodrigues De Moura, et al. "Distribution of pesticides in agricultural and urban soils of Brazil: A critical review." *Environ Sci Process Impacts* 22 (2020): 256-270.
3. Negatu, Beyene, Sisay Dugassa, and Yalemshay Mekonnen. "Environmental and health risks of pesticide use in Ethiopia." *J Health Pollut* 11 (2021): 210601.
4. Teklu, Berhan M, Paulien I. Adriaanse, Mechteld MS Ter Horst, and John W. Deneer, et al. "Surface water risk assessment of pesticides in Ethiopia." *Sci Total Environ* 508 (2015): 566-574.
5. Si, Youbin, Kazuhiro Takagi, Akio Iwasaki, and Dongmei Zhou. "Adsorption, desorption and dissipation of metolachlor in surface and subsurface soils." *Pest Manag Sci* 65 (2009): 956-962.
6. Boesten JJTI, and van der Linden AMA. "Modelling the influence of sorption and transformation on pesticide leaching and persistence." *J Environ Qual* 20 (1991): 425-435.
7. Park, Jeong-Hun, Yucheng Feng, Pingsheng Ji, and Thomas C. Voice, et al. "Assessment of bioavailability of soil-sorbed atrazine." *Appl Environ Microbiol* 69 (2003): 3288-3298.
8. Alfonso, Lorenzo-Flores, Giacomán Vallejos Germán, Ponce Caballero María Del Carmen, and Ghozeisi Hossein. "Adsorption of organophosphorus pesticides in tropical soils: the case of karst landscape of northwestern Yucatan." *Chemosphere* 166 (2017): 292-299.
9. Olvera-Velona, Angeluz, Pierre Benoit, Enrique Barriuso, and Laura Ortiz-Hernandez. "Sorption and desorption of organophosphate pesticides, parathion and cadusafos, on tropical agricultural soils." *Agron Sustain Dev* 28 (2008): 231-238.

How to cite this article: Alemu, Bereket Ayenew and Endalkachew Getu. "Prediction of Adsorption Capacity, Degradation and Leaching Potential of Metolachlor in Selected Agricultural Soils of Ethiopia." *Pollution* 9 (2026): 400.