Adsorption and Desorption of Chlorsulfuron in Agricultural Soils of Mara River Basin, Kenya

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Authors' contributions

This work was carried out in collaboration between all authors. Author JAO designed the study, involved in data collection, data analysis, interpretation and wrote the first draft of the manuscript. Authors POO, COK and JOL guided on data collection, evaluation, interpretations and review. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Chlorsulfuron is a sulfonylurea herbicide widely used in Kenya to control broadleaf and grass weeds in wheat. Its sorption was studied in five wheat growing soils from Mara River Basin in Kenya using batch sorption method. Freundlich adsorption equation described the sorption mechanism of chlorsulfuron with adsorption coefficients (K_f) ranging between 0.46 and 0.75. The K_f showed positive and negative correlation ($P \leq 0.05$) with organic carbon (r = 0.7882) and soil pH (r = 0.8111) respectively. Adsorption isotherms were L-type suggesting the herbicide sorption was inversely related to the initial concentration of chlorsulfuron in solution. Desorption of the herbicide was concentration dependent and hysteresis effect was present in three soils implying that sorbed chlorsulfuron was not easily released possibly leading to phytotoxicity to rotational crops. Chlorsulfuron was poorly sorbed on to the soils demonstrating its high leaching potential onto the lower profiles and carry over that would injure susceptible plants in the future.

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1. INTRODUCTION

Sulfonylureas herbicides are assumed to be safe within the environment due to their low application rates and low toxicity to mammals [1,2]. However, wide-spread use of sulfonylureas herbicides can have devastating influence on the productivity of non-target crops, the makeup of natural plant communities and wildlife food chains [3]. Off-site transport of sulfonylureas by drift or leaching may have negative ecological effects due to their high phytotoxicity. Sulfonylureas can persist in the soil and may affect plant reproduction and crop or rotational crop yields beyond the application season [4-7]. Also, sulfonylureas are relatively mobile in soils because of their anionic character, and may leach to the groundwater. In general, sulfonylureas have been found in both surface and underground water [1,2]. Besides, the sulfonylureas pose potential risks to soil microorganisms and non-target organisms [8-10]. Chlorsulfuron is a sulfonylurea herbicide widely used as a pre- and post- emergent herbicide to control broadleaf and grass weeds in cereal crops due to its effectiveness and low mammalian toxicity [11]. In Kenya, chlorsulfuron is one of the most widely used herbicides in large scale wheat farms within the Mara River Basin. Use of chlorsulfuron reduces the growth of Pseudomonas soil bacteria [12] causing major changes in species composition and diversity thus affecting soil fertility. Despite the widespread use of chlorsulfuron, its potential hazards in the Mara Basin have not been evaluated.

The adsorption–desorption process is of great importance for evaluation of mobility of herbicides in the environment and their bioavailability to agricultural crops [13,14]. Generally sorbed chemicals are unavailable to microorganisms and plants prior to desorption [6, 15-16]. Therefore, desorption plays an important role in the biodegradation and transport of herbicides in soil. The amount and shape of soil micropores, which are related to the content of organic matter and clay, are the main factors influencing desorption of organic chemicals from soil [17]. Sorption of chlorsulfuron in soils was reported to be strongly related to the soil organic matter and pH with high sorption in soils with high organic matter and acidic pH [18,19]. Clay content has been reported to be negatively related to sorption of chlorsulfuron in three Spanish soils [20]. Despite chlorsulfuron

extensive use, very little is known about its sorption behavior under tropical conditions. This study investigated the sorption-desorption of chlorsulfuron in five typical soils from wheat fields in Mara River Basin, Kenya.

2. MATERIALS AND METHODS

2.1 Soil Sampling and Characterization

Soil samples were obtained from five wheat growing locations; Mau Central (latitude 1°06'S, longitude 35°92'E, altitude, 1902 m asml), Olokurto (latitude 0°80'S, longitude 35°89'E, altitude 2788 m asml), Mau East A (latitude 1°04S', longitude 35°16'E, altitude 2296 m asml), Ololulunga (latitude 1°01'S, longitude 35°64'E, altitude 2132 m asml) and Mau East B (latitude 1°10'S, longitude 35°15'E, altitude 1869 m asml), within the Mara River Basin, Kenya. Fifteen soil samples in each location were picked from randomly selected points, 0-20 cm depth, air dried, homogenized and sieved through 2-mm sieve and stored in plastic bags in the laboratory ensuring no possibility of exposure. The soil physical chemical parameters were determined as described previously [21]. The characteristics of the soils are shown in Table 1.

2.2 Chemicals

Chlorsulfuron (99% purity, analytical grade) (Fig. 1) was supplied by Sigma- Aldrich (Germany). Methanol and acetonitrile were of ultra-high performance liquid chromatography (UHPLC) grade. NaOH, $CaCl_2$, HCl and NaN_3 were of analytical grade. Chlorsulfuron stock solution (100 mg/l) was prepared in methanol and stored in darkness at 4°C. Details of the analytical methods for chlorsulfuron were as described previously [21].
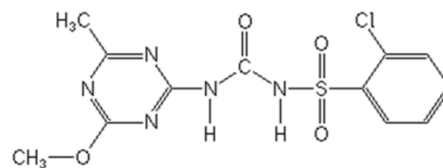
Fig 1. Chemical structure of chlorsulfuron

2.3 Adsorption and Desorption Experiments

The batch equilibrium technique [22] was used to determine the soil adsorption constants of

chlorsulfuron for all the soils samples. Triplicate samples (10 g) of air-dried soil and 10 mL of aqueous chlorsulfuron solutions at concentrations of 0.625, 1.25, 2.5, 5.0 and 10.0 mg/L was added to 50 mL polyallomer centrifuge tubes. $CaCl_2$ (0.01 M) was added as the background electrolyte, to keep the ionic strength of the soil solution constant and to facilitate flocculation. NaN_3 (1 ml) (0.01 M) was used to restrain microbial degradation. Blanks with the solutions without soil were also prepared. The tubes were shaken at 150 rpm in the dark for 24 hr at 25±2°C using an overhead mechanical shaker. After equilibration, the suspension was centrifuged at 4000 r/min for 10 min, and then the supernatant solutions decanted and filtered through a 0.45-µm filter. Chlorsulfuron quantitation was done using a HPLC-MS.

The amount of herbicide adsorbed by each soil was calculated from the difference between the initial and final concentrations of chlorsulfuron in solution.

Desorption experiments were performed immediately after decanting the supernatant and adding same volume of 0.01 M $CaCl_2$ solution into the tubes. The soils were re-suspended by shaking the tubes at 150 rpm for a further 24 h. After equilibration, the suspension was centrifuged at 4000 r/min for 10 min, and then the supernatant solutions decanted, filtered through a 0.45-µm filter and chlorsulfuron present in the samples quantified by HPLC –MS. The process was repeated three times. The amount of chlorsulfuron desorbed was calculated as amount of pesticide released into the solution during the process and expressed as a percentage of the amount adsorbed. Sorption isotherms were obtained by plotting the amount of chemical sorbed per unit weight of soil at equilibrium versus chlorsulfuron concentration at equilibrium.

2.4 Limit of Detection (LOD) and Limit of Quantification (LOQ)

Validation of the method was performed with different known concentrations of chlorsulfuron in methanol by diluting the stock solution of the analytical standard in the range of 0.01-5 mg/l. Recovery study was conducted by spiking 0.4 mg kg^{-1} and 4 mg kg^{-1} chlorsulfuron in soil, and recoveries of 92.1% and 88.3%, respectively were achieved. The limit of detection based on the signal to noise ratio of 3:1 was established as 0.003 mg kg^{-1} in soil.

2.5 Data Analysis

The amount of chlorsulfuron adsorbed after equilibrium was calculated according to the difference between the initial and final equilibrium concentrations by following Eq. (1):

$$S_e = (Co - C_e) * V/m \qquad (1)$$

where S_e (mg/ Kg) was the amount of chlorsulfuron adsorbed by a soil; C_o (mg/L) and C_e (mg/L) were the initial and equilibrium aqueous concentrations, respectively. V (L) was the solution volume; m (Kg) the mass of the soil [22].

Amount of chlorsulfuron desorbed from the soils was calculated by following Eq. (2):

$$S_{des} = \{C_{des} - \{C_e * (V- V_{ex})/V\}\}*V/m \qquad (2)$$

where S_{des} (mg/Kg) was the amount of chlorsulfuron released from the soil; C_{des} (mg/L) was the analytically determined chlorsulfuron concentration; V_{ex} (L) is the volume of chlorsulfuron solution removed from each tube and replaced by the same volume of 0.01M $CaCl_2$.

Adsorption and desorption were described by the linearized form of the Freundlich Eq. (3):

$$logS_e = logK_f + 1/n_flogC_e \qquad (3)$$

where, K_f was the adsorption coefficient characterizing the adsorption- desorption capacity, and n_f was the Freundlich equation exponent related to the adsorption intensity that was used as an indicator of the adsorption isotherm nonlinearity [22]. K_{f-ads} and K_{f-des} were the adsorption and desorption coefficients of the Freundlich equation respectively.

The OC normalized adsorption constant (K_{OC}) was calculated by normalizing K_{f-ads} to the fraction of OC [23] as in Eq. (4):

$$K_{OC} = K_{f-ads} /OC * 100\% \qquad (4)$$

The hysteresis coefficient, H, for the adsorption and desorption isotherms was calculated according to Eq. (5):

$$H = (1/n_{f-des})/ (1/n_{f-ads}) \qquad (5)$$

Where, n_{f-ads} and n_{f-des} were the Freundlich constants obtained for the adsorption and desorption isotherms, respectively [24].

The statistical analysis was done using MSTATC as a factorial one design and the separation of means done by least significance difference (LSD) at p≤0.05.

3. RESULTS AND DISCUSSION

The physicochemical parameters of the five soils studied are presented in Table 1. Mau East A had the lowest pH (5.47) and increased in the order Mau East A< Mau central< Olololunga < Olokurto< Mau East B. Mau east A soil had the highest organic carbon content (3.88%) while Mau East B had the lowest (2.71).

% clay content was in the order Mau East B > Mau central > Olololunga> Mau East A > Olokurto. The soils from Mau Central, Olokurto and Olololunga were classified as clay loam, Mau East A soils as sandy clay loam and soils from Mau East B were classified as clay. All the soil physicochemical parameters determined varied significantly (P =.05) with the sites. Soil physicochemical parameters highly influence the sorption of sulfonylurea herbicides. Medium- and fine-textured soils with organic matter content of more than 3 percent have the greatest potential to bind or hold herbicides and injure sensitive rotation crops [25]. Since all soils were medium textured the adsorption of the herbicide was expected to be high. The persistence and activity of the sulfonylureas were affected by soil pH. At soil pH of 7.0 and greater, some sulfonylurea herbicides tend to persist for longer periods [26]. The soils in Mara River Basin had pH below7.0; therefore the adsorption of chlorsulfuron was expected to be low. Percent clay content, OC content and pH were reported to be the main properties that determine the extent of adsorption for sulfonylurea herbicides [27,28], with high adsorption in soils with high clay and OM content and pH. Soil moisture content below the permanent wilting point resulted in a loss of herbicidal activity since virtually all of the herbicide were adsorbed to the soil and could not move to the plant by diffusion or mass movement [29]. Sulfonylurea herbicides had high carryover under dry soil conditions because of tight sorption of the herbicides to the soil colloids due to low soil moisture content [30]. Based on the results above, Mau East B and Mau Central soils with low moisture content the amount of herbicide adsorbed onto the soils would be high and hence insufficient herbicide could be available to the soil solution for effective weed control. On the contrary for Mau East A, Olokurto and Olololunga soils with high moisture content,

more herbicide would be released on to the soil solutions therefore posing leaching risks to the surface and underground waters.

3.1 Sorption Kinetics

Sorption of chlorsulfuron with time was plotted (Fig. 2) and was biphasic in all the soils. The first phase was characterized by quick increase in sorbed chlorsulfuron during the first 3 hours of soil- solution contact followed by slower progress towards equilibrium at 12 hours (Fig. 1). After 12 h, chlorsulfuron sorption slowed and change in chlorsulfuron concentration did not vary after 24 hours. The adsorption equilibrium was reached after 12 h for all soils, although the amounts adsorbed per mass of soil varied and increased in the order Mau East B< Olokurto<Mau Central <Olololunga<Mau East A indicating that the sorption kinetics of chlorsulfuron in the wheat growing soils of Mara River Basin was dependent on soil pH, moisture content and soil organic content.
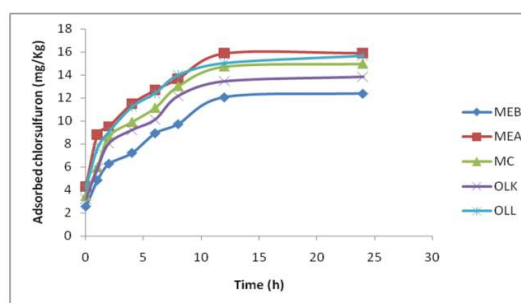

Fig 2. Kinetics of chlorsulfuron (10 mg/L initial concentration) sorption in the soils at 25±2°C

MEA- Mau East Central; MEB-Mau East B; MC-Mau Central; OLK- Olokurto; OLL- Olololunga

Chlorsulfuron was rapidly adsorbed during the first stage since the soils had readily available vacant adsorption sites. A pesticide mixed with soil reacts with the active sites that are available on the soil surfaces [31]. Some of the soils were very reactive, and held the pesticide strongly, while others had lower reactivity which resulted in different adsorption kinetics. The loosely bound pesticide molecules desorbed, so that the adsorption and desorption processes occurred concurrently, but the adsorption efficiency was greater than that of desorption [31]. The soil adsorption-desorption behavior of pesticides reported by Gilchrist et al. [31] were similar to the soil adsorption kinetics of chlorsulfuron observed. The results imply that if low levels of

chlorsulfuron are applied in the Mara River Basin soils, most of it will be adsorbed onto the soil colloids decreasing the amount of herbicide available for the control of weeds in wheat.

3.2 Sorption Isotherm

The sorption of chlorsulfuron in the soils was fitted into the Freundlich model. The adsorption coefficients K_{f-ads} were 0.46 (Mau East B), 0.57 (Olokurto), 0.61 (Mau Central), 0.73 (Olololunga) and 0.75 (Mau East A) for chlorsulfuron (Table 2). Mau East A soils showed the maximum sorption possibly due its low pH and the high organic matter content as had been observed in previous studies [19,29].

Chlorsulfuron is a weakly acidic herbicide and exists in the anionic form in mildly acidic agricultural soils. Since the pH of the soils were greater than their pK_a (3.3), especially for soils at Olokurto and Mau East B, there were increased amounts of anionic molecules in the solutions leading to lack of charged molecules and higher lipophilicity of the neutral molecular species thus reducing its sorption. High organic carbon content in Mau East A soil compared to the rest could be responsible for the high adsorption coefficient [26]. Increase in soil pH increased solubility of molecules due to either particle dispersion increase or the repulsion of the increasing negative charges on both organic matter and soil inorganic solids [32]. Since the

pH of soils at Olololunga, Olokurto, Mau Central and Mau East B were higher than Mau East A; there was increase in dissolved organic matter in the soil solutions consequently reducing the sorption ability of the soils, compared to Mau East A. Sorption of sulfonylureas has been shown to be favoured in low pH soils and soils with high organic matter [33]. The extent of monosulfuron adsorption on soils was at rather high levels under low pH value conditions, and it decreased with increasing pH value. The content and chemical characteristic of the soil organic matter was one of the important factors leading to differences in sorption capacity of monosulfuron ester [34].

Generally, chlorsulfuron sorption onto the five soils from the Mara River Basin was low as predicted by the low K_d values (0.59 – 2.52) thus raising concerns about its leaching potential. Alvarez-Benedi et al. [20] reported low sorption for chlorsulfuron in three Spanish soils with increase in ionic strength. Similarly, low sorption of chlorsulfuron was reported in fresh and amended soils with composted olive cake [35]. These results were also supported by [36] who also reported low sorption of [14]C- chlorsulfuron in fourteen Chinese soils. Sorption of chlorsulfuron in all the five soils was nonlinear, since all the $1/n$ values were less than unity (Fig. 3). This predicted the L-type adsorption isotherm usually characterized by strong interaction between the adsorbent and adsorbate [37], implying that

Table 1. Physico-chemical parameters of wheat growing soils within Mara River Basin

Site	pH	% MC	CEC	% OC	% sand	% clay	% silt	Texture
Mau Central	5.53	10.48	22.95	2.89	27.00	38.00	35.00	Clay loam
Mau East A	5.47	13.24	17.54	3.88	45.67	33.00	21.33	Sandy loam
Olokurto	6.13	11.17	22.68	2.83	33.33	32.00	34.67	Clay loam
Olololunga	5.62	11.78	17.64	3.18	31.33	36.67	32.00	Clay loam
Mau East B	6.57	9.116	28.24	2.71	22.33	44.00	33.67	Clay
LSD (*P*=.05)	0.12	1.14	0.09	0.02	0.56	1.63	0.53	

MC-Moisture content; CEC- cation exchange capacity; OC-organic carbon

Table 2. Chlorsulfuron: adsorption isotherms, coefficients of determination (r^2), adsorption coefficient (K_{f-ads}), distribution coefficient (K_d), organic carbon-normalized distribution coefficients (K_{oc}) and n_{f-ads} is a describer of adsorption isotherm curvature in topsoil of Narok soils

Soil	K_d	K_{OC}	K_{f-ads}	$1/n_{f-ads}$	r^2	P≤0.05
Mau Central	0.88±0.03	21.03	0.61±0.07	0.87± 0.11	0.978	0.00
Mau East A	2.52±0.07	19.54	0.75±0.13	0.91±0.08	0.890	0.04
Olokurto	1.87±0.11	21.58	0.57±0.11	0.99±0.21	0.983	0.00
Olololunga	2.35±0.03	22.93	0.73±0.03	0.86±0.10	0.939	0.01
Mau East B	0.59±0.09	15.91	0.46±0.08	0.99±0.05	0.986	0.00

chlorsulfuron could adsorb to the clay fraction of the soils as well as the organic matter in the soils. Nemeth- Konda et al. [38] described this type of curve in the case of cultivated soils in Hungary. For the Mara River Basin soils, the L-type curve could have been caused by decrease of accessibility of the free adsorption sites in the soils and subsequently decreased adsorbed amounts even when chlorsulfuron concentration was high.
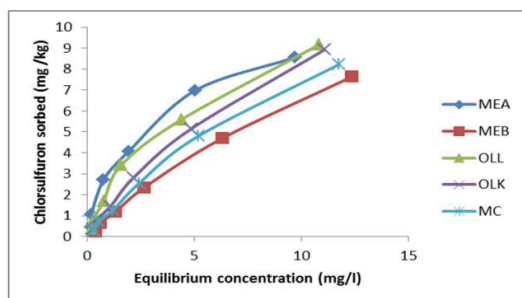

Fig 3. Sorption isotherms of chlorsulfuron in soils of Mau East A (MEA), Mau East B (MEB), Mau Central (MC), Olokurto (OLK) and Olololunga (OLL)

The sorption coefficient K_{oc} is commonly a measure of pesticide sorption to soil organic carbon and is useful in predicting the mobility of soil contaminants. Higher K_{oc} values (50-150) correlate with less mobile organic chemicals while lower K_{oc} values (< 50) correlate to more mobile organic chemicals [39]. The K_{oc} values calculated by normalizing chlorsulfuron sorption to soil organic carbon in all the five soil types were below 50 suggesting that chlorsulfuron could be more mobile in these soils which could lead to its leaching into the sub soils. The correlation of the sorption coefficient K_{fads} and the soil properties was done to determine the factors responsible for chlorsulfuron adsorption in the five soils. Sorption of chlorsulfuron showed an inverse correlation with the soil pH and a positive correlation with the organic carbon content (Table 3). This further confirmed that soil organic carbon and

pH affected the sorption of chlorsulfuron in the soils.

Similar observations have been reported for other sulfonylureas. Negative correlation (r = 0.993, P =.05) was reported between soil pH and metsulfonyl-methyl sorption but not with organic matter [33]. Monosulfuron sorption was inversely correlated to pH (r = -0.783, p≤0.01) and positively correlated to organic matter (r = 0.848, P =.05) [34]. Similarly, a correlation coefficient (r) of -0.87 (P =.05) between pH and sorption of metsulfuron methyl has been reported [40]. The sulfonylureas adsorptions were higher in soils with low pH and high with organic matter [41,42]. Although Alvarez-Benedi et al. [20] observed that the sorptions of chlorsulfuron, tribenuron-methyl and imazamethabenz-methyl were positively correlated with organic matter and clay content, no positive sorption correlation with clays was observed in this study. Mau East B soils with the highest clay content had a lower adsorption coefficient. Due to anionic nature, sulfonylureas generally exhibit very low adsorption on clay minerals especially at a pH above their pKa, as more of the herbicide is in anionic form and repelled by the negatively charged soil colloids. However, there have been instances of binding of sulfonylurea herbicides to clay. Soils containing amorphous iron oxides have a high capacity for adsorption of sulfonylureas although the forces are relatively weak [18]. These results imply that chlorsulfuron applied on the wheat growing soils within the Mara River Basin was lowly sorbed on the soils therefore the herbicide was available for herbicidal activity. On the contrary, this low sorption could make the herbicide easily available to the soil solution thus increasing the leaching potential to the surface and underground waters.

3.3 Desorption Isotherms

Desorption isotherms were fitted to the Freundlich isotherm and the constants are as shown in Table 4.

Table 3. Coefficient of determination (r) values for chlorsulfuron sorption

	pH	CEC	OC	Sand	Clay	Silt
Kf	-0.8111*	-0.3163	0.7882*	-0.7719	-0.6286	-0.6607
P	0.004	0.3732	0.0068	0.1262	0.2560	0.2248

Significant at P =.05; these values were obtained by determining the correlations between Freundlich coefficient (Kf) and the soil properties

Table 4. Chlorsulfuron desorption isotherms, coefficients of determination (r^2), desorption coefficient (Kf_{des}) and hysteresis coefficient (H) obtained for the top soils of Mara River Basin

Soil	$K_{f\text{-}des}$	$1/n\text{-}_{f\ des}$	r^2	P =.05	Hysteresis (H)
Mau Central	1.16	0.89	0.982	0.02	1.02
Mau East A	2.49	0.73	0.962	0.00	0.80
Olokurto	1.44	1.10	0.988	0.01	1.11
Olololunga	1.90	0.55	0.972	0.01	0.63
Mau East B	1.03	0.72	0.952	0.05	0.72

The Kf_{des} values of chlorsulfuron in all the five soils were higher than the Kf_{ads} implying that the sorption process was not fully reversed and some sorbed chlorsulfuron was retained in the soils [43]. Soils from Mau East A had the highest Kf_{des} suggesting it retained more chlorsulfuron compared to the other soils, while the Mau East B soil had the lowest. Desorption isotherms were nonlinear ($1/n_{des}$<1) for all the soils except Olokurto. Two soils from Mau Central and Olokurto had higher values of $1/n_{des}$ than their respective $1/n_{ads}$ suggesting the rates of desorption for these soils were faster than adsorption [44]. Studies by Mersie and Foy [45] also reported nonlinearity of chlorsulfuron desorption in soils. This observation has also been reported for other sulfonylureas such as bensulfuron [35]. Soils from Mau East A, Olololunga and Mau east B had lower $1/n_{des}$ than their respective $1/n_{ads}$, implying that chlorsulfuron adsorbed on these soils were not easily desorbed. Therefore the herbicide applied in these soils will have decreased herbicidal activity and a greater potential for carryover, hence injuring susceptible crops in the future.

The hysteresis coefficient, H, is a measure of the extent of hysteresis in desorption. A value of H>1 means that desorption proceeds as fast as adsorption and no hysteresis occurs. However if the value, a value of H < 1 indicates that the rate of desorption is slower than the rate of adsorption, and therefore hysteresis occurs [46]. The H values for the soils ranged from 0.63-1.11 (Table 4), with Mau East A, Olololunga and Mau East B showing hysteresis effect.

Desorption hysteresis has been reported for several sulfonylureas with varying H values including monosulfuron which had hysteresis effects in eight Chinese soils with H values ranging from 0.14 to 0.63 [34], metsulfuron-methyl (0.79 - 0.98) and sulfosulfuron (H= 0.87) [43] and H of 0.35-0.64 for monosulfuron-methyl [33], primisulfuron [47], triasulfuron [48] and chlorimuron-ethyl [49]. Hysteresis effect can be as a result of irreversible binding and sequestration of solute to the OC and/ or clay mineral of soil aggregates [49,50] and entrapment of sorbed molecules in meso and microporous structures within the mineral structures and OC matrix of soil aggregates [51]. Chemical or biological transformation, non-equilibrium conditions and high–energy bonding have also been proposed as explanation for hysteresis for a number of soil organic compound systems [34,48,51]. In the two soils; Mau Central and Olokurto, the desorption rates were faster than adsorption rates suggesting that chlorsulfuron initially sorbed is readily released into the solution therefore higher leaching potential in to the surface and underground waters for the two soils. Sorption-desorption studies indicated that chlorsulfuron was weakly sorbed on the Mara River basin soils and the process was dependent on the soil physicochemical parameters. The low sorption implied that within the basin chlorsulfuron had a potential of leaching to the surface and ground waters. Soil pH and soil organic matter were the main factors that affected sorption of chlorsulfuron. There was hysteresis effect in three soils as chlorsulfuron sorbed was not easily desorbed. This phenomenon may lead to injury of susceptible plants in the future due to carryover.

4. CONCLUSIONS

Chlorsulfuron dissipation within the five wheat growing regions is dependent on the soil physicochemical parameters of the soils on which it is applied. However it is positively influenced by soil organic matter while negatively correlated to the soil pH. This implies that in soils with high soil organic matter, more herbicide will be adsorbed therefore reducing the bioavailability of the herbicide for weed eradication. Moreover its weak adsorption on to the wheat growing soils of the Mara River Basin raises its leaching potential into the subsurface and ground waters.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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