UNDER PEER REVIEW

Original Research Article

Effect of Copper (II) on the Sorption/Desorption of Chlorsulfuron In Five Wheat Growing Regions of the Mara River Basin, Kenya.

ABSTRACT

Aim: To study the effect of copper ions on the sorption and desorption of chlorsulfuron in five wheat growing soils from Mara River Basin, Kenya.

Study design: The experiments were laid down in a Completely Randomized Design (CRD) with three replications. Control experiments were carried our using soils without history of application of chlorsulfuron.

Place and duration of study: Department of Chemistry, Maseno University and Centre of Analytics, Jülich Research Centre from April 2014 to May 2015

Methodology: Adsorption of chlorsulfuron (0.625–15mgl^{-1}) in the presence of Cu^{2+} (0, 50 and 100 mg l^{-1}) was studied using batch sorption method and the data fitted on Freundlich adsorption equation. Fourier Transform Infrared (FTIR) analysis was done to one soil type to establish the mechanism of sorption on soil.

Results: Chlorsulfuron was sorbed on the soils with adsorption coefficients (K_f) ranging between 0.51 and 1.49. Increasing Cu^{2+} concentration increased the sorption of chlorsulfuron in all the five soils possibly due to decreased equilibrium solution pH and formation of Cu-chlorsulfuron complexes which were preferentially sorbed via the carboxylic and hydroxylic functional groups of the soil. Moreover, Cu^{2+} decreased hysteresis effects on desorption of chlorsulfuron.

Conclusions: The increase in sorption of chlorsulfuron in the presence of Cu^{2+} could suppress the bioactivity of the herbicide. However, Cu^{2+} decreased hysteresis effects on desorption of chlorsulfuron implies that more of sorbed chlorsulfuron can be released to the soil solution increasing the leaching potential onto the lower profiles and surrounding aquatic systems.

Keywords: Chlorsulfuron, Copper, Adsorption, desorption, Mara River Basin

UNDER PEER REVIEW

1. INTRODUCTION

Chlorsulfuron is a sulfonylurea herbicide widely used in wheat crops for its good agronomic characteristics and low toxicity to mammals [1]. It is selective and effective both pre and post emergence at field doses as low as 10-40 g a.i. ha-1 against a wide spectrum of broad-leaved weeds [1]. In Kenya, chlorsulfuron is one of the most widely used herbicides in large scale wheat farms within the Mara River Basin. Its adsorption–desorption process is of great importance for evaluation of mobility of herbicides in the environment and their bioavailability to agricultural crops [2-3]. Chlorsulfuron adsorption in soil is affected by several physicochemical parameters including soil properties like soil organic matter (SOM), clay content, pH and environmental factors including soil moisture and temperature [4-6]. Previous studies have reported that chlorsulfuron adsorption is positively correlated to high SOM and clay content [7] and negatively correlated to soil pH [8].

Copper, is an essential micronutrient for normal growth and metabolism of plants [9], with important roles in protein and carbohydrate metabolism as well as enzymatic systems [10]. The soils within Narok District (part of Mara River Basin) have been classified as copper deficient [11-13] and therefore the use of copper fertilizers has been recommended to optimize wheat yields. Different types of copper foliar fertilizers such as copper sulphate, copper oxychloride and copper chelate are used in the region to correct copper deficiency in wheat farming [11,14].The timing of the foliar fertilizer application is crucial for maximum grain yield and it is recommended that it be applied early, not later than the 6th leaf stage [15]. This timing sometimes coincides with the application of chlorsulfuron herbicide potentially causing an interaction between Cu and chlorsulfuron which might lead to changes in the adsorption and desorption patterns of chlorsulfuron. Several studies have reported the deficiencies on the uptake and utilization of copper in wheat by chlorsulfuron [16-18] , but there is limited information on effect of copper on the behavior of chlorsulfuron in soil. Interactions of sulfonylurea with metallic cations have been reported. Cu (II) increased the sorption of metsulfuron- methyl to peat and soil through the formation of Cu-Me complexes [19] while the presence of Cu (II) in the soils promoted the adsorption of chlorimuron ethyl by slightly altering the pH of the soil-solution [20]. It is not documented, if there is an interaction between copper ions and chlorsulfuron in the soils within Mara River Basin. This study investigated the interactive effects of copper ions on chlorsulfuron in five typical soils from wheat fields in Mara River Basin, Kenya.

2. MATERIAL AND

2.1 Soil sampling and characterization

Soil samples were obtained from five wheat growing locations; Mau Central (latitude 1o06'S, longitude 35°92'E, altitude, 1902m asml), Olokurto (latitude 0o80'S, longitude 35°89'E, altitude 2788 m asml), Mau East A (latitude 1o04S', longitude 35°16'E, altitude 2296 m asml), Ololulunga (latitude 1o01'S, longitude 35°64'E, altitude 2132 m asml) and Mau East B (latitude 1o10'S, longitude 35°15'E, altitude 1869 m asml), within the Mara River Basin, Kenya. The soils were sampled in triplicate from randomly selected points, 0- 20cm depth, air dried, homogenized and sieved through 2-mm sieve and stored in plastic bags in the laboratory ensuring no possibility of exposure. Soil pH was measured with a glass electrode in 1:2.5 1M $CaCl_2$ [21]. Texture of the soils was analyzed by the hydrometer technique [22]. Organic carbon was determined by the LECO RC612 multiphase carbon analyser (Mönchengladbach, Germany), cation exchange capacity (CEC) by ammonium acetate exchange [23] and total copper content in the soils was determined using a Thermo Scienitific iCAP6500 Inductively Coupled Plasma with Optical Emission Spectrophotometer (ICP-OES) after HF-HClO4-HCl digestion [24]. The characteristics of the soils are shown in Table 1.

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

Site	pH	% MC	CEC	% OC	% Sand	% Clay	% Silt	Cu (ppm)	Texture
Mau	5.53	10.48	22.95	2.89	27.00	38.00	35.00	5.67	Clay loam

UNDER PEER REVIEW

Central									
Mau East A	5.47	13.24	17.54	3.88	45.67	33.00	21.33	7.33	Sandy loam
Olokurto	6.13	11.17	22.68	2.83	33.33	32.00	34.67	6.33	Clay loam
Olololunga	5.62	11.78	17.64	3.18	31.33	36.67	32.00	4.00	Clay loam
Mau East B	6.57	9.116	28.24	2.71	22.33	44.00	33.67	9.33	Clay

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

2.2. Chemicals

Chlorsulfuron (99% purity, analytical grade) was supplied by Sigma- Aldrich (Germany). Methanol and acetonitrile were of ultra-high performance liquid chromatography (UHPLC) grade. NaOH, CaCl2, HCl and NaN3 were of analytical grade. Copper (II) ions were used as analytic grade copper nitrate salt. Chlorsulfuron stock solution (100mg/l) was prepared in methanol and stored in darkness at 4oC. Copper (II) ions (100 mg/l) stock solution was prepared in Millipore water.

2.3 Sorption and desorption of chlorsulfuron as affected by copper ions

The batch equilibrium sorption experiments [25] were carried out in triplicate by mixing 2g of soil samples with 10 ml background solution containing various concentrations of chlorsulfuron (0.625–15mgl–1) and Cu2+ (0, 50 and 100 mg l–1) in 50-ml glass centrifuge tubes sealed with Teflon-lined screw caps. The background solution was 0.01M CaCl2 solution containing 100 mg l–1NaN3 as a biocide. The initial pH of the solutions were recorded and the tubes shaken in an overhead shaker (150 rpm) at 25°C for 24 hours in the dark. After equilibration, the tubes were centrifuged at 4000 r/min for 10 minutes. The pH of the equilibrium solution was recorded and a 5-ml aliquot of supernatant was removed and filtered through 0.45-µm pore-size cellulosic membrane filters, transferred into vials and stored at 4◦C before analysis. The concentration of chlorsulfuron in the supernatant was determined by HPLC-MS. Control samples were also treated in the same way to quantify the loss of chlorsulfuron through mechanisms other than sorption to soils.

HPLC-MS analyses were performed using an Agilent (Palo Alto, CA, USA) 1100 Module equipped with a quarternary pump, an autosampler and a column oven. Separation was achieved on a Kinetex™ 2.6 µm Biphenyl 100 Å column (Phenomenex, Germany, 100 mm × 4.6 mm) kept at 27 ℃ during analysis. The mobile phases were 100% water (A) and acetonitrile-0.1% formic acid (v/v) (B). Chlorsulfuron was eluted with the following gradient program: from 95% A at t = 0 to 5% A at t = 15 min, maintaining at 5% for 5 min and returning to 95% A up to t = 26 min at a constant flow rate of 700 µl min-1. The injection volume was 10 µl.

The HPLC was interfaced with a 4000 Q-TRAP MS (ABSciex, Darmstadt, Germany) fitted with a ESI-Turbo Ion spray Source. Quantification of chlorsulfuron was done using the multiple reaction monitoring (MRM) mode. The transitions were m/z 358 →167, 358→ 141, 360→167 and 360 → 141. All analyses were performed in the positive mode using the following settings: de-clustering potential 50 arbitrary units; Ion spray 5500 eV, curtain gas (nitrogen) 20 arbitrary units, temperature of the source 500 ℃, nebulizer gas (nitrogen) 50 psi and heater gas (nitrogen) 50 arbitrary units at a flow rate of 0.8 l min^{-1}; collision energy 20 eV and cell exit potential of 10 V. MultiQuant 2.0 was used for MS data processing. The

UNDER PEER REVIEW

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

The desorption experiments were conducted by adding an extra amount (5 ml) of freshly prepared background solutions to the soils remaining in the centrifuge tubes and maintaining the total amount of the solution exactly at 10 ml. The soil in the centrifuge tubes was re-suspended using a vortex mixer and then the suspensions were agitated in an overhead mechanical shaker at 150 rpm for 24 hours to attain a desorption equilibrium. Subsequently, the desorbed solutions were centrifuged, decanted and analyzed as described for the sorption experiment.

2.3.1 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 0.4mg kg-1 and 4mg 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.

2.3.2 Fourier Transform Infrared (FTIR) Analysis

In order to identify the adsorption sites of chlorsulfuron and Cu2+ on the soil matrix, an FTIR spectral study was performed [20]. To 100 mg of the soils, 1 ml of 100 mg l-1 initial concentration of both chlorsulfuron and Cu2+ was added. Controls of 100mg l-1 chlorsulfuron mixed with the soils and 100mg l-1 Cu2+ solutions mixed with soils and a blank of the soils with 0.01 M CaCl2 solutions were also prepared. The suspensions were equilibrated for 16 hours, and the aqueous solutions decanted. The sorption process was repeated three times and after the third process the aqueous suspensions were filtered through a 0.45µm cellulosic membrane. The soil samples on the filter were freeze-dried and the soil removed from the filter by running it over a knife edge. FTIR were recorded on an RX FTIR spectrometer (Perkin-Elmer, Germany) equipped with a deuterated L-alanine doped triglycine sulfate detector and a KBr beamsplitter in the range of 700- 4000cm-1 with a resolution of 4.0 cm-1 from a collection 500 scans per sample.

2.3.3 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):

$$Se = (Co - Ce) * V/m \quad (1)$$

where Se (mg/ Kg) was the amount of chlorsulfuron adsorbed by a soil; Co (mg/L) and Ce (mg/L) are the initial and equilibrium aqueous concentrations, respectively. V (L) is the solution volume; m (Kg) is the mass of the soil [25].

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

$$Sdes = \{Cdes - \{Ce * (V- Vex)/V\}\}*V/m \quad (2)$$

UNDER PEER REVIEW

where Sdes (mg/Kg) was the amount of chlorsulfuron released from the soil; Cdes (mg/L) was the analytically determined chlorsulfuron concentration; Vex (L) was the volume of chlorsulfuron solution removed from each tube and replaced by the same volume of 0.01M CaCl2.

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

$$\text{Log Se} = \log Kf + 1/nf \log Ce \qquad (3)$$

where, Kf was the adsorption coefficient characterizing the adsorption- desorption capacity, and nf is the Freundlich equation exponent related to the adsorption intensity that is used as an indicator of the adsorption isotherm nonlinearity [25]. Kf-ads and Kf-des were the adsorption and desorption coefficients of the Freundlich equation respectively.

The OC normalized adsorption constant (KOC) was calculated by normalizing Kf-ads to the fraction of OC [26] as in Eq. (4):

$$KOC = Kf\text{-}ads / OC * 100\% \qquad (4)$$

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

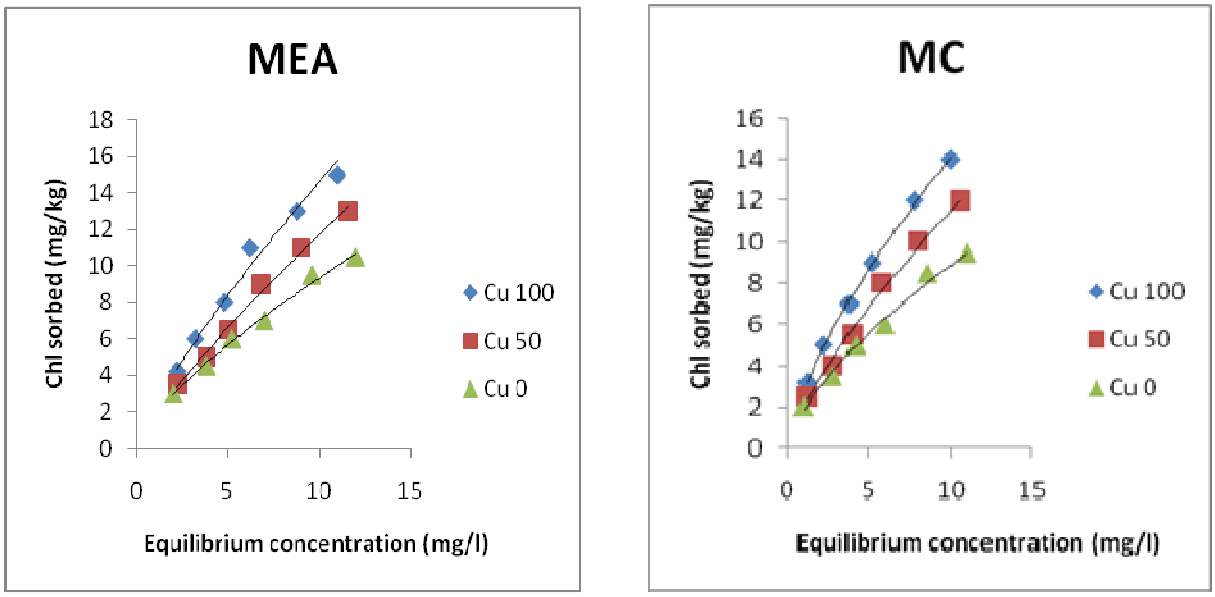
$$H = (1/nf\text{-}des)/ (1/nf\text{-}ads) \qquad (5)$$

Where, nf-ads and nf-des were the Freundlich constants obtained for the adsorption and desorption isotherms, respectively.

3. RESULTS AND DISCUSSION

3.1.Interaction of copper ions with chlorsulfuron

Sorption isotherms of chlorsulfuron in the five soils in the absence and presence of Cu (II) were fitted in the Freundlich equation. The presence of Cu (II) ions in the solution increased the adsorption of chlorsulfuron in all the soil types and the effect was more pronounced with increase in the concentration of Cu^{2+} (Figure 1). However, these increases caused by Cu^{2+} ions were seen more significantly at equilibrium concentrations > 5 mg/L.



UNDER PEER REVIEW

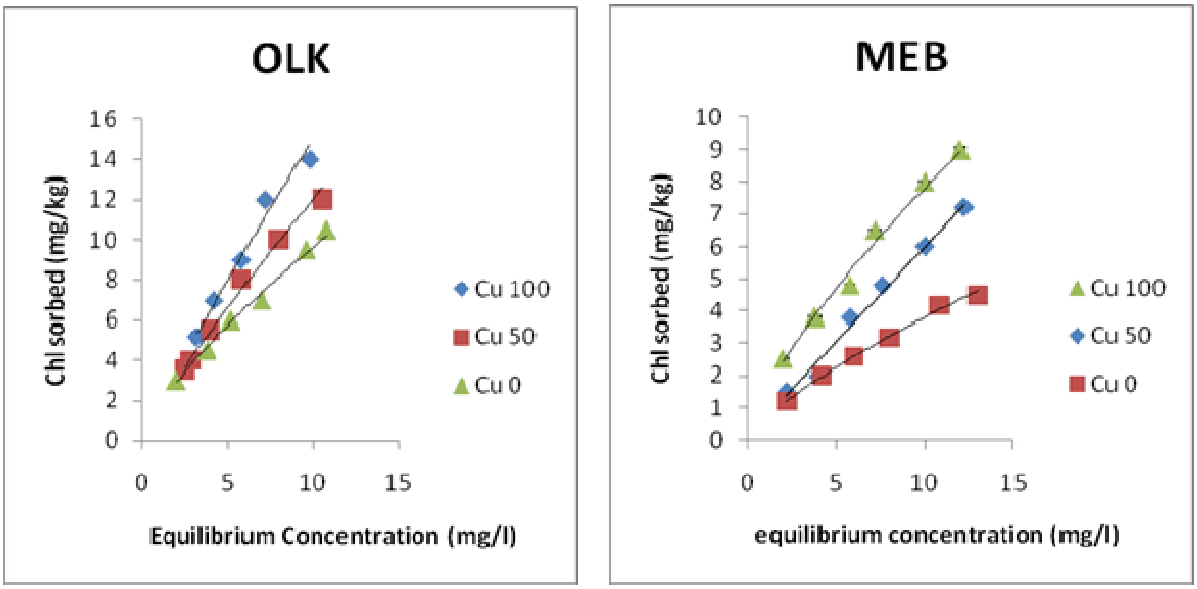


Figure 1. Sorption isotherms of chlorsulfuron in Mau Central (MC), Mau East A (MEA), Olokurto (OLK) and Mau East B (MEB) soils in presence and absence of Cu (II).

The adsorption constants K_f; which gives an estimate of the extent of adsorption at a concentration and *n* which represents the variation in adsorption with concentration of the herbicide are presented in Table 2. Mau East A soil showed the highest sorption for chlorsulfuron while soil Mau East B had the lowest sorption. The sorption of chlorsulfuron in the absence and presence of Cu (II) ions for the five soils was in the order Mau East A > Olololunga > Olokurto >Mau Central>Mau East B.

Table 2: Freundlich constants (K_f and n) and coefficient of determination (r^2) for chlorsulfuron sorption on Mau Central (MC), Mau East A (MEA), Olokurto (OLK), Olololunga (OLL) and Mau East B (MEB) soils.

		Sorption			Desorption			
	Cu^{2+} mg l^{-1}	K_f	n	r^2	K_f	n	r^2	H
MC	0	0.55±0.04	0.76±0.07	0.985	0.77±0.04	0.71±0.03	0.987	0.93
	50	0.64±0.03	0.73±0.04	0.966	0.91±0.02	0.69±0.05	0.994	0.95
	100	0.81±0.09	0.64±0.08	0.976	1.04±0.05	0.66±0.03	0.989	1.03
MEA	0	0.79±0.07	0.77±0.04	0.990	1.01±0.05	0.71±0.05	0.996	0.92
	50	1.12±0.13	0.81±0.10	0.993	1.36±0.09	0.78±0.09	0.981	0.96
	100	1.49±0.24	0.75±0.05	0.998	1.65±0.05	0.79±0.04	0.992	1.05
OLK	0	0.64±0.05	0.72±0.05	0.938	0.89±0.04	0.67±0.04	0.988	0.93
	50	0.82±0.03	0.75±0.07	0.986	1.02±0.07	0.76±0.05	0.990	1.01
	100	1.14±0.05	0.76±0.02	0.966	1.29±0.09	0.77±0.11	0.983	1.01
OLL	0	0.71±0.06	0.84±0.09	0.992	0.99±0.07	0.77±0.07	0.967	0.91
	50	0.93±0.05	0.91±0.11	0.988	1.13±0.12	0.87±0.05	0.975	0.95
	100	1.37±0.16	0.77±0.03	0.965	1.48±0.06	0.78±0.05	0.991	1.01
MEB	0	0.51±0.23	1.01±0.08	0.991	0.69±0.08	0.98±0.02	0.989	0.94
	50	0.59±0.09	1.14±0.13	0.993	0.75±0.03	1.14±0.04	0.998	1.00
	100	0.72±0.06	0.99±0.05	0.991	0.97±0.05	1.04±0.06	0.986	1.05

With increasing concentration of Cu^{2+}, the *n* values for all the five soils gradually decreased. For all the soils the K_f values in the presence of copper ions were greater than those obtained in Cu^{2+} absence (Table 2), indicating increase in sorption. Changes in sorption of herbicide in the presence of cations have also been observed by [20] for Cu ions which significantly increased the sorption of chlorimuron-ethyl

UNDER PEER REVIEW

in two Chinese soils. Similarly, the presence of Cu^{2+} in soil solution increased the sorption of anionic metsulfuron-methyl in soil and peat by decreasing the repulsion between soil surface and metsulfuron-methyl herbicide [19]. Also the sorption of glyphosate increased when Cu ions were present in solution treatments [27]. On the contrary the presence of Cu ions in soil solutions suppressed the sorption of cationic difenzoquat on peat and soils due to competitive sorption of the two for the same sorption sites [19].The desorption coefficient Kf values were greater than those for sorption indicating that some amount of chlorsulfuron was held in the soils after desorption cycles at all the concentrations. The results imply that the existence of both copper ions and chlorsulfuron in the Mara River Basin soils lowers the effectiveness of the herbicide in eradicating the broadleaf and grass weeds in the wheat farms since the increase in sorbed amounts reduce availability of the herbicide for herbicidal activity.

There was a slight decrease in pH of the equilibrium solution with the introduction of Cu^{2+} (Table 3). This observation could explain the increase in sorption since the decreased pH caused the variable charge surface of the soil oxides to be more protonated thus reducing the soil surface negative charges [27]. Since chlorsulfuron is anionic in nature, the repulsion between the herbicide and the soil surface decreased thus increasing the adsorption. This behavior has also been observed by [20] for Cu ions which decreased the soil solution pH therefore increasing the sorption of chlorimuron-ethyl. In fields with large concentrations of copper ions the pH of the soil will be lowered, increasing the sorption of chlorsulfuron herbicide in the soils thus compromising its efficiency in eliminating weeds. Farmers will therefore use higher application rates, increasing the amounts of chlorsulfuron into the soils.

Table 3: Soil solution pH for the five soils after equilibration with and without Cu^{2+}

Soil	Initial Cu (II) (mg l^{-1})	Initial chlorsulfuron concentration (mg l^{-1})				
		0.625	1.25	2.5	5.0	10
MC	0	5.55	5.57	5.53	5.56	5.53
	50	5.53	5.55	5.49	5.52	5.49
	100	5.53	5.52	5.49	5.49	5.47
MEA	0	6.01	6.03	5.99	6.00	5.88
	50	5.88	5.85	5.88	5.85	5.76
	100	5.71	5.68	5.65	5.67	5.61
OLK	0	6.44	6.41	6.38	6.40	6.37
	50	6.39	6.41	6.33	6.37	6.33
	100	6.33	6.36	6.29	6.37	6.31
OLL	0	5.83	5.81	5.80	5.81	5.83
	50	5.79	5.77	5.79	5.75	5.76
	100	5.71	5.75	5.79	5.71	5.69
MEB	0	6.64	6.60	6.49	6.57	6.44
	50	6.41	6.43	6.30	6.29	6.33
	100	6.29	6.28	6.20	6.17	6.15

MC-Mau central, MEA-Mau East A, OLK-Olokurto, OLL-Olololunga, MEB- Mau East B

Formation of complexes between chlorsulfuron and cationic Cu^{2+} could also increase adsorption since the complexes could be sorbed easily than chlorsulfuron itself. The organic amine and compounds containing the NH-group like chlorsulfuron are efficient ligands for divalent metal ions [28]. Cu^{2+} can coordinate with the N-H in the ureic bridge and the pyrimidine ring of chlorsulfuron to form a six membered ring chelate, with reduced negative charges compared to chlorsulfuron. This would favour the adsorption of the chelate to the negatively charged soil surface. Previous study on the effect of pH on the adsorption of anionic sulfathiozole on peat and soil demonstrated that sulfathiozole adsorption on soil was increased at a pH greater than 5.0 since sulfathiozole could form a complex with Cu or through the formation of Cu bridge which enhanced its adsorption [29].

To verify if Cu (II) acted as a bridge between chlorsulfuron and soil and to demonstrate the sorption sites of chlorsulfuron and Cu (II), FTIR spectroscopy analysis [20] was carried out using soil from Mau East A. There was strong peak at 1003 cm^{-1} corresponding to C-O stretch, the peak at 1633 cm^{-1} was assigned to the C=O while the broad peak at 3406 corresponded to -COOH or –OH stretch vibrations of the soil (Figure 2). With the introduction of both copper (II) and chlorsulfuron, the shift at C-O stretch was not significant. However, the sorption of chlorsulfuron, Cu (II) or a mixture of chlorsulfuron and Cu (II), the peaks at 1633 cm^{-1} and 3406 cm^{-1} shifted to 1634 and 3372 cm^{-1}, 1635 and 3369 cm^{-1} and 1637 and

UNDER PEER REVIEW

3357 cm^{-1} respectively suggesting interaction between chlorsulfuron, copper and the soil. Increase in the intensity of O-H band (3600-3300 cm^{-1}) could be attributed to the adsorption of the copper herbicide complex onto the soil. The displacement of C = O band (1633 cm^{-1}) to higher wavenumbers (1635 and 1637 cm^{-1}) suggested an increase in the double-bond character of the C = O group, more likely owing to the electron-withdrawing effect from a protonated neighboring group in this case Cu(II), or to the loss of intermolecular hydrogen bonding. Similar red shifts on the C = O group on the addition of cations was reported for the sorption of Zn^{2+} and *p*-nitrophenol on wheat ash when C = O band (1592 cm^{-1}) on ash was shifted to 1622 cm^{-1} and 1632 cm^{-1} on addition of Zn^{2+} and *p*-nitrophenol respectively [30]. Similarly, the addition of Cu^{2+} and chlorimuron-ethyl on a Chinese soil caused a blue shift on the –OH vibration from 3418 cm^{-1} to 3428 cm^{-1} and 3432 cm^{-1} respectively [20]. Complexation of soil surface with exchangeable multivalent cations has been suggested as a sorption mechanism for sulfonylurea and many ionic herbicides [31]. In another study, Cu-bridging was reported to be the main sorption mechanism for chlorimuron-ethyl in soil [20]. Similarly, rimsulfuron was adsorbed mainly on to Cu (II)-clays due to formation of a complex with the saturating Cu (II) ion [32]. Interaction of copper ions with chlorsulfuron in the Mara River Basin soils will lower the activity of chlorsulfuron on the targeted weeds due to the formation of complexes. Besides non availability of the copper ions to the wheat plant uptake will affect the yields.

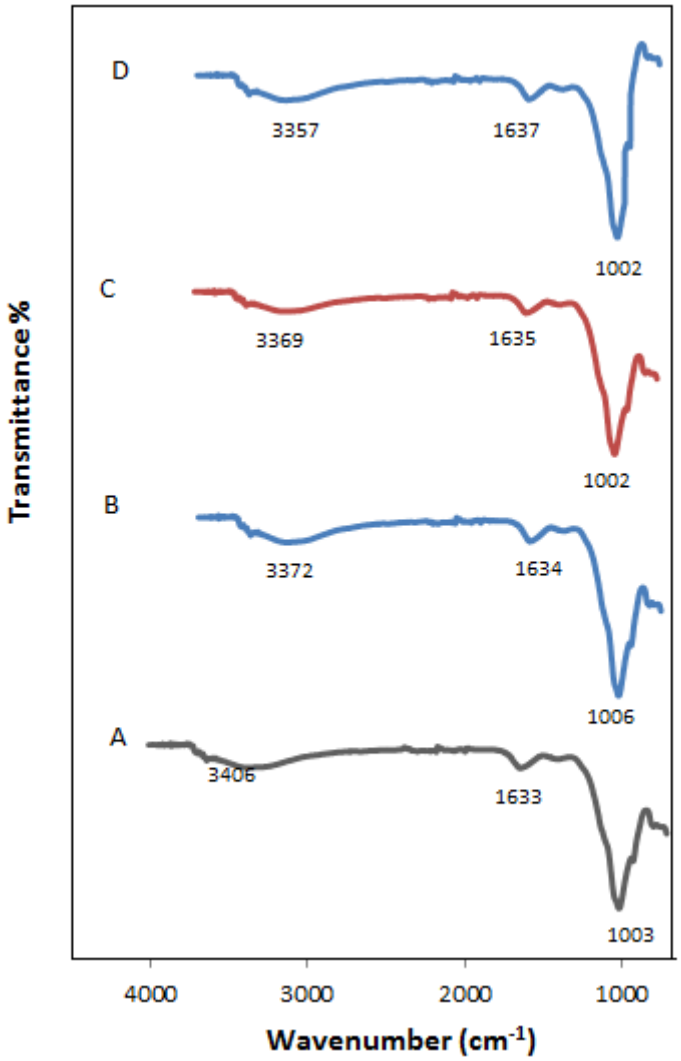


Figure 2. FTIR spectra of (A) soil, (B) soil with chlorsulfuron, (C) Soil with Cu (II), and (D) soil with chlorsulfuron and Cu (II).

UNDER PEER REVIEW

4. CONCLUSION

The presence of Cu (II) enhanced chlorsulfuron sorption in all the soils through change of solution pH and formation of complexes through the carboxylic and hydroxylic groups which decreases the repulsive forces between negatively charged soil surfaces. However, Cu (II) decreased the hysteresis effect on the desorption process. This effect increased with increase in Cu (II) concentration implying that wheat fields with high copper ions concentrations more chlorsulfuron can be sorbed thus reducing the effectiveness of the herbicide on the target weeds leading to losses.

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