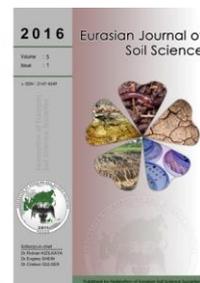




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Adsorption and desorption characteristics of chlorosulfuron in selected minerals and Pakistani soils

Khuram Shahzad Ahmad ^{a,b}, Naghmana Rashid ^b, Sundus Azhar ^{a,*}

^a Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi, Pakistan

^b Department of Chemistry, Science Block, Research Complex, Allama Iqbal Open University, Islamabad, Pakistan

Abstract

Sorption and desorption efficiency of Chlorosulfuron that is sulfonylurea herbicide was checked by selecting different minerals and two types of Pakistani soils that were different on spatial scale. In Pakistan, sulfonylurea herbicide is being used against wide varieties of broad leaf weeds and for some grasses as well. Results obtained after the experimental work showed that adsorption co-efficient isotherm for Chlorosulfuron in tested soils data well fitted the Freundlich equation. In all the cases, slope $n < 1$ was resembling the C type curve and isotherm was nonlinear. Due to low adsorption, distribution co-efficient (K_d) parameters were also low. Results indicated that soil samples (silt loam) collected from northern hilly areas Ayubia, Khyber Pukhtunkhwa showed more adsorption for Chlorosulfuron herbicide i.e. 25.5% than the sandy soil of Multan Punjab. The major difference between the sorption capacities of both of the soil was due to the difference in soil organic matter and soil pH. Among both these factors, organic matter plays more significant role in sorption. Adsorption efficiency of synthesized compounds on different soil types of known composition can be predicted by the adsorption and desorption results of the present study.

Keywords: Chlorosulfuron, sorption, desorption, physicochemical properties

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Introduction

One substance or mixture of different substances that are used for repelling, preventing, destroying, controlling and mitigating the undesirable effect caused by pests is called as pesticide (Kuwatsuka and Yamamoto, 1997). In the recent modern agricultural farming operations, pesticides have become an inevitable part. Almost 48 % of the world's total food production is either consumed, destroyed or lost due to different pests like insects, parasites, birds, weeds, fungi, bacteria and rodents. Pesticides are used to overcome this much loss of food production. For controlling pests, different practices have been applied since long ago like neem oil and green olive etc. These natural pesticides have been modified into broad range of chemical compounds to kill the wide varieties of pests and weeds (Hemmamda et al., 1995). Different characteristics of the pesticide like its binding capability, vapor pressure, solubility in water and degradation have an effect on its movement from the site of the application. Different physic chemical properties of soil like its texture, pH and amount of organic matter also influence the amount of pesticides migrated from an area (Cozza and Woods, 1991; Koleli et al., 2006). Soil nature and its composition also determine the amount of pesticides retained in the soil (Marinas et al., 2001).

It is necessary to understand the pesticide behavior in the natural environment to reduce the risks of contaminants for preserving the environment specially its sorption behavior. There are different active sites

* Corresponding author.

Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi, Pakistan

Tel.: +92519270050169

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E-mail address: Sundus_azhar2001@yahoo.com

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available on the surface of the soil. When a pesticide is applied to soil it may be attached to soil very strongly while loosely bound pesticide molecules desorb from active sites (Wu et al., 2012). Biological efficacy and persistence of a pesticide in soil is determined by its adsorption and desorption capacity. Both these capacities not only determine the migration of pesticides in different environmental components like soil and water but also have an influence on their uptake and metabolism by different microbes and plants (Konda et al., 2002).

Distribution of pesticides in the different phases can be investigated by the nature of the soil components with different adsorption efficiency and by the physicochemical properties of the pesticides (Monkiedje and Spitteler, 2003). Electronic structure and water solubility of pesticides are the most important properties for their adsorption and desorption study. Different intermolecular forces like Vander-Waals forces, hydrogen bonding, charge transfer, ligand exchange, direct and induced ion-dipole, dipole-dipole interaction and chemisorptions monitor the sorption of pesticides (Ali and Baugh, 2003). Clayey soil with amorphous mineral matter and organic matter controls the adsorption phenomena.

In agricultural sector, large number of urea based herbicides has been used extensively. Sulfonylurea are group of herbicides applied on different crops and vegetables like wheat, barley, oats, rice, maize, turf, soybean, oil seed rap, flax, sugar beets, plantation crops, forestry, blueberries, potatoes, and tomatoes to control the growth of weeds and grasses (Verschueren, 2001). Sulfonylurea is applied in lower rates (10-40 g ha⁻¹) than higher application rate of other herbicides (e.g. 2-5 Kg ha⁻¹ for atrazine) (Sarmah and Sabadie, 2002).

Sulfonylurea is less toxic to mammals and applied in low rate so it is considered safe within the environment. Except its low toxicity, it still has some other environmental concerns. It is highly toxic to plants and it can be transported to other sites by leaching and air drift. It is very persistent in the environment and affects the reproduction capability of plants specially the rotational crops. It is found both in surface water and ground water due to its higher mobility and anionic character. It has a severe effect on the non target organisms and soil microorganism (Cessna et al., 2006).

As compared to the conventional herbicides, sulfonylurea can be degraded under the field conditions and at faster rate. There are different modes of degradations but the two important modes are chemical hydrolysis and microbial breakdown (Nyström et al., 1999). At 30°C, Nicosulfuron herbicide undergoes breakdown of the urea part of the molecules by alcoholysis and hydrolysis (Schneiders et al., 1993).

In alkaline soil, microbial breakdown is major degradation pathway while in acidic soils, chemical hydrolysis predominates (Sabadie, 2002). Faster degradation of pesticide is favored by warmer, moist soil with low texture and low pH while slow degradation is associated with dry, heavy textures and high pH soil (Mishra and Patel, 2008). Increase in soil pH and decrease in organic matter content of soil is also associated with the higher mobility of certain sulfonylurea herbicides. There are some cases where the situation is opposite like Nicosulfuron has irreversible sorption capacity on clay particles that is a sulfonylurea herbicide (Laird et al., 1994). In agricultural sector, many organic herbicides and insecticides have been used in past few decades that ultimately accumulate in the soil. These compounds can also enter into human food chain through drinking water and pose serious threat to human health. So there is a need of integrated research to understand the behavior and fate of the pesticides and all other organic molecules.

The sulfonylurea herbicide, Chlorosulfuron 1-(2-chlorophenyl) sulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) is shown in figure 1 is a broad spectrum herbicide used against a wide range of broadleaf weeds as well as some grasses. Sulfonylurea herbicide is mostly used to control a wide range of weeds in crops of wheat in Pakistan with the Trade name of Alkanak and Logran, in which Chlorosulfuron and Triasulfuron are present (Ukrainczyk and Rashid, 1995). Different researches have indicated that the activity and adsorption efficiency of Chlorosulfuron depend on pH of soil. Like a weak acid with pKa of 3.3, Chlorosulfuron is present in ionic form in both neutral and alkaline soil solution. It has also been observed in the previous studies that there is a negative relationship soil pH and sorption of sulfonylurea herbicides (Khan et al., 2003). Nonionic pesticide has a different mechanism of binding with the soil components and it depends on the chemistry of pesticides and physicochemical properties of soil (Stork, 1998; Bailey et al., 1968). Generally, binding of pesticide with soil by physical sorption is reversible while by chemisorptions it is irreversible. Apparent hysteresis or irreversibility may be caused by some other factors than chemisorptions, such as equilibrium is not attained during desorption, pesticide loss due to biological and

chemical degradation, volatilization and precipitation. Depending upon the nature of chemical bond or desorption methodology chemisorbed pesticides can be partially desorbed (Chen, 1990).

Pakistan is a country where economy is largely dependent on agricultural sector therefore most of the parts of its land are used for cultivation of crops. So pesticides are applied extensively to protect crops. Sulfonylureas based pesticides are used widely in Pakistan on different crops. Pesticides are used frequently in Pakistan but the knowledge about their toxicity is lacking. The main aim of the present research is to identify the effects of these pesticides in terms of their persistence and toxicity on different soils of Pakistan and in different environments. Four types of soils were selected from the different agricultural areas of Pakistan and main focus was on agricultural areas of KPK, central and southern Punjab districts. The selection of these areas was based on the use of pesticides. Wheat was grown in the south Punjab while other selected sites had more fruit growing area. Extensive use of sulfonylurea has raised concerns as it has potential to contaminate environment. Adsorption processes in soil play a significant role in all physical processes affecting the residue behavior of pesticides in the agro environment.

Material and Methods

Chemicals

Acetone and Methanol used were 99.9 % pure from Merck, Germany. Sodium chloride and calcium chloride anhydrous powder, extra pure used were products of Sigma Aldrich Company Germany. Analytical standard Chlorosulfuron was purchased from ACCU Standard USA.

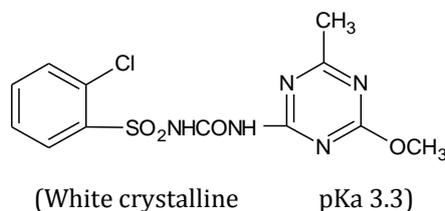


Figure 1. Chemical structure of Chlorosulfuron

Soil samples

Two soils (0-10cm) were collected from different cultivated soil areas of Punjab and KPK, with no recent history of pesticide application. Among them one was from the province of Punjab while the other one was from the KPK in Pakistan. Soil 2 was taken from chak no. 136 WB Tehsil Harpa District Multan, and soil 1 was from Ayubia, KPK. These soils having substantial differences representing a range of physical properties i.e. differences in level of clay organic matter and pH (Afyuni et al., 1997).

Sub samples of soils were mixed thoroughly, air dried at room temperature disaggregated manually using a marble mortar and a pestle. After this the soil was passed through a 2-mm screen sieve, and mixed manually to achieve homogeneity. Samples of homogenized soils were analyzed for moisture content, organic matter percentage and pH. In order to find out the moisture content of the soils, the soils were dried at 105°C until a constant weight was achieved and the moisture content was determined by the difference in the pre and post oven weights. Organic matter content was determined by the loss on Ignition Method, in this method the soil samples were heated to a temperature of 400°C in a Ney Vulcan burnout in oven for 24 hours in order to oxidize any volatile organic matter present in the soil (Afyuni et al., 1997).

Table 1. Physiochemical properties of soils

Sample	Location	Soil Texture	OC (%)	Clay (%)	Sand (%)	Silt (%)	pH	% C	Primary Crops
Soil 1	Ayubia (KPK)	SiL	6.51	44	24	41	7.6	3.79	Maize, French beans
Soil 2	Multan (Punjab)	SC	1.89	12	52	13	8.1	1.10	Wheat, Cotton

Organic content was deduced from the loss of weight as a result of heating in the furnace. Organic carbon was determined by elemental analysis. Soil pH was measured by mixing 10 gm of dry soil and 10 ml of deionized water, after one hour of contact time the pH of the slurry was measured using Orion 420 plus pH meter equipped with a glass electrode (Laird et al., 1994; Zhang et al., 2009). The relevant physiochemical properties of two soils are given in Table 1.

Table 2. Relative physicochemical properties of selected minerals

Minerals	Formula	pH	AEC (cmol kg ⁻¹)	CEC (cmol kg ⁻¹)	d-spacing (Å)	Specific Surface Area m ² g ⁻¹	Types of Lattice
Goethite	FeOOH	6.0	7.0	0.4	9.6	36	N/A
Bentonite	BaTiSi ₃ O ₉	9.7	N/A	10	12.06	N/A	2:1

Adsorption experiments

All experiments have been performed under isothermal conditions at 25±1°C (Walker and Welch, 1989). Pesticide solutions were prepared in deionized water and stored at 4 °C. For Chlorosulfuron eight different concentrations 0.25, 0.5, 0.75, 1.0, 2.5, 5.0 and 7.5 ppm were prepared, Sorbent/solution ratio was kept at 1:20. Depending on the desired Chlorosulfuron concentration, 10 ml of 0.1M sodium chloride was added as background electrolyte in each concentration to simulate ionic strength similar to that of natural soil solution. It was also added as an aqueous solvent phase in order to improve centrifugation and to minimize cation exchange.

Each sample consisted of 0.5g of soil or mineral mixed with 10ml of pesticide solution in 1:10 soil /solution ratio, placed in a 15ml Pyrex glass centrifuge tube, fitted with a screw cap. The tubes were continuously agitated on a Stuart Orbital Shaker at 90 rpm for 24 hours at room temperature (25°C) in order to attain equilibrium. The adsorption equilibration process was done in duplicate for each concentration. In addition a blank sample containing only dissolved fungicides and 0.1M NaCl background electrolyte without any mineral or soil was prepared and treated in parallel with each set of batch experiment in order to quantify the losses and to account for possible degradation during adsorption process. The data was analyzed using XRD and HPLC techniques.

Desorption experiment

Desorption studies was conducted on the same herbicide soil solutions. After the sorption experiment, the remainder of the supernatant was decanted and the tubes were reweighed. After this 9 ml of freshly prepared 0.01M CaCl₂ solution was added to the soil remaining in the centrifuge tubes and the samples were again shaken for 24 hr and XRD and HPLC techniques were utilized to manipulate the data. Desorption, expressed as micrograms adsorbed/gram of soil (µg/g' soil), was obtained from the difference, taking into account the solution remaining in the soil after the supernatant was poured off.

Data analysis

The amount of the Chlorosulfuron adsorbed (µg/g of soil) was calculated by using Equation (1).

$$C_s = \frac{V}{m} \cdot (C_b - C_a) \quad (1)$$

where C_s is the amount adsorbed, V is the volume of solution, m is grams of soil taken, C_b is equilibrium concentration of blank and C_a is equilibrium concentration of treatment supernatant. The adsorption values obtained from Equation (1) were used to construct following linear type of isotherm:

$$K_{d(ads)} = \frac{C_s}{C_e} \quad (2)$$

Where K_{d(ads)} is linear or sorption equilibrium distribution co-efficient in (ml/µg). C_e is the concentration (µg/ml) at the equilibrium concentration. Desorption is expressed as micrograms adsorbed/gram of soil (µg/g soil) and was calculated from the difference of solution remaining in the soil after the supernatant was decant off. The sorption equilibrium distribution co-efficient K_{d(des)} in (ml/µg) was calculated as:

$$K_{d(des)} = \frac{C_s}{C_e} \quad (3)$$

The adsorption isotherms of pesticides in all the soils fitted the Freundlich adsorption relationship equation (4):

$$C_s = K_f C_e^{\frac{1}{n}} \quad (4)$$

where C_s is the amount of adsorbed (ug/g), C_e is the equilibrium concentration (ug/ml) and K_f and n are constants determined by applying the linearized form of the Freundlich equation. The Freundlich constant normalized to organic carbon (K_{foc}) was calculated by using equation (6).

$$K_{oc} = \frac{K_d}{\%C} \cdot 100 \quad (5)$$

Where K_{foc} and K_f are related as:

$$K_{foc} = \frac{K_f}{\%C} \cdot 100 \quad (6)$$

The equilibrium organic matter (K_{OM}) by normalizing K_d or by normalizing K_f with the content of was calculated according to equation (7) and equation (8) respectively.

$$K_{OM} = \frac{K_d}{\%OM} \cdot 100 \quad (7)$$

$$K_{OM} = \frac{K_f}{\%OM} \cdot 100 \quad (8)$$

The hysteresis coefficient (H) for the adsorption isotherm was calculated using the relation;

$$H = n_d / n_a$$

Where n_a and n_d are the Freundlich constants of the adsorption and the desorption isotherms. The standard free energy change of adsorption (ΔG) from the isotherm can be calculated using the following relation: (Abdullah et al., 2001; Tahir et al., 2008).

$$\Delta G = -RT \ln K_{OM} \quad (9)$$

The ΔG can be used to judge the adsorption reaction. Its value ≤ -40 kJmol⁻¹ indicates physical adsorption of herbicide with the soil.

Results

Chlorosulfuron adsorption and desorption were studied by HPLC attached UV- detector at λ_{max} 230 nm for Chlorosulfuron.

Adsorption isotherm

Comparative adsorption of Chlorosulfuron on 2 studied soils and selected minerals i-e Goethite and Bentonite is shown in Figure 2 and Figure 3.

Distribution coefficient (K_d), Freundlich constant (K_f), Gibbs free energy (ΔG) and Hysteresis (H) were calculated from the isotherm by using formulae given in data analysis.

Table 3. Adsorption coefficients of chlorosulfuron in selected soils

Soil	K_d	R^2	K_{oc}	K_f	n_a	R^2	K_{foc}	K_{OM}	G
Soil1	5.4	0.83	142	20	1.64	0.65	527	317	-13.31
Soil2	3.3	0.82	300	27	1.84	0.78	2454	1443	-16.81

Table 4. Adsorption coefficients of chlorosulfuron in selected minerals

Mineral	K_d	R^2	K_f	n_a	R^2
Bentonite	3.156	0.76	5.12	0.79	0.87
Goethite	2.598	0.91	4.06	1.03	0.84

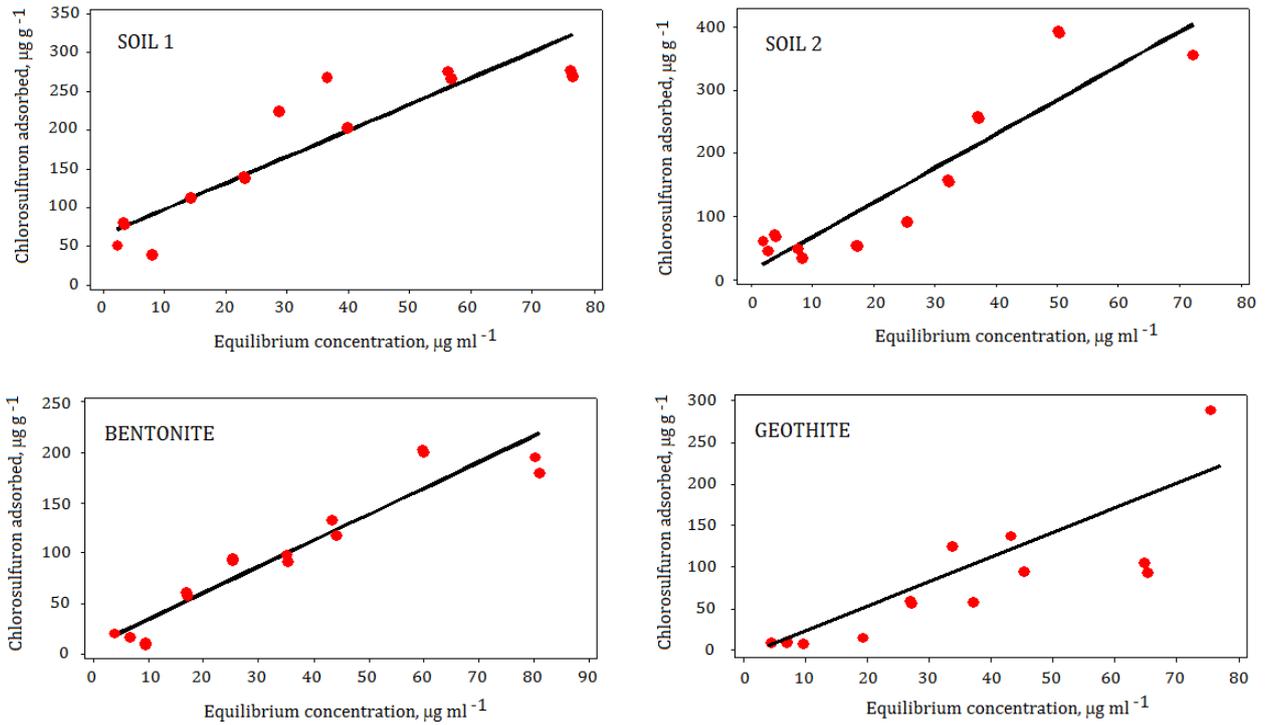


Figure 2. Simple sorption isotherms of Chlorosulfuron by soil 1, soil 2, Bentonite and Goethite.

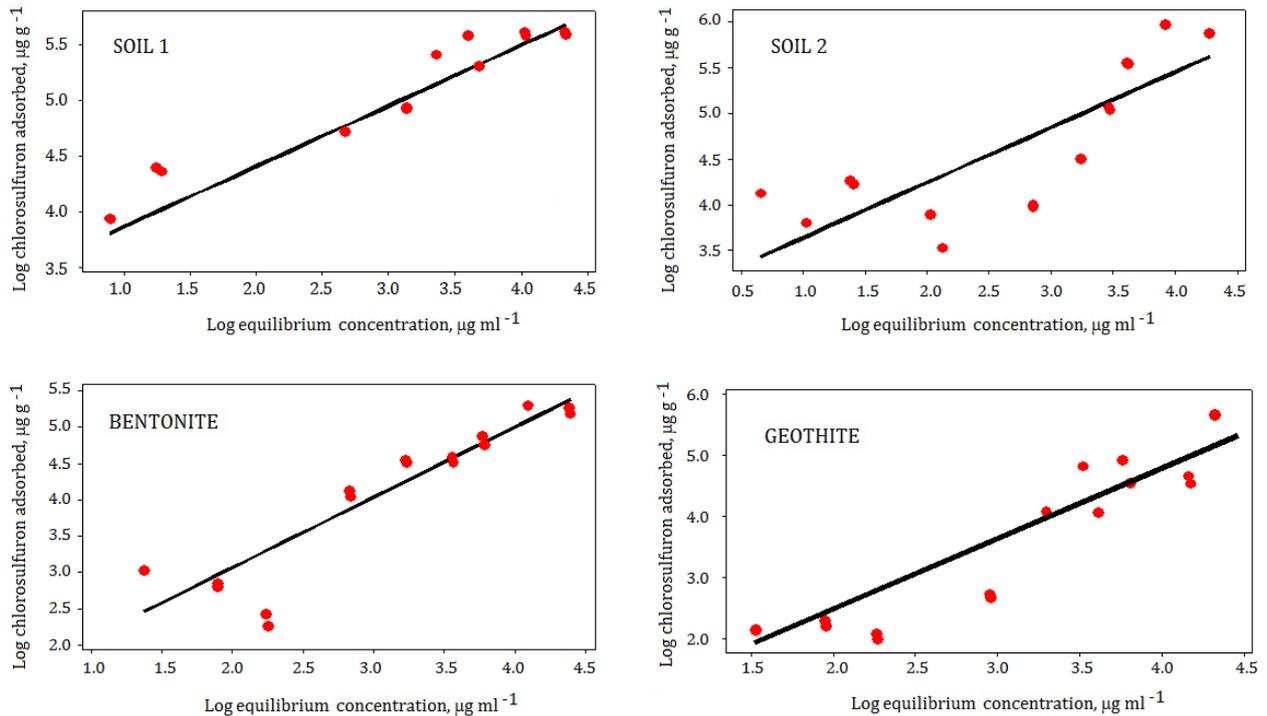


Figure 3. Freundlich Adsorption Isotherms Chlorosulfuron by soil 1, soil 2, Bentonite and Goethite

Desorption

Desorption equilibrium distribution co-efficient ($K_{d(des)}$) was calculated by plotting the desorbed pesticide concentration ($C_{s(des)}$) against the equilibrium pesticide concentration ($C_{e(des)}$) and are shown in Figure 4 while Figure 5 shows Freundlich desorption isotherms.

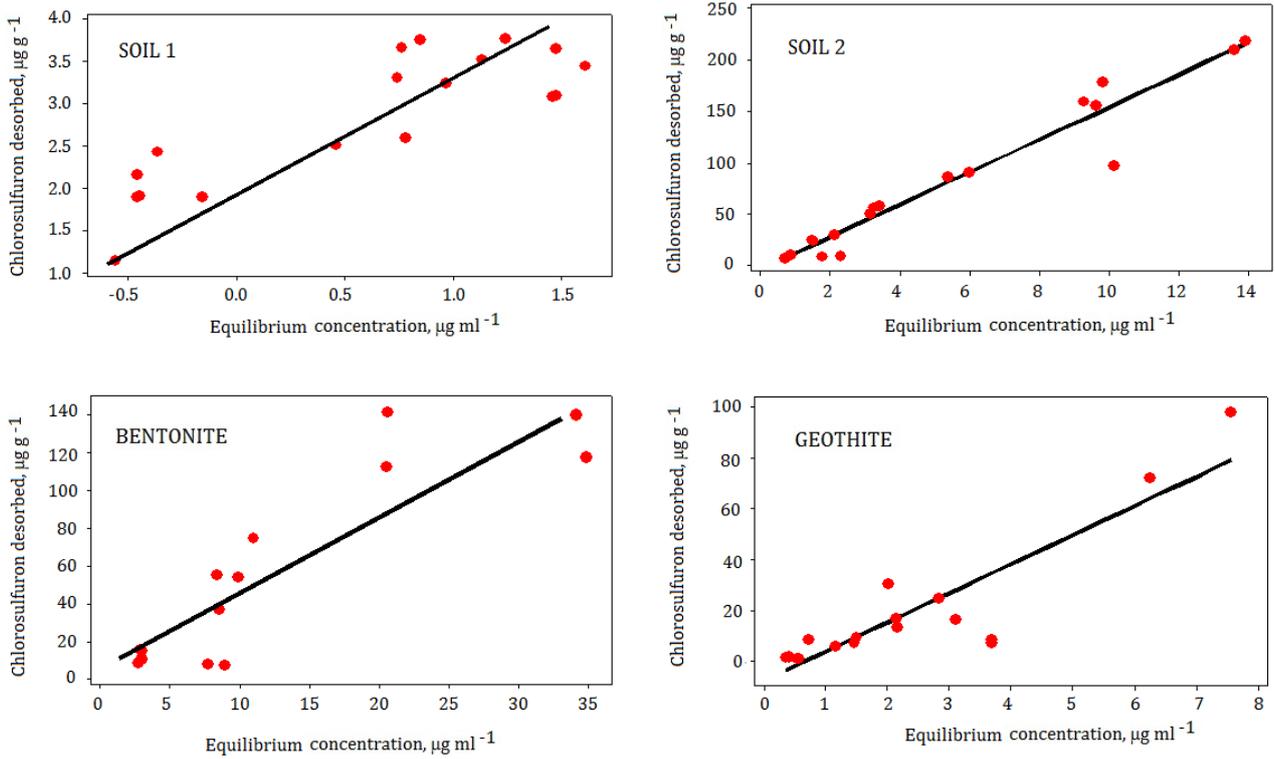


Figure 4. Simple desorption isotherms of Chlorosulfuron by soil 1, soil 2, Bentonite and Geothite

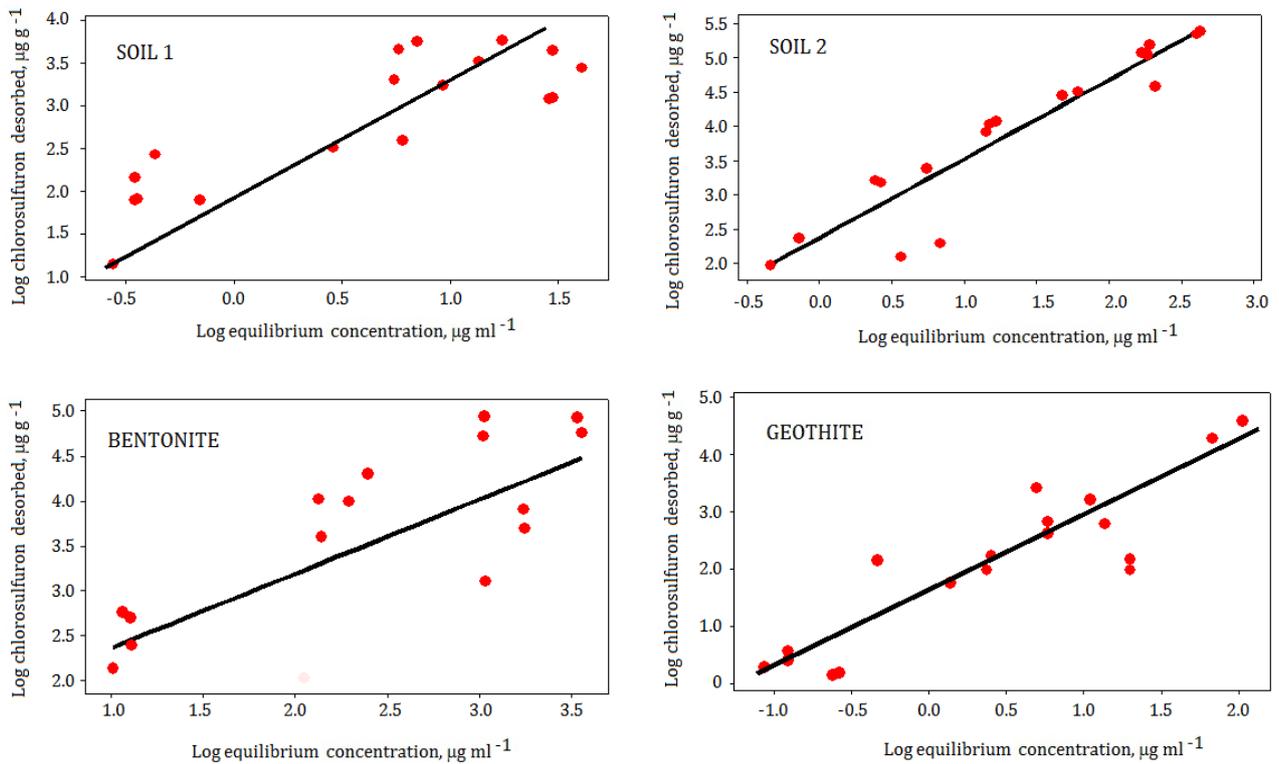


Figure 5. Freundlich desorption isotherms of chlorosulfuron by soil 1, soil 2, bentonite and geothite

Desorption kinetic studies were conducted to assess the desorption potential of adsorbed chlorosulfuron herbicide in different soils and minerals and the results are shown in Table 5 and Table 6.

Table 5. Desorption Coefficients of Chlorosulfuron in Selected Soils

Soil	$K_{d(des)}$	R^2	$K_{f(des)}$	n	R^2	H
Soil1	15.80	0.93	10.32	0.63	0.88	0.38
Soil2	6.389	0.48	10.32	1.15	0.73	0.62

Table 6. Desorption Coefficients of Chlorosulfuron in Selected Minerals

Mineral	$K_{d(des)}$	R^2	$K_{f(des)}$	n	R^2	H
Bentonite	3.044	0.48	4.60	1.19	0.51	0.9
Geothite	11.45	0.79	4.86	0.79	0.80	1

XRD Results

In XRD studies, sorptions of pesticides with minerals and soil were measured by the change in basal spacing. Results of XRD Studies for Bentonite mineral are given in figure 6 and table 7.

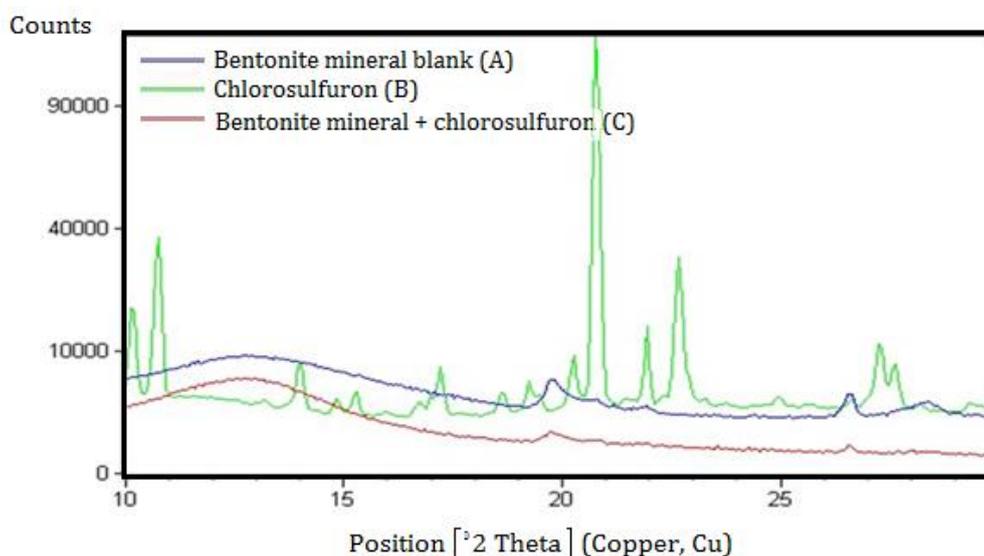


Figure 6. Bentonite Mineral (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

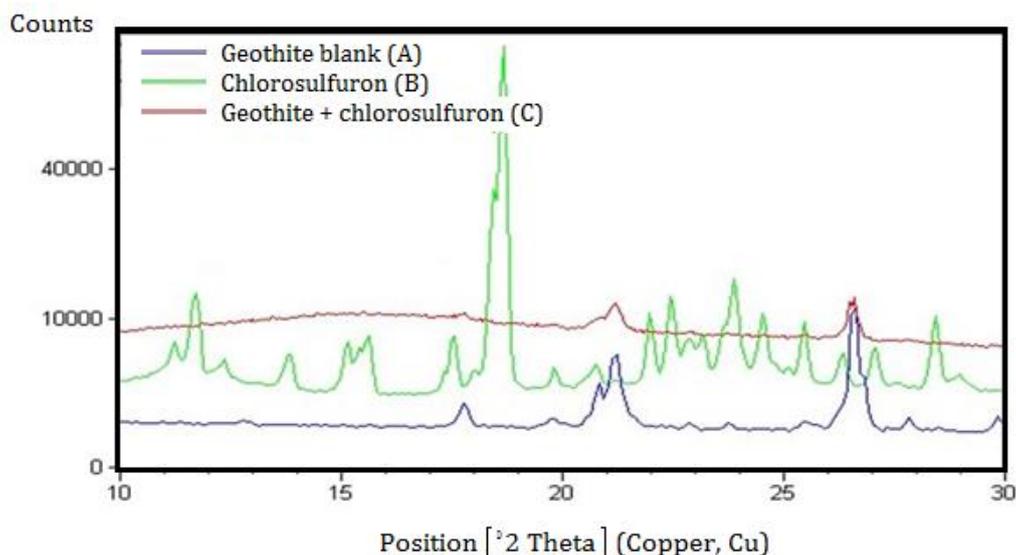


Figure 7. Geothite Mineral (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

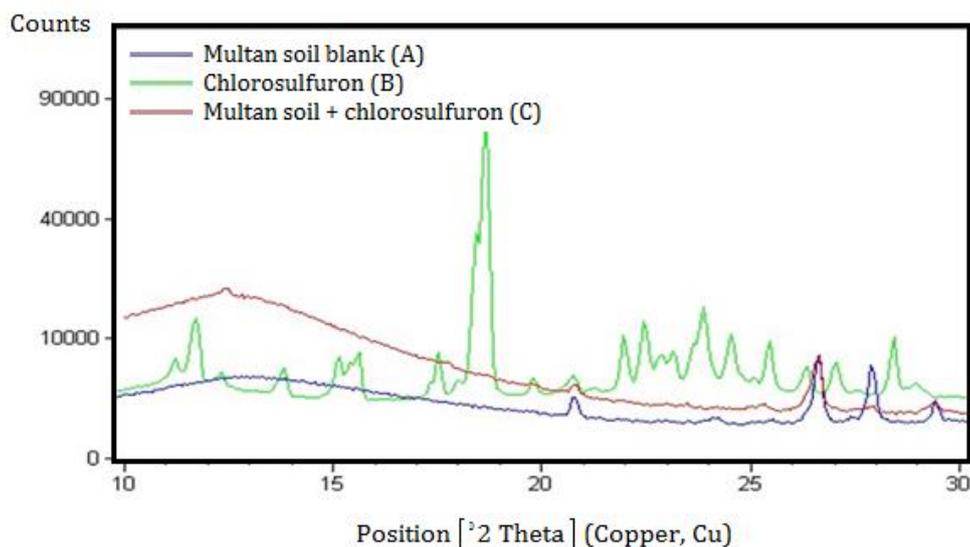


Figure 8. Multan Soil (A) Untreated (B) Chlorosulfuron (C) Treated with Chlorosulfuron

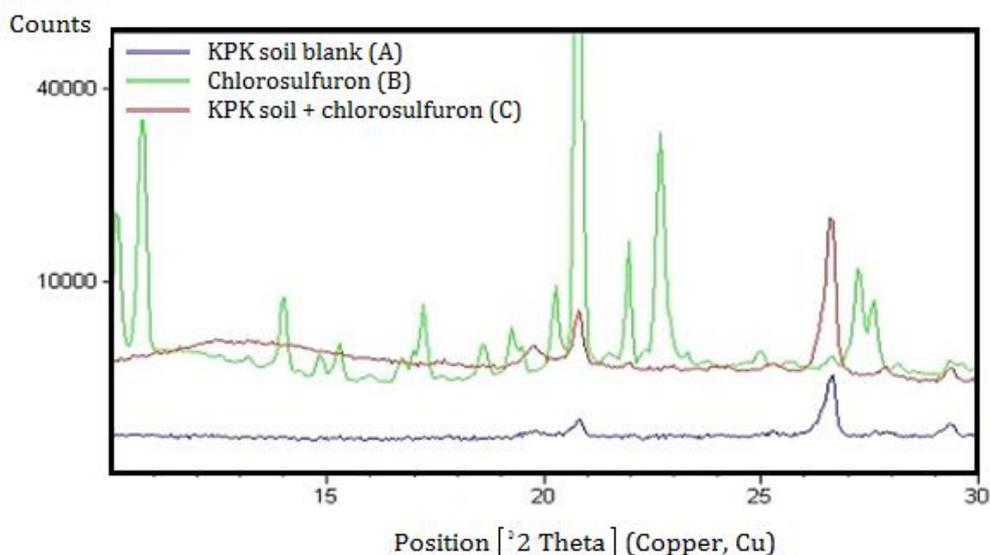


Figure 9. KPK Soil (A) Untreated (B).Chlorosulfuron (C) Treated with Chlorosulfuron

Table 7. Basal Spacing (A°) for clay minerals and soils

	MULTAN Soil	KPK Soil	Goethite Mineral	Bentonite Mineral
Untreated d (001)	9.99	9.97	10.03	12.06
Treated with Chlorosulfuron d (001)	9.99	9.97	10.03	12.06

Discussion

Adsorption studies

In this study the different values of K_f are also presented evidently in table 3 suggesting different adsorption capacities in these two soils. Further table showed that the predicted capacity for Chlorosulfuron retention normalized to the OC content (i.e. K_{foc}) differentiated significantly in these two soils. Among them soil 2 had biggest K_{foc} values. If organic matter in soils had a common capacity for Chlorosulfuron then K_{foc} value might be expected to be nearly constant. Adsorption of chlorosulfuron in soil is highly dependent on the organic matter content. Along with organic matter, iron oxide and aluminium oxides are also the important adsorbent of chlorosulfuron. Soil pH also determines the fate of chlorosulfuron in soil giving maximum adsorption at low pH and minimum at high pH. So if chlorosulfuron is applied to alkaline or neutral soils having less organic matter content and oxides, then there are more chances of leaching causing the ground water pollution (Borggaard and Streibig, 1998).

The result of the present study well agreed with the results obtained by walker *et al.* 1989, in which a significant positive correlation between organic matter contents of soil with the extent of adsorption of pesticide was observed (Walker and Welch, 1989). Soil having high sand content had less vacant sites/surface areas and probably resulted in minimum adsorption (Sprynskyy *et al.*, 2008).

Organic carbon is crucial parameter affecting the sorption capacity of the herbicides especially when OC is greater than 2 % with the nature, form and functionality of OC not being much important in this case. In present study, soil type 1 had 6.51 % OC while soil type 2 had 1.89 % OC as shown in table 1. It means in soil 1, OC is responsible for the sorption irrespective of its nature. Presumably, when the OC of soils and their size fractions is lower than 2%, the difference in the nature and functionality of the OC makes a difference in terms of sorption as in soil 2. As compared to K_f, K_{oc} still provides a better way for predicting hydrophobic pesticide sorption (Wang and Keller, 2009).

Shan *et al.* suggested grouping of pesticide on the basis of K_{oc} values and concluded that K_{oc} values less than 50 as a highest mobility group and those having K_{oc} values between 50 and 500 as medium mobility group (Li *et al.*, 2003). All the K_{oc} values observed in this study suggested that Chlorosulfuron had moderately to high mobility in different soil types which might result in a leaching problem working with Chlorosulfuron.

To identify the physical and chemical mechanism of adsorption, Gibbs free energy change (ΔG) of 40 kJ/mol is considered as a threshold (Carter *et al.*, 1995). Physical adsorption has value below the threshold. The ΔG values of Chlorosulfuron within studied soils (Table 3) ranged from -16.81 to -13.31 kJ/molsuggesting that physical adsorption have taken place. The adsorption of Chlorosulfuron by soils was also a spontaneous process for the negative value of ΔG .

Desorption characteristics

Desorption study of herbicide is very important as it controls the release rate, mobility of herbicides in soil and also the treatment processes for the contaminated soils. Lower rate of desorption of an herbicide means that it can cause higher risk to the crops (Singh and Cameotra, 2013). Thus, desorption kinetic studies were conducted to assess the desorption potential of adsorbed chlorosulfuron herbicide in different soils and minerals and the results are shown in Table 5 and Table 6.

Results indicated that K_d (des) values were higher as compared to K_d (ads) in the two selected sites. Higher values of desorption of soil for chlorosulfuron showed that adsorption was reversible and chlorosulfuron did not retain after desorption has occurred. Soil type 2 was more efficient in releasing the adsorbed chlorosulfuron as the K_d (des) for soil 2 was lower (6.389) as compared with soil type 1 (15.80). The organic matter content may play an important role in the desorption process. The K_f values of the desorption process suggested that both soil types had higher desorption rate as compared to minerals. Among the minerals, Geothite had better desorption (4.86) than Bentonite (4.60). This observation may be attributed to the different solubility of chlorosulfuron in different media (Schneiders *et al.*, 1993).

Hysteresis in adsorption and desorption processes shows that there are less chances of reversibility of adsorbed herbicide depending on physic chemical properties of soil and herbicides (Flores *et al.*, 2009; Kovaos *et al.*, 2006). Hysteresis index close to 1 indicates that sorption and desorption occur at same rate while the value less than 1 means that desorption is lower than adsorption and thus hysteresis takes place (Tang *et al.*, 2009). Many scientists explain hysteresis in different ways as irreversible binding or sequestration of solute to the OC and/or clay mineral of soil aggregates and entrapment of sorbed molecules into meso and micropore structures within mineral structures and OC matrix of soil aggregates. Second type is called structural hysteresis (Cason and Lester, 1977).

In the both studied soils, hysteresis index values for chlorosulfuron were less than 1 as given in table 5. On the other hand, both minerals had hysteresis value 1 or close to 1 as shown in table 6. It is indicated by results that organic matter and aqueous solubility of herbicide influences the desorption hysteresis. Entrapment of herbicide in the organic matter have a significant effect on the desorption hysteresis. Hysteresis is also controlled mostly by entrapment of pesticides sorbed inside micropores, i.e., structural hysteresis. From a contaminant transport perspective, higher hysteresis associated with these fractions (clay and silt fractions) implies that these fractions bind the pesticides more 'strongly' than the bulk soils (Wang and Keller, 2009).

Soil minerals composition has also a major role in the desorption hysteresis of herbicides. The hysteresis index values observed in the present study, suggest that the adverse effect of chlorosulfuron on the succession crops should be noticed, especially when it is applied on soils with high organic matter content.

While applying it to soil with low organic matter content attention should be paid to the risk of groundwater and surface water contamination from the herbicide.

XRD of selected minerals

In XRD studies, sorptions of pesticides with minerals and soil were measured by the change in basal spacing. Results of XRD Studies for Goethite mineral are given in figure 6 and table 5 while XRD studies for Bentonite mineral are given in figure 6 and table 7. The basal spacing of Goethite did not change by the sorption of the chlorosulfuron, relative smaller difference indicates parallel arrangement of pesticide into the interlayer of mineral. In the case of Bentonite mineral again there was no change in the basal spacing by the sorption of the pesticides. When the pesticides were arranged perpendicularly in the interlayer of clay content then an increase in the basal spacing was observed while parallel arrangement of pesticides indicated relatively smaller difference. There was no significant change in the basal spacing however HPLC technique showed sorption, which may be due to surface adsorption. It can be concluded that intercalation of sulfonylurea pesticides with Bentonite mineral would not occur that why Bentonite mineral didn't show any expansion of the basal spacing.

Sorption of pesticides with soil was measured by the change in basal spacing in XRD. Results of XRD Studies for Multan soil are given in figure 8 and table 7. The basal spacing of Multan soil has no-effect with Chlorosulfuron. Results of XRD Studies for KPK are given in figure 8 and table 5. The basal spacing of KPK soil showed no effect with Chlorosulfuron whereas relative smaller difference indicates parallel arrangement of pesticide into the interlayer of mineral. In XRD, there was no any penetration observed while in HPLC, penetration may be due to surface adsorption in all six cases.

The basal spacing obtained for both soils and minerals showed no change after chlorosulfuron adsorption. The chlorosulfuron-soils and chlorosulfuron-minerals basal spacings were the same as those for the untreated soils and minerals (9.99 Å for Multan soil, 9.97 Å for KPK soil, 10.03 Å for goethite and 12.06 Å for bentonite) suggesting the absence of interlamellar adsorption ([Hermosin and Perez-Rodriguez, 1981](#)).

No change in basal spacing indicated that minerals are nonexpanding and organic herbicide was sorbed around the edges of the clay particle, owing to broken-bond charges there, rather than the interlayer structure and did not increase or decrease the 2Φ value or the d-spacing value ([Cason and Lester, 1977](#)).

Conclusion

The present study revealed that Chlorosulfuron showed weak to moderate adsorption capacity with the agricultural soils that can lead to its leaching losses creating different problems in soil. The adsorption and desorption study of Chlorosulfuron soils well fitted with the Freundlich isotherm and depended significantly on the properties of soils. Adsorption behavior of Chlorosulfuron determined by the soil pH value, organic carbon, clay contents, organic matters. Increase in pH values decreased the adsorption of the chlorosulfuron while increase in adsorption was observed with the increase in organic carbon, clay contents and organic matters. Similar to other weak sulfonylurea herbicides, in this study the desorption hysteresis of Chlorosulfuron decreased from low to high solution concentrations and correlated significantly with the content of SOM, OC, Clay. Suggesting that both solute concentration gradient and physico-chemical properties of soil commonly controlled the adsorption-desorption behavior of this herbicide. XRD results show no increase or decrease in basal spacing in any of the case. This study can be used to predict the sorptive behavior of other soils.

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