

# Adsorption and Desorption Behavior of Chlorotriazine Herbicides in the Agricultural Soils

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## Abstract

The chlorotriazine herbicides have been applied worldwide for controlling of broadleaf weeds. These herbicides are known carcinogen and thus, their occurrence in surface and ground water is a cause of concern. In the present study, adsorption-desorption behavior of chlorotriazine herbicides namely simazine and atrazine was investigated. For the study, two different types of agricultural soil A (loam, 13.7% organic matter content) and soil B (clay-loam, 4.8% organic matter content) was collected from Punjab, India. The adsorption-desorption study was carried out by batch equilibration procedure. The data fitted well into the Freundlich equation. The adsorption  $K_f$  values indicated that the simazine has more soil adsorption ability than atrazine. The extent of herbicides adsorbed to the soil was more under low pH conditions and decreased with the increase in pH value. Increase in temperature decreased herbicides adsorption ability for both the soil types. The Gibb's free energy ( $\Delta G$ ) values were found less negative with the increase in temperature. Atrazine exhibited better desorption behavior than simazine. Soil A with high organic matter content exhibited sorption-desorption hysteresis. The results indicate that the soil organic matter content and aqueous solubility play an important role in the adsorption-desorption behavior of chlorotriazine herbicides. The present understanding of chlorotriazine herbicides sorption-desorption process will help to determine the herbicides fate and availability in soil, biodegradation, runoff and leaching.

**Keywords:** Simazine; Atrazine; Organic matter; Clay; Sorption-desorption hysteresis

## Introduction

The chlorotriazine herbicides namely atrazine and simazine have been widely used since 1950s for controlling of broadleaf weeds and annual grasses in agricultural and non-crop fields [1]. A very small fraction of applied herbicides reaches the target weeds, while the large fraction enters the environment, causing soil and water pollutions [2]. Consequently, the chlorotriazine herbicides have been detected in the surface and groundwater of the United States, Europe and Australia [3,4].

United States Environmental Protection Agency (EPA) has reported atrazine and simazine as potential carcinogenic herbicides. Owing to their carcinogenic potentials, the presence of these herbicides in water is a cause of concern for public and regulatory agencies [5,6]. Atrazine and simazine has been reported to cause tumors and cancers, including breast, ovarian, and uterine, leukemia and lymphoma [1,7-9]. Atrazine is an endocrine disrupting chemical, interrupting regular hormone function, causing birth defects, reproductive tumors and weight loss particularly in amphibians as well as humans [7-9].

Literatures suggest that adsorption of herbicide to the soil is the key process that affects their ecotoxicological impact, environmental mobility and the rate of degradation [10,11]. The desorption process of herbicides is also important since it determines the release rate and the potential mobility of herbicides in the soil [10]. The adsorption-desorption process of herbicide is influenced by several factors like organic matter content, soil texture, pH, temperature, etc. [10-13]. The risk of herbicide entering the surface water and groundwater mainly comes from the adsorbed herbicide present in the soil. To protect surface and groundwater from pesticide contamination and evaluate their impact, extensive knowledge concerning degradation and sorption-desorption processes in the environment is required [13,14].

The use of herbicides in India had gradually increased in recent years especially in the state of Punjab [15]. In 1999-2000 Punjab

used nearly 923g/ha of pesticides which was highest among all the Indian states [15]. According to the Directorate of Plant Protection, Quarantine and Storage, Government of India, Punjab is among the top pesticide consuming state in India, thus having high risk of soil and water pollution. In Punjab chlorotriazine herbicides are mainly used for non-selective weed control on waste land and selective weed control in crops such as sorghum, maize, sugarcane, etc [11].

The aim of this work was to determine adsorption-desorption behavior of chlorotriazine herbicides namely atrazine and simazine in the typical agricultural soils of Punjab, India. Kinetics and isotherm adsorption experiments were carried out to have a better insight into the adsorption process. Factors affecting the adsorption efficiency of herbicides such as initial pH of the solution and temperature were also studied.

## Material and Methods

### Chemical and physical characterization of agriculture soil

The two representative soils used in the present study were collected from two different agricultural sites namely soil A (Rajpura; 30.48°N, 76.6°E) and soil B (Kharar; 30.74°N, 76.64°E) from Punjab, India. The soils were collected from the surface layer (0-20 cm depth), air-

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dried, and sieved to pass through 2.0 mm mesh. Chemical and physical characterization of agriculture soil was performed following previously described methods [16,17].

### Chlorotriazine adsorption to the soil

The atrazine and simazine herbicides adsorption isotherms of both the soils were performed using the batch equilibration procedure. To minimize changes in the ionic strength and avoid dispersion, 5mM CaCl<sub>2</sub> solution was used as a background. First, herbicides were dissolved in methanol. Then the methanol solution was diluted by 5mM CaCl<sub>2</sub> solution to obtain the working solutions of different concentrations (5, 10, 20, 50 and 100 mg/l). The concentration of methanol in the working solution was kept constant at 0.1%. Aliquots (8ml) of aqueous herbicide solution were added to 2g of soil. Soil slurries were shaken on a horizontal shaker at 200rpm for a period of 24 h at 25 ± 1°C. Aliquots (600µl) were sampled from the supernatant at different time interval of 0, 0.5, 1, 6, 12 and 24 h. The samples were mixed with methanol 1:1 v/v, centrifuged (4000 rpm for 5 min) for soil separation and then quantified by High-Performance Liquid Chromatography (HPLC). The amount of pesticide adsorbed was calculated as the average of the three replicates. A blank sample was also kept to assess the effects of chlorotriazine herbicide adsorption onto the tubes and the following possible degradation during the process.

### Chlorotriazine desorption from the soil

Desorption experiments were performed instantly after the adsorption experiments. Supernatant was decanted and the herbicides residue present in the soil was analyzed. Then equal volume of the fresh 5 mM CaCl<sub>2</sub> solution was added. The mixtures were shaken on a horizontal shaker at 200rpm for 8 h at 25 ± 1°C. These steps were repeated three times consecutively.

### Chlorotriazine herbicides adsorption enthalpy

Chlorotriazine herbicides adsorption enthalpy on both the soils was determined using the batch experiments as described above. The adsorption process was performed at two different temperatures (25°C and 35°C). Herbicides concentrations used for the study were 5, 10, 20 and 50 mg/l, respectively.

### Effect of pH on chlorotriazine herbicides adsorption

The pH values of 5mM CaCl<sub>2</sub> solutions were adjusted to 5.0, 7.0 and 9.0 with the help of 5N HCl or 5 N NaOH. The chlorotriazine herbicides were then added to the solution so as to have concentrations of 5, 10, 20 and 50 mg/l. Further, the experiment was performed in the same way as done for the kinetic study described above.

### Chlorotriazine quantification

Chlorotriazine herbicides used in the present study were quantified using HPLC. Chromatographic analysis was performed with a Prominence HPLC system (Shimadzu, Japan) equipped with a UV-VIS detector. The column was Phenomax- C18 (5µ, 250 mm x 4.6 mm) while mobile phase was methanol: water (40/60, v/v) at a flow rate of 0.5mg/ml. The samples were injected with constant injection volume of 20 µl and detected at 254 nm absorbance wavelength. The chlorotriazine herbicides were identified and quantified by comparing the retention peaks of samples and authentic standard procured from Sigma-Aldrich, USA. External calibration curves with standard solutions between 1 and 50 mg/l were used for the calculations. The chemical structure of atrazine and simazine is shown in Figure 1.

### Data analysis

Adsorption - desorption data were fitted on the Freundlich model:  $S = K_f \cdot C^{1/n}$ , where S is the amount of herbicides sorbed per mass of soil (mg/ kg soil), C is the concentration of the herbicide in the liquid phase (mg/l),  $K_f$  is the Freundlich sorption coefficient (l/kg), and

n is a dimensionless parameter. Sorption coefficients  $K_f$  and n were determined by plotting the logarithmic form of the Freundlich equation.

The adsorption coefficient ( $K_f$ ) was also calculated as a function of the Organic Carbon (OC) content and Organic Matter (OM) of the soil following equations  $K_{OC} = K_f/\%OC \times 100$  and  $K_{OM} = K_f/\%OM \times 100$ , respectively. The free energy change ( $\Delta G$ , cal/ mol) in the adsorption process was calculated by the following equation  $\Delta G = -RT \ln K_{OM}$ , where R is the gas constant (2.0 cal/K/ mol), and T is Kelvin temperature.

Hysteresis coefficient, H, is calculated for the adsorption-desorption isotherms according to the following equation  $H = (n \text{ desorption}) / (n \text{ adsorption})$ , where n desorption and n adsorption are the Freundlich constants obtained for desorption and adsorption isotherms, respectively.

### Results and Discussion

#### Chemical and physical characterization of soil

Table 1 shows chemical and physical features of agricultural soil samples used in the present study. Soil A showed higher organic matter content (13.7%) than soil B (4.8%). The chlorotriazine herbicides used in the present study were not detected in the soil samples, thus suggesting absence of atrazine and simazine pre-contamination.

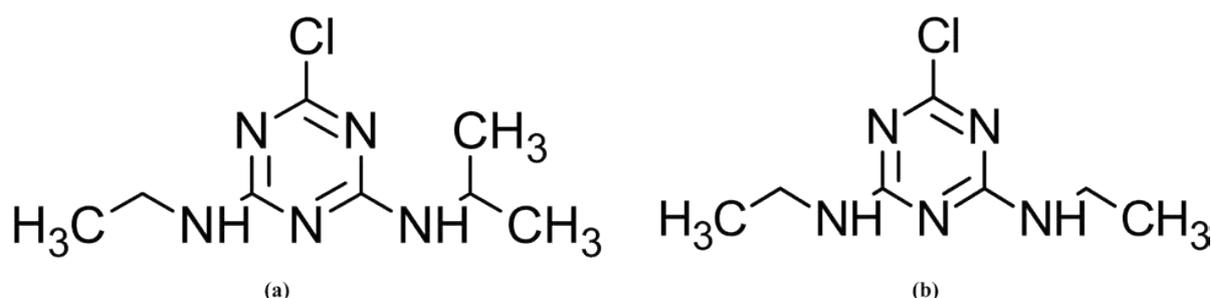


Figure 1: Chemical structure of (a) atrazine [1-Chloro-3-ethylamino-5-isopropylamino-2, 4, 6-triazine] and (b) simazine [6-chloro-N, N'-diethyl-1, 3, 5-triazine-2, 4-diamine]. The solubility of atrazine and simazine in water is 5 mg/l and 30mg/l (pH 7, 25°C).

### Chlorotriazine adsorption kinetics

A preliminary adsorption experiment was performed to determine the contact time required for attaining adsorption equilibrium. As evident from Figure 2 the adsorption kinetics exhibited two distinct stages in both the soil types. The initial step was a very rapid adsorption followed by a slow adsorption. This observation is due to the fact that in initial stage a large number of vacant surface sites were available for adsorption, but once the vacant surfaces were occupied, the repulsive forces between the solute molecules of the solid and bulk phases came into play, thus delaying the adsorption process. Similar observation has been reported for few other organic herbicides [18,19].

Herbicides adsorption equilibrium was reached within 5h of incubation in both the soil types. The maximum chlorotriazine herbicides adsorption was observed in soil A. This may be due to high organic matter content in the soil [2]. As compared to atrazine, simazine exhibited better adsorption on both the soil. This may be attributed to the different water solubility of the herbicides [19]. Simazine with very low water solubility has greater tendency to get adsorbed to the soil.

### Chlorotriazine adsorption isotherms

In the present study, no detectable amount of chlorotriazine

degradation was found in the supernatant during the adsorption process. Thus, the reduction in the herbicide concentration in the solution was considered to be due to soil adsorption. The chlorotriazine herbicides exhibited non-linear sorption isotherms on soil A and B (Figure 3). Table 2 shows the adsorption parameters of chlorotriazine in soils A and B. The sorption of chlorotriazine herbicides in both the soil types fitted well within the Freundlich model. According to Calvet shape of the adsorption isotherm provides information regarding the adsorption mechanisms [19]. The value of the exponent  $1/n$  gives an indication of the favorability and the capacity of the adsorbent-adsorbate system. Values  $n > 1$  represent favorable adsorption conditions and  $1 < n < 10$  shows beneficial adsorption. The soils A and B showed non-linear isotherm ( $n \neq 1$ ), which indicated that chlorotriazine could adsorb to the clay fraction of soil as well as organic matter present in the soil. Similar adsorption isotherms have been previously reported for simazine [13,20] and atrazine adsorption [21,22]. Apart from soil organic matter, clays can also be an important sorbents for the adsorption of organic pesticides in the soil [23]. Simazine can sorb on hydrophobic microsites of smectites [24], and montmorillonite clay minerals [23]. Celis et al. [25] has reported that atrazine and simazine initially sorbed as neutral species on hydrophobic microsites of clay (montmorillonite).

Soil	pH	Organic matter (%)	Organic carbon (%)	Conductivity ( $\mu\text{S}/\text{cm}$ )	Texture	Particles Size		
						Clay	Silt	Sand
A	6.4	13.7	8.6	186.2	Loam	25	30	45
B	8.0	4.8	2.1	178.1	Clay Loam	37	36	27

Table 1: Physical and chemicals properties of the agricultural soils collected from Punjab, India.

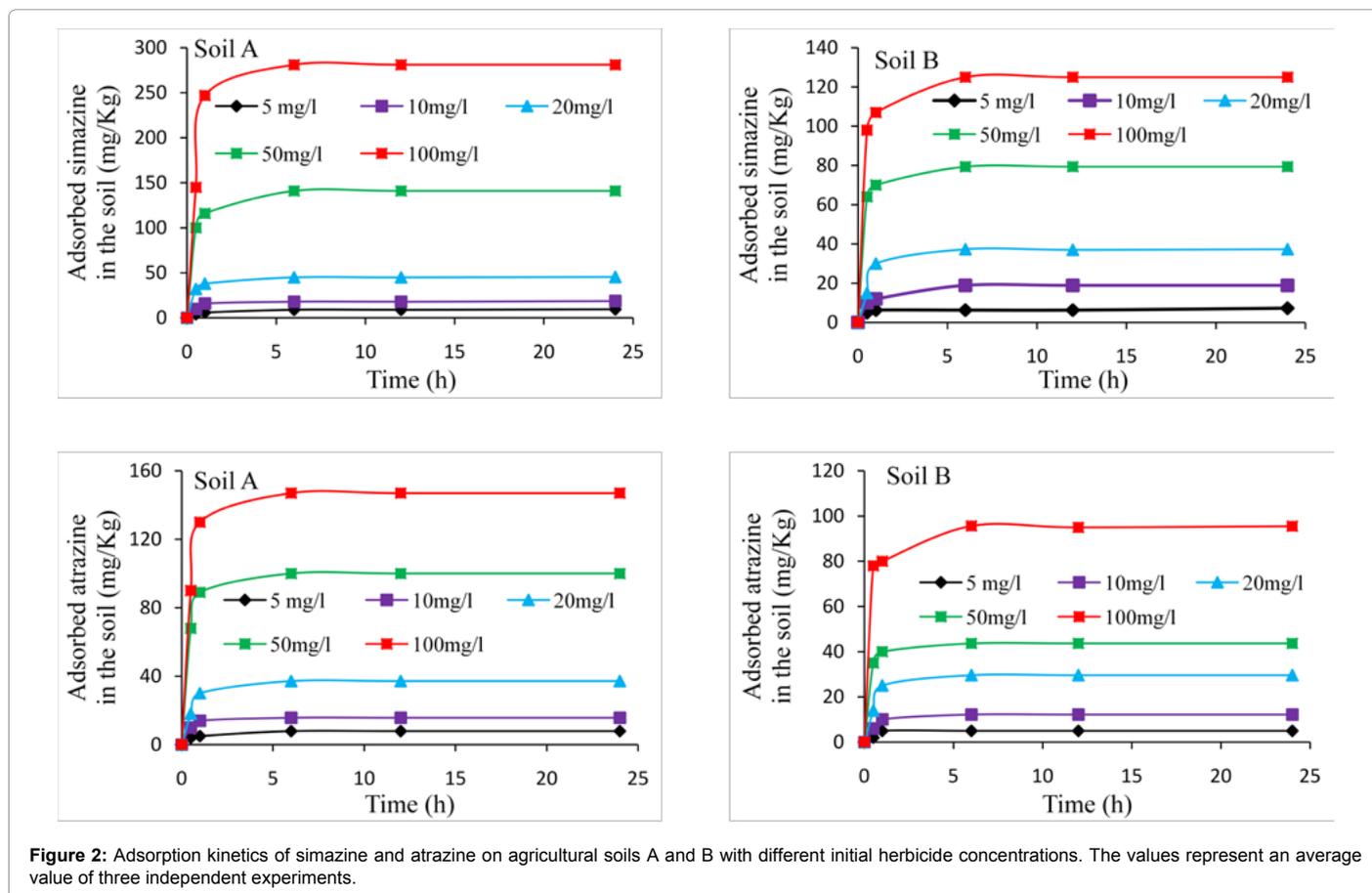


Figure 2: Adsorption kinetics of simazine and atrazine on agricultural soils A and B with different initial herbicide concentrations. The values represent an average value of three independent experiments.

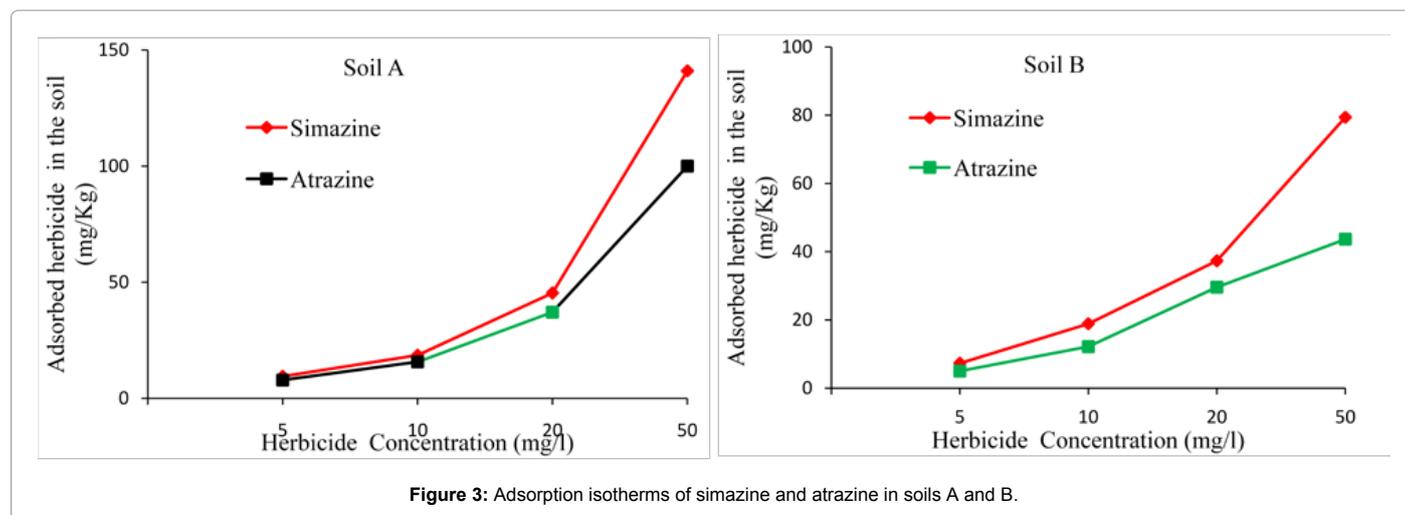


Figure 3: Adsorption isotherms of simazine and atrazine in soils A and B.

Herbicides	Temperature (K)	Soil	$K_f$ (mg/Kg)	1/n	$R^2$	$K_{oc}$ (mg/kg)	$K_{om}$ (mg/kg)
Simazine	298	A	1.1581	0.1496	0.9978	13.4662	8.4532
		B	0.9138	0.3251	0.9868	43.5142	19.0357
	308	A	0.8559	0.3293	0.9933	17.8312	6.2474
		B	0.6039	0.4747	0.9925	28.7571	12.5812
Atrazine	298	A	1.0113	0.2121	0.9889	11.7593	7.3817
		B	0.8395	0.2865	0.9811	39.9762	17.4896
	308	A	0.8009	0.3598	0.9846	9.3128	5.8459
		B	0.5898	0.3876	0.9942	28.0857	12.2875

Table 2: The adsorption parameters of simazine and atrazine in agricultural soils at different temperature. The values represent an average value of three independent experiments.

Soil organic matter plays a crucial role in the adsorption of organic pesticides [2]. In the present study soil A with high organic matter content exhibited better herbicide sorption ability. In the soil A 47.5-70.5% and 40.0-50.0% of available simazine and atrazine was adsorbed, respectively. The soil B, with less organic matter content exhibited 36.4-47.1% and 25.0 -36.9% of adsorption for simazine and atrazine, respectively. The sorption of s-triazines on organic matter is governed by H bonds and proton transfer between s-triazines and acidic groups of humic substances [10]. The  $K_{oc}$  values observed in the present study suggest that mineral constituents as well as soil organic matter contribute towards sorption of herbicides. Literatures suggest that the adsorption of chlorotriazine is more hysteretic for humic acid than for the clay [13]. Herbicide desorbs relatively easily from clay than from the organic matter, suggesting a stronger interaction between chlorotriazine and organic matter than between the chlorotriazine herbicides and clay. Thus, soil B that has more clay and less organic matter exhibited comparative low herbicide sorption.

### Chlorotriazine adsorption enthalpy

Temperature play crucial role in determining the extent of herbicide that gets adsorbed on the soil. To determine chlorotriazine herbicides adsorption enthalpy in the agricultural soils, adsorption experiments were conducted at 25°C and 35°C. Table 2 shows Freundlich constants at 25°C and 35°C. At higher temperature,  $K_f$  values declined for both the herbicides used in the present study. The values of the Freundlich exponent 'n' also decreased when the temperature increased from 298 K to 308 K. In the soils A the  $\Delta G$  values for simazine changed from -1272 kJ/mol to - 1128 kJ/mol when the temperature was increased from 298K to 308 K, thus indicating the feasibility and spontaneous nature of adsorption process at lower temperature. A similar observation was

also made in soil B where  $\Delta G$  values increased from -1756 kJ/mol to -1559 kJ/mol with change in the temperature. In the soils A the  $\Delta G$  values for atrazine was found to change from -1191 kJ/mol to - 1087 kJ/mol when the temperature was increased from 298K to 308 K. A similar observation was also made in soil B where  $\Delta G$  values changed from -1705 kJ/mol to -1545 kJ/mol. Decrease in  $\Delta G$  value suggest the feasibility and spontaneous nature of the adsorption process [13].

The chlorotriazine herbicides adsorption increased at lower temperature, indicating that the process is exothermic. The exothermic adsorption of chlorotriazine on soil may be explained by the fact that the adsorbate-adsorbent bonds were weakened with increasing temperature. Temperature induced change in aqueous solubility of herbicides may also influence the adsorption process [26]. Higher temperatures increase herbicides solubility and lower the tendency to get sorbed on the soils. During summer in Punjab temperature generally remain higher than 25°C. Thus, the probability of surface and ground water contamination with chlorotriazine herbicides is more during summer rains than in the winter. Chlorotriazine herbicides applied during winter (when temperature remains below 25°C) have more tendency to remain adhered to the soil.

### Effect of pH on chlorotriazine adsorption

The adsorption capacity of herbicides is significantly influenced by the initial pH of the solution. In the present study adsorption of chlorotriazine herbicides in the soils were more at low pH and decreased with the increase in pH of the solution (Table 3). Thus, indicating that the availability of the adsorption sites to chlorotriazine molecules reduced as the pH value increased. This observation is in accordance with the general trend observed for many other pesticides [13,27,28]. The number of protonated surface on the adsorbent increases with

decreasing pH and thus the coulombic attractive forces between more positively charged surfaces and herbicide increases at lower pH values [13]. In soil A, the  $K_f$  value for simazine was 1.6235 mg/kg at pH 5, which is 3.2 times higher than those of corresponding value at pH 9. For soils B the  $K_f$  value for simazine at pH 5 was 1.1610 mg/kg which is 2.3 times higher than the corresponding value at pH 9. Similarly in soil A, the  $K_f$  value for atrazine was 1.4938 mg/kg at pH 5, which was 2.7 times higher than those of corresponding value at pH 9. In soils B, the  $K_f$  value at pH 5 and pH 9 changed by ~ 1.5 times only. The differences may be due to the different concentration of organic matter. Soil A with high organic matter content has a better buffer capacity for pH change [13]. Organic matter present in the soil is known to act as a pH buffering agent in nature [29].

### Desorption behavior of chlorotriazine on soils

Looking into the desorption process of herbicides is vital since it determines the release rate and the potential mobility of herbicides in the soil as well as the treatment strategy for the contaminated soils. The herbicides with a lower desorption rate may possess higher risk to the successive crops. Thus, desorption kinetic studies were conducted to assess the desorption potential of adsorbed chlorotriazine herbicides and the results are shown in Table 4. The rate of desorption was comparatively fast in soil B as compared to the soil A. The organic matter content may play an important role in the desorption process [13]. Soil B with little organic matter content exhibited the highest desorption  $K_f$  for both the herbicides (Table 4). The  $K_f$  values of the desorption process suggested that atrazine has better desorption ability as compared to simazine. This observation may be attributed to the different solubility of atrazine and simazine. Atrazine with a comparatively better water solubility has higher tendency to enter the aqueous phase and get desorbed from the soil.

### Hysteresis in adsorption and desorption

Occurrence of hysteresis in adsorption-desorption reaction in the soils suggests that adsorption of pesticides occurs with a limited degree of reversibility depending upon both the physico-chemical properties of the molecules and the soils involved in the process [13,30]. Generally,

a value of hysteresis index close to 1 means that desorption and sorption has similar rate, therefore, hysteresis is absent. On the other hand, a value of hysteresis index less than 1 indicates that the rate of desorption is lower than that of sorption, thus hysteresis takes place [31]. In the soil A, the hysteresis index was less than 1 for both the herbicides (Table 4). However, in the soil B the hysteresis index for simazine and atrazine was less than 1 and nearly equal to 1, respectively. The soil B with low organic matter content and atrazine with a higher water solubility supported desorption process in the present study. Results suggest that organic matter and aqueous solubility of herbicides significantly influence the adsorption-desorption hysteresis. The entrapping of herbicide molecules within the condensed soil organic matter makes a significant contribution to adsorption-desorption hysteresis. In soils with high organic matter content, the adsorption-desorption hysteresis is mainly controlled by organic matter. However, involvement of the soil mineral composition in desorption behavior of herbicides cannot be ignored [14]. The hysteresis index values observed in the present study, suggest that the adverse effect of simazine and atrazine on the succession crop should be noticed, especially when chlorotriazine were applied on soils with high organic matter content, for example, soil A. While applying atrazine to soil with low organic matter content like soil B, attention should be paid to the risk of groundwater and surface water contamination from the herbicide.

### Conclusions

This study contributes to the understanding of simazine and atrazine sorption-desorption process in the two types of agricultural soil of Punjab, India. Organic matter content of soil has significant influence on the adsorption of simazine and atrazine. Soil with high organic matter content has better herbicide's adsorption ability. Soils of Punjab with higher organic matter content exhibited enhanced simazine and atrazine sorption capacity. The increase in temperature and pH of the solution had a negative effect on the adsorption process. Organic matter content also contributed significantly towards simazine and atrazine desorption process. The results from the present study would help in designing of effective herbicide management strategies in Punjab, India. This also highlights the feasibility of adverse effect of soil adsorbed chlorotriazine on the succession crops.

Herbicides	pH	Soil	$K_f$ (mg/Kg )	1/n	$R^2$	$K_{oc}$ (mg/kg)	$K_{om}$ (mg/kg )
Simazine	5	A	1.6235	0.0376	0.9928	18.8779	11.8503
		B	1.1610	0.2881	0.9926	55.2857	24.1875
	7	A	1.1581	0.1496	0.9978	13.4662	8.4532
		B	0.9138	0.3251	0.9868	43.5142	19.0357
	9	A	0.5071	0.2296	0.9894	5.8965	3.7014
		B	0.4994	0.3865	0.9874	23.7809	10.4041
Atrazine	5	A	1.4938	0.0024	0.9794	17.3697	10.9036
		B	1.0956	0.2132	0.9878	52.1714	22.825
	7	A	1.0113	0.2121	0.9889	11.7593	7.3817
		B	0.8395	0.2865	0.9811	39.9762	17.4896
	9	A	0.5459	0.3301	0.9744	6.3476	3.9846
		B	0.6968	0.3231	0.9719	33.1809	14.5166

**Table 3:** The adsorption parameters of simazine and atrazine in agricultural soils at different pH. The values represent an average value of three independent experiments.

Herbicides	Soil	$K_f$ (mg/Kg )	1/n	$R^2$	$K_{oc}$ (mg/kg)	$K_{om}$ (mg/kg )	Hysteresis index
Simazine	A	0.5717	0.4738	0.9957	6.6476	4.1729	0.315
	B	0.4979	0.4940	0.9814	23.7095	10.3729	0.658
Atrazine	A	0.5238	0.4043	0.9936	6.090	3.8233	0.525
	B	0.6780	0.3015	0.9774	32.285	14.125	0.950

**Table 4:** The desorption parameters of simazine and atrazine in the soils.

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