Sorption-desorption behavior of atrazine for calcareous soil from Antalya, Turkey

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Abstract: - The aim of this work was to determine sorption-desorption behavior of atrazine in soil from Antalya, Turkey. Batch experiments were conducted to investigate the sorption isotherm and sorption-desorption characteristics of atrazine. The sorption isotherm and kinetic studies showed that the sorption of atrazine was described by nonlinear and rate-limited processes for soil. Results indicate that organic matter content of soil has played major role on sorption behavior of atrazine (Kf= 3). Inorganic components could have contribution for influencing the sorption of atrazine. Results summarize that sorption of atrazine to calcareous soil with sandy loam texture was moderate which could lead to a possibility of contamination of groundwater resources. The results from the present study would also help in designing of effective herbicide management strategies in Antalya, Turkey.

Key-Words: - Antalya, atrazine, heterogeneous soils, isotherm, kinetic, sorption.

1 Introduction

Contamination of soils, surface and groundwater by pesticides has been recognized as an important environmental issue. Particularly, herbicides such as *s*-triazines are priority pollutants as they are widely used all over the world [1]. Among the various herbicides, atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine] takes significant attention as it is one of the most heavily applied types [2]. Atrazine has been used to increase crop production by targeting pre- and post-emergent grassy weeds due to its high efficiency and low cost.

Atrazine has been extensively used in recent decades for agricultural control in vicinity of Antalya. Although, atrazine exhibits broad distribution in Mediterreanen Region, there is limited information in the literature regarding the sorption and desorption behavior in various soils around Antalya. Akyol, investigated sorption behavior of atrazine in non-amended and stable manure-amended agricultural soils from Mersin and Antalya [3,4]. It was revealed that sorption of atrazine to soil component was moderate and concentration dependant (Freundlich isotherm n<1). In addition, sorption of atrazine exhibited much greater sorption affinity when soil was amended with stable manure, indicating the impact of organic carbon fraction on sorption of atrazine.

The aim of this work was to determine sorption-desorption behavior of atrazine in calcareous soil from Antalya, Turkey. Sorption isotherm and sorption-desorption kinetic experiments were carried out to have a better understanding for contamination risk of high permeability overlying karstic aquifer system of Antalya.Different isotherm and kinetic models (Linear, Freundlich and Langmuir isotherms) were applied to experimental data obtained from batch experiments to investigate sorption mechanism.

2 Metarials and Methods

2.1 Soils and solitions

Soil used in this study was calcareous collected from overlying highly permeable travertine aquifer in Antalya. Samples were dried at 105 °C for 48 hours and sieved through 2 mm prior to batch experiments. Selected physical and chemical properties of the soil are presented in Table 1. Calcareous soil comprises of calcium carbonate, intermediate organic carbon content and minor amounts of quartz [4,5]. Calcareous soil was used for batch experiments. Batch experiments were conducted using analytical-grade atrazin [2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine],which was dissolved in a 0.1% methanol background electrolyte solution of 0.02 M $CaCl_2$.

Table 1. Physical and chemical properties of soils

	Calcareous [a]
Sand (%)	67
Silt (%)	30
Clay (%)	3
Texture	Sandy Loam
Bulk Density, ρ_b (g/cm^3)	1.34
Total Organic Carbon (%)	0.97
Hard Carbon (kerogen and black carbon), (%)	22
Soft Carbon (fluvic/humic acid and lipids), (%)	78
$pH_{1:1}$	8.4

[a] Akyol et al., 2015

2.2 Experimental Studies

Batch experiments were conducted to determine the sorption isotherm and the sorption–desorption kinetics of atrazine for soil. Sorption isotherms were performed in duplicate at different atrazine concentrations (0, 0.2, 0.5, 1, 5, 10 mg/L) at room temperature. A predetermined volume of atrazine solutions and 5 g of soil samples were added in 50 mL polyethylene centrifuge tubes and shaken at 450 rpm for 48 hours. At the end of the required agitation period, supernatants were filtered through 0.2 PTFE filter and analyzed for atrazine. The amount of atrazine sorbed to the soil was calculated by subtracting supernatant concentration in equilibrium from the initial atrazine concentration. Potential loss of atrazine in the absence of soil was also investigated under the same experimental conditions.

Atrazine sorption kinetic experiments were performed at two different initial concentrations (2 and 10 mg/L) for calcareous soil. For the atrazine sorption experiments, 5 gram of soil and 25 ml atrazine solution were placed in polyethylene centrifuge tube and shaken at 450 rpm for 72 hours. At the different time periods; aliguots (2 ml) were sampled from each tube at only once. The supernatants were filtered through 0.2 PTFE filter and analyzed for atrazine.

Atrazine desorption kinetic experiments were conducted by replacing supernatant with de-ionized water in each centrifuge tubes after sorption reached equilibrium (24 hrs). After de-ionized water replaced with supernatant, same experimental procedure was followed as in determination of sorption kinetics. Some of the experiments were duplicated to check the reproducibility of the results.

2.3 Analysis

Atrazine was analyzed by UV–VIS technique at wavelength of 222 nm (for high concentrations: >0.05 mg/L) and by using enzyme-linked immune-sorbent assay (ELISA) at wavelength of 450 nm (for low atrazine concentrations: 0.05–5 mg/L). Consumer-based ELISA kits have become available for atrazine analysis and manufactured by Abraxis TM [6]. Samples were also filtered and centrifuged prior to analysis to avoid interference for analysis.

2.4 Isotherm and kinetic models

In the study isotherm and kinetic models were applied to experimental data in order to investigate the adsorption characteristics of atrazine.

2.4.1 Used isotherm models

Langmuir and Freundlich isotherm models were applied considering the amount of adsorbed atrazine (q_e) per unit soil mass. q_e values were calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)/V}{m}$$

In the equation $C_0$and C_e(mg/L) are the initial and equilibrium atrazine concentrations, V(L) is the sample volume, and m(g) is the soil amount.

Linear isotherm; $q_e = K_p / \quad C_e$

Langmuir isotherm model;

$$\frac{C_e}{q_e} = \frac{1}{\mathrm{k}\mathrm{V}_m} + \frac{C_e}{V_m}$$

Freundlich isotherm model;

$$\log q_e = \log K_f + 1/n \log C_e$$

In linear isotherm $K_p$shows the adsorption coefficient whereas k and $V_m$denote the equilibrium constant and monolayer adsorption capacity, respectively. K_f and $n$are adsorption capacity and intensity, respectively. $1/n$ value in the range 0-1 denote favorable characteristic of the adsorption process.

2.4.2. Pseudo-first orderreaction kinetics

The following linear equation can be used to develop pseudo-first-order kinetic model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

In the equation k_1 denotes the rate constant of the first order reaction kinetic. q_e and q_t show the amount of adsorbed material at time t and saturation (mg/g), respectively.

3 Results and Discussions

3.1 Atrazine sorption isotherm

Batch experiments were conducted to determine the sorption isotherm of atrazine in calcareous soil in the range of 0.2–10 mg/L initial atrazine concentrations. Langmuir, Freundlich and Linear isotherms were applied to experimental data and obtained results are illustrated in Fig. 1 and Table 2. Langmuir isotherm values have not been reported due to having poor results.

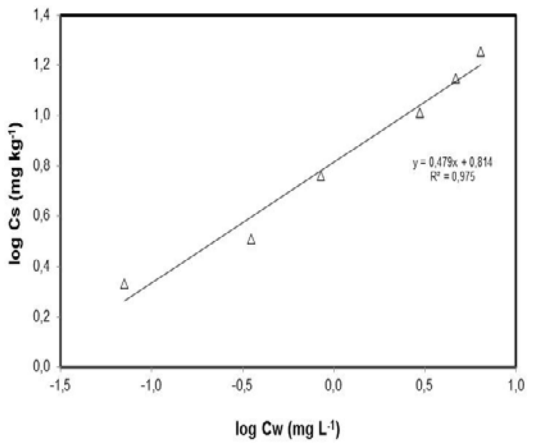

Figure 1. Results of isotherm for the soil.

Table 2. Results of linear and Freundlich isotherm

Soil	Linear isotherm		Freundlich isotherm		
	K_d	R^2	K_f	n	R^2
Calcareous	2.98	0.91	3.02	0.48	0.98

Isotherm results showed that sorption of atrazine was represented well with Freundlich isotherm for both soils suggesting that atrazine sorption has occurred on heterogeneous surfaces [15]. The Freundlich soil–water partitioning coefficients (Kf) calculated from the isotherm was 3.02 L/kg for calcareous soil. It was indicated that atrazine sorption is concentration dependent and the degree or rate of sorption decreases with increasing atrazine concentration for soil.

As noted in the previous studies, soil organic carbon fraction (>O.C=0.1) plays dominant role on the sorption of atrazine for soils [2,7,16]. In addition, the non-linearity exponent values (n) calculated from the Freundlich isotherm were 0.48 for calcareous soil. Values of (n) basically represent the degree of non-linearity and could be related to hard carbon component of soils [4].

Apart from soil organic carbon, the contribution of the inorganic soil components such as clay minerals could have slight impact on the sorption behavior of atrazine in soil. The contribution of carbonate content of soil on atrazine sorption could have negligible impact for soil [7, 8, 9].

3.2 Atrazine sorption-desorption kinetics

Batch sorption kinetic tests were performed at 2 and 10 mg/L atrazine concentrations for calcareous soil. Calculated sorption rate coefficients obtained from pseudo-first-order kinetic model were presented in Table 3.

Table 3. Sorption rate coeffecients

Atrazine	Rate of sorption k' (s^{-1})	r^2
2	4.86E-4	0.98
10	3.01E-4	0.99
	Rate of desorption k'' (s^{-1})	
2	7.81E-6	0.98
10	2.04E-5	0.97

As seen in Fig 2, sorption kinetics exhibited two distinct behaviors soil system. The initial step was shown as rapid drop in atrazine concentration indicating fast sorption mechanism. In the second step; drop of atrazine concentration continued at a slower rate by reaching to equilibrium.

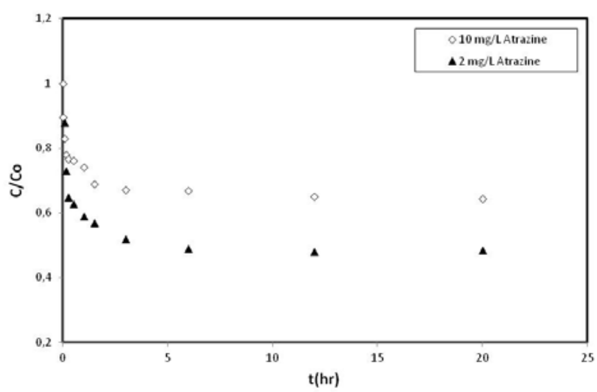

Figure 2. Sorption kinetics for the soil

This two step observation indicated that a large number of vacant surface sites were available for adsorption at the beginning. After the vacant surfaces were occupied by atrazine molecules, the repulsive forces become active, thereby slowing down the kinetic of adsorption process. Similar observation has also been observed in prior studies for organic herbicides [10, 11, 12]. Despite 5 time difference in initial atrazine concentrations (2 and 10 mg/L), similar values were observed in the sorption rate coefficients (Table 3).

Desorption kinetics of atrazine was determined following the completion of sorption kinetics experiments conducted at two different initial atrazine concentrations (2 and 10 mg/L). As seen from Fig 3, desorption of atrazine was also initially rapid then continued slower at the studied concentrations. This phenomenon was described as hysteresis indicating chemically non-ideal behavior (rate-limited desorption) [4].The rapid desorption can be attributed to soft carbon fraction (humic/fluvic acid and lipids) whereas slower desorption can be responsible by hard carbon fraction (black carbon, kerogen) of soils that led to chemically non-ideal behavior.

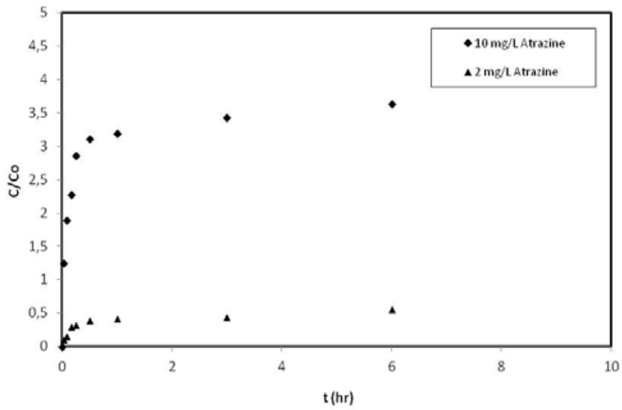

Figure 3. Desorption kinetics for the soil

According to the kinetic data; desorption rate of atrazine at later stage (>30 min) was about 10-100 times slower than the early stage (30 min) rate of desorption, indicating the presence of rate-limited desorption effect. Akyol et al., also postulated the rate-limited desorption of hydrophobic organic compounds due to the effect of organic carbon fraction in such calcareous soils [4,5]. Based on both the sorption isotherm and the sorption/ desorption kinetic studies, it can be concluded that non-linear sorption and rate-limited desorption processes predominantly influence the fate and transport of atrazine herbicide in such soil conditions.

4 Conclusion

Pesticide contamination of soil and groundwater is a common problem in the environment. The aim of this work was to determine sorption-desorption behavior of atrazine in calcareous soil from Antalya, Turkey. Batch experiments were conducted to investigate the sorption isotherm and sorption-desorption characteristics of atrazine in calcareous soil. Linear, Langmuir and Freundlich isotherm models were applied to evaluate the emprical values. The sorption isotherms for soil conditions were non-linear and could be accurately described by a Freundlich isotherm over a wide range of atrazine concentration. Results indicate that organic matter content of soil has played major role on sorption of atrazine for soil and exhibited sorption–desorption hysteresis (rate-limited desorption).

As a result, sorption of atrazine onto calcareous soil was moderate which could lead to contamination risk of groundwater resources. The results from the present study would also help in designing of effective herbicide management strategies in Antalya, Turkey.

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