PESTICIDE ADSORPTIONON SOIL: ASSESSMENT OF CALCULATION METHODS

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Abstract- It is important to get correct results of adsorption coefficients, as the adsorption is the major process in order to describe the fate of pesticides in soil. In this study, Batch equilibrium method was compared with centrifugation method for measurement of adsorption by using pesticide (captan) on six different types of soil. The results showed that the batch method overestimates both adsorption and desorption process when compared to centrifugation method. This result explained by the use of low soil/solution ratios and extreme shaking process in batch method. The centrifugation method was accepted as more realistic method for the measurement of adsorption as it uses the high soil/solution ratios and more realistic experimental conditions. It is concluded that the overestimation of sorption leads the misinterpretation of adsorption and it may increase the probability of pesticide leaching into groundwater.

Keywords- Adsorption; batch method; captan; centrifugation method, pesticide

I. INTRODUCTION

Sorption is one of the most important factors that affect the fate of pesticides in soil. The extent of sorption will affect the amount in solution and thus both the bioavailability and potential loss of the pesticide. Sorption studies provide quantitative information regarding pesticide movement and the distribution of the compound within the environmental compartment. Most of the transport processes of pesticides such as volatilization to atmosphere, leaching into groundwater and runoff to surface water are described by the sorption coefficient. All pesticide transport models use adsorption coefficients in order to estimate the probable transport pathways. Therefore, correct estimation of sorption is very important issue especially in decision-making of environmental behavior of pesticides. (Cornejo, 2000; Walker, 2000; Kennedy, 2003; Walker, 2003)

Pesticide soil/solution distribution coefficients (Kd), commonly referred to as pesticide soil sorption values, are utilized to predict soil mobility of the compounds.The most commonly used method for the measurement of adsorptionKd is Batch Equilibrium Method developed by OECD (1997). Soil is shaken with an aqueous solution of pesticide, after which the solid and aqueous phase are separated by centrifugation, and the concentration of pesticide in the aqueous phase determined by a suitable analytical technique. Despite its advantages, the main shortcoming of the method is its unrealistic experimental conditions. For example, the method uses higher soil:solution ratio comparing to field conditions. Although, sieved and air dried soils are used in the experiments, the soils in the field conditions contain aggregates, which have a diversity of sizes and during leaching water will transport a proportion of the applied pesticide with it. Additionally, the period of contact between pesticide and soil is prolonged and degradation may occur (Koskinen and Harper, 1990; Sykas, 2003).

Besides the batch method, a number of techniques are available which allow the measurement of sorption in intact soils at more realistic solid: solution ratios. Several methods may be used to extract soil solution from unsaturated soil and pesticide concentration in order to calculate sorption. As well as being more representative of field conditions, pesticide sorption in soils at different moisture contents can be compared (Kennedy, 2003; Sykas, 2003).

Roy et al. (2000) used glass microfibre filters to directly sample soil solution. Sorption of several fungicides was measured in soils at 26.1% and 46.6% (w/w) water content. Sorption in the wetter soil was similar to that measured by the batch method, but it was greater in the drier soil. Centrifugation method, one of newly developed one by Walker (2000), is an easy method to measure the adsorption. The method estimates sorption of pesticides at more realistic soil: solution ratio and accepts soil aggregates without running any shaking operation. Walker & Jurado-Exposito (1998) studied isoproturon, diuron & metsulfuron-methyl sorption in soils using this technique. On comparing the centrifugation method to the batch method, the former indicated less sorption, attributed to fewer sorption sites being readily available than in the batch method (Kennedy, 2003). The aim of this study is to compare sorption and desorption measurement of batch and centrifugation method by using popular fungucide, captan, and to examine the kinetics of adsorption with both methods.

II. MATERIAL

A total of six different soils were used in experiments examining the sorption of captan. Soil samples were

collected from different sites in Marmara Region of Turkey and were selected to give a range of soil properties expected to influence pesticide sorption. All soils selected for use in this study are frequently used for agricultural cultivation.

Soil was collected from the upper 20cm of the soil profile. Several samples were taken from each site and then combined. Soil was air dried sufficiently to pass a 2 mm mesh sieve and stored in loosely closed polythene bags, refrigerated at 4°C. Before the experiments, soil properties such as soil texture, pH, organic carbon content and cation exchange capacity were determined (Table 1).

Table 1. Physical and chemical properties of selected soil

Soil	% OC	pH (in H_20)	CEC, (meq/100 g)
Loamy sand	2,0	6,1	13,4
Sandy loam	2,3	7,4	11,2
Loam	2,8	6,8	24,1
Sandy clay loam	2,5	7,8	19,3
Clay loam	3,1	6,9	15,5
Clay	2,9	7,5	32,8

The test compound used in this study is funguicide captan (N-(trichloromethylthio) cyclohex-4-ene-1,2dicarboximide) (Fig. 1). It is one of the commonly used fungucide with protective and curative action in vegetables and fruits (Tomlin, 1998).

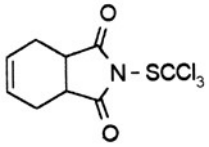


Fig. 1. Molecular structure and properties of captan (Tomlin, 1998)

III. METHODS

3.1.Batch equilibrium method

The details of the method are described in the OECD guideline 106 (OECD, 1997). An equilibrium period of 24 hours is commonly assumed. Sorption and desorption experiments were conducted at room temperatures.

Six pesticide concentrations from 0 to 25 microgram pesticides per gram of soil were used. Triplicates were prepared for each concentration for each soil. To measure sorption of the pesticides, each soil samples were placed in polypropylene centrifuge tubes (45ml maximum capacity) with 23 ml of 0.01M $CaCl_2$ solution in deionised water. 0.01M $CaCl_2$ solution was used to minimize disruption to the ionic composition of the soil solution. The tubes were shaken for 6h using an orbital shaker at 150 rpm. After the soil was pre-equilibrated, appropriate volumes from aqueous pesticide solutions were added in order to obtain the above concentrations. The stock solution did not exceed 10% of the final volume of the aqueous phase so as to limit any change of the pre-equilibration solution. The final volume of 25 ml aqueous phase was obtained by addition of 0.01M $CaCl_2$ solution giving a soil: solution ratio of 0.2. Tubes were then transferred to the orbital shaker for 24 h. After the agitation of the mixture, the soil suspensions were separated by centrifugation at 4500 rpm for 10 minutes. An aliquot (1ml) from the supernatant was pipetted into a 2 ml GC vial.

The amount of pesticide sorbed on the soil sample was calculated as the difference between the amount of test substance, which was initially presented in solution and amount of pesticides that existed after equilibration in the aqueous phase.

1.2. Centrifugation method

Disposable polypropylene syringe (10 ml capacity) with the outlet plugged with a small amount of nonabsorbent cotton wool was used in the experiments. The same amount (5g) of soil was placed into the syringe. Pesticide solutions from the stock solution were added in order to achieve the suitable concentrations of pesticide. Deionised water was added to reach 80% of the maximum water capacity of each soil. The top of the syringe was covered with self-adhesive tape to prevent evaporation of water and volatilization of pesticide. The outlet of the syringe entered the neck of a GC vial (2ml). The whole apparatus was fixed into a centrifuge tube (45 ml) in order to be centrifuged later.

For each pesticide concentration and soil, triplicates were made. The experiments were conducted in room temperature. After 24 hours equilibration the whole unit was centrifuged for 10 minutes at 4500 rpm and the sample solution that was collected in the GC vials was then analyzed with GC. The same pesticide concentrations were used in both methods for comparison purposes. The amount of pesticide sorbed on the soil sample was calculated similarly as in batch method.

3.3.Chromatographic method

A HP 6890 model gas chromatograph and 5973 MS detector was used with an 30 m x 0.25 mm x 0.25 µm HP-5MS column. Quantification was achieved by use of a computer integrator and the detection limits were 0.001 µg/l.

IV. RESULTS AND DISCUSSION

Sorption of captan on the soils was measured by the batch and the centrifugation method. Freundlich isotherms were used in order to assess the adsorption. Isotherms were obtained by plotting the mean concentration of the pesticide in the aqueous phase [C_{aq}] versus the mean concentration of pesticide [C_s] sorbed on the soil samples for each concentration. Partition coefficient values (K_d) were obtained from the slope.

$K_d = [C_s] / [C_{aq}]$

Sorption isotherms were also expressed using the linear form of Freundlich equation

$\log [C_s] = \log K_f + 1/n \log [C_{aq}]$

The K_f value was derived from the intercept of the linear form of Freundlich equation and 1/n from the slope.

Adsorption isotherms of captan on selected soils obtained by batch and centrifugation methods are given in Fig 2 and Fig 3, respectively.

From the figures the adsorption of captan presents L shape isotherms. It is the most observed type of isotherm for pesticide sorption in soil indicating that the initial slope of the isotherm is non linear and concave with respect the concentration in the aqueous phase. It also implies that sorption decreases as the number of pesticide molecules sorbed increases and the availability of free binding sites declines. This shows that specific binding sites are involved (Weber and Miller, 1989).

Details of adsorption results of captan are given in Table 2.

From Table 2, it is clear that adsorption coefficients obtained from batch method is gretaer than that of centrifugation method. Mean Kd and Kf values for batch method are 2,99 and 3,62, respectively. Similarly they are 1,63 and 2,18 for centrifugation methods. 1/n values are less than one indicating that the isotherms are L shape as explained before.

The correlation of pesticide sorption with soil properties is often complicated. Generally, properties of soil are themselves interrelated which tends to obscure any causal effects. However, very high correlation was found between adsorption coefficients and clay ratio for the adsorption of captan (Table 3). This shows that, captan adsorption is mainly controlled by the clay particles. The correlation for CEC and organic matter are also high and they also have positive effects on the extent of adsorption.

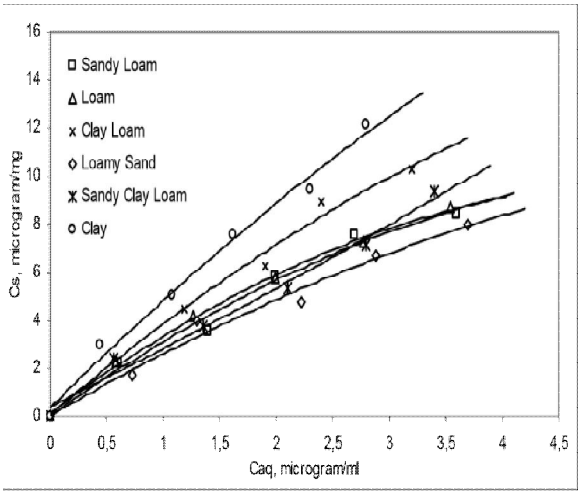


Fig.2 Adsorption isotherms of captan for six soil samples by batch method

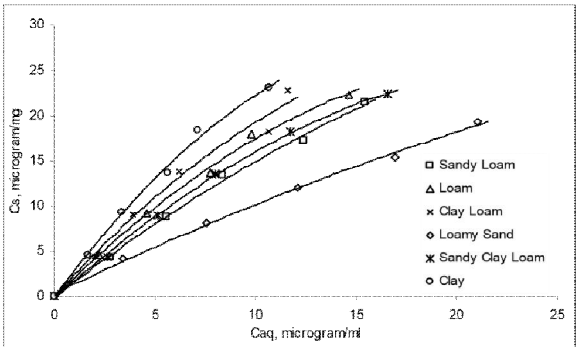


Fig.3 Adsorption isotherms of captan for six soil samples by centrifugation method

In order to compare the results in both methods, the percentage differences in Kd and Kf values between two methods are given in Table 4. From Table 4, it is clear that there is a significant difference between adsorption coefficients of two methods and batch method overestimates the adsorption. Mean Kd values of batch method are 45,8 % and mean Kf values 39,9 % higher than those of centrifugation method

The results are in agreement with other studies using similar experimental conditions. Walker and JuradoExposito (1998) compared the batch method with a similar centrifugation technique for measurement of sorption of isoproturon, diuron and metsulfuron-methyl and obtained greater $K_f$values in batch method. Kennedy et al,(2002) and Yazgan et al. (2004) obtained the similar results for ^{14}C anthranilate fungicide and carbofuran and imidacloprid pesticides, respectively.

Desorption, as the reverse process of sorption, determines the distribution of pesticides in the soil and therefore it has implications both for their mobility and availability. Desorption values are calculated as percentage in this study and given in Table 5. Desorption percentages refer to the percentage of removed pesticide from soil after adsorption process.

Table 2. Adsorption coefficients of captan obtained by batch and cenrifugation methods

	Kd	r^2	Kf	r2
		Batch method		
Loamy sand	2,26	0,97	2,54	0,95
Sandy loam	2,59	0,96	3,19	0,97
Loam	2,65	0,96	3,46	0,99
Sandy clay loam	2,68	0,98	3,38	0,97
Clay loam	3,42	0,98	3,94	0,99
Clay	4,36	0,98	5,23	0,99
		Centrifugation method		
Loamy sand	0,94	0,99	1,49	0,99
Sandy loam	1,43	0,99	1,72	0,99
Loam	1,67	0,97	2,36	0,99
Sandy clay loam	1,48	0,97	1,93	0,98
Clay loam	1,93	0,97	2,52	0,98
Clay	2,34	0,98	3,07	0,99

Table 3. Correlation of adsorption coefficients with soil properties

	OC, %	Clay, %	PH	CEC meq/100 g
Batch	0,726	0,970	0,406	0,739
Centrifuge	0,881	0,951	0,506	0,751

Table 4. Comparison of adsorption coefficients between two methods

	Kd differences, %	Kf differences, %
Loamy sand	58,4	41,3
Sandy loam	44,8	46,1
Loam	37,0	31,8
Sandy clay loam	44,8	42,9
Clay loam	43,6	36,0
Clay	46,3	41,3

The results shows that more desorption occur in batch method comparing to the centrifugation method similar to adsorption results.

Table 5. Desorption results (%) for captan with both methods

	Batch method	Centrifugation method
Loamy sand	52,1	33,0
Sandy loam	43,4	31,7
Loam	48,7	28,3
Sandy clay loam	45,9	30,1
Clay loam	42,2	28,2
Clay	29,5	19,2

CONCLUSIONS

The results of the comparison of batch with the centrifugation methods for captan pesticides indicate that the batch method overestimates sorption and desorption in comparison to the centrifugation method. This overestimation can be explained by use of different soil/solution ratios in two methods. Extreme shaking process in batch method could also be another reason of the greater sorption observed in comparison to the centrifugation method as the shaking process increases the disintegration of the soil aggregates. The size of aggregates was showed to be a significant factor that influences sorption in the same manner (Walker and Jurado-Exposito, 1998).

Adsorption coefficient is the major parameter in order to describe the fate of pesticides in soil. Many pesticide transport models use sorption coefficients in order to estimate probable transport pathways. Overestimation of sorption leads the misinterpretation of adsorption and the other process that affects the movement of pesticides. In the condition that real sorption rate of a pesticide is calculated to be higher in laboratory conditions, a greater proportion will be bioavailable for degradation or plant uptake or for transportation in the field conditions, which may increase the risk of leaching into the groundwater. Therefore, reliability of extent of sorption that is measured with the batch method must be questionable whether it reflects the real extent of sorption of a particular pesticide under natural conditions.

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