（15）　　　## Sorption and Transport of Asulam in Soils

<div align="center">土壌内におけるアシュラムの吸着・脱離と移動</div>

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ABSTRACT; Adsorption and desorption of asulam, a polar herbicide, on decomposed granite (DG), two sand size fractions of DG (0.212-0.425 mm and 0.075-0.150 mm), and two natural loam soils were studied under both batch and transport conditions. In the batch experiments, equilibrium was obtained within the first 10 minutes in the DG soils and after 36 hours in the organic matter-rich loam soils. Freundlich isotherm models best describe the measured adsorption/desorption data. Asulam adsorption was highly correlated with Cation Exchange Capacity (CEC) for the five soils, suggesting that both soil organic matter and clay minerals controlled sorption. Different sorption time-dependency (kinetics) were observed when comparing initially non-polluted with initially already asulam-polluted soil. During the transport (micro-column) experiments, significant differences in the shape and tailing of the breakthrough curves and in asulam retardation were observed for the two soil types. A Two-Sites Non-Equilibrium (TNE) model was used to describe and interpret the transport measurements. Pronounced non-equilibrium sorption and transport processes in the more organic and clay-rich loam soil gave a significant tailing of breakthrough curves while a symmetric breakthrough was seen for the more coarse-textured DG, probably due to the immediate sorption equilibrium in the DG. Slightly different values of pesticide retardation factors were obtained from the batch and transport experiments in the case of loam soil, likely due to the observed sorption non-equilibrium, sorption non-linearity, and sorption hysteresis processes.

KEYWORDS; Asulam, soil size fractions, adsorption, desorption, sorption kinetics, retardation factor

1. INTRODUCTION

Within the last few decades the use of pesticides has increased continuously. As a consequence, soil and groundwater are now frequently found to be contaminated with pesticides. Many studies have focused on the adsorption phenomena, but there is a lack of literature concerning the desorption; therefore less is known about this process[1]. Also, little is known about the time-dependency (kinetics) of pesticide sorption in soils. Therefore, in order to predict the risk of soil and groundwater contamination with pesticides, knowledge about sorption (adsorption and desorption) of pesticides on soils and soil particle size fractions is necessary.

Organic matter is recognized as the primary factor controlling sorption of non-polar organic chemicals in soils[2-3], but for polar organic compounds the behavior is not expected to be the same[4-6]. Mineral soil colloids play an important role in adsorption of polar organic compounds due to the high surface areas associated to their small particle size.

The batch technique is not considered fully representative for the pesticides transport under field situations because the transport parameters which can influence the adsorption rates should be taken into account[7-8]. Differences in adsorption between transport and batch systems have been frequently noted[9].

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There is few and contradictory information about asulam behavior in soils. Asulam adsorbs very little[10] and it is hardly degraded in dry soils according to Sczerzenie et al.[11]. Asulam and similar compounds are readily degraded by soil microorganisms according to Bartha and Pramer[12], Clark and Wright[13], and Kaufman[14].

Our objectives were 1) to investigate the influence of soil properties such as soil type (using two different soils, a low-organic compared to a higher-organic matter containing soil), soil texture (using different soil particle size fractions), organic C content, and CEC on the adsorption and desorption processes and 2) to investigate possible differences between sorption parameters estimated from batch and transport experiments

2. MATHEMATICAL MODELS FOR PESTICIDE SORPTION AND TRANSPORT

In this study a modified form of the Freundlich kinetics type equation was used to describe the time-dependency (kinetics) as the Freundlich type equation has been suggested to best describe short-term sorption kinetics[15]. The modified two-parameters Freundlich equation used in this study is

$$C/C_0 = K(t-t_0)^{-N}, \qquad t > t_0 \qquad [1]$$

where C is asulam concentration in the liquid phase (solution concentration) at time t (hours), C_0 is asulam concentration in the liquid phase at time t_0 (mg l^{-1}), and K and N are sorption parameters (assumed constant).

The models for characterizing the equilibrium sorption are well known from the literature. The Henry's region (linear) sorption model describes adsorption at very low solution concentration and for solids of low sorption potential:

$$S = kC \qquad [2]$$

where S is the amount of pesticide adsorbed per unit mass of soil (mg kg^{-1}), and k is the linear distribution coefficient (l mg^{-1}).

The Freundlich isotherm equation is the most common non-linear equilibrium model used to describe pesticide sorption:

$$S = k_f c^n \qquad [3]$$

where k_f relates to sorption capacity, and n to sorption intensity. Eqs. (2) and (3) were fitted to the batch equilibrium measurements.

To analyze the transport experiments, the Two-Site Non-Equilibrium (TNE) model by Parker and van Genuchten [16] was used. The basic idea of this model is that the solid phase of the soil is made up of different constituents and a chemical will react with these constituents at different rates and intensities, an instantaneous reaction on "type-1" sites , and a time dependent reaction on "type-2" sites.

The following linear adsorption equations are considered in the TNE model:

$$S_1 = k_1 C = FkC, \qquad [4]$$

$$S_2 = k_2 C = (1- F)kC. \qquad [5]$$

At equilibrium the total adsorption is:

$$S = S_1 + S_2 = kC. \qquad [6]$$

"Type-1" sites are always at equilibrium, thus:

$$\frac{\partial S_1}{\partial t} = Fk\frac{\partial C}{\partial t} \qquad [7]$$

and the adsorption rate for the "Type-2" non-equilibrium (kinetic) sites is given by a linear and reversible rate equation of the form:

$$\frac{\partial S_2}{\partial t} = \alpha(k_2 C - S_2). \qquad [8]$$

The combined transport model can then be written as:

$$\left(1+\frac{F\rho k}{\theta}\right)\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial S_2}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x}, \qquad [9]$$

$$\frac{\partial S_2}{\partial t} = \alpha[(1-F)kC-S_2]. \qquad [10]$$

At equilibrium, the pesticides retardation factor "R" is given as:

$$R = 1 + \frac{\rho k}{\theta}. \qquad [11]$$

In the above Eqs. [4] - [11] the subscript numbers 1 and 2 refer to the first type "equilibrium" sites or to the second type "kinetics" sites, x is the distance (cm), t is time (hours), D is the dispersion coefficient (cm^2 hour^{-1}), u is the average pore-water velocity (cm hour^{-1}), ρ is the soil bulk density (g cm^{-3}), θ is the volumetric soil-water content (cm^3 cm^{-3}), k is the distribution coefficient as previously also defined in Eq.[2], α is a first-order rate coefficient (hour^{-1}) and F is the

fraction of the total amount of adsorption sites that are "Type-1" sites.

3. MATERIALS AND METHODS

3.1 Batch Adsorption Experiments

The soils used were the whole soil (<1.0 mm) and two grain size fractions (0.212-0.425 mm, and 0.075-0.150 mm) of a Hiroshima type weathered granitic soil, decomposed granite (DG), and two natural loam soils (Hiroshima type A and B) with different organic matter contents. The characteristics of the soils are given in Table 1.

Table 1. Physical and chemical properties of the soils and soil size fractions used. The whole soil is represented by the fraction <1.0 mm. Two types of whole loam soil (labeled A and B) with different organic matter content were used. DG is Decomposed Granite, SA is Soil Surface Area, CEC is Cation Exchange Capacity, and TOC is Total Organic Carbon

Soil size fraction (mm)	SA (m^2/g soil)	CEC (meq/100 g soil)	TOC (%)
Loam(A);<1.0	13 1	13.0	1.3
Loam(B);<1.0	10.6	9.8	0.4
DG; <1.0	9.1	3.0	<0.1
DG; 0.212-0.425	7.6	2.7	<0.1
DG; 0.075-0.150	13.9	6.9	<0.1

Asulam (N-acetyl p amino sulphone amide), is a herbicide from the large family of thiocarbamates and it has a high aqueous solubility (5000 mg l^{-1}). This herbicide is used on reforestation areas, Christmas tree plantings, sugarcane and noncrop areas. According to the US regulations, no amount of asulam is legally allowed to appear on food [18].

The pesticide solutions were made in 0.005 M $CaSO_4$ and contained 10, 20, 30, 40, and 50 mg l^{-1} asulam. The 0.005 M $CaSO_4$ was used in order to avoid changing the ionic strength of the soils when the pesticide solution was added to the soils, i.e. to avoid changing the soil surface structure.

In the adsorption experiments 10 ml of pesticide solutions were added to 5 g of dried soils in 100 ml brownish screw cap tubes. The sample tubes were shaken mechanically using a top table shaker at 25°C. The shaking time varied between 10 min. to 36 hours to investigate the adsorption time-dependency (kinetics). In addition to this, two-step kinetics sorption were followed as described by Farcasanu et al.[17]. After 36 hours adsorption (Step I), 70% of liquid phase were replaced with fresh 0.05 M $CaSO_4$ solution (asulam free) and the equilibration was followed for additional 36 hours (Step II). After various times 7 ml of supernatant

were extracted and centrifuged for 30 min. at 8000 rpm.

All samples were filtered through a 0.20 μm membrane filter (type calc 20 ASTROPORE). Pesticide solutions were analyzed by HPLC (Shimadzu C-R6A Chromatopac), using STR ODS-2 column (Shinwa Chemical Industries, Ltd.) (4.0 *150 mm), UV detector (270 nm), and 20 μl sample loop (manual injection). The mobile phase consisted of methanol/water solution (ratio: 1/2), buffered with 0.05 M ammonium acetate to a pH 6.8.

3.2 Batch Desorption Experiments

The samples were first equilibrated for 4 hours in the case of DG and 36 hours in the case of loam soils; sufficient to obtain an apparent equilibrium according to the batch adsorption experiments. Seven ml of supernatant were removed from the equilibration tubes and replaced with 7 ml fresh 0.005 M $CaSO_4$ solution. For equilibrium desorption experiments the shaking times were 4 (DG) or 36 hours (loam) and the replacing-shaking process was repeated three times to obtain three points on the desorption isotherm.

All experiments were run at 25°C using duplicate for each concentration and grain size. All solutions were filtered before use. At the end of each experiment the recovery of asulam was computed based on mass balance. Stock solutions of pesticide kept in vials in the same conditions did not change their initial concentration during the experimental period.

3.3 Transport Experiments

Stainless steel microcolumns (25 cm length and 1.0 cm diameter) were packed with dry soil to bulk densities of 1.26 g cm^{-3} (decomposed granite, 0.425-0.212 mm) and 1.5 g cm^{-3} (loam B), respectively.

D_2O and $CaCl_2$ solutions used as tracers were passed through the soil microcolumns at a constant flow rate ranging from 0.04 to 0.1 ml min^{-1} with an HPLC pump (Shimadzu, LC-10AD). Breakthrough curves (BTCs) were monitored in the effluent with a UV detector (Shimadzu, SPD-10A UV-VIS), and recorded with a Shimadzu, C-R3A recorder. The transport parameters (u and D) were estimated from the tracer BTCs by the First-Term Method[19].

Subsequently, the solutions of pesticide (10 mg l^{-1}) were passed through the soil columns by shifting suddenly the pump from mobile phase (0.005 M $CaSO_4$ solution, or water) to the pesticide solution, at the same flow rate of the mobile phase and the BTCs were monitored in the same way as

previously described. The Parker and van Genuchten [16] Two-Site Non-Equilibrium model (Eqs. [4]-[11]) was then fitted to the pesticide BTCs to estimate the remaining parameter values.

4. RESULTS AND DISCUSSION

4.1 Equilibration time and sorption kinetics during batch experiments

Figure 1 shows the liquid phase asulam concentration as function of time. Equilibrium is already obtained within the first 10 minutes in the case of DG soil and soil size fractions, i.e., no adsorption kinetics were seen for the DG. However, a pronounced adsorption kinetics were seen for the loam where almost 36 hours were needed for both type of loam soils to obtain adsorption equilibrium during Step I (0 - 36 hours).

Table 2. The modified Freundlich equation, (Eq. [1]), parameters determined from the asulam adsorption data. Step I (0 - 36 hours) represents adsorption kinetics of asulam on unpolluted loam soils (A or B) and Step II (36 - 72 hours) represents adsorption kinetics of asulam on initially polluted loam soils i.e. after being exposed for asulam during 36 hours. In Eq. [1] t_0 is set at 10 min (Step I) and 36 hours and 10 min (Step II).

Soil size fraction (mm)	Step I			Step II		
	K	N_I	R^2	K	N_{II}	R^2
Initial asulam concentration in step I = 20 mg l^{-1}						
<1.0(A)	0.97	0.013	0.96	0.99	0.002	0.82
<1.0(B)	0.98	0.008	0.98	0.99	0.003	0.97
Initial asulam concentration in step I = 50 mg l^{-1}						
<1.0(A)	0.98	0.010	0.88	0.97	0.002	0.88
<1.0(B)	0.98	0.009	0.94	0.99	0.003	0.94

In the first 10 minutes of Step II (36 -72 hours; soil initially exposed for asulam in 36 hours during Step I) a combination of very rapid desorption and adsorption processes likely took place but this could not be followed with sufficient temporal resolution in the measurements to separate the adsorption and desorption processes. The existence of micropores not easily accessible for the chemicals may explain the delay in the adsorption of asulam on loam soils. Thus, our sorption kinetics data suggest that in the case of loam soils "two sites" kinetics (equilibrium "Type 1" sites and slower, non-equilibrium "Type 2" sites) have to be taken into account. The modified form of

Freundlich equation (Eq.[1]) was used to fit the measured data and very well described the two-step sorption process (Fig. 2A,B). The values of the modified Freundlich equation parameters are shown in Table 2. Adsorption kinetics were found in both loam soils probably due to slow diffusion in the soil organic matter. The experiments suggested that a real equilibrium can be obtained only within a time scale of days for organic-matter containing soils.
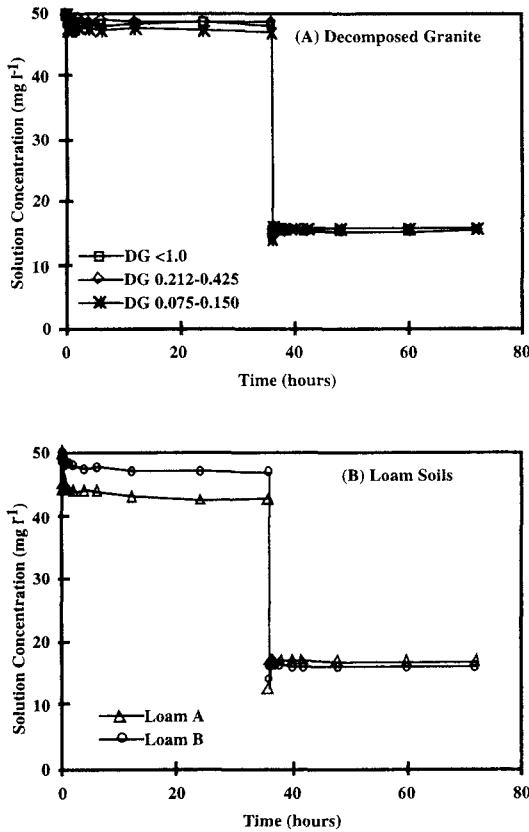

Fig. 1 Two-step adsorption kinetics of asulam (50 mg l^{-1} initial concentration) on decomposed granite (DG <1.0 mm), two particle size fractions of DG (0.212-0.425 mm and 0.075-0.150 mm) and two natural Hiroshima type loam soils (<1.0 mm) with different organic matter contents

The sorption process slowed down in the loam soils during Step II (soil already exposed to asulam in 36 hours) compared to Step I (initially asulam-free soil), see Fig. 2. Likely, a part of the easily accessible sorption sites in the soil organic matter and on the clay minerals have been occupied by slowly desorbable asulam during Step I. Our data

shows that the previous sorption story (degree and duration of previous exposure to the pesticide) in part controls the actual sorption kinetics.
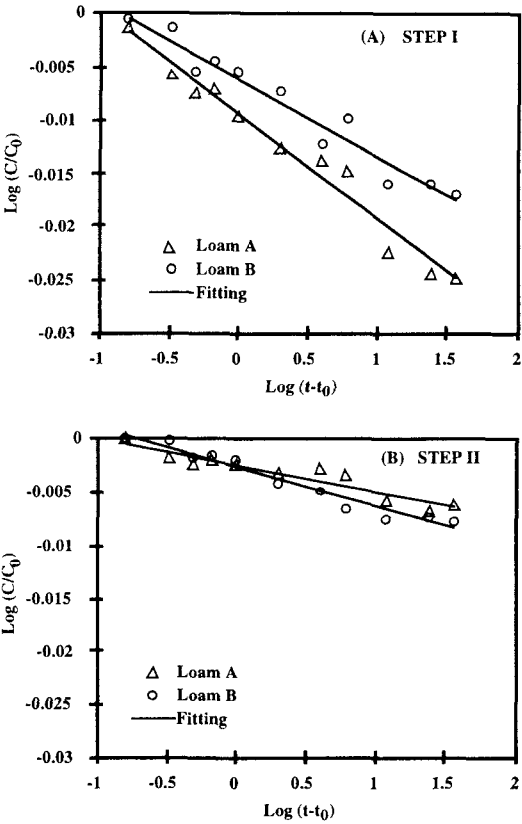
more clay minerals and higher organic matter content.

Table 3. Freundlich adsorption isotherm parameters (k_f and n) from batch experiments.

Soil size fraction (mm)	k_f	n	R^2
Loam(A);<1.0	0.31	0.71	0.96
Loam(B);<1.0	0.26	0 73	0.96
DG; <1.0	0.12	0 64	0.95
DG; 0.212-0.425	0.10	0.62	0.91
DG; 0.075-0.150	0.15	0 65	0.93

Fig 2 Fitting of the modified Freundlich adsorption equation (Eq [1]) to the measured adsorption kinetics data. Two-Step adsorption kinetics of asulam (20 mg l^{-1}) on two loam soils with different organic matter contents. Step I represents initially unpolluted soils and Step II initially asulam-exposed soils during 36 hours C_0 is solution concentration of asulam at t = 10 minuttes after the start of Step I or Step II experiments.
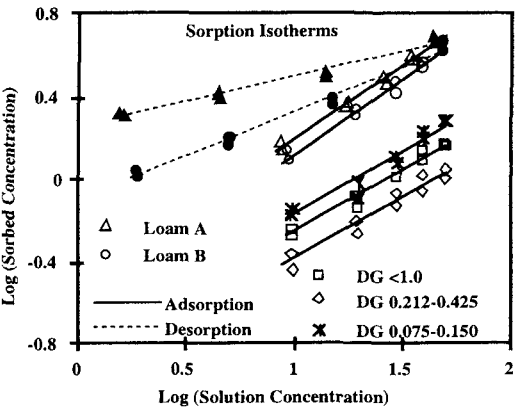
Fig. 3 Illustration of sorption hysteresis (difference between adsorption and desorption isotherms) for the two loam soils. Measured adsorption isotherms (open symbols) and desorption isotherms (50 mg l^{-1} initial solution concentration, closed symbols) for whole soils and soil size fractions. Lines and dotted lines are best-fit Freundlich adsorption and desorption (loam soils) isotherms (Eq [3]). No sorption hysteresis was found for the DG soil and particle size fractions.

4.2 Equilibrium adsorption and desorption results from batch experiments

There was relatively little asulam adsorbed in all soils and soil size fractions investigated. In Table 3, the results of batch adsorption isotherm experiments are shown. In all cases, the Freundlich isotherm model (Eq. [3]) fitted the data better than the linear model (Eq. [2]). In Figure 3 the adsorption and desorption isotherms are shown. More asulam was adsorbed on the loam soils with

The adsorption coefficients increased with increasing CEC (Fig. 4) and also, to some extent, with increasing surface area. Asulam adsorption increased with Cation Exchange Capacity (CEC) for the five soils, suggesting that not only the soil organic matter but also the clay minerals controlled sorption of the polar herbicide. The highest amount of simazine was adsorbed on the loam soil (A) with the high organic matter content and surface area. Despite the DG 0.075-0.150 mm fraction has the highest surface area (13.9 m^2 g^{-1}) the highest

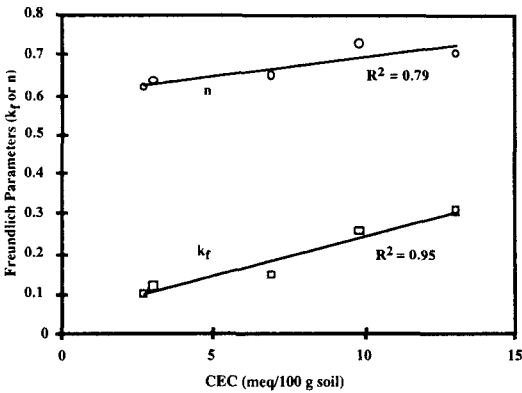amount of asulam was adsorbed on the loam soil which has the highest CEC (13.0 meq/100g soil).

Fig. 4 Relation between the Freundlich adsorption parameters (k_f and n) and Cation Exchange Capacity (CEC) for the five (three DG and two loam) soils.

The k_f values for desorption (Table 4) were consistently higher than those for adsorption (Table 3) for the loam soils showing a hysteretic behavior of asulam on the loam soils. For the DG soil and soil size fractions no hysteresis was seen.

Table 4. Freundlich desorption isotherm parameters (k_f and n). Desorption parameters are shown for 20 and 50 mg l^{-1} initial asulam solution concentration, respectively.

Soil size fraction (mm)	20 mg l^{-1}			50 mg l^{-1}		
	k_f	n	R^2	k_f	n	R^2
Loam(A);<1 0	1.11	0.26	0.95	1.82	0.24	0.90
Loam(B);<1.0	0.62	0.39	0.95	0.80	0 43	0.96

4.3 Sorption and retardation results from transport experiments

The simulated and observed data are presented in Figure 5. Using the First-Term Method [19], the transport parameters (u and D) were estimated from the breakthrough curves. The sorption data were fitted to the TNE model by a numerical program CXTFIT[16]. The fractions (type "1" and "2") and their rate coefficients, according to the equations for both type of sites are given in Table 5. A combination of rapid and slow rates of sorption was as discussed, likely due to diffusion of asulam into the organic matter structure and also,

possibly due to the presence of different types of reaction sites in the soils (organic matter, clay minerals).
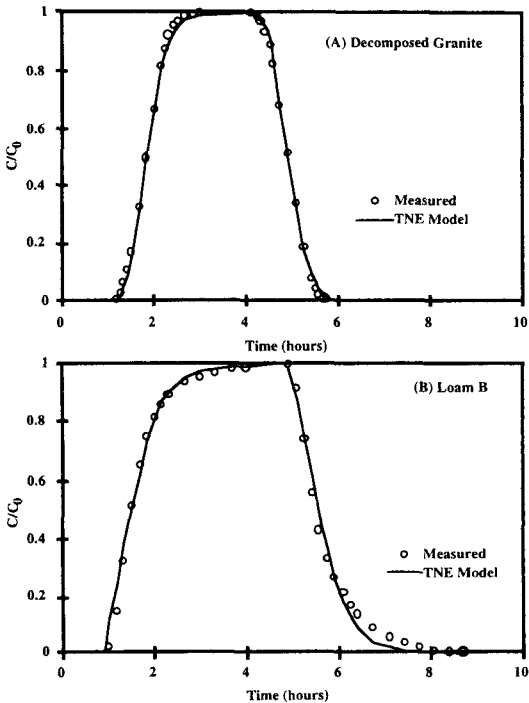

Fig. 5 TNE model (Eqs. [4] - [11]) fitted to the measured data. A pulse application of asulam with concentration $C_0 = 10$ mg l^{-1} eluted symmetrically in DG 0.212-0.425 mm while tailing was observed in the loam B column

The BTCs of asulam was symmetrical in the case of decomposed granite while tailing was observed in the case of loam (Fig. 5). In the case of decomposed granite the retardation factor R obtained from the breakthrough curve (BTC) was 1, and R calculated from the batch experiments data (Eq. [11]) was 1.06. This suggested that asulam was not significantly adsorbed onto decomposed granite during the transport experiments. For the loam soil, the retardation factor values determined using the BTC and batch experiment data were 1.16 and 1.29 respectively, and the fraction "F" in the TNE model was 0.844. Thus, the R estimated from batch experiments did not describe the transport experiments well for the loam soil. The differences between the values of retardation factor obtained from the BTCs (R=1.16) and batch data (R=1.29) may in part be due to the different solid/liquid ratio in batch and flow method but also,

the sorption non-equilibrium processes observed in the batch experiments. The value of the fraction "F" < 1 for the loam soil (F = 0.84) and F = 1 for DG shows that the "Type - 2" non-equilibrium kinetics in the loam soil is mostly associated with the soil organic matter since the DG does not contain organic matter.

Table 5 Selected adsorption and transport parameters.

	Soil Type	
	DG	Loam B
u (cm min^{-1})	0.25	0.33
D (cm^2 min^{-1})	0.02	0.44
k	0.01	0.04
F	1.00	0.84
Rf	1.00	1.16
Rb	1.06	1.29

DG - decomposed granite 0.212-0.425 mm
Loam B - loam soil <1.0 mm
Rf - retardation factor computed from BTC experiments
R_b - retardation factor computed from batch experiments

5. CONCLUSION

Asulam sorption was highly influenced by the CEC and thus by both the organic matter and the clay minerals of the soils. Pronounced non-equilibrium sorption and transport processes in the more organic and clay-rich loam soil gave a significant tailing of breakthrough curves while a symmetric breakthrough was seen for the more coarse-textured DG, probably due to the immediate sorption equilibrium in the DG. Slightly pesticide retardation factors were obtained from the batch and transport experiments in the case of loam soil, likely due to the sorption non-equilibrium (time dependency during the first 36 hours), non-linearity (Freundlich isotherm behavior) and hysteresis (difference between adsorption and desorption isotherms) observed in the batch experiments. However, from the viewpoint of solute transport modeling, the difference in retardation factors between batch and transport experiments was insignificant.

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