

## Evaluation of Sorption and Leaching Potential of Malathion and Atrazine in Agricultural Soils of India

Kulluru, P. P. \*, Das, B. S. and Panda, R. K.

Agricultural and Food Engineering Department, Indian Institute of Technology,  
Kharagpur, India

Received 20 Feb. 2009;

Revised 16 June 2009;

Accepted 25 July 2009

**ABSTRACT:** Movement of pesticides through soils to groundwater and surface water has long been considered a potentially serious environmental problem in different parts of the world. Remediation of such problems requires monitoring of site specific data. Considering these facts a laboratory based investigation was carried out to determine the sorption and leaching parameters of two contrasting and widely used pesticides (malathion and atrazine) in three different agricultural soils: loamy sand (Typic Xerosament), sandy loam (Acid Lateritic Haplustalf) and clay loam (Hyperthermic Typic Haplusterts). Standard batch sorption technique was used to determine the sorption coefficient ( $K_d$ ) and organic carbon distribution coefficient ( $K_{oc}$ ). Miscible displacement experiments were conducted to determine the transport parameters such as pore water velocity ( $v$ ), dispersion coefficient ( $D$ ), retardation factor ( $R$ ) and degradation rate constant ( $\lambda$ ). The results of batch sorption experiments revealed that malathion had higher  $K_d$  values as compared to atrazine for all soils. The grouping of soils according to sorption capacity followed the order: clay loam > sandy loam > loamy sand, for both malathion and atrazine. The results of miscible displacement experiments revealed that malathion could leach up to 30 cm depth whereas atrazine could leach up to 65 cm depth in the test soils. The values of transport parameters determined by method of moments ranged from 0.79 to 1.63 cm/h for  $v$  and 3.15 to 12.26, cm<sup>2</sup>/h for  $D$  in the test soils. The  $R$  values of malathion obtained using  $K_{d,were}$  3.1 to 3.4 times higher than atrazine for the test soils. The half life of malathion and atrazine obtained from  $\lambda$  ranged from 0.3 to 1.7 days and 50 to 64 days, respectively in the above mentioned soils.

**Key words:** Sorption, Leaching, Malathion, Atrazine, Method of moments

### INTRODUCTION

Pesticide use is a major chemical method of controlling insects, diseases and weeds in different crops and is established as an effective technology. Although the annual consumption of technical grade pesticides exceeds 40,000 tones, chemical pest control continues to be an immature practice in India because of over-application of pesticides, repeated application of the same pesticide and poor application methods. In fact, improper handling procedures may have led to frequent pesticide detections in groundwater and surface water bodies in recent years (Apel and Richter, 2000; Konda *et al.*, 2002; Shetty, 2004; Alam *et al.*, 2000). Malathion and atrazine are two widely used

pesticides in India. These two pesticides are also considered among the largest groundwater pollutants of the world (Droflur, *et al.*, 1997; Apel *et al.*, 2002; Konda *et al.*, 2002; Shetty, 2004; Alam *et al.*, 2000). Malathion is mainly used for controlling different pests in cereals and vegetables in India. Although it is reported to have less persistence (Sujatha *et al.*, 1991), only limited data is available on its sorption and leaching behavior. Similarly, relatively fewer reports exist on atrazine behavior for Indian soils although it is extensively studied in temperate regions of world (Squillace and Thurman, 1992; Kolpin *et al.*, 1996; Lesan and Bhandari, 2003). Because pesticide usage remains an effective technology, there is a

\*Corresponding author E-mail: kpriyaiit@gmail.com

great need for generating region-specific detailed data on pesticide behavior for ensuring maximum safety and effectiveness for their use (Anonymous, 1998).

The vulnerability of pesticides in the ecosystem is controlled by its mobility and persistence (Bedmar, 2004). Mobility of a pesticide is controlled by the structure of soil and its hydraulic conductivity, whereas persistence is influenced by soil-pesticide interactions (Gustafson, 1995). The soil pesticide interactions in turn determine the physical and biological availability of chemicals in soil through the process of sorption. For majority of pesticides, soil organic matter and clay colloids control the sorption process (Weber *et al.*, 2004). The sorption of pesticide in soil is evaluated by linear sorption coefficient- $K_d$  obtained through laboratory batch sorption experiments. The laboratory studies are simple and easy to carry out and provide a useful means for quality control purposes (Ronnenfart, 1997). The  $K_d$  values are useful in computer and decision aid models for predicting pesticide mobility in soils (Weber, 2004).

Simulation models are valuable research tools for predicting pesticides fate under wide range of environmental scenarios. Soil parameters such as organic carbon, structure and texture have similar effects on pesticides distribution and degradation globally, but specific characteristics are strongly influenced by climatic conditions (Langenbatch *et al.*, 2001; Sharma, *et al.*, 2004; Coreria, 2007). The quantitative prediction of pesticides fate is both pesticide- and soil-specific. Therefore, site specific experimental data is crucial input to simulation models for accurate prediction of environmental risks. Inasmuch as fewer reports are available on malathion and atrazine persistence and mobility in Indian soil, the present study was conducted to assess sorption and leaching characteristics of these two pesticides under laboratory conditions.

## MATERIALS & METHODS

Soils used in this study were collected from three different locations of India: farmer's field in Kapgari, Midnapur, West Bengal (22°40' N and 86°45' E); Experimental Farm of the Indian Institute of Technology, Kharagpur, West Bengal (22°19' N and 87°19' E); Central Research Station, Panjabrao Deshmukh Krishi Vidyapeeth, Akola,

Maharashtra (20°5' N and 77°52' E). Soil samples were collected from 15, 30, 45 and 60 cm depths, respectively. Collected samples were air-dried, crushed with wooden mortar and sifted through 2 mm sieve. Dried and sieved soil samples were placed in sealed glass jars and stored at room temperature. The soils collected from Kapgari, Kharagpur and Akola were classified as loamy sand (Typic Xerosament), sandy loam (Typic Haplustalf), and clay loam (Typic Haplustert), respectively. The general properties of these soils determined by using standard methods are shown in Table 1.

To reduce the number of batch experiments, surface (0-30 cm) and subsurface (30-60 cm) soil samples were obtained by combining soils collected from 0-15 and 15-30 cm and from 30-45 and 45-60 cm soil layers, respectively, for the Kapagari and Kharagpur soils. Similarly, only the surface (0-30 cm) soil sample was obtained by combining soils collected from 0-15 and 15-30 cm soil layers for Akola soil. Malathion and atrazine (both 99% pure) were supplied by Aldrich Chemicals, Germany. Other chemicals used in this study were of analytical and HPLC grade. The physicochemical properties of the selected pesticides malathion and atrazine are shown in Table 2.

Batch sorption experiments were performed by mixing 2 g of surface and subsurface soils with 10 mL of malathion and atrazine solutions prepared using 0.01 M  $\text{CaCl}_2$  solution in 100 mL glass centrifuge tubes. Five different pesticide concentrations (2, 4, 6, 8 and 10  $\mu\text{g}/\text{mL}$ ) along with a blank treatment were used in triplicate for these batch equilibrium studies. The pesticide solution also contained 0.01 M  $\text{NaN}_3$  to inhibit microbial degradation. The soil slurries were shaken for 48 hours at  $25 \pm 2$  °C and then centrifuged at 12000 rpm for 15 minutes to separate the solution and solid phases. The pH of the samples was recorded before and after equilibration. The supernatant was decanted and an aliquot was used for analyzing equilibrium phase pesticide concentration,  $C_e$  ( $\mu\text{g}/\text{mL}$ ) using an Ion Chromatography system (Mertrohm, Switzerland). The centrifuge tubes were individually weighed before and after the removal of the aqueous phase to estimate the amount of solution that remained in the soil. The sorbed concentration,  $S$  ( $\mu\text{g}/\text{g}$ ) was calculated from the

**Table 1. Physical and chemical properties of soils at different depths**

	Loamy sand			Sandy loam			Clay loam
	0-30 (cm)	30-60 (cm)	Mean	0-30 (cm)	30-60 (cm)	Mean	0-30 (cm)
Sand (%)	72.00	70.00	71.00	59.60	52.35	55.97	19.40
Silt (%)	20.00	18.00	19.00	22.75	19.70	21.22	24.20
Clay (%)	8.00	12.00	10.00	17.65	27.95	22.8	56.40
Organic carbon (%)	0.28	0.25	0.26	0.32	0.18	0.25	0.50
Cation Exchange Capacity (cmol/kg)	22.11	20.50	21.30	31.62	22.45	27.03	78.15
pH	5.30	5.00	5.15	5.55	5.85	5.78	5.80
Bulk density (g/cm <sup>3</sup> )	1.55	1.50	1.55	1.38	1.42	1.40	1.22
*Saturated Hydraulic conductivity (cm/day)	8.50	6.50	18.50	11.5	8.90	10.32	7.68
Iron [oxalate extractable] (g/kg)	6.10	ND	-	ND	ND		10.30

ND- not detected

\*Saturated hydraulic conductivity for loamy sand and sandy loam soils are depth weighted average

**Table 2. Properties of selected pesticides**

Properties	Malathion	Atrazine
Log K <sub>oc</sub>	3.25	1.96
Henry's Law constant at 25 °C (atm m <sup>3</sup> / mol)	4.9 × 10 <sup>-9</sup>	2.96 × 10 <sup>-9</sup>
Application Dose ( kg a.i./ha)	1.0 - 1.5	1.0 - 2.0
Class	Organophosphate, Insecticide	Triazine, Herbicide
IUPAC Name	O,O-dimethyl-s-(1,2-carbethoxyethyl) phosphorodithioate.	2-chloro-4-ethylamino-6-isopropylamino- 1,3,5-triazine
Half life (Days)	1 to 25	60 to 100
EPA limit ( μg/L)	0.1	0.3

Source: FAO, 2003

difference between the initial and final concentration of pesticide in solution.

Malathion and atrazine concentrations were determined by Metrohm modulator, Ion Chromatography/HPLC system. This system contained the 762 IC Interface, 709 IC pump, 733 IC separation centre, Lambda 1010 UV/VIS detector, IC Net 2.1 software (designed by Metrohm AG, Switzerland), and a RPC-18 column (150×4.6 mm, 5 μm, Prontosil 60-5-C18-H). Pesticide detections were made in the UV region (λ = 210 nm for malathion and λ = 254 nm for atrazine). The composition of mobile phase for malathion consisted of acetonitrile (70 %) plus water (30%) with pH 3.5 (30 %) and for atrazine it was acetonitrile (35 %) plus 0.025 M dipotassium hydrogen phosphate (pH 3.0 with acetic acid) (65 %). The flow rate and injection volume for both the pesticides was 1.0 mL/min and 20 μL,

respectively. The retention times for malathion and atrazine were 5.2 and 11.08 min, respectively under the chromatographic conditions. The quantitative determination of pesticides was performed by using external standards. A stock solution of 100 mg/L malathion and atrazine (dissolved in acetonitrile) was prepared with distilled water and serial dilutions (0.03 to 27 mg/L) were made. Thereafter a calibration curve for malathion and atrazine was plotted between peak base area from the chromatogram and different concentrations. Detection limit was 0.1 μg/L.

A cylindrical methacrylate tube (75 cm length, 0.5 cm thickness and 12.5 cm inner diameter) was used for packing soil. The tube was designed to have outlets at side and bottom for leachate collection. The bottom of the tube was sealed and was spread with a layer of sand. Over this, soils collected from 45-60, 30-45, 15-30 and 0-15 cm

soil layers were gently added to form a 65 cm soil profile. The surface of each soil layer was scratched to discourage formation of layer boundaries. It was ensured that the base of each soil layer was overlapped with the side outlet. Thus, soil columns were prepared representing field bulk densities for the 0-60 cm soil profile. In case of clay loam, a soil column of 0-40 cm depth was prepared with top 15 cm using soil from 0-15 cm depth and rest 15 cm using soil from 15-30 cm depth. The column had 30 cm of clay loam soil and 10 cm sand. A thicker sand layer was used to reduce solute travel time through this soil column. The flow setup consisted of soil column, water reservoir and a pressure head regulator. The water reservoir and pressure head regulator as a unit were mounted above the prepared soil column. The water reservoir was a perplex cylinder of 4 L capacity, used to store and supply water to the soil column. It had the dimensions of 35 cm length, 12.5 cm internal diameter and 5 cm thickness, with two perplex plates cemented, one each at the lower and upper end, of thickness 1 cm and 2 cm, respectively. A valve was provided at the lower end of the water reservoir to regulate the flow of water into the column. A glass pipe (internal diameter 0.5 cm) taken out through the rubber cork provided in the upper perplex plate, connected the water reservoir with the pressure head regulator using flexible polyethylene tube. A measuring scale was fixed on the water reservoir to know the volume of water withdrawn from it. Pressure head regulator maintained constant head of water over the column, so as to get a desired flow rate. It was a 30 cm long perplex cylinder of 5 cm internal diameter with wall thickness of 0.5 cm. A stopper was provided at the bottom end to regulate the flow from it. At the upper end, one rubber cork fitted with two glass tubes was used to control flow rate. A measuring scale was attached to the side of the pipe for measuring water level in the pressure head regulator.

The miscible displacement technique was employed to conduct the column leaching experiment. Separate transport experiments were conducted, alternately for loamy sand, sandy loam and clay loam soils. All the three experiments were undertaken at room temperature ( $24^{\circ}\text{C}\pm 1$ ). The experiments began with water saturation of the columns, achieved through capillary rise of distilled

water. After saturation, each column received an application of solute mixture for 50 hours. The solute mixture contained 30 mg/L of atrazine, 125 mg/L of malathion and 100 mg/L of KBr. The application of tracer was used to characterize the water flow behavior in packed soil columns. During the experiment, effluent was collected at constant time intervals, from the side and bottom outlets of the columns. The effluent from the side outlets was collected by vacuum pump, whereas that from bottom was collected by gravity drain. The effluent was monitored until solute pulse was almost completely displaced. The collected effluents were either analyzed immediately or stored at  $4^{\circ}\text{C}$  till further analysis. Experimental conditions of solute transport experiments are presented in Table 3.

The sorption data were fitted to Freundlich equation,

$$S = K_f C^n \quad (1)$$

where,  $S$  is the sorbed phase concentration (mg/kg),  $C$  is the solution phase concentration (mg/L),  $K_f$  is the Freundlich's sorption coefficient ( $\text{mg}^{1-n} \text{L}^n/\text{kg}$ ), and  $n$  is a dimensionless parameter that accounts for nonlinearity of an isotherm. When  $n$  is equal to 1.0, the isotherm is linear with  $K_f$  replaced by a linear distribution coefficient,  $K_d$  (L/kg). The organic carbon normalized distribution coefficient ( $K_{oc}$ ) can be estimated by normalizing  $K_d$  with the organic carbon content of the soils expressed as

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (2)$$

where  $f_{oc}$  is the fraction of organic carbon in soil.

Solute transport processes under steady water flow conditions in the undisturbed soil columns were modeled using the one-dimensional form of the advection-dispersion equation (ADE):

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \lambda c \quad (3)$$

where  $c$  is volume-averaged concentration ( $\text{M}/\text{L}^3$ ),  $D$  is the dispersion coefficient ( $\text{L}^2/\text{T}$ ),  $v$  is the pore water velocity ( $\text{L}/\text{T}$ ),  $x$  is the distance ( $\text{L}$ ),  $t$  is the time ( $\text{T}$ ),  $R$  is the dimensionless

**Table 3. Experimental conditions for solute transport experiments**

Soil	Loamy sand	Sandy loam	Clay Loam
Volume of soil (cm <sup>3</sup> )	7972.00	7972.00	3679.00
Bulk density (g/cc)	1.55	1.4	1.22
Darcy's Flux (cm/h)	0.74	0.42	0.33
Pore water velocity (cm/h)	1.76	0.93	0.61
Pulse duration (h)	50.00	50.00	50.00
Volumetric water content (cm <sup>3</sup> /cm <sup>3</sup> )	0.42	0.45	0.54
Flow rate (cm/h)	0.74	0.42	0.33
Pore volume (cm <sup>3</sup> )	3348.00	3587.00	1985.00
Duration of experiment (h)	268.00	384.00	456.00

retardation factor representing the effect of sorption on transport, and  $\lambda$  is the first-order degradation rate constant for the liquid phase in soil (Gershon and Nir, 1969; van Genuchten and Wagenet, 1989).

$$R = 1 + \rho_b \frac{K_d}{\theta} \quad (4)$$

where  $\rho_b$  is the bulk density and  $\theta$  is the volumetric water content. In this study, solutes were applied as pulse inputs of duration  $t_0$ . Soils used in each column experiment were assumed to be devoid of applied solutes before their application. Thus, the following initial and boundary conditions were used for modeling the experimental data:

$$c(0, t) = 0 \quad t_0 < t < \infty \quad (4a)$$

$$c(0, t) = c_0 \quad 0 < t < t_0 \quad (4b)$$

$$c(x, 0) = 0 \quad 0 < x < \infty \quad (4c)$$

$$c(\infty, t) = 0 \quad 0 < t < \infty \quad (4d)$$

where  $c_0$  is the initial solution concentration (Pang *et al.*, 2003). Experimental BTCs were analysed using the method of moments (MOM) and moments were estimated using the trapezoidal rule (Mishra and Mishra, 1977; Haas, 1996). The  $i^{\text{th}}$  temporal moment for a concentration distribution at a location  $x$  is defined as

$$M_i = \int_0^{\infty} t^i c(x, t) \partial t \quad (5)$$

The  $i^{\text{th}}$  normalized moment of the distribution is defined as

$$\mu_i = \frac{M_i}{M_0} = \frac{\int_0^{\infty} t^i c(x, t) \partial t}{\int_0^{\infty} c(x, t) \partial t} \quad (6)$$

Eqns. 5 and 6 may be used to obtain experimental temporal moments from measured BTCs. Solute transport parameters such as  $v$ ,  $D$  and  $\lambda$  may be estimated by setting the experimentally determined moments equal to theoretical moments as follows (Pang *et al.*, 2003):

$$v = \frac{L}{\mu_1 - 0.5t_0} \quad (7)$$

$$D = \frac{v^3}{2L} \left( \mu_2 - \mu_1^2 - \frac{t_0^2}{12} \right) \quad (8)$$

$$\lambda = \frac{v^2}{4D} \left[ \left( 1 - \frac{2D}{Lv} \ln \frac{M_0}{C_0 t_0} \right) - 1 \right] \quad (9)$$

$$R = \frac{(\mu_1 - 0.5t_0) \sqrt{v^2 + 4D\lambda}}{x} \quad (10)$$

where  $L$  is the column length.

The column length ( $L$ ), diameter ( $d$ ),  $\rho_b$ , and porosity ( $\eta$ ) were determined to compute the column's pore volume under saturation. The pore volume (PV) of the packed soil column was estimated by multiplying total soil volume with the porosity Darcy's flux ( $J_w$ ) was calculated from saturated steady state flow experiment.

$$J_w = \frac{V_w}{At} \quad (11)$$

where  $V_w$  is the water volume,  $t$  is the time and  $A$  is the area of soil column. Pore water velocity ( $v$ ) was calculated to compute solute travel or arrival time

$$v = \frac{J_w}{\theta} \quad (12)$$

The dispersivity coefficient ( $\varepsilon$ ) was estimated using  $D$  obtained from temporal moment as:

$$\varepsilon = \frac{D}{v} \quad (13)$$

The half lives of pesticides were obtained by using

$$t_{1/2} = \frac{0.693}{\lambda} \quad (14)$$

In the present study, the HYDRUS-1D model was also used, which simulates water flow and transport of solutes in variably saturated porous media (Simunek, 1998, 2003). The computer program numerically solves the Richards' equation for saturated-unsaturated water flow and the Fickian-based ADE for solute transport. The model analyses different equilibrium and non-equilibrium flow and transport process in both direct and inverse mode. The following transport processes can be used to analyze experimental BTC's; i) physical and chemical equilibrium transport (Lapidus and Amundson, 1952); ii) Chemical non-equilibrium transport using the two-site chemical non-equilibrium model (Cameron and Klute, 1977); iii) Physical non-equilibrium transport using two-region model (mobile-immobile water) (van Genuchten and Wierenga, 1976); iv) Physical non-equilibrium transport using dual permeability model (Gerke and van Genuchten, 1993); and v) Simultaneous physical and chemical non-equilibrium transport using the dual permeability model (Gerke and van Genuchten, 1993) combined with two-site chemical model. The governing flow and transport equations are solved using a Galerkin type linear finite element scheme. Solute-soil interactions in the present study showed linear sorption and steady-state water flow was also maintained, therefore, the physical and chemical equilibrium transport process was used for simulation.

The size of model domain for the soil columns of loamy sand and sandy loam soils was 65 cm soil profile, using single layer for mass balance. The soil profile consisted of 65 nodes and three observation nodes at 15, 30 and 65 cm depth. Each of these layers was assumed to have uniform physical and chemical properties except for the column containing clay loam soil where the 40 cm profile was divided into 2 layers for mass balance i.e. 0-30 cm clay loam soil and 30-40 cm of sand. Initial time step of two hours, minimum time step of one to four hours and maximum time step of 10 hours were used during simulations. Column experiments were conducted under saturated steady state flow conditions with a constant pressure head. The solute was applied to the completely saturated soil column at the same pulse duration of 50 hours and at different flow rates as per the soil conditions as explained (Table 3). The upper boundary condition for water flow was constant pressure head and that for solute transport was concentration boundary condition. The lower boundary condition for water flow was seepage face and that for solute transport was zero gradient.

Measured and estimated values of physical and chemical parameters were used as fixed inputs for the HYDRUS-1D model. For describing soil moisture behavior, van Genuchten model was chosen. The soil separates and hydraulic parameters were taken as input and were predicted by Neural network predictions. For describing solute transport, parameters such as bulk density, diffusion coefficient and dispersivity were used for conservative solute and parameters such as  $K_d$  and degradation rate constant ( $\lambda$ ) were used for sorbing chemicals as input. The model was first evaluated for its simulation of water flow in the experimental conditions with estimated  $D$  and  $\rho_b$  without any calibration. When the simulated data obtained using the inverse optimization function fitted the observed data reasonably well, the model was then calibrated for  $\varepsilon$  using the observed bromide data. The value for  $\varepsilon$  (as estimated by Eqn. 13) was calibrated as it is needed for conservative bromide in different soil conditions. After obtaining satisfactory match similar calibrations were performed for malathion and atrazine considering  $K_d$  and  $\lambda$  for different soil conditions.

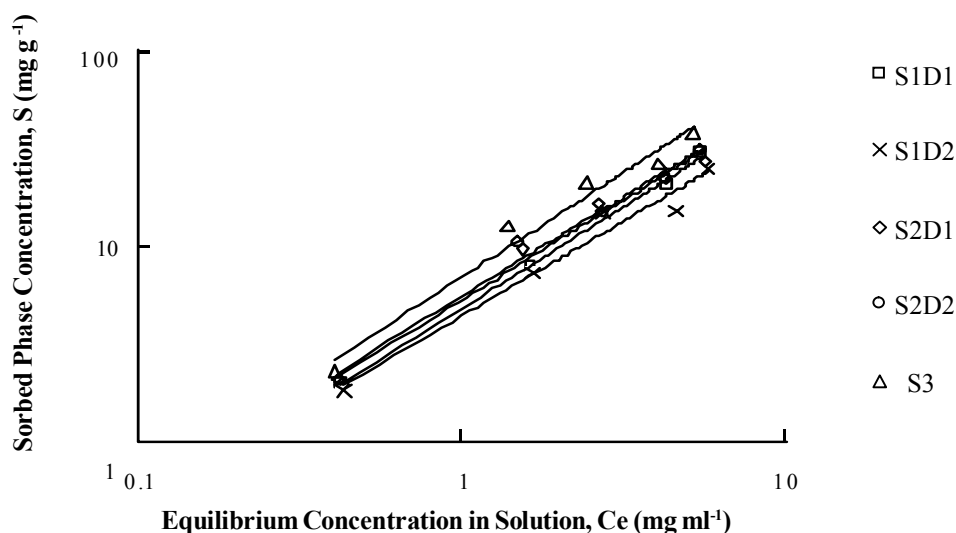
**RESULTS & DISCUSSION**

Pesticide sorption isotherms for malathion and atrazine for three different soils are shown in Fig. 1. All sorption isotherms were adequately described by linearised Freundlich's equation with R<sup>2</sup> greater than 0.96 for malathion and 0.91 for atrazine. The estimated K<sub>d</sub> values for malathion and atrazine ranged from 3.61 to 7.30 L/kg and 0.37 to 1.05 L/kg, respectively, for the three test soils (Table 4). Sorption for both the pesticides varied in the order of clay loam > sandy loam (surface) > sandy loam (subsurface) > loamy sand (surface) > loamy sand (subsurface) soils. The extent of sorption decreased with decreasing organic carbon content in all three soils. Generally, higher K<sub>d</sub> for both the pesticides was obtained for clay loam soil and lower K<sub>d</sub> values were obtained for loamy sand soil. With respect to depth, both the pesticides showed higher K<sub>d</sub> values for surface soil compared to subsurface soil and the effect of soil depth on pesticide sorption was more pronounced in malathion than in atrazine (Table 4). Also, malathion had higher sorption coefficient than atrazine in all soils.

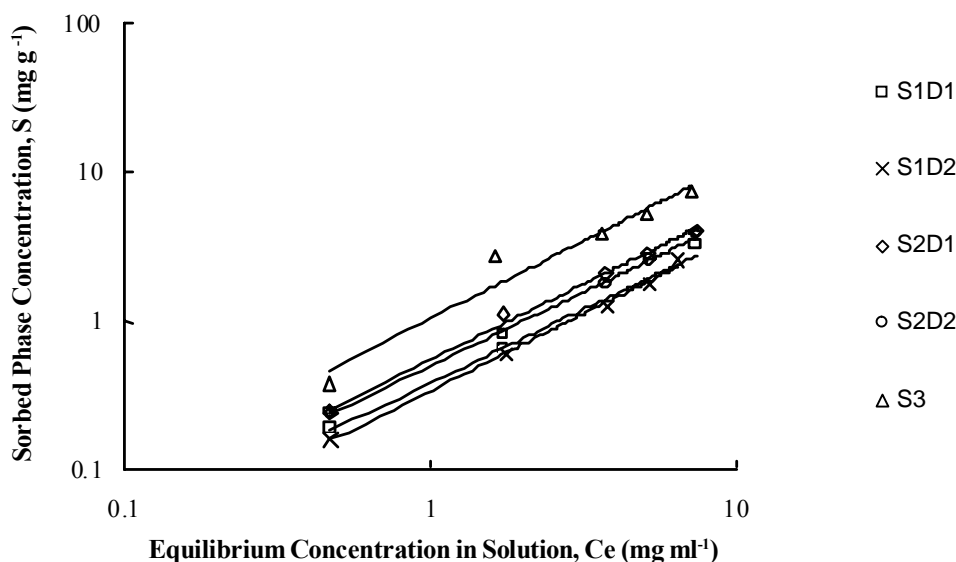
**Table 4. Estimated sorption parameters for malathion and atrazine by different soils**

	Depth	K <sub>d</sub>	R <sup>2</sup>	K <sub>oc</sub>
A. Malathion				
Loamy sand	0-30 (Surface)	4.00	0.99	1846.42
	30-60 (Subsurface)	3.61	0.90	1656.00
Sandy loam	0-30 (Surface)	4.80	0.98	1632.35
	30-60 (Subsurface)	4.30	0.96	1726.66
Clay loam	0-30 (Surface)	7.30	0.96	1116.92
B. Atrazine				
Loamy sand	0-30 (Surface)	0.40	0.96	142.85
	30-60 (Subsurface)	0.37	0.91	148.00
Sandy loam	0-30 (Surface)	0.56	0.99	155.55
	30-60 (Subsurface)	0.51	0.99	154.54
Clay loam	0-30 (Surface)	1.05	0.96	161.53

There are limited literatures stating the K<sub>d</sub> of malathion in soils (Apel *et al.*, 2002). The mean K<sub>d</sub> of malathion reported by EPA is 8.25 times higher than that reported by Apel *et al.* (2002) in loamy sand soil. Comparison of mean K<sub>d</sub> of malathion in loamy sand soil of the present study showed that it is 19 times higher than that reported by Apel *et al.* (2002). Malathion sorption has been reported to be influenced by organic carbon and clay content of soils (McNamara and Toth, 1970). The mean organic carbon and clay content of studied soils were found to be 1.5 to 3.8 times lower and 2-5 times higher than those published in the literature. The difference in K<sub>d</sub> values may be attributed to variation in these soil properties. Estimated K<sub>d</sub> values from the present study were also compared with published values to understand the variation of atrazine sorption to soils (Figs. 2 and 3). The K<sub>d</sub> values of atrazine obtained in the present study are within the range of previously reported values in literature (Parez *et al.*, 1992; Dousset *et al.*, 1994; Baskaran *et al.*, 1996; Celis *et al.*, 1998; Rochette and Koskinen, 1998; Johnson, 2001; Konda *et al.*, 2002, Lesan and Bhandari, 2002; Bouchard, 2002; Coquet, 2003; Close *et al.*, 2006). Only organic carbon and clay content of soils were taken into account for comparison as they are reported to be the main factors influencing atrazine sorption (Baskaran *et al.*, 1996; Wouchope 2000; Leasan and Bhandari, 2003). Fig. 2 shows that K<sub>d</sub> values increased with increase in organic carbon and clay contents. However, the K<sub>d</sub> values of observed soils did not show an increasing trend with clay, especially at higher clay content. The reason for the variation may be the difference in organic carbon and clay content of the compared soils. Fig. 2 also shows that the effect of organic carbon on atrazine sorption is more pronounced than clay content in the present study. Similar results were reported by Felsot and Dahm (1979), Rao and Davidson (1979), Barriuso *et al.* (1992) and Jhonson and Sims (1993). The difference in atrazine K<sub>d</sub> values of test soils and published literature may be due to differences in the amount and nature of organic carbon of soils from temperate regions. This is consistent with literature of Ahmed *et al.* (2001) and Corrirea *et al.* (2007) who suggested that K<sub>d</sub> values of tropical and temperate regions may not be always comparable.



(a) Malathion



(b) Atrazine

S1D1: loamy sand surface soil, S1D2: Loamy sand subsurface,  
 S2D1: Sandy loam surface soil, S2D2: Sandy loam subsurface  
 S3: Clay loam

**Fig. 1. Observed (symbols) and predicted (lines) sorption isotherms for malathion and atrazine in different soils**

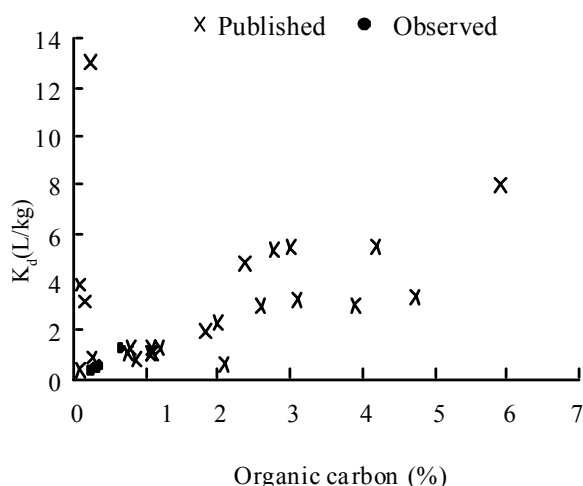
To account for the differences in organic carbon content between soils  $K_{oc}$  values are used as they reduce the variability in  $K_d$  (Gerstl, 2000).

The  $K_{oc}$  values of malathion and atrazine found in the present work range from 1435 to 2388 L/kg and 142 to 161 L/kg, respectively (Table 4). Still the  $K_{oc}$  values obtained in the present study were compared with those published in literature to understand the extent of variability (Fig. 4 & 5). Fig. 4 shows that almost all malathion  $K_{oc}$  values

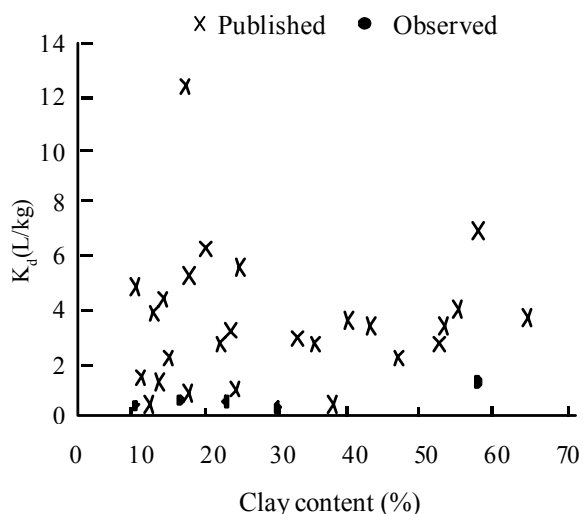
are within  $\pm 25\%$  of average values of published  $K_{oc}$  confirming the similarity of observed and published data points. Fig. 5 shows that the observed data points of atrazine were within  $+25\%$  of average value of published data, which is acceptable in agricultural soils. This indicates the variability in  $K_{oc}$  is much less than that of  $K_d$  of a pesticide in a given soil.

Both simple and multiple linear regression analysis were carried out for  $K_d$  of both pesticides with selected soil properties with the help of SPSS





**Fig. 2. Comparison of observed and estimated  $K_d$  values as influenced by organic carbon content**



**Fig. 3. Comparison of observed and estimated  $K_d$  values as influenced by clay content**

10.0. Results of simple correlation analysis are summarized in Table 5. The analysis revealed that the influence of organic carbon on the sorption of malathion and atrazine is highly significant followed by clay content and CEC of soil. The correlation between  $K_d$  and pH was not significant in this study. Similar significant correlations were also obtained for atrazine by Jhonson and Sims (1993), Konda et al. (2002) and Weber et al. (2004). Following multiple linear regression relationships were also found for malathion and atrazine, respectively:

$$K_d = 3.563 + 3.551 \text{ OC (\%)} + 0.017 \text{ Clay (\%)} + 0.010 \text{ CEC (cmol/kg)} \quad R^2 = 0.94$$

$$K_d = 0.010 + 0.802 \text{ OC (\%)} + 0.003 \text{ Clay (\%)} + 0.013 \text{ CEC (cmol/kg)} \quad R^2 = 0.99$$

The regression results indicated by the combination of organic carbon, clay and CEC, was necessary to explain the variability of malathion and atrazine retention by the various soils. Similar interaction of soil properties on sorption parameters was reported by Jonge et al. (2000), Mallawatantri et al. (1996) and Pusino et al. (1994). Higher  $K_d$  values of malathion in present study are indicative of strong retention by soil and consequently tending to its limited mobility (Ghezal *et al.*, 1997; Andradea *et al.*, 2000). However, its appearance in drinking water (Shankaramkrishna et al. 2005; Clark *et al.*, 1993, Kimbrough and Litke 1996; Kucklick and Bidleman 1994; Larson et al. 1995) despite its strong sorption to soils may be due to agricultural runoff resulting from extensive agricultural activities (Shankaramkrishna et al. 2005). The experimental  $K_d$  values suggest that sorption of atrazine is weak in test soils. Weak sorption implies that atrazine may have a moderate to high leaching potential, especially in light textured soils, and the sorption will not adversely affect the efficacy of atrazine in different soil types.

Measurement of pesticide retardation allows a first approximation of vulnerability of a system of mobility of pesticides (Praiba and Spadotto, 2003). Observed and estimated R for atrazine is in accordance with literature values (Singh *et al.*, 1996; Pang *et al.*, 2003). Results obtained from soil column experiments are shown in the form of breakthrough curves (BTCs) with number of pore volumes (PV) as abscissa and relative solute concentration ( $C/C_0$ ) as ordinate. Observed and calculated bromide effluent concentrations are shown in Fig. 6. The distributions indicated that the concentrations at the breakthrough and elution sides adjust rapidly to the changing input concentrations. The percolation curve of bromide showed a maximum concentration peak at a leachate volume of 1.6, 1.42 and 1.1 PV in loamy sand, sandy loam and clay loam soils, respectively (Fig. 6). All these values are close to 1 PV as generally occurs in the percolation of conservative ions (Bigger and Nielson, 1962). Table 6 shows the depth wise elution of bromide in three different soils, the elution reached 97.5, 93.7 and 63% in loamy sand, sandy loam and clay loam soils, respectively.

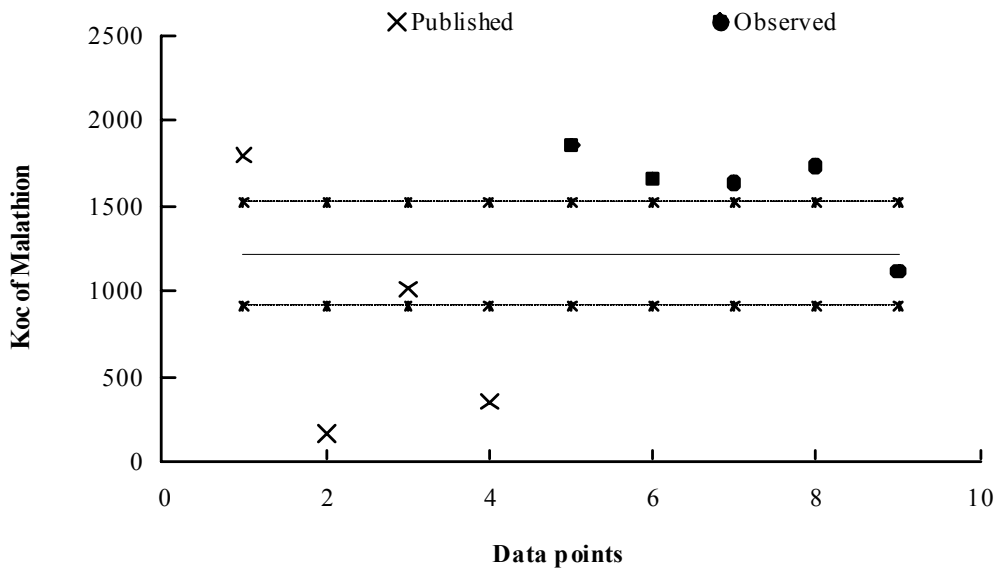


Fig. 4. Relative difference between the  $K_d$  values of malathion obtained from measurement and published

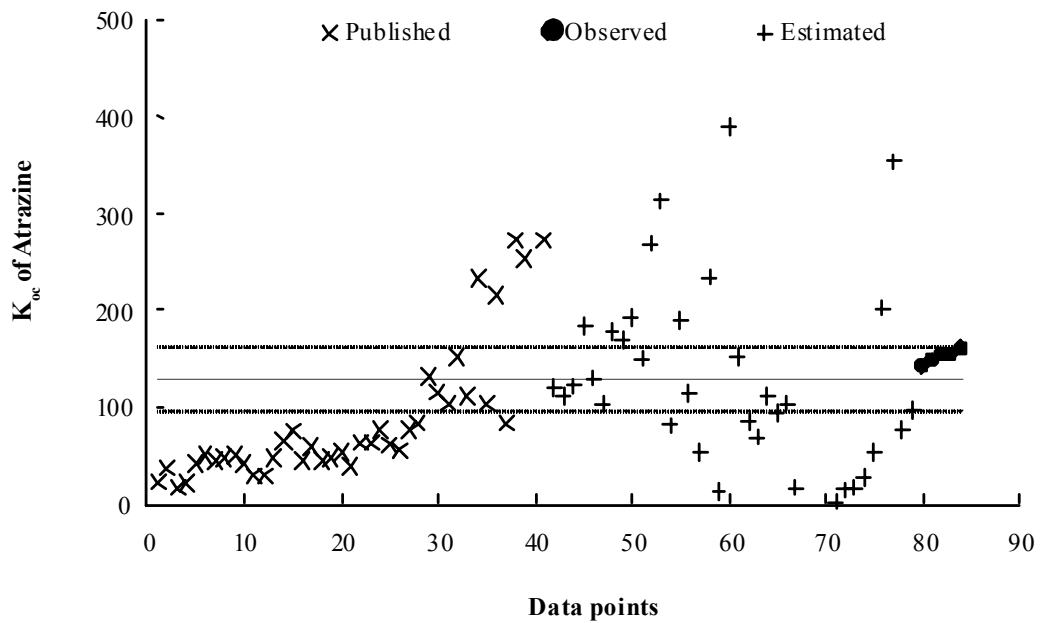


Fig. 5. Relative difference between the  $K_d$  values of atrazine obtained from measurement and published

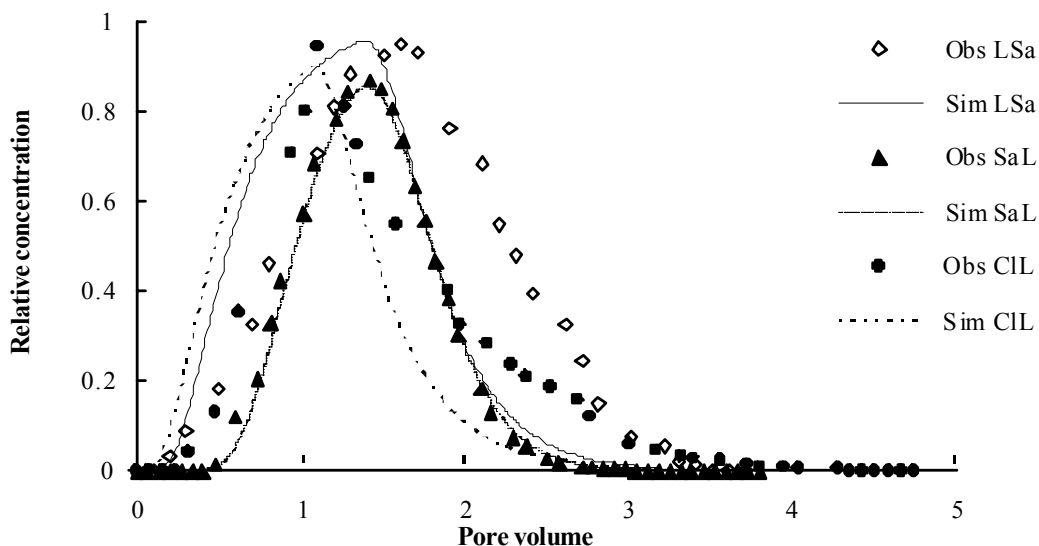
Table 5. Linear regression analysis for malathion and atrazine sorption coefficient with selected soil roperities

Pesticide	Property	Intercept	Slope	R <sup>2</sup>	Significance level
Malathion	OC (%)	-0.594	15.801	0.99	0.012
	Clay (%)	2.910	0.077	0.99	0.051
	CEC (cmol/kg)	2.728	0.058	0.99	0.06
	pH	-13.656	3.381	0.45	0.528
Atrazine	OC (%)	-0.446	2.998	0.99	0.028
	Clay (%)	-0.218	0.014	0.99	0.035
	CEC (cmol/kg)	0.185	0.011	0.98	0.059
	pH	-3.023	0.659	0.48	0.358

Pesticide mobility parameters such as  $v$ ,  $D$  and  $\mu$  were estimated for bromide BTC data using Eqns. 7, 8 and 14 (Table 7). The pore water velocities obtained in this study ranged from 0.79 to 1.63 cm/h,  $D$  values ranged from 3.15 – 12.26 cm<sup>2</sup>/h and  $\mu$  values ranged from 2.83 to 8.44 cm. The table shows that the values of pore water velocity obtained using temporal moments were within a variation of 7 to 22 % of those determined experimentally (using Eqn. 13). The value of dispersion coefficient for loamy sand soil was 1.8 and 3.8 times higher than the clay loam and sandy loam soils, respectively. The larger degree of dispersion in loamy sand soil was the consequence of wider distribution of pore water velocities (1.5 and 2.05 in sandy loam and clay loam soils). The

increase in dispersivity and dispersion coefficient with increasing flow velocity was consistent with results reported in the literature (Cote *et al.*, 2001). Malathion BTCs for two test soils loamy sand and sandy loam are shown in Fig. 7. The measured BTCs exhibited asymmetry as illustrated by the differences in shape of their effluent and desorption sides. In addition to these asymmetries, a sharp front of the BTC for loamy sand soil was observed which is in contrast with more gradual change of effluent concentrations for the sandy soils.

No residue of malathion could be detected in the first 24 hrs and 500 mL of leachate in any of the three test soils, whereas the pesticide residue was detected in the further fraction leachate in loamy sand soil. The concentration of malathion



LSa= loamy sand soil, SaL = sandy loam soil, CIL = clay loam soil, Obs=Observed  
Sim= Simulated

Fig. 6. Observed and simulated BTC of Bromide from soil columns of different soils

Table 6. Percentage of applied bromide, malathion and atrazine eluted from leachate

Tracer/ Pesticide	Depth (cm)	Loamy sand	Sandy loam	Clay loam
Bromide	Upto 15	8.1	6.79	NA <sup>?</sup>
	Upto 30	9.1	6.27	50
	Upto 65	80.3	80.7	ND
	Total	97.5	93.7	62.9
Malathion	Upto 15	15.87	7.76	NA
	Upto 30	4.69	1.16	NA
	Total	20.56	8.92	NA
Atrazine	Upto 15	15.7	15.1	-
	Upto 30	15.4	14.3	41.8
	Upto 65	61.9	53	-
	Total	87.9	79	41.8

\*ND- not applicable

was increased in the 48 to 100 hrs in loamy sand and sandy loam soils, at 15 cm depth but decreased thereafter. Table 6 shows the percentage of malathion eluted at 15 cm depths in loamy sand and sandy loam soils. Since the leaching study was carried out under saturated water flow conditions, the initial fractions mainly contained displaced soil water, previously entrapped in voids. As the subsequent movement of malathion front could have been much slower compared to the percolating water, may be the reason for no detectable residue of malathion in first 500 mL leachate. From the elution curves of malathion in soils, it was observed that the maximum concentration was observed at 6.7 and 7.4 PV in loamy sand and sandy loam soils. Since, no leachate was detected in clay loam soil the distribution of malathion in soil cores at different depths had been determined.

Out of 275 mg of malathion added to the column, 4.8 mg (1.74 %) was recovered, after 550 hours of application. A loss of approx. 270 mg of malathion might be attributed to its degradation in soil and partly to the losses during the process of sampling. The mobility of malathion was restricted up to 15 cm depth, as limited amount of malathion could be detected in depth beyond 15 cm in the test soil. The reason for negligible detection of malathion residue beyond 15 cm depth may be attributed to its higher sorption to soil and faster degradation. The  $\bar{v}$  values ranged from 0.07 to 0.09/h, which indicated a half life ranging from 3.9 day to 3.3 days (Eqn. 16) for loamy sand and sandy loam soils.

Observed atrazine BTCs for the three soils are depicted in Fig. 8. There was a slight tailing in case of clay loam soil compared to other two soils. The tailing in clay loam soil may have been due to slow release of atrazine by the clay loam soil because of its higher water holding capacity. The

time (or pore volumes) of the arrival of the BTC peak or the concentration maximum varied among the different soil columns, i.e. 1.74, 2.72 and 4.0 in loamy sand, sandy loam and clay loam soils, respectively. Atrazine leached very rapidly through the loamy sand soil, because of its lower organic matter content and higher porosity compared to other two soils (Table. 6). Leaching was slower for sandy loam and clay loam soils. The early arrival of the BTC peak for loamy sand soil ( 4 pore volumes) is indicative of lower retardation and thus relatively higher atrazine mobility among the different soils. Ryang et al. (1989) also recorded a faster movement of herbicide in coarse texture soil. Celis et al. (2001) reported similar link between the leaching of two polar herbicides in sandy and clay loam soils. The half life estimated from degradation rate constant ranged from 47 to 61 days depending on the soil type. The results are consistent with the values reported in literature (Singh *et al.*, 1996). Table 6 showed the atrazine elution from different soils, maximum elution was obtained for loamy sand soil. For sandy loam and clay loam soils the duration of experiment was longer than loamy sand soil, probably some degradation took place in these soils due to longer contact time. In fact the lowest recovery of atrazine was in clay loam soil with which it had the highest contact time.

The results obtained from the experiments were simulated by HYDRUS 1D using the inverse optimization approach. The model fitted the experimental BTC well, with R<sup>2</sup> values ranging from 0.65 to 0.99 (Table 8). Estimated parameters of bromide, malathion and atrazine are described in Table 8. The measured bromide BTC data for all soils could be fitted well with HYDRUS 1D model. The comparison of observed and simulated dispersivity in loamy sand, sandy loam and clay loam soils depicted a variation of 22, 29 and 9%,

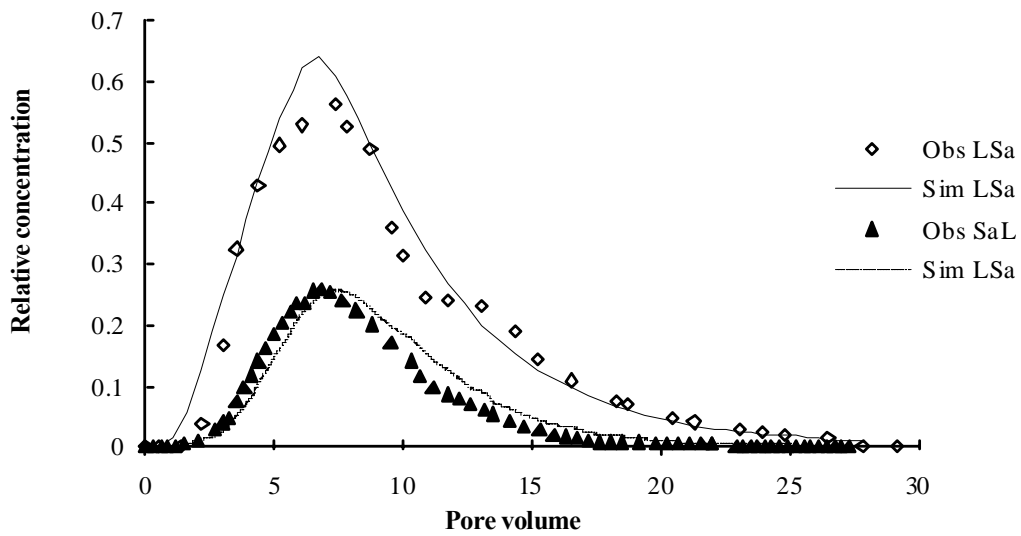
**Table 7. Comparison of pore water velocities estimated by two different methods**

Soils	$v^a$ (cm/h)	$v^b$ (cm/h)	Absolute Variation (%)	D (cm <sup>2</sup> / h)	$\epsilon$ (cm)
Loamy sand	1.76	1.63	7.38	12.26	7.52
Sandy loam	0.93	1.11	16.20	3.15	2.83
Clay loam	0.61	0.79	22.30	6.7	8.44

$v^a$  = Experimental pore water velocity

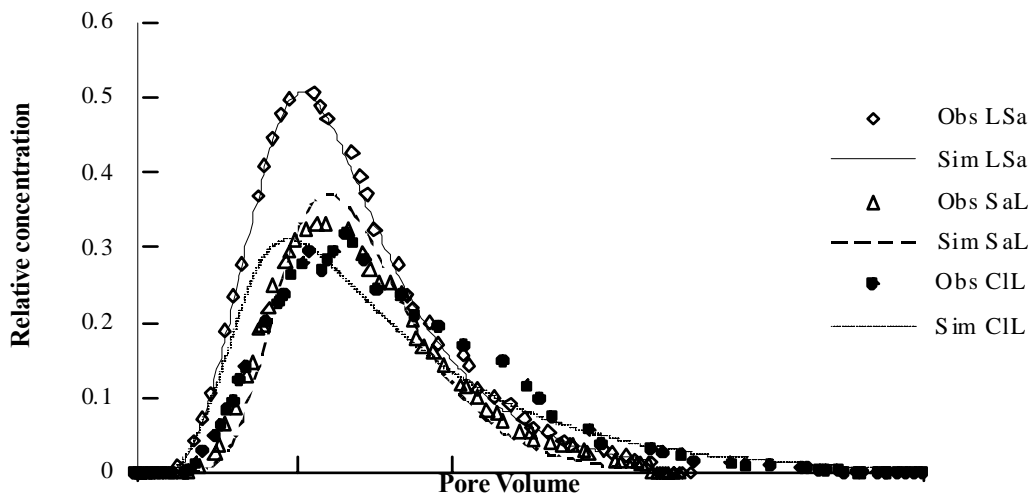
$v^b$  = Estimated pore water velocity by MOM

$(1 - v^a / v^b) \times 100$  = absolute variation



LSa= loamy sand soil, SaL = sandy loam soil, CIL = clay loam soil, Obs=Observed  
Sim= Simulated

Fig. 7. Observed and simulated BTC of malathion from soil columns of sandy loam and loamy sand soils



LSa= loamy sand soil, SaL = sandy loam soil, CIL = clay loam soil, Obs=Observed  
Sim= Simulated

Fig. 8. Observed and simulated BTC of atrazine from soil columns of different soils

Table 8. Comparison of observed (Obs)/ estimated (Est) and simulated (Sim) parameters of mobility experiments for bromide, malathion and atrazine in three different soils

		Parameters								
		$\epsilon$ (cm)			$K_d$ (mL/g)			$\lambda$ (per hour $\times 10^{-4}$ )		
		Est	Sim	$R^2$	Obs	Sim	$R^2$	Est	Sim	$R^2$
Loamy sand	Bromide	7.52	8.2	0.65	0	0	0	0	0	0
	Atrazine	7.52	8.2	0.65	0.38	0.38	0.99	3.0	3.0	0.99
	Malathion	7.52	8.2	0.65	3.8	4.3	0.71	365	590	0.71
Sandy loam	Bromide	2.83	2	0.99	0	0	0	0	0	0
	Atrazine	2.83	2	0.99	0.53	0.42	0.98	5.7	5.7	0.98
	Malathion	2.83	2	0.99	4.5	4.5	0.92	90	157	0.92
Clay loam	Bromide	8.44	6.5	0.77	0	0	0	0	0	0
	Atrazine	8.44	6.5	0.77	1.05	2.0	0.82	6.1	0.4	0.82
	Malathion	8.44	6.5	0.77	NA			NA		

NA: data not available

respectively. Average  $K_d$  values derived from the HYDRUS 1D model for both malathion and atrazine were close to the observed ones with a slight variation ranging from 0-40% (Table 9). However, the variation in observed and simulated  $K_d$  values for malathion was slightly 0-13%. In addition, degradation rate constant estimated from the HYDRUS 1D model were almost similar to observed except for clay loam soil which did not match with observed value. The greater variation in clay loam soil may be due to different soil layers with different properties during simulation. However, a good fit could not be obtained for the degradation rate constant for malathion. A plausible reason for the somewhat different behavior of malathion and atrazine could be the difference in physico-chemical properties of compounds.

**Table 9. Comparison of retardation factors obtained by MOM and using batch results**

	Malathion		Atrazine	
	R (Using $K_d$ )	R mom	R (Using $K_d$ )	R mom
Loamy Sand	15.02	5.68	2.4	2.05
Sandy Loam	15.00	8.74	2.65	2.50
Clay Loam	17.50	NA	3.37	1.68

## CONCLUSION

The test soils can be grouped according to their sorption capacities as clay loam > sandy loam > loamy sand for both malathion and atrazine. The range of  $K_d$  and  $K_{oc}$  for malathion obtained from the study are 3.8 - 7.3 and 1116 - 1846, respectively and that for atrazine are 0.37 - 1.05 and 142 - 161, respectively. Under saturated flow conditions, malathion and atrazine could leach up to 65 cm and 15 cm respectively. Leaching losses were higher in case of coarse textured soils as compared to fine textured soils. HYDRUS 1D successfully predicted the sorption and degradation of atrazine and malathion in repacked type of soil columns.

## ACKNOWLEDGEMENTS

Financial support for this study was provided by Ministry of Water Resources, Government of India. The authors would like to thank them.

## REFERENCES

- Ahmad, R. and Kookana, R. S. (2002). Extrapolation of pesticide environmental sorption data between agroclimatic regions. In 'environment protection and risk assessment of organic contaminants.' (Eds R.S. Kookana, R. Sadler, N. Sethunathan, R. Naidu). 93-119. (Science Publishers, Inc: Enfield, NH).
- Ahmad, R., Kookana, R. S., Alston, A. M. and Bromilow, R. H. (2001). Differences in sorption behaviour of carbaryl Phosalone in soils from Australia, Pakistan and the UK. Australian Journal of Soil Research. **39**, 893-908.
- Alam, J. B., Dikshit, A. K. and Bandyopadhyay, M. (2000). Efficacy of adsorbents for 2,4-D and atrazine removal from water environment. Global nest: Int. J., **2** (2), 139-148.
- Andrade, L., Marcet, P., Covelo, E. O. and Reyzabal, M. L. (2000). Persistence and mobility of malathion and parathion in horticultural semiarid soils. ISHS Acta Horticulturae 664: IV International Symposium on Irrigation of Horticultural Crops.
- Anonymous. (1998). Production and use of pesticides in Asia. Proceedings of Food and Fertilizers TC International Seminar. Tokyo, Japan.
- Barriuso, E. C., Feller, Ch., Calvet, R and Cerri, C. (1992). Sorption of Atrazine, Terbutyrn, and 2,4-D Herbicides in Two Brazilian Oxisols. Geoderma, **53**, 155-167.
- Baskaran, S., Bolan, N. S., Rahman, A. and Tillman, R. W. (1996). Pesticides sorption by allophane and non-allophonic soils of New Zealand. New Zealand Journal of Agricultural Research, **39**, 297-310.
- Bedmar, F. Costa, J. L., Seuro, E. and Giamenez, D. (2004). Transport of Atrazine and Metribuzin in Three soils of Humid Pampas of Argentina. Weed Technology, **18**, 1-8.
- Bouchard, D. C. (2002). Cosolvent effects on sorption isotherm linearity. Journal of Contaminant Hydrology. **56**, 159-174.
- Cameroon, D. R. and Klute, A. (1977). Convective dispersive solute transport with a combined equilibrium and kinetic adsorption model. Water Res. Res., **13**, 183-188.
- Celis, R., Barriuso, E. and Houout, S. (1998). Effect of liquid sewage sludge on Atrazine adsorption desorption by soil. Chemosphere, **37** (6), 1091-1107.
- Clark, J. R., Lewist, M. A. and Pait, A. S. (1993). Pesticides inputs and risks in coastal wetlands. Environmental Toxicological Chemistry, **12**, 2225-2233.
- Close, M. E., Dann, R. L., Lee, R. and Pang, L. (2006). Impact of data quality and model complexity on

- prediction of pesticide leaching. *J. Environ. Qual.*, **35**, 628-640.
- Coquet, Y. (2003). Sorption of pesticides Atrazine, Isoproturon and Metamitron in Vadose zone. *J. Environ. Qual.*, **2**, 40-51.
- Correia, F. V., Macrae, A., Guileherme, L. R. G. and Langenbatch, T. (2007). Atrazine sorption and fate in Ultisol from humid tropical Brazil. *Chemosphere*, **67** (5), 847-854.
- Dousset, S., Mouvet, C. and Schiavon, M. (1994). leaching of atrazine and some of its metabolites in undisturbed field lysimeters of three soil types. *Chemosphere*, **30** (3). 511-524.
- Droflur, U., Feicht, E. A. and Scheunert, I. (1997). S-Triazine residues in groundwater. *Chemosphere*, **35**, 99-106.
- Felsot, A. and Dahm, P. A. (1979). Sorption of organophosphorus and carbamate insecticides by soil. *J. Agric. Food Chem.*, **3**, 557-563.
- Gerke, H. H. and van Genuchten, M. Th. (1993). A dual porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resour. Res.*, **29**, 305-319.
- Gershon, N. D. and Nir, A. (1969). Effect of boundary conditions on the models on tracer distribution in flow through porous medium. *Water Resour. Res.*, **5**, 830-839.
- Gerstl, Z. (2000). An update on the concept of  $K_{oc}$  in regard to regional scale management. *Crop Protection*, **19**, 643-648.
- Ghezal, F. and Bennaceur, M. (1996). Mobility and degradation of  $^{14}C$ -malathion in soil. X-Symposium Pesticide Chemistry-Last Minute Communication .
- Graymore, M., Stagnitti, F. and Allison, G. (2001). Impacts of atrazine on aquatic ecosystems. *Environment international*, **26** (7-8), 483-495.
- Gustafson, D. I. (1995). Development of novel active ingredients. In M. Vighi and E. Funari, eds. *Pesticide Risk in Groundwater*. Boca Raton, FL: CRC., 153-161.
- Haas, C. N. (1996). Moment analysis of tracer experiments. *J. Environ. Eng.*, **122**, 1121-1123.
- Johnson, A. B. (2001). Saturated transport of Atrazine under two tillage system. This paper was peer reviewed for scientific content. Pages 283-287. In : D. E. Stott, R. H. Mohtar and G. C. Steinhardt (eds). *Sustaining the Global Farm. Selected papers from the 10<sup>th</sup> International Soil Conservation Organisation Meeting held May 24-29, 1999, Purdue University and the USDA – ARS National Soil Erosion Laboratory*.
- Johnson, R. M. and Sims, J. T. (1993). Influence of surface and subsoil properties on herbicide sorption by atlantic and costal plain soils. *Soil science*, **155**, 339-348.
- Jonge, H., Jonge, L. W. and Jacobsen, O. H. (2000). [ $^{14}C$ ]Glyphosate transport in undisturbed topsoil columns. *Pesticide Management Science*, **56**, 909-915.
- Kimbrough, R. A. and Litke, D. W. (1996). Pesticides in streams draining agricultural and urban areas in Colorado. *Environ, Sci. Tech.*, **30**, 908-916.
- Konda, L. N., Fuleky, G., Morovjan, G. and Csokan, P. (1991). Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil. *Chemosphere*, **48**, 545-552.
- Koplin, D. W., Thurman, E. M. and Goosby, D. A. (1996). Occurrence of selected pesticides and their metabolites in near surface aquifers of Midwestern US. *Environ. Sci & Tech.*, **30**, 335-340.
- Kucklick, J. R. and Bidleman, T. (1994). Organic contaminants in Winyah Bay, South Carolina I: Pesticides and polycyclic aromatic hydrocarbons in subsurface and microlayer waters. *Mar. Environ. Res.*, **37**, 63-78.
- Langenbach, T., Schroll, R. and Scheunert, I. (2001). Fate of  $^{14}C$  terbutylazine in Brazilian soils under various climatic conditions. *Chemosphere*, **45**, 387-398.
- Lapidus, S. and Amundson, N. R. (1952). Mathematics of adsorption in beds: VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *J. Phys. Chem.*, **56**, 84-998.
- Larson, S. J., Capel, P. D. and Goolsby, D. A. (1995). Relations between pesticide use and riverine flux in the Mississippi river basin. *Chemosphere*, **31**, 3305-3321.
- Lesan, H. M. and Bhandari, A. (2003). Atrazine Sorption on surface soils: time dependent phase distribution and apparent desorption hysteresis. *Water Research*, **37**, 1644-1654.
- MacNamara, G. and Toth S. (1970). Adsorption of linuron and malathion by soils and clay mineral. *Soil Sci.*, **109** (4), 234-240.
- Mallawantri, A. P. and Mulla, D. J. (1994). Herbicide adsorption and organic carbon contents on adjacent low input versus conventional farms. *Journal of environmental quality*, **21**, 546-551.
- Mishra, C. and Mishra, B. K. (1977). Miscible displacement of nitrate and chloride under field conditions. *Soil. Sci. Soc. Am J.*, **41**, 496-499.

- Parez, A. B. P., Cortes, A., Sala, M. N. and Larsen, B. (1992). Organic matter fractions controlling sorption of atrazine in soils. *Chemosphere*, **25** (6), 887-898.
- Paraiba, L. C. and Spadotto, C. A. (2002). Soil temperature effect in calculating attenuation and retardation factors. *Chemosphere*, **48**, 905-912.
- Liu, P. A. and Gessa, C. (1994). Adsorption of Triclopyr on soil and some of its components. *J. Agri. Food Chem.*, **42**, 1026-1029.
- Rao, P. S. C. and Davidson, M. (1979). Adsorption and movement of selected pesticides at high concentrations in soils. *Water Res.*, **13** (4), 375 – 380.
- Ronenfart, L., Traub-Ebenhard, U., Kordel, W. and Stein, B. (1997). Comparison of the fate of isoproturon in small and large scale water/sediment systems. *Chemosphere*, **35**, 181-189.
- Rosette, E. A. and Koskinen, W. (1997). Atrazine sorption in field moist soil. Supercritical carbon dioxide density effects. *Chemosphere*, **36** (8), 1825-1839.
- Sankaramakrishnan N., Sharma, A. K. and Sanghi R. (2005). Organochlorine and organophosphorous pesticide residues in ground water and surface waters of Kanpur, Uttar Pradesh. India. *Environment International*, **31**, 113-120.
- Shetty, P. K. (2004). Pesticide stewardship and food security in India. Socio-ecological implications of pesticide use in India. NIAS Report RP1. National Institute of Advanced Studies, Bangalore (India).
- Simunek, J., Jarvis, N. J., van Genuchten, M. Th. and Gardenas, A. (2003). Review and comparison of models for describing non equilibrium and preferential flow and transport in the vadose zone. *J. Hydrol.*, **272**, 14-35.
- Simunek, J., Sejna, M. and van Genuchten, M. Th. (1998). The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 2.0, IGWMC-TPS-70. International Ground Water Modeling Center, Colorado School of Mines, Golden, Colorado. 202.
- Singh, G., Van Genuchten, M. TH., Spencer, W. F., Clith, M. M. and Yates, S. R. (1996). Measured And Predicted Transport Of Two S-Triazine Herbicides Through Soil Columns. *Water, Air and Soil Pollution.*, **86**, 137-149.
- Squillace, P. J. and E. M. Thurman. (1992). Herbicide transport in rivers: Importance of hydrology and geochemistry in non point-source contamination. *Environ. Sci. Tech.*, **26**, 538-545.
- Sujatha, C. H. and Chako, J. (1991). Malathion sorption from sediments of a tropical estuary. 1991. *Chemosphere*, **23** (2), 167-180.
- van Genuchten, M. Th. and Wierenga, P. J. (1976). Mass transfer in sorbing porous media. Analytical solutions. *Soil Sci. Soc. Am. J.*, **40**, 473-480.
- van Genuchten, M. Th. and Wagenet, R. J. (1989). Two site /two region models for pesticide transport and degradation: theoretical development and Analytical solutions. *Soil Sci. Soc. Am J.*, **5**, 1303-1309.
- Wauchope, R. D., Yeh, S., Linders, J. B. H. J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M. and Unsworth, J. B. (2002). Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Management Science*, **58** (5), 419-445.
- Weber, J. B., Wilkerson, G. G. and Reinhardt, C. F. (2004). Calculating pesticides sorption coefficient using selected soil properties. *Chemosphere*, **55**, 157-166.