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Behavior of Atrazine and Malathion Pesticides in Soil: Simulation of Transport Process using Numerical and Analytical Models

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ABSTRACT

The objectives of present study were to investigate the transport and distribution of Atrazine and Malathion in soil columns and to determine the transport parameters by using numerical and analytical models. The soil sample used in the study was collected from the surface layer (0-30 cm) of Kharj Province, Riyadh, Saudi Arabia. The soil has a sandy loam texture. Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) as herbicide and Malathion (diethyl (dimethoxy thiophosphorylthio) succinate) as insecticide was used as tested pesticides. The PVC columns, 30.0 cm long and 6.0 cm ID with closed bottoms were used. The columns were hand-packed with air dried sandy loam soil to the desired bulk density. Atrazine and Malathion sorption isotherms were done according to the recommended method to determine the sorption characteristics. Water was added to the soil surface at constant water flow rate (0.182 and 0.282 cm min⁻¹). Atrazine or Malathion was applied with concentration of 300 µg L⁻¹ with a pulse period of 60 min. and then water flow lasted to 360 min with constant water flux, respectively. Pesticide residues in soil or solution were extracted with acetone: hexane, 3:2 extracting solution using Microwave-Assisted Extraction Technique (MAE) and determined with GC-MS. The water flow and pesticides transport equations were solved numerically using the HYDRUS-2D and analytically with CXTFIT code. The present results showed that Atrazine was reached the lower boundary at only the high rate of water flux, but the low water flux did not drained from lower boundary. Both low and high water flux are able to move Malathion to the lower boundary with different magnitude. High and low water flux led to leach Atrazine downward and the maximum concentration was at 17.5 and 12.5 cm depth. In case of Malathion, the water flux leached Malathion out of soil column with high rate, while low rate led to concentrate the Malathion at lower depth of soil column. Numerical and analytical analysis did not differ from experimental data. Thus, the HYDRUS-2D and CXTFIT models successfully predicted Atrazine and Malathion distribution profiles under the present conditions.

Key words: Convection-dispersion equation, breakthrough curve, fate of pesticides in soil, column experiment

INTRODUCTION

It is clear that chemicals applied to soil surface may be transported rapidly to groundwater assign into the unsaturated soil zone (Johnson *et al.*, 1995). Toxic materials especially pesticides

are being used for many purposes in the environment. These substances are adsorbed in soil environment through natural processes occurring in soil-water-plant interface. Adsorption is one of the most important behavior that affects the fate of pesticide in soils and determine their distribution in the soil/water environment (Kah and Brown, 2007).

The environmental fate of herbicides can be studied at different levels: in the lab with disturbed or undisturbed soil columns (Mallawantantri *et al.*, 1996; Abdel-Nasser, 2000, 2001, 2006), or in the field with suction cup lysimeters (Byers *et al.*, 1995) or soil enclosure lysimeters (Bergstrom, 1990; Lennartz *et al.*, 2001). The first type of lysimeters are used particularly for studying the transport processes of herbicides from surface soil to ground water (Guzzella *et al.*, 2000), while the second type for measuring the mass balance of the herbicides in different environmental compartments (Bergstrom, 1990). In the latter type, the quantification of the amount of leaching herbicides is very accurate and precise, because the pore water is collected at the bottom of the different lysimeters and it can be used to quantify water volume collected and herbicide amount leached. The amount of herbicide leached from the bottom of lysimeters takes into account both matrix transport and preferential flow transport in soil. The latter is one of the most important factors in significantly increasing the risk of ground water contamination. In fine textured soils, large and discontinuous macropores consisting of shrinkage cracks, earthworm channels, or root holes operate as preferential flow pathways and can cause rapid movement of chemicals through the unsaturated zone (Klavidko and Timmenga, 1990).

Atrazine is one of the most extensively used herbicides for weed control (Wollenhaupt and Springman, 1990). It is also widely used in many developed and developing countries. With increasing awareness and concern for environmental quality, it is important that we consider not only the effectiveness of a pesticide, but also its interaction and persistence and mobility in soil (Bergstrom *et al.*, 1991). Many pesticides are non-polar and their adsorption on soils is predominantly due to the Organic Carbon (OC) content (Nkedi-Kizza *et al.*, 1983). Understanding sorption, degradation and transport of pesticides and other organic contaminants in soil and aquifers is essential in predicting their fate and transport in the environment. The sorption of uncharged organic compounds by soils has been shown to be highly correlated with soil Total Organic Carbon (TOC) content (Chiou *et al.*, 1979; Briggs, 1981; Karickhoff, 1984). It is therefore generally accept that the predominant sorbent of uncharged organic compounds is organic carbon, as long as the TOC is larger than 0.1% (Schwarzenbach and Westall, 1981).

Once atrazine has been applied to soils, it has the ability to associate with various soil compounds, including Soil Organic Matter (SOM). In general, SOM becomes an important factor with atrazine adsorption in soils with high SOM content (>6%), Shea (1989). Barriuso *et al.* (1992) and Xing *et al.* (1996) examined atrazine sorption to two Brazilian oxisols and concluded that SOM was the most important factor effecting atrazine adsorption. Piccolo *et al.* (1998) found that the type of SOM plays an important role in atrazine adsorption. Roy and Krapac (1994) found that atrazine sorption to low organic carbon sand, till and alluvial samples conformed to linear isotherms. Atrazine adsorption was not proportional to the organic carbon content, indicating mineral surface interactions.

Some researches provided a model for predicting the fate of nonvolatile pesticides (Wagenet and Hutson, 1986, 1987; Wagenet *et al.*, 1989). In many cases, they considered a

distribution coefficient for this case (Deeley *et al.*, 1991). Developing models with molecular diffusion and other important factors have been done by other researchers (Jury *et al.*, 1983; Kalita *et al.*, 1998).

The increasing concern over pesticides in surface and groundwater has required the evaluation of their mobility as a basis of risk assessment. Columns and Lysimeters offer good possibilities to conduct such tests, because they carry on in the closed systems, with the control of water leaching through the soil (Bergstrom, 1990; Hance and Fuhr, 1992). The objectives of this study were to investigate the transport and distribution of Atrazine and Malathion in arid land soil to determine the transport parameters using numerical and analytical models.

MATERIALS AND METHODS

The present study was carried out at year of 2008 in the Soil Physics Laboratory, Soil Sciences Department, King Saud University, Saudi Arabia.

Soil: The soil sample used in the present study was collected from the surface layer (0-30 cm) of Kharj Province, Haradh road, Riyadh, Saudi Arabia, 24° 27' 5.8" N and 47° 40' 23.1" E and 445 m.a.s.l. (Al-Turki *et al.*, 2009). The soil has sandy loam texture and some of its physical and chemical characteristics as determined by recommended procedures (Klute, 1986; Carter, 1993) are presented in Table 1. The texture of soil is sandy loam and has 81.9% sand, 2.50% silt and 15.6% clay with electrical conductivity of 0.92 dS m⁻¹.

Pesticides: Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) of 99.8% purity, which is an herbicide used for selective control of grassy weeds. It has a water solubility of 33 mg L⁻¹ and half-life of 64 days (Singh *et al.*, 1990a, b) (Table 2).

Malathion is known technically as diethyl (dimethoxy thiophosphorylthio) succinate. Malathion is a non-systemic, organophosphate insecticide. Main uses are agricultural and domestic,

Table 1: Some physical and chemical characteristics of soil used in present study

Parameters	Values	Units
Particle size distribution		
Sand	81.9	%
Silt	2.5	%
Clay	15.6	%
Textural class	Sandy loam	
Bulk density	1.6	g cm ⁻³
Calcium carbonate content	9.29	%
Organic matter content	0.05	%
pH	8.30	
EC _w	0.92	dS m ⁻¹
Soluble cations		
Ca ²⁺	6.25	mg L ⁻¹
Mg ²⁺	2.00	mg L ⁻¹
Na ⁺	1.60	mg L ⁻¹
K ⁺	0.45	mg L ⁻¹
Soluble anions		
CO ₃ ⁻²	0.00	mg L ⁻¹
HCO ₃ ⁻	3.00	mg L ⁻¹
Cl ⁻	2.00	mg L ⁻¹
SO ₄ ⁻²	5.30	mg L ⁻¹

Table 2: Selected physical and chemical properties of Atrazine and Malathion

Properties	Atrazine	Malathion
Molecular formula	C ₈ H ₁₄ ClN ₅	C ₁₀ H ₁₉ O ₆ PS ₂
MW (g mol ⁻¹)	215.68	330.36
Melting point (°C)	175-177	2.9
Aqueous solubility (S _w) (mg L ⁻¹)	33	145
Vapour Pressure (mPa, 25°C)	0.038	5.3
pK _a (25°C)	1.70	2.61
Henry's Law Constant (Pa·m ³ ·mol ⁻¹ , 25°C)	2.5E-04	2.35E-05
Log K _{oc} (Octanol-water partition coefficient)	2.68	2.89
Half-life time (days)	68	7
Partition coefficient (K _d) (L g ⁻¹)	3.2997	1.1162
First order rate constant for degradation in dissolved phase (μ _w) (day ⁻¹)	0.0102	0.1053
Molecular diffusion coefficient in free water (D _w) (cm ² min ⁻¹)	0.005	0.005

Source: Capel *et al.* (1999) and Acero *et al.* (2000)

mainly for the control of sucking and chewing insects including mosquitoes, aphids, turf insects and many floral and vegetable crops. It has a water solubility of 145 mg L⁻¹ and half-life of 4-6 days (Singh *et al.*, 1990a) (Table 2).

Soil columns: A PVC columns, 30.0 cm long and 6.0 cm ID with closed bottoms were used in the present study. The base of the columns tightly sealed with silicon adhesive. The bottom 1 cm layer in the columns comprised fine gravel (drainage layer). A perforated plastic tube of 1.0 cm diameter fitted into the drainage layer to collect the drainage water. The columns were hand-packed with air dried sandy loam soil to the desired bulk density by gently tapping (1.6 g cm⁻³).

Soil hydraulic parameters: Soil water retention, θ(h) and soil hydraulic conductivity K(h) functions are specified. The soil water retention curve was determined using the pressure plate extractor according the method described in Klute (1986). The water retention data was described using the van Genuchten analytical expression (Van Genuchten, 1980):

$$S_e = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1 + |\alpha h|^n)^m} \quad (1)$$

The hydraulic conductivity function was described using the capillary model (Mualem, 1976) as applied to the van Genuchten function (Van Genuchten, 1980):

$$K(h) = K_s S_e^\tau \left[1 - \left(1 - S_e^{1/m} \right)^m \right]^2 \quad (2)$$

In Eq. 1 and 2, θ_r and θ_s denote the residual and saturated volumetric water content, respectively (L³L⁻³); S_e is effective saturation (-); K_s the saturated hydraulic conductivity (LT⁻¹); τ a pore connectivity coefficient; and α(L⁻¹), n and m (m=1-1/n) are empirical coefficients. The saturated hydraulic conductivity (K_s) was determined using constant head permeameter method as describe in Klute (1986).

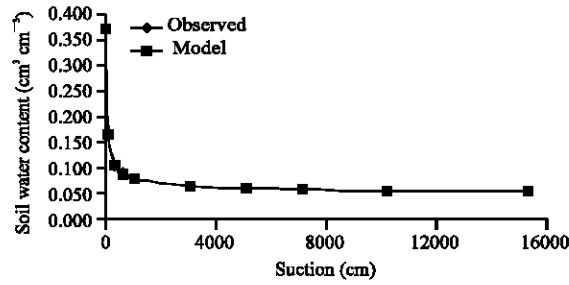


Fig. 1: Soil water retention curve of used soil

The soil hydraulic parameters were fitted using the RETC model (Van Genuchten *et al.*, 1991) and the soil moisture retention curve is shown in Fig. 1. The soil hydraulic parameters were; $\theta_r = 0.0482 \text{ cm}^3 \text{ cm}^{-3}$, $\theta_s = 0.3728 \text{ cm}^3 \text{ cm}^{-3}$, $\alpha = 0.0508 \text{ cm}^{-1}$, $n = 1.6080$, $m = 0.3781$ and $K_s = 0.656 \text{ cm min}^{-1}$.

Pesticides adsorption isotherm: Atrazine and Malathion adsorption isotherms were done according to the method of USEPA (1991) as described in Abdel-Nasser (2005) using linear adsorption isotherm (Simcnek *et al.*, 1999). The partition coefficient (K_d) was calculated and then the retardation factor (R).

$$S = K_d C \tag{3}$$

where, C is the total dissolved adsorbate remaining in solution at equilibrium (M L^{-3}) and S is the adsorbate on the solid phase at equilibrium (M M^{-1}).

The theoretical retardation factor R was calculated according to Rao *et al.* (1985):

$$R = 1 + \frac{\rho_b \times K_d}{\theta} \tag{4}$$

where, ρ_b is soil bulk density (M L^{-3}), θ is the effective volumetric soil water content ($\text{L}^3 \text{ L}^{-3}$).

Water and pesticides application: Before starting the experiment, each soil column was connected to a suction pump and subjected to -10.0 cm water tension. Water was added to the column soil surface at constant state water flow rate (0.182 and 0.282 cm min^{-1}). Atrazine or Malathion were applied at a constant rate with concentration of 300 $\mu\text{g L}^{-1}$ using CaCl_2 (0.001 M) as a background solution with a pulse period of 60 min., then water flow lasted to 360 min with constant water flux. The suction head (h) in the soil columns were monitored periodically during the application period using small mercury tensiometers located at depths of 2.5, 7.5, 12.5, 17.5, 22.5 cm below the soil surface. Soil columns were monitored for drainage water at desired times. Collected drainage water at different periods was measured as volume per surface area of soil columns (cm).

Pesticide residues extraction and analysis: Pesticide residues in soil samples or solution were extracted with acetone: hexane, 3:2 extraction solution using Microwave-Assisted Extraction (MAE)

technique as described by Westbom *et al.* (2008). The pesticide concentrations in the extract were analyzed by gas chromatography (Hewlett-Packard, Agilent 6890N), equipped with Nitrogen-Phosphorus Detector (NPD) and Electron Capture Detector (ECD) detectors (Westbom *et al.*, 2008). The clear supernatant was used for analyzing the pesticides concentration (C_e) using gas chromatography, GC-MS (Agilent-6890, USA, using 30 m×0.25 mm×0.25 μm film cross-linked with 5% phenyl methyl silicone capillary column and a N/P detector). The operational conditions of the gas chromatography were: injector temperature 250°C, detector temperature 320°C, initial oven temperature 80°C with a holding time of 2.5 min, increased to 230 at 40°C min⁻¹ with a final holding time of 3 min and carrier flow rate 1.5 mL min⁻¹. All the solutes were rectified using external standard solution of Atrazine or Malathion. The detection limit was below 5 μg L⁻¹.

Theory

Water flow: Variably saturated water flow in porous media usually described using Richards, (1931):

$$\frac{\partial\theta(h)}{\partial t} = \frac{\partial}{\partial z} \left(K(h) \frac{\partial h}{\partial z} + K(h) \right) \quad (5)$$

where, t is time (min) and z (cm) is depth (positive upward) and θ (cm³ cm⁻³) and h (cm) denote the volumetric water content and the soil water matric pressure head, respectively. The Richards equation can be solved numerically when the initial and boundary conditions are prescribed and two constitutive relations are specified, i.e., the soil water retention, $\theta(h)$ and soil hydraulic conductivity, K(h) functions (Eq. 1 and 2).

Solute transport: Solute transport (single reactive solute) in variably saturated porous media is described in one-dimensional homogeneous system using the convection-dispersion equation (Nielsen and Biggar, 1962) as:

$$R \frac{\partial\theta C}{\partial T} = \frac{\partial}{\partial Z} \left(\theta D \frac{\partial C}{\partial Z} \right) - \frac{\partial v\theta C}{\partial Z} \quad (6)$$

where, C is the solute concentration (μg L⁻³), R is the retardation factor (-), D is the effective dispersion coefficient (cm² min⁻¹) and v is the pore water velocity (cm min⁻¹). The retardation factor R (Hasimoto *et al.*, 1964; Singh *et al.*, 1996) and the dispersion coefficient D (Bear, 1988) are defined as:

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (7)$$

$$D = \lambda |v| + \tau(\theta) * D_0$$

where, K_d is the linear adsorption distribution coefficient (L³ g⁻¹), ρ_b is the soil bulk density (g cm⁻³), $\tau(\theta)$ is the tortuosity factor, D₀ is the ion diffusion coefficient (cm² min⁻¹) and λ is the longitudinal dispersivity (L). Tortuosity factor (τ) can be calculated as follows (Millington and Quirk, 1961):

$$\tau(\theta) = \frac{\theta^{(7/3)}}{\theta_s^2} \quad (8)$$

Initial and boundary conditions: The initial condition for the present experiment was obtained by establishing steady state downward water flow with a constant water flux and a constant solute concentration. Then at initial time ($t = t_0 = 0$, both matric pressure head (h_i) and solution concentration (C_i) were constant with depth:

$$\begin{aligned} h(z, t_0) &= h_i = -10\text{cm} & z > 0, t = 0 \\ C(z, t_0) &= C_i = 0 \end{aligned} \quad (9)$$

The upper boundary conditions (at $z = 0$) for the water flow (flux-type boundary condition) are given by:

$$\begin{aligned} -K \left(\frac{\partial h}{\partial z} + 1 \right) &= q_{\text{top}}(t) & z = 0, t \geq 0 \\ -\theta D \frac{\partial C}{\partial z} + qC &= q_{\text{top}}(t)C_{\text{top}}(t) \end{aligned} \quad (10)$$

where, q_{top} and C_{top} are water flux and input solute concentration applied at the soil surface, respectively.

A zero matric pressure head gradient (free drainage, $q = -K(\theta)$) and a zero concentration gradient are used as the lower boundary conditions (at $z = -L$) for water flow and solute transport, respectively.

$$\begin{aligned} \left(\frac{\partial h}{\partial z} \right)_{z=-L} &= 0 & z \rightarrow \infty, t \geq 0 \\ \left(\frac{\partial C}{\partial z} \right)_{z=-L} &= 0 \end{aligned} \quad (11)$$

The water flow and pesticides transport equation subjected to initial and boundary conditions were solved numerically using the HYDRUS-2D code (Simunek *et al.*, 1999).

The Eq. 4 was solved analytically and the data were fitted using the CXTFIT program (Parker and van Genuchten, 1984; Toride *et al.*, 1999). For pulse time, t_0 ($t_0 = T$) and for times greater than T , the solution can write as follows (Van Genuchten and Wierenga, 1986):

$$\frac{C(z,t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left\{ \frac{z - v^*t}{\sqrt{4D^*t}} \right\} + \left(\frac{v^*t}{\pi D^*} \right)^{\frac{1}{2}} \exp \left\{ -\frac{(z - v^*t)^2}{4D^*t} \right\} - \frac{1}{2} \left(1 + \frac{v^*z}{D^*} + \frac{v^{*2}t}{D^*} \right) \exp \left(\frac{v^*z}{D^*} \right) \operatorname{erfc} \left\{ \frac{z + v^*t}{\sqrt{4D^*t}} \right\} \quad (12)$$

Equation 12 can be simplified (Lapidus and Amundson, 1952) as:

$$\frac{C(z,t)}{C_0} = \frac{1}{2} \operatorname{erfc} \left\{ \frac{z - v^* t}{\sqrt{4D^* t}} \right\} + \frac{1}{2} \exp \left(\frac{v^* z}{D^*} \right) \operatorname{erfc} \left\{ \frac{z + v^* t}{\sqrt{4D^* t}} \right\} \quad (13)$$

where,

$$D^* = \frac{D}{R} \quad \text{and} \quad v^* = \frac{v}{R}$$

All three parameters v , D and R were unknown and can be fitted by program. Following Buckingham's theorem (Bird *et al.*, 2001), only two of them can simultaneously fit.

RESULTS AND DISCUSSION

The transport parameters used in the simulation of pesticides transport in soil columns were shown in Table 3.

Pesticides flux at lower boundary condition: Atrazine and Malathion fluxes at lower boundary conditions are shown in Fig. 2a and b. The data indicated that Atrazine was reached the lower boundary for only the high rate of water flux, but the lower flux of water did not drained from lower boundary. The high water flux is able to leach atrazine out of soil column. In the case of Malathion, both low and high water flux are able to move Malathion to the lower boundary but with different magnitude. The high water flux reached the peak concentration firstly at about 210 min. But the low water flux retarded and reached the maximum peak at about 330 min. This result may be attributed to that the low water flux did not able to fill soil pores with water that responsible to movement of pesticide out of the soil column (Al-Darby and Abdel-Nasser, 2006). The differences between Atrazine and Malathion in behavior are attributed to the difference in partition coefficient. Amount of leached Atrazine was 6.64 and 0.05 μg for high and low water flux, respectively. While the corresponding values for Malathion were 128.1 and 58.7 μg , respectively.

Table 3: Pesticides transport parameters used in the present simulation

Parameters	Symbol	Atrazine	Malathion	Unit
Longitudinal pore scale dispersivity	λ_L	0.5	0.5	cm
Transverse pore scale dispersivity	λ_T	0.1	0.1	cm
Ionic diffusion coefficient in free water	D_0	0.0558	0.0558	$\text{cm}^2 \text{min}^{-1}$
Partition coefficient	K_d	3.2997	1.1162	L g^{-1}
Pulse time	T_0	60	60	min
Simulation time	T	360	360	min
Initial condition				
Initial water potential	h_i	-10.0	-10.0	cm
Initial concentration	C_i	0.0	0.0	$\mu\text{g cm}^{-3}$
Upper boundary condition				
Steady state water flux	q_0	Variable	Variable	cm min^{-1}
Inflowing concentration	C_0	300	300	$\mu\text{g L}^{-1}$
Lower boundary condition				
Free drainage	dq/dt	0.0	0.0	cm min^{-2}
Conservative flow	dc/dx	0.0	0.0	

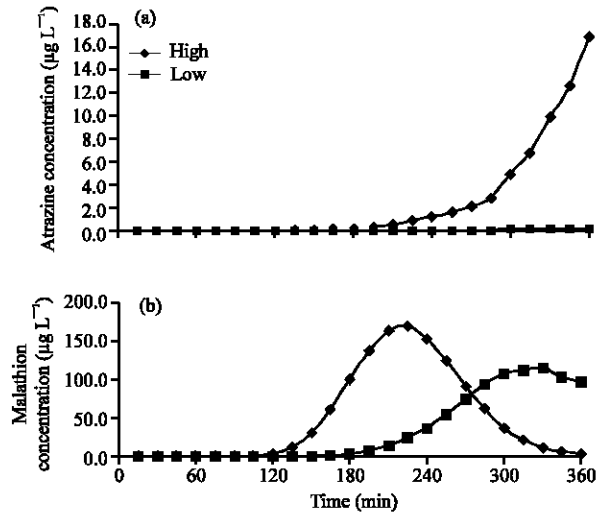


Fig. 2: Pesticides distribution with time in column leachate ($\mu\text{g L}^{-1}$). (a) Atrazine concentration in column leachate and (b) Malathion concentration in column leachate

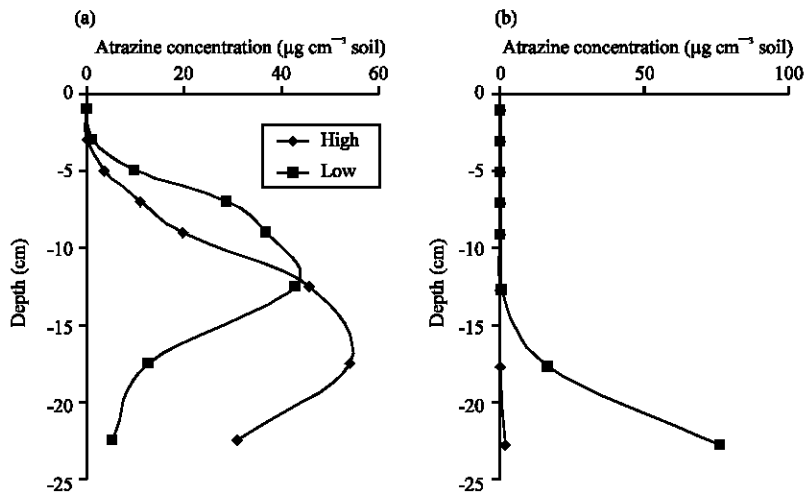


Fig. 3: Pesticide distribution profile. (a) Atrazine soil profile distribution and (b) Malathion soil profile distribution

The Leaching Fraction (LF) represents the mass of pesticide passing through the lower boundary against the mass of pesticide added. At low water flux, the LF of Atrazine and Malathion was 0.06 and 70.29%, respectively. The corresponding values for high water flux were 5.10 and 98.92%, respectively. This means that Malathion is more leachable than Atrazine.

Pesticides distribution profile: Pesticides distribution profiles at the end of experimental period are shown in Fig. 3a and b. The data clearly indicate that the water flux density has an important role in distribution pattern of pesticides in soil columns.

High water flux led to leach Atrazine downward and the maximum concentration was at 17.5 cm depth, while the low water flux reached the maximum concentration at 12.5 cm depth.

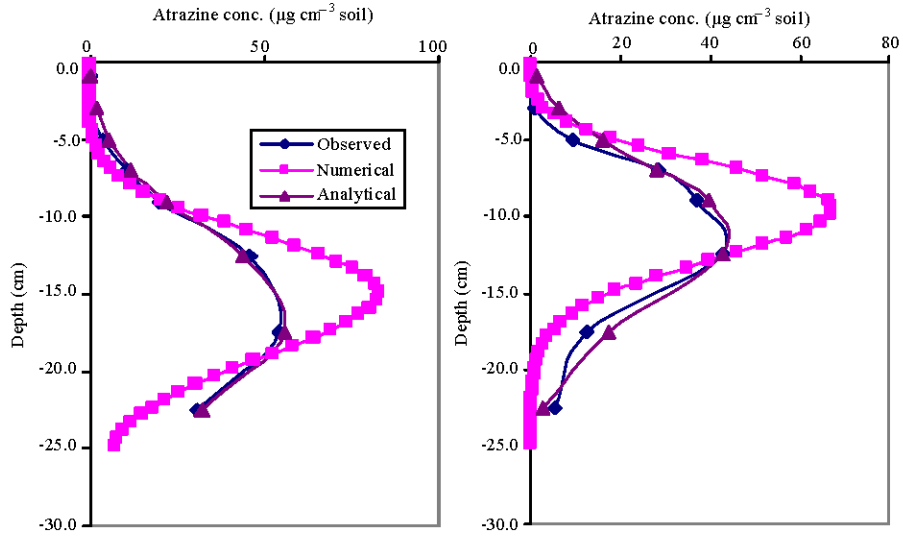


Fig. 4: Comparison between experimental data and numerical and analytical analysis for Atrazine distribution profile. (a) high water flux and (b) low water flux

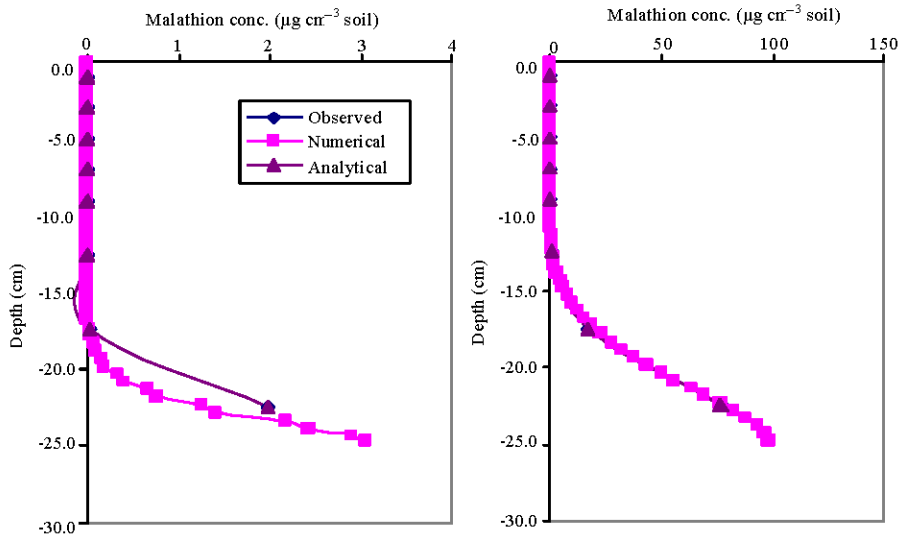


Fig. 5: Comparison between experimental data and numerical and analytical analysis for Malathion distribution profile. (a) high water flux and (b) low water flux

In case of Malathion, the water flux leached Malathion out of soil column with high rate, while low rate led to concentrate the Malathion at lower depth of soil column. The decreased movement of atrazine through soil columns was due to the great ability of soil to adsorb the Atrazine than Malathion as indicated by increasing the partition coefficient (K_d) and retardation factor, R (Abdel-Nasser, 2005, 2006).

Numerical and analytical analysis did not differ from experimental data. The results showed that the numerical and analytical analysis is close up the experimental data (Fig. 4, 5). Thus,

Table 4: Mass balance calculations (μg) for Atrazine transport in soil columns

Soil depth (cm)	High water flux		Low water flux	
	Sorbed	Solution	Sorbed	Solution
-1	0.000	0.000	0.004	0.000
-3	0.003	0.000	0.338	0.020
-5	0.705	0.041	2.908	0.169
-7	2.908	0.169	8.627	0.500
-9	4.984	0.289	11.11	0.644
-12.5	32.967	1.912	32.213	1.868
-17.5	40.583	2.353	9.613	0.557
-22.5	22.585	1.310	3.94	0.228
Total	104.70	6.100	68.80	4.000
Total in soil	110.80		72.80	
Leachate	6.61		0.05	
Total Atrazine detected	117.41		72.85	
Inflowing solution	129.50		83.30	
Mass balance recovery (%)	90.66		87.45	

Table 5: Mass balance calculations (μg) for Malathion transport in soil columns

Soil depth (cm)	High water flux		Low water flux	
	Sorbed	Solution	Sorbed	Solution
-1	0.000	0.000	0.000	0.000
-3	0.000	0.000	0.000	0.000
-5	0.000	0.000	0.000	0.000
-7	0.000	0.000	0.000	0.000
-9	0.000	0.000	0.001	0.000
-12.5	0.000	0.000	0.158	0.029
-17.5	0.008	0.001	4.064	0.737
-22.5	0.479	0.087	18.413	3.339
Total	0.487	0.088	22.636	4.105
Total in soil	0.575		26.60	
Leachate	128.10		58.70	
Total Malathion detected	128.68		85.30	
Inflowing solution	129.50		83.30	
Mass balance recovery (%)	99.36		102.40	

the HYDRUS-2D and CXTFIT models successfully predicted Atrazine and Malathion distribution profiles under the present conditions. According to the goodness index, modeling efficiency, EF (Loague *et al.*, 1989), the values of EF ranged between 0.997 and 0.999. Also the coefficient of determination, CD (Loague *et al.*, 1989) was ranged from 0.992 to 0.998.

Mass balance of pesticides in soil column: Table 4 and 5 shown the mass balance calculations of Atrazine and Malathion in soil columns at different water flux. The mass recovery percent ranged between 90.66 and 87.45% for Atrazine and ranged between 99.36 and 102.40% for Malathion. Therefore the error percent did not exceed 12.65% that is allowed in laboratory - experiments. Atrazine concentration in liquid phase (soil solution) equal to 4.71%, in solid phase

(adsorbed) is 80.85% and in leachate is 5.1% of applied Atrazine in case of high water flux. While the values for low water flux were 4.80, 82.59 and 0.06%, respectively.

Malathion concentration in liquid phase (soil solution) equal to 0.07%, in solid phase (sorbed) is 0.38% and in leachate is 98.92% of applied Malathion in case of high water flux. While, the values for low water flux were 4.92, 27.17 and 70.47%, respectively.

The values resulted from the analytical solution (CXTFIT model) did not differed from the numerical solution (HYDRUS-2D model) and observed values. This means that compatibility between the numerical and analytical solutions in this case is very good (Fig. 4, 5).

This result is useful as a mean for reducing the groundwater pollution with pesticides. Also, the water flux or irrigation rate plays an important factor for groundwater pollution, in with increasing irrigation capacity will increased the pesticides leaching into groundwater (Abdel-Nasser, 2001). Therefore, soil and water management considered as major factor in reducing groundwater pollution with pesticides.

CONCLUSION

The present study shows a primary data about the behavior of Atrazine and Malathion in soil, but the behavior of pesticides in soil differs according many factors such as soil type and properties, pesticide properties and environmental factors. Thus, the complete information about the behavior of pesticides in soil requires studying the behavior of these pesticides in different soil types and properties under different environmental conditions. This is more important if we need to draw general policy for using the pesticides under varying conditions to draw an integrated program to conserve soil and groundwater against pollution, then protect human from pesticides pollution.

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REFERENCES

- Abdel-Nasser, G., 2000. Numerical Simulation of Water Flow and Solute Transport into Subsurface Tile Drains. Washington State University, Pullman, WA, USA.
- Abdel-Nasser, G., 2001. Predicting atrazine transport into subsurface tile-drained soil using HYDRUS-2D model: Lysimeter study. Proceedings of BCPC Symposium on Pesticide Behaviour in Soils and Water, Nov. 12-15, Brighton, UK., pp: 301-306.
- Abdel-Nasser, G., 2005. Impact of olive pomace on atrazine transport parameters in sandy soil. I. partition coefficient and retardation factor. *J. Saudi Soc. Agric. Sci.*, 4: 1-17.
- Abdel-Nasser, G., 2006. Impact of olive pomace on atrazine transport parameters in sandy soil. II: Simulation of atrazine transport with numerical and analytical models. *J. Saudi Soc. Agric. Sci.*, 5: 1-19.
- Acero, J.L., K. Stemmler and U. Von-Gunter, 2000. Degradation kinetics of atrazine and its degradation products with ozone and OH radicals: A predictive tool for drinking water treatment. *Environ. Sci. Technol.*, 34: 591-597.
- Al-Darby, A. and G. Abdel-Nasser, 2006. Nitrate leaching through unsaturated soil columns: comparison between numerical and analytical solutions. *J. Applied Sci.*, 6: 735-743.
- Al-Turki, A.M., G. Abdel-Nasser, M.I. Al-Wabel and M.H. El-Saeid, 2009. Evaluation of pollutants in agricultural soils in Saudi Arabia. Financial Supported from Deanship of Scientific Research, King Saud University. Two Parts, pp: 649.

- Barriuso, E., Ch. Feller, R. Calvent and C. Cerri, 1992. Sorption of atrazine, terbutyrn and 2,4-D herbicides in two Barazilian Oxisols. *Geoderma*, 53: 155-167.
- Bear, J., 1988. *Dynamics of Fluids in Porous Media*. Dover Publ., New York.
- Bergstrom, L., 1990. Use of lysimeters to estimate leaching of pesticides in agricultural soils. *Environ. Pollut.*, 67: 325-347.
- Bergstrom, L., A. McGibbon, D. Day and M. Snel, 1991. Leaching potential and decomposition of clopyralid in Swedish soils under field conditions. *Environ. Toxicol. Chem.*, 10: 563-571.
- Bird, R.B., W.E. Stewart and E.N. Lightfoot, 2001. *Transport Phenomena*. 2nd Edn., John Wiley and Sons, New York, ISBN-10: 0471410772, pp: 912.
- Briggs, G.G., 1981. Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors and the parachor. *J. Agric. Food Chem.*, 29: 1050-1059.
- Byers, M.E., D. Tyess, G.F. Antonious, D. Hilborn and L. Jarret, 1995. Monitoring herbicide leaching in sustainable vegetable culture using tension lysimeters. *Bull. Environ. Contamination Toxicol.*, 54: 848-854.
- Capel, P.D., A.H. Spexet and S.J. Larson, 1999. Occurance and behavior of the herbicide prometon in the hydrologic system. *Environ. Sci. Technol.*, 33: 674-680.
- Carter, M.R., 1993. *Soil Sampling and Methods of Analysis*. Canadian Society of Soil Science. Levis Publishers, London, pp: 823.
- Chiou, C.T., L.J. Peters and V.H. Freed, 1979. A physical concept of soil-water equilibria for nonionic organic compounds. *Science*, 206: 831-832.
- Deeley, G.M., M. Reinhard and S.M. Stearns, 1991. Transformation and sorption of 1, 2-dibromo-3-chloropropane in subsurface samples collected at Fresno, California. *J. Environ. Qual.*, 20: 547-556.
- EPA., 1991. *Site Characterization for Subsurface Remediation*. EPA., Cincinnati, Ohio.
- Guzzella, L., F. Pozzoni and G. Giuliano, 2000. Field study on mobility and persistence of linuron and monolinuron in agricultural soil. *Int. J. Environ. Anal. Chem.*, 78: 87-106.
- Hance, R.J. and F. Fuhr, 1992. *Methods to Study Fate and Behaviour of Pesticides in the Soil*. In: *Lysimeter Studies of the Fate of Pesticides in the Soil*, Fuhr, F. and R.J. Hance (Eds.). Vol. 53, British Crop Protection Council Publisher, UK., pp: 9-21.
- Hasimoto, I., K.B. Deshpande and H.C. Thomas, 1964. Peclet numbers and retardation factors for ion exchange columns. *Ind. Eng. Chem. Fundamentals*, 3: 213-218.
- Johnson, D.C., H.M. Selim, I. Ma, L.M. Southwick and G.H. Willis, 1995. *Movement of Atrazine and Nitrate in Sharkey Clay Soil: Evidence of Preferential Flow*. Louisiana State University Agricultural Center, Los Angeles, USA.
- Jury, W.A., W.F. Spencer and W.J. Farmer, 1983. Behavior assessment model for trace organics in soil: I. model description. *J. Environ. Qual.*, 12: 558-564.
- Kah, M. and C.D. Brown, 2007. Changes in pesticide adsorption with time at high soil to solution ratios. *Chemosphere*, 68: 1335-1343.
- Kalita, P.K., A.D. Ward, R.S. Kanwar and D.K. McCoo, 1998. Simulation of pesticide concentrations in groundwater using Agricultural Drainage and Pesticide Transport (ADAPT) model. *Agric. Water Manage.*, 36: 23-44.
- Karickhoff, S.W., 1984. Organic pollutant sorption in aquatic systems. *J. Hydraul. Eng.*, 110: 707-735.

- Klavidko, E.J. and H.J. Timmenga, 1990. Earthworms and Agricultural Management. In: Rhizosphere Dynamics, Box, J.E. and L.C. Hammond (Eds.). Westview Press, Boulder, USA., pp: 154-159.
- Klute, A., 1986. Methods of Soil Analysis. American Society of Agronomy, Madison, WI, USA.
- Lapidus, L. and N.R. Amundson, 1952. Mathematics of adsorption in beds: VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *J. Phys. Chem.*, 56: 984-988.
- Lennartz, B., E. Simic and G. Destouni, 2001. Field-scale variability of herbicide transport. Proceedings of a Symposium on Pesticide Behaviour in Soils and Water, Brighton, UK., Nov. 13-15, pp: 165-170.
- Loague, K.M., R.S. Yost, R.E. Green and T.C. Liang, 1989. Uncertainty in a pesticide leaching assessment for Hawaii. *J. Contaminant Hydrol.*, 4: 139-161.
- Mallawantantri, A.P., B.G. McConkey and D.J. Mulla, 1996. Characterization of pesticide sorption and degradation in macropore linings and soil horizons in thatuna silt loam. *J. Environ. Qual.*, 25: 227-235.
- Millington, R.J. and J.P. Quirk, 1961. Permeability of porous solids. *Trans. Faraday Soc.*, 57: 1200-1207.
- Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resour. Res.*, 12: 513-522.
- Nielsen, D.R. and J.W. Biggar, 1962. Miscible displacement. 3. Theoretical considerations. *Soil Sci. Soc. Am. Proc.*, 26: 216-221.
- Nkedi-Kizza, P., P.S.C. Rao and J.W. Johnson, 1983. Adsorption of diuron and 2,4,5-T on soil particle-size separates. *J. Environ. Qual.*, 12: 195-197.
- Parker, J.C. and M.T. van Genuchten, 1984. Determining transport parameters from laboratory and field tracer experiments. *Virginia Agric. Exp. Stat. Bull.*, 84: 83-83.
- Piccolo, A., P. Conte, I. Scheunert and M. Paci, 1998. Atrazine interaction with soil humic substances of different molecular structure. *J. Environ. Qual.*, 27: 1324-1333.
- Rao, O.S.C., A.G. Hornsby and R.E. Jessup, 1985. Indices for ranking the potential for pesticide contamination of groundwater. *Soil Crop Sci. Soc. Florida*, 44: 1-8.
- Richards, L.A., 1931. Capillary conduction of liquids through porous mediums. *Physics*, 1: 318-333.
- Roy, W.R. and I.G. Krapac, 1994. Adsorption and desorption of atrazine and deethylatrazine by low organic carbon geologic materials. *J. Environ. Qual.*, 23: 549-556.
- Schwarzenbach, R.P. and J. Westall, 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.*, 15: 1360-1367.
- Shea, P.J., 1989. Role of humified organic matter in herbicide adsorption. *Weed Technol.*, 3: 190-197.
- Simcnek, J., M. Seja and M.T. van Genuchten, 1999. The HYDRUS-2D Software Package for Simulating the Two-Dimensional Movement of Water, Heat and Multiple Solutes in Variably-Saturated Media Version 2.0. USDA/ARS, California, USA.
- Singh, G., W.F. Spencer, M.M. Cliath and M.T. Van-Genuchten, 1990a. Sorption behavior of s-triazine and thiocarbamate herbicides on soils. *J. Environ. Qual.*, 19: 520-525.
- Singh, G., W.F. Spencer, M.M. Cliath and M.T. van Genuchten, 1990b. Dissipation of s-triazines and thiocarbamates from soil as related to soil moisture content. *Environ. Pollut.*, 66: 253-262.
- Singh, G., M.Th. Van Genuchten, W.F. Spencer, M.M. Cliath and S.R. Yates, 1996. Measured and predicted transport of two s-triazine herbicides through soil columns. *Water Air Soil Pollution*, 86: 137-149.

- Toride, N., F.J. Leij and M.Th. van Genuchten, 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.1, Research Report No. 137, U.S. Salinity Laboratory, USDA-ARS, Riverside, CA.
- USEPA, 1991. Site characterization for subsurface remediation. EPA/625/4-91/026, Office of Research and Development, US. Environmental Protection Agency, Cincinnati, Ohio. <http://www.epa.gov/oust/cat/sitchasu.pdf>.
- Van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, 44: 892-898.
- Van Genuchten, M.T. and P.J. Wierenga, 1986. Solute Dispersion Coefficients and Retardation Factors. In: *Methods of Soil Analysis Part 1*, Klute, A. (Edn.). 2nd Edn., ASA and SSSA, Madison, WI., pp: 1025-1054.
- Van Genuchten, M.T., F.J. Leij and S.R. Yates, 1991. The RETC Code for Qualifying the Hydraulic Functions of Unsaturated Soils. Agricultural Research Services, California, USA.
- Wagenet, R.J. and J.L. Hutson, 1986. Predicting the fate of nonvolatile pesticides in unsaturated zone. *J. Environ. Qual.*, 15: 315-322.
- Wagenet, R.J. and J.L. Hutson, 1987. LEACHM: Leaching Estimation and Chemistry Model: A Process Based Model of Water and Solute Movement Transportation, Plant Uptake and Chemical Reactions in Unsaturated Zone. Vol. 2, Water Resources Institute, Ithaca, New York, USA.
- Wagenet, R.J., J.L. Huston and J.W. Biggar, 1989. Simulating the fate of a volatile pesticide in unsaturated soil: A case study with DBCP. *J. Environ. Qual.*, 18: 78-84.
- Westbom, R., A. Hussen, N. Megersa, N. Retta, L. Mathiasson and E. Bjorklunda, 2008. Assessment of organochlorine pesticide pollution in Upper Awash Ethiopian state farm soils using selective pressurized liquid extraction. *Chemosphere*, 72: 1181-1187.
- Wollenhaupt, N.C. and R.E. Springman, 1990. Atrazine in Groundwater: A Current Perspective. Univ. of Wisconsin-Extension Publ., Madison.
- Xing, B., J.J. Pignatello and B. Gigliotti, 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ. Sci. Technol.*, 30: 2432-2440.