Int. J. Environ. Res., 3(4):545-556, Autumn 2009 ISSN: 1735-6865

# **Pollution Migration Study in Subsurface Environment**

Sadashiva Murthy, B.M.\*, Ramesh, H.S. and Mahadevaswamy, M.

Department of Environmental Engineering, Sri Jayachamarajendra College of Engineering, Mysore – 570 006, Karnataka, India

Received 5 Aug. 2008;	Revised 24 Jan. 2009;	Accepted 12 April 2009
100001.0000 11000. 20000,	100 1300 2 1 Valii 2009,	incerpted in inpin 2009

**ABSTRACT:** The sources of groundwater pollution such as, industrial effluents, sewage and extensive farming have lead to agrochemical pollution. Mathematical modeling helps to analyze the existing situation, allows forecasting, and to evaluate the effects of changes in the surrounding water quality. The present research has been focused mainly towards understanding the various processes affecting the transport of chemicals in soils. Dispersion coefficient for the sandy loam soil was found to be  $0.247 \text{ m}^2/\text{d}$ ,  $0.150 \text{ m}^2/\text{d}$  and  $0.01 \text{ m}^2/\text{d}$  for nitrates, phosphates and Chlorpyriphos through column, and  $0.337 \text{ m}^2/\text{d}$ ,  $0.217 \text{ m}^2/\text{d}$  and  $0.077 \text{ m}^2/\text{d}$  for nitrates, phosphates and Chlorpyriphos through channel studies, respectively. For similar analysis of the breakthrough curves, dispersion coefficient for the clay soil was found to be  $0.0835 \text{ m}^2/\text{d}$ ,  $0.0632 \text{ m}^2/\text{d}$  and  $0.008 \text{ m}^2/\text{d}$  for nitrates, phosphates and Chlorpyriphos through column and  $0.147 \text{ m}^2/\text{d}$ ,  $0.0848 \text{m}^2/\text{d}$  and  $0.022 \text{ m}^2/\text{d}$  for nitrates, phosphates and Chlorpyriphos through channel studies in sandy loam and clay soils and compared with model output (in which total elimination rate "K" is considered as zero). From this a variation of about 40-60 percent in the leaching characteristics of pollutants was being observed (nitrates, phosphates and chlorpyriphos).

Key words: Contaminant, Vadoze zone, Transport, Plume Model, Total Elimination Rate

## **INTRODUCTION**

Chemical pollutants such as fertilizers (like nitrates and phosphates) and pesticides (like chlorpyriphos) reach soil by direct application, by drift during aerial application and due to washingoff from the foliage. Irrespective of the methods of application, chemicals ultimately find their way into soil, which finally acts as a reservoir where persistent chemicals remain (Asi, et al., 2008; Shahidi Bonjar, 2007; Nouri et al., 2008; Borujeni et al., 2007). They may form complexes with humic and fulvic acids which are very resistant to breakdown. As a consequence, they may disturb the local metabolic activity, the fertility of soil and also the chemical degradation processes. Further, the characteristics of recharge mechanisms are also undergoing drastic change leading to different rates of recharge into groundwater medium. These issues can be addressed through mathematical modeling.

Concern over groundwater contamination by chemicals entering subsurface environment have created a greater impetus for the development of quantitative tools for predicting the spread of pollutants in the unsaturated (vadose) zone at the field scale. Effective groundwater management requires a good acquaintance of the aquifer system; secondly, practical measures to control abstraction that can be identified and, thirdly augmentation groundwater resources through artificial recharge (Thangarajan, 2004). While properly designed field experiments provide a relatively high degree of confidence in predicting contaminant fate under particular experimental conditions, extrapolation of experimental data to other locations or cropping scenarios is often impossible. It is, therefore indispensable to quantify the response of the aquifer under study to diverse input/output stresses. A groundwater model is thus

<sup>\*</sup>Corresponding author E-mail:bmsada@yahoo.com

a simplified version of the real system that approximately simulates the input/output stresses and response relation of the system. The modeling technique is very powerful tool and many of the very complex problems can be addressed through these tools (Mohankumar, 2005). Accurate measurement of soil water flux, containing any solute, remains a challenge and the lack of measurements of these solutes, limits our understanding of solute transport in porous media. Protection and remediation of groundwater resources require an understanding of processes that affect fate and transport of contaminants in the subsurface environment. The unsaturated or vadose zone (between water table and groundwater) is generally more favorable for pollutant attenuation and elimination. It is evident that vadose zone plays a significant role in groundwater studies, as it is the hydrological connection between the surface water component of hydrological cycle and groundwater component (Inayathulla, 2005).

To assess the risk of groundwater contamination by excess nutrients allied chemicals, their mobility and persistence in the soil need to be determined. To account for contaminant transport along preferential pathways the contaminant concentration needs to be monitored when percolating through soil environment. In temperate regions, many studies were conducted to assess the leaching potential of nutrients in field experiments and to evolve the influence of soil properties, soil management, and application mode on output from soils (Paramasivam et al., 2002 and Logsdon et al., 2002). However, data on medium to long term leaching of nutrients in representative soils of the tropics are completely lacking for most compounds in the literature (Laabs et al., 2002). Adsorption - Desorption of Imidacloprid on five Indian soils (Alfisol, Vertsol, Oxisol, Ultisol, Inceptisol) were studied by Kalpana et al., 2002 using batch equilibration technique. Equilibration time was determined using preliminary kinetic study.Suman et al., 2002 have investigated the adsorption, persistence and leaching of dithiopyr. The sorption experiment was conducted by the batch equilibrium technique and preliminary kinetic studies were carried out to determine equilibration time.

Degradation studies of many chemicals in soil have been reported in large numbers during the last decade. Of all the reviewed subsoil studies, only few of them took into account the vulnerability of microorganisms to changes in their environment caused by actions such as sieving and drying the soil (Fomsgaard, 1997). Degradation of chemicals can follow either chemical or a microbial pathway or a combination of both. Contaminant degradation studies in soil are often performed at higher concentrations of contaminant than the concentrations actually present in soil after leaching through normal agricultural use (Fomsgaard, 1997). Vanderbroght et al., 2000, evaluated the effect of flow rate and flow regime on solute transport in two soils, sandy loam and loam. For each type leaching experiments were carried out in two large undisturbed soil columns of 0.3 m inner diameter and 1 m length for three different flow rates and transient flow regimes. Solute concentrations were measured in the drain and break through curves was used to optimize convective dispersion equation. The experiment revealed that due to the activation of macro-pores, the lateral solute mixing decreases with increasing flow rate, which resulted in the increase of dispersivity with increasing depth at higher flow rates.

A standard method for estimating solute transport properties is to conduct a steady-state transport experiment and to measure solute flux concentrations in the soil or a breakthrough curves at various depths. Such studies are essential to address the question whether or not detected contaminants are likely to persist in the vadose zone. Retention processes deserve attention as well, since they generally play a major role in the fate and transport of pesticides in the subsurface, (Cokca, 2002). Retention in the vadose zone delays the appearance of pollutants in groundwater, and increases their migration time, thereby allowing more time for the chemical to undergo degradation in the vadose zone, (Cokca, 2002). Also, simulating field studies in laboratory provides valuable in sign about the porous media, the behaviors of chemicals, and associated processes such as diffusion, dispersion, anion exclusion, sorption or exchange during transport (Shukla et al., 2003). The physical and chemical composition of soil like particle size, organic content, bulk density, porosity,

maximum water holding capacity, pH and conductivity influence the sorption, leaching and mobility behavior of fertilizers and pesticides in soil. The chemical structure of the fertilizers and pesticides defines its intrinsic properties such as adsorption characteristics, chemical reactivity, biological activity and photolytic stability. The fate of fertilizers and pesticides is also determined by the adsorption, desorption, volatilization of the chemical in the soil and its rate of degradation either biotically or abiotically. Leaching and mobility are important routes of pesticides and fertilizers transport in soil. Climatologically parameters such as temperature, sunlight, rainfall and evaporation rates determine microbial degradation and leachate volumes. The fate and behavior of the fertilizers and pesticides in the environment is governed by the complex interaction of these mechanisms.where,

C, the solute concentration (ML<sup>-3</sup>), Ds ,the solute dispersion coefficient ( $L^2 T^{-1}$ ),

V ,the average pore water velocity  $(LT^{-1})$ , Z ,the longitudinal distance (L) and t, the time (T).

$$(\partial \mathbf{C} / \partial \mathbf{t}) = \mathbf{D}_{s} (\partial^{2} \mathbf{C} / \partial z^{2}) - \mathbf{V} (\partial \mathbf{C} / \partial z)$$
(1)

Under steady state condition, one-dimensional transport equation for the transient transport of contaminants with advection, adsorption, and dispersion, is given by (Domenico and Schwartz., 1998).

$$(\partial C / \partial t) = D [(\partial^2 C / \partial z^2) / R_d] - [V (\partial C / \partial z) / R_d] - K C$$
 (2)

where,

R<sub>d</sub> - Retardation Factor

 $R_d = [1+(\rho_b/n) \ K_d]$ 

 $r_{\rm b}$  - Bulk mass density of the porous medium (g/ cm<sup>3</sup>).

 $K_{d}$  - The distribution Coefficient (cm3/g).

$$K = k_{d} + k_{v} + k_{l} + k_{u}$$
(3)

n - Effective porosity.

- D Hydraulic Dispersion Coefficient (m<sup>2</sup>/d)
- V Average Linear Velocity, (m/d)
- K Total Elimination Rate, (d<sup>-1</sup>)

The one dimensional analytical model developed includes the term total elimination rate (K) which specifies the rate constants such as, degradation, volatilization, leaching and plant root uptake defined in Equation (3). where,

 $k_d$  - Degradation Rate Constant, (d<sup>-1</sup>)

 $k_{v}$  - Volatilization rate constant, (d<sup>-1</sup>)

 $k_1$  Rate of leaching, (d<sup>-1</sup>)

 $k_{n}$  Rate of plant root uptake, (d<sup>-1</sup>)

#### **Biodegradation Rate Constant**

The Biodegradation rate constant is given by

$$\mathbf{C} = \mathbf{C}_0 \, \mathrm{e}^{\mathrm{kd} \, \mathrm{t}} \tag{4}$$

where, C the solute concentration and k is the rate constant for the reaction  $(T^{-1})$ . From the plot of ln  $(C/C_0)$  versus t. rate constant  $(k_d)$  can be determined directly from slope of the line.

#### **Volatilization Rate Constant**

The volatilization rate constant is given by

$$V = k_V R C$$
 (5)

where, V - Chemical vaporized from surface vegetation during hour t, (g ha<sup>-1</sup>)

R - Relative volatility of the chemical and water during hour t, (d<sup>-1</sup>)

C - Chemical available for volatilization on vegetation at the beginning of hour t, (gha<sup>-1</sup>)

 $k_{y}$  - Volatilization constant, (d<sup>-1</sup>)

#### Leaching Rate Constant

The Leaching rate constant is given by

$$\mathbf{k}_{\mathrm{I}} = (\mathbf{PL}_{\mathrm{t}} - \mathbf{BC}) / \mathbf{FC}_{\mathrm{t}}$$
 (6)

where,

 $PL_t$  - Chemicals leached from vegetation during hour *t*, (g ha<sup>-1</sup>)

BC - Background concentration of the chemicals, (g ha<sup>-1</sup>)

 $FC_t$  - Actual amount of chemicals applied in field, (g ha<sup>-1</sup> d<sup>-1</sup>)

#### Plant Root Uptake Rate Constant

The Plant root uptake rate constant is given by

$$k_{\rm U} = FS \tag{7}$$

Where,

F - Transpiration stream concentration factor

S - Actual rate of water uptake by the crop,  $\left[1/T\right]$ 

Analytical solutions obtained with simplified assumption include the following:

- The traces are ideal with constant density and viscosity
- The fluid is incompressible
- The medium is homogeneous and isotropic Only saturated flow is considered

# AnalyticalSolutionsforPulse (Instantaneous) Model

A pulse input of contamination, such as leaking from underground storage tank or from the site of an accidental hazardous materials spill has been derived for the injection of a tracer with background concentration zero. The analytical solution for the Equation (2) with initial and boundary condition given

as:

I.C. : 
$$C(z, 0) = 0$$
 for  $z \ge 0$   
B.C. 1:  $C(0, t) = C_0$  for  $t > 0$   
B.C. 2:  $\partial c / \partial z = 0$  at  $z = \infty$   
 $C(z, t) = \{M/(4 \pi D | t) 0.5\} \exp(-\{(z - V | t)/(4 D | t)\}) \exp(-K | t)\}$ 
(8)

Where,

M - Mass spilled per cross sectional area,  $(g / m^2)$ T - Time, (Days)  $D^{I} - D/R_d$ 

 $V^{I} - V/R_{d}$ 

 $K^{\text{I}}\,$  - K/  $R_d$ 

# Analytical Solutions For Plume (Continuous) Model

The continuous input of hazardous wastes from a landfill, surface impoundment or similar sources can be calculated at any distance with respect to time. The solution to Equation (2) based on its integration using the appropriate boundary condition is as follows:

I.C.: C (z, 0) = 0 for 
$$z \ge 0$$
  
B.C.1: C (0, t) = C<sub>0</sub> for t > 0  
B.C.2:  $\partial c / \partial z = 0$  at  $z = \infty$   
C/C<sub>0</sub> = 0.5 [exp {z/2D<sup>1</sup> (v<sup>1</sup> - (v<sup>1 2</sup> + 4D<sup>1</sup>K<sup>1</sup>)}  
{erfc ((z - t (v<sup>1 2</sup> + 4D<sup>1</sup>K<sup>1</sup>/(4D<sup>1</sup>t)<sup>0.5</sup>} + Exp {z<sup>1</sup> 2D<sup>1</sup> (v<sup>1</sup> + (v<sup>1 2</sup> + 4D<sup>1</sup>K<sup>1</sup>)} (9)  
erfc ( (z + t (v<sup>1 2</sup> + 4D<sup>1</sup>K<sup>1</sup>/(4D<sup>1</sup>t)<sup>0.5</sup>}]

Where,

The complementary error function (erfc) is given by the following relations.

erfc  $(-\beta) = 1 + erf(\beta)$ erfc  $(\beta) = 1 - erf(\beta)$ 

## **MATERIALS & METHODS**

A computer program developed for personal computers under the windows environment using V.B language is used in this study. This Visual basic is a Rapid Application Development tool that allows programmers to create windows application in very little time.It is the most popular programming language in the world and has more programs or lines of code, which is very simple and user friendly. In this program, equations 4, 5, 6, 7, 8 and 9 are programmed.

#### Validation Of The Model

Model Validation is testing the model on another independent data set or to verify the model, that is to make sure that the computer simulation acts as it is intended to against the conceptual model that has been designed. This validation is done by comparing the models to what is generally accepted as the real system, and real system for this exercise can be thought of as the laboratory results and characteristics of the sources.

## Sensitivity Analysis

The analysis of sensitivities is the study of model behavior in response to perturbations in parameters. Sensitivity analysis has been applied generally to solutions of time-dependent, physically based differential equations, and applied specifically to chemical kinetics. The purpose of these applications of sensitivity analysis is to indicate which model parameters are most important to estimate accurately and to gain insight on how a system should be sampled to refine estimates of parameters (Knopman and Voss, 1987).

The one dimensional Advection Dispersion Equation has been chosen to illustrate the behavior and role of sensitivities to parameter estimation and sampling design for transient transport problems. An advantage of choosing the one dimensional model is the availability of the closed form analytical solutions (Knopman and Voss, 1987). Derivatives thus are exact and integrals are formed from exact integrands. This lessens the chance that results will be marred by unspecified error. The model was found to be very sensitive to increase in dispersion coefficient and degradation rates i.e., the peak concentration was increased to about 87 % with decrease in dispersion coefficient by 90 % from the actual dispersion coefficient.

## Hydrodynamic Dispersion Co-Efficient for the Combined Leaching Characteristics of Nitrates and Phosphates

From Fried and Cumbernous (1971), equation:

$$D = (1/8) [\{(z - u t_{0.84})/(t_{0.84})^{0.5}\} - \{(z - u t_{0.16})/(t_{0.16})^{0.5}\}]^2$$
(10)

where,

D - Hydrodynamic dispersion coefficient in  $m^2/d$ Z - Depth of the soil layer in m,

U - Velocity of the tracer solution in the soil layer in m/d,

t  $_{0.84}$  and t $_{0.16}$ . Time required for the relative concentrations at 0.840 and 0.160 to reach a particular depth Z.

The hydrodynamic dispersion Coefficient values obtained considering Break through Curves for Nitrates, Phosphates and Chlorpyriphos using laboratory leachate column and channel studies are as in Table 1,2,3 and 4 respectively.

### **RESULTS & DISCUSSION**

Leaching studies were carried out on sandy loam and clay soils using column and channel with similar initial concentrations of nitrate, phosphate and chlorpyriphos of 11 mg /L, 0.3 mg/L and 0.1  $\mu$ g/l, respectively, under steady state condition. The constant head maintained was ranging between 50 mm and 90 mm. In order to study the leachate characteristics of nitrate, phosphate and chlorpyriphos through the column and channel, breakthrough curves were drawn.

The Figs. (1), (2) and (3) shows concentration profiles in terms of breakthrough curves for nitrate, phosphate and chlorpyriphos with time in column for sandy loam soil. From figs. (1) and (2), it is observed that the concentration of nitrates and phosphates in the column increased steadily during first few days (around 7 days), which further increased rapidly between 10 to 15 days and continued till 25 days. However, after 25 days it attained its equilibrium. Further, chlorpyriphos concentration in the column in sandy loam soil increased steadily during first few days (around 12 days), which further increased rapidly between 18 to 27 days and continued till 45 days as shown in Fig.3. However, after 45 days it attained its equilibrium. The Figs. (4), (5) and (6) show concentration profiles in terms of breakthrough curves for nitrate, phosphate and chlorpyriphos with time in column for clayey soil. It was observed that the concentration of nitrates and phosphates in the

 Table 1. Dispersion Coefficient Values Obtained Considering BTC curves Of Nitrates, Phosphates and Chlorpyriphos in Sandy loam soil (Column studies)

Nitrate (C <sub>o</sub>	= 11 mg/L)		Phosphat	$e (C_0 = 0.3 r)$	ng/L)	Chlorpyr	Chlorpyriphos ( $C_o = 0.1 \mu g/L$ )		
t 0.16(Days)	t. <sub>0.84</sub> (Days)	$D(m^2/d)$	t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	t 0.16(Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	
0.6525	13	0.2476	0.4	8	0.150	11	15	0.010	

 Table 2. Dispersion Coefficient Values Obtained Considering BTC curves of Nitrates, Phosphates and Chlorpyriphos in Clay soil(Column Studies)

Nitrate ( $C_0 = 11 \text{ mg/L}$ )			Phosphate (	$(C_0 = 0.3 \text{ mg/I})$	L)	Chlorpyriphos( $C_0 = 0.1 \mu g/L$ )		
t 0.16(Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	t 0.16(Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	t 0.16(Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$
5	40	0.0835	9	43	0.0632	33	49	0.008

Table 3. Dispersion Coefficient Values Obtained Considering B.T.C. Curves Of Nitrates, Phosphates and
Chlorpyriphos in Sandy loam soil (Channel Studies)

Nitrate ( $C_o = 11 \text{ mg/L}$ )			Phosphate	$e (C_0 = 0.3 m)$	g/L)	Chlorpyriphos(Co = 0.1µg/L)			
t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	D( m <sup>2</sup> /d )	t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	
0.4	10	0.337	0.3	5.5	0.217	17	31.9	0.077	

 Table 4. Dispersion Coefficient Values Obtained Considering B.T.C. Curves of Nitrates, Phosphates and Chlorpyriphos in Clay soil (Channel Studies)

Nitrate ( $C_0 = 11 \text{ mg/L}$ )			Phosphate ( $C_0 = 0.3 \text{ mg/L}$ )			Chlorpyriphos(Co = 0.1 µg/L)		
t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Day)	$D(m^2/d)$	t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$	t <sub>0.16</sub> (Days)	t <sub>0.84</sub> (Days)	$D(m^2/d)$
1	15	0.147	4	20	0.0848	29.9	47	0.022

column for clay soil increased steadily during first few days (around 11 days), which further increased rapidly between 15 to 20 days and continued till 30 days as shown in Figs .(4) and (5). However, after 30 days it attained its equilibrium. Further, it is also observed that the rate of leachate as well as concentration of chlorpyriphos was more pronounced in sandy loam soil as compared with clay soil.

The concentration profile in the form of ratio for nitrates, phosphates and chlorpyriphos (channel studies) in sandy loam soil at various time intervals are presented in Figs. (7), (8) and (9), respectively. From Figs. (7) and (8), it was observed that the concentration of nitrates and phosphates increased steadily in the first few days (3 to 5 days), then it increased rapidly after 18 to 25 days, thereafter it attained equilibrium. From Fig. (9) it was observed that the concentration of chlorpyriphos increased steadily in the first few days (10 to 15 days) and then it increased rapidly after 20 to 35 days and thereafter it attained equilibrium.

In the channel studies the concentration profile in the form of concentration ratio in clay soil at various time intervals for nitrates, phosphates and chlorpyriphos are presented in Figs. (10), (11), and (12), respectively. From the Figs. (10) and (11), it can be observed that the concentration of nitrates and phosphates is increasing steadily in the first few days (8 to 10 days) and then increasing rapidly

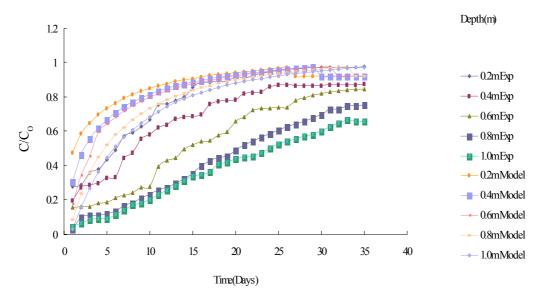


Fig. 1. B.T.C for Concentration versus Time for Nitrates In Sandy loam soil (Column Studies and Model Output, Total Elimination Rate, K =0)

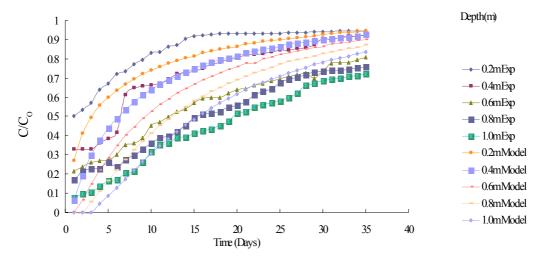


Fig. 2. B.T.C for Concentration versus Time for Phosphates In Sandy loam soil (Column Studies and Model Output, Total Elimination Rate, K =0)

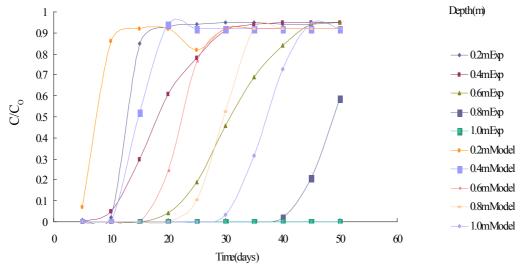


Fig. 3. B.T.C for Concentration versus Time for chlorpyriphosIn Sandy loam soil (Column Studies and Model Output, Total Elimination Rate, K =0)

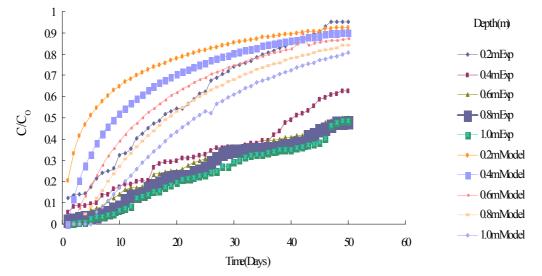


Fig. 4. B.T.C for Concentration versus Time for Nitrates In Clay soil (Column Studies and Model output, Total Elimination Rate, K =0)

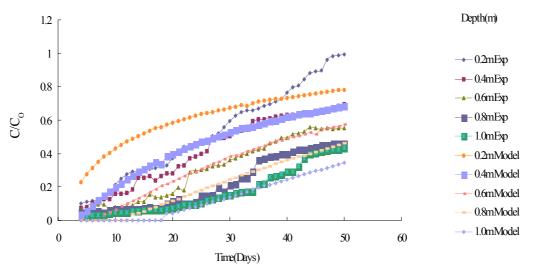
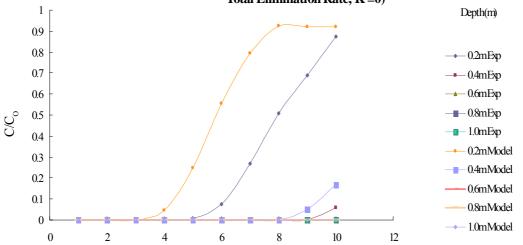


Fig. 5. B.T.C for Concentration versus Time for PhosphatesIn Clay soil (Column Studies and Model Output, Total Elimination Rate, K =0)



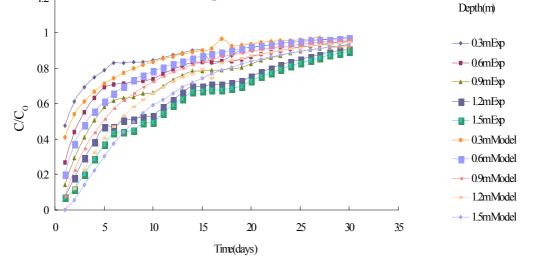


Fig.7 . B.T.C f or Concentration versus Time for Nitrates In Sandy loam soil (Channel Studies and Model Output, Total Elimination Rate, K =0)

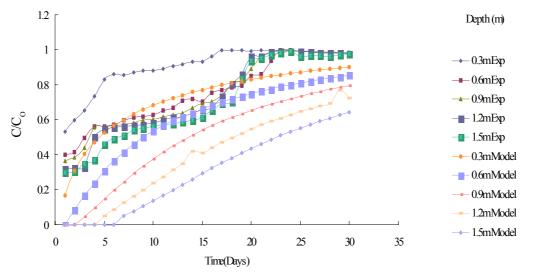


Fig. 8. B.T.C for Concentration versus Time for Phosphates In Sandy loam soil (Channel Studies and Model Output, Total Elimination Rate, K =0)

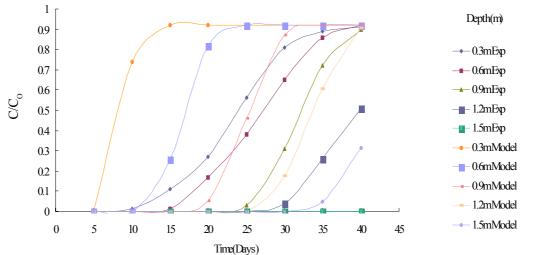


Fig. 9. B.T.C for Concentration versus Time for ChlorpyriphosIn Sandy loam soil (Channel Studies and Model output, Total Elimination Rate, K =0)

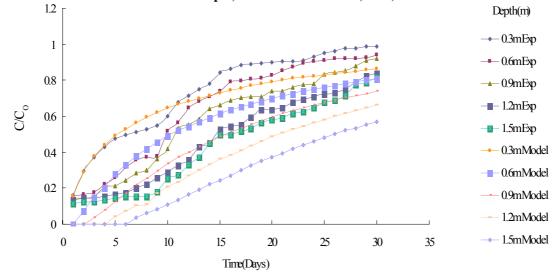


Fig. 10. B.T.C for Concentration versus Time for Nitrates In Clay (Column Studies and Model Output, Total Elimination Rate, K =0)

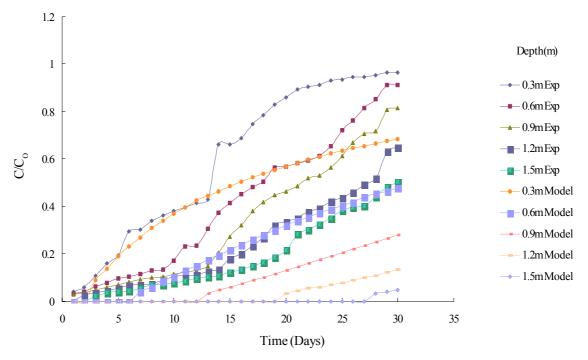


Fig. 11. B.T.C for Concentration versus Time for Phosphates In Clay soil (Channel Studies and Model Studies, Total Elimination Rate, K =0)

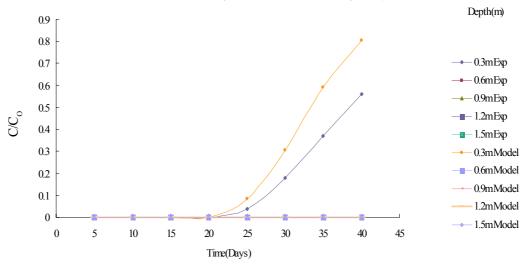


Fig. 12. B.T.C for Concentration versus Time for Chlorpyriphos In Clay soil (Channel Studies and Model Studies, Total Elimination Rate, K =0)

after 20 to 35 days and thereafter it attains equilibrium. As shown in Fig. (12) chlorpyriphos leachate was found only at 0.3 m in clay soil and thus, the rate of leachate as well as concentration of chloropyriphos was more in sandy loam soil as compared to clay soil.

In order to study the leaching characteristics of pollutants through sandy loam and clayey soil, hydrodynamic dispersion co-efficient was determined from the breakthrough curves, for which one-dimensional analytical model has been used. The soil column and channel studies are compared with analytical model considering the term total elimination rate, K as zero. The breakthrough curves of concentration versus time and depth from the model output for both sandy loam and clay soil with column and channel studies are as shown in the Figs. (1) to (12). The comparative study revealed that, model output data for soil column and channel studies is greater by 40 to 60 % than the experimental studies which may be due to non-consideration of total elimination rate (K) in the model analysis.

# CONCLUSION

Based on the extensive laboratory studies and analytical review, the following conclusions were drawn:

The laboratory column studies of nitrates, phosphates and chlorpyriphos revealed that, in sandy loam soil, concentration profile of the nitrate and phosphate increased steadily during first few days (about 7 days) and thereafter it increased rapidly from 10-15 days and attained its equilibrium after 25 days. Similarly, for chlorpyriphos it indicated an increase in chlorpyriphos concentration profile during 12 days from startup thereafter increased linearly from 12-18 days and attained its equilibrium after 45 days. As given in Table 1the hydrodynamic dispersion coefficients are found to be 0.2476 m<sup>2</sup>/day, 0.15m<sup>2</sup>/day and 0.01 m<sup>2</sup>/day, for nitrate, phosphate and chlorpyriphos respectively. The laboratory column studies of nitrates, phosphates and chloropyriphos revealed that, in clay soil the concentration profile of the nitrate and phosphate increased steadily during first few days (about 11 days) and thereafter it increased rapidly from 15-20 days and attained its equilibrium after 30 days and It was also observed that the rate of leachate as well as concentration of chloropyriphos is more in sandy loam soil as compared with clay soil. As given in Table 2 the hydrodynamic dispersion coefficients are found to be  $0.0835 \text{ m}^2/\text{day}, 0.0632$ ,  $m^2/day$  and 0.008  $m^2/day$ , for nitrate, phosphate and chlorpyriphos respectively.

The channel studies for leachate of nitrate and phosphate through sandy loam soil showed that there was gradual increase in the nitrate and phosphate concentration upto first 3 to 5 days, and then it varied linearly upto 18 to 25 days and thereafter it attained its equilibrium. Similarly, for chlorpyripos through sandy loam soil showed that there was gradual increase in the chloropyripos concentration upto first 10 to 15 days, and then it varied linearly upto 20 to 35 days and thereafter it attained its equilibrium. As given in Table 3 the hydrodynamic dispersion coefficients are found to be  $0.337 \text{ m}^2/\text{day}$ ,  $0.217 \text{ m}^2/\text{day}$  and  $0.077 \text{ m}^2/\text{day}$ , for nitrate, phosphate and chlorpyriphos respectively.

The channel studies for leachate of nitrate and phosphate through clay soil showed that there was

gradual increase in the nitrate and phosphate concentration upto first 8 to 10 days, and then it varied linearly up to 20 to 30 days and thereafter it attained its equilibrium .Similarly, for chloropyripos through sandy loam soil showed that there was gradual increase in the chloropyripos concentration upto first 8 to 10 days, and then it varied linearly upto 20 to 35 days and thereafter it attained its equilibrium. Similarly, channel leachate studies for nitrate, phosphate and chlorpyriphos through clay soil revealed that time of travel for nitrate, phosphate and chlorpyriphos was more than that for sandy loam soil. As given in Table 4 the hydrodynamic dispersion coefficients are found to be 0.147 m<sup>2</sup>/day, 0.0848 m<sup>2</sup>/day and 0.022 m<sup>2</sup>/ day, respectively. It was also observed that the hydrodynamic dispersion coefficient for nitrate, phosphate and chlorpyriphos in sandy loam of column studies was 3, 2.3 and 1.25 times greater than that recorded in clay soil and 2.3, 2.5 and 3.5 for channel studies respectively. Comparative study of model output with the soil column and channel experimental data revealed a variation of 40 to 60% in the leaching characteristics of pollutants (nitrate, phosphate and chlorpyriphos).

#### REFERENCES

Asi, M. R.; Hussain, A. and Muhmood, S. T.(2008). Solid phase extraction of pesticide residues in water samples: DDT and its metabolites. Int. J. Environ. Res., **2(1)**, 43-48.

Akhtar, M.S, Richards, B.K., Medrano, P.A., Groot, M. and Steenius, T.S. (2003). Dissolved Phosphorous From Undisturbed Soil Cores; Related To Adsorption Strength, Flow Rate, Or Soil Structure? Soil Science Society Of American Journal, **67**, 458-470.

Borujeni, F. G., Mahvi, A. H., Nouri, J. and Dobaradaran, S., (2007). Removal of cadmium from aqueous solution by Platanus orientalis leaves. Trop. Med. Int. Health. **12**, 194-194.

Choi, Y. H., Lim, K. M., Choi, H. J., Choi, G. S., Lee H. S. and Lee, C. W. (2004). Analytical Model For Vadose Zone Solute Transport With Root Water and Solute Uptake. Vadose Zone Journal., **1**, 158-171.

Chu, X. and Marino, M. A. (2004). Semi Discrete Pesticide Transport Modeling and Application. Journal Of Hydrology, **285**, 19–40.

Cokca, E. (2002). Computer Program For The Analysis Of 1-D Contaminant Migration Through The Soil Layer. Int. Environmental Modeling and Software, **18**, 147-153. Dejong H., Jacobsen O.H., De Jonge L.W. and Moldrup, P. (1998). Colloid-Facilitated Transport Of Pesticide In Undistributed Soil Columns. Phys. Chem. Earth, **23(2)**, 187-191.

Domenico, P.A. and Schwartz, F. (1998). Physical and Chemical Hydrogeology. Second Edition, John Wiley and Sons, New York, 506.

Fomsgaard, I.S. (1997). Modeling the Mineralization Kinetics for Low Concentration of Pesticides in Surface and Subsurface Soil. Ecological Modeling, **102**, 175 – 208.

Gupta, S. and Gajbhiye V.T., (2002). Adsorption – Desorption, persistence, and leaching behavior of dithiopyr in an alluvial soil in India. Journal of Environmental science and Health, **37(6)**, 573-586.

Haith, D. A., Lee, P. C., Clark, M., Roy, G. K., Imboden, M. J. and Walden, R.R. (2002). Modeling Pesticide Volatilization From Turf. J. Environmental Quality, **31**, 724-729.

Hamilton, D. A., Wiggert, D.C. and Wright, S. J. (1985). Field Comparison Of Three Mass Transport Models. J. Hydraulic Engineering, **111(1)**, 1-11.

Inayathulla, M. (2005). Migration of Pollutants through Unsaturated Porous Media. Proceedings of Fourth DST-SERC School on Mathematical Modeling of Groundwater Quality and Pollution. UGC- Center for Advanced Studies in Fluid Mechanics, Department of Mathematics, Bangalore University and National Research Institute for Applied Mathematics, Bangalore, 331-357.

Kalpana, P., Agnihotri, N. P. and Gajbhiye V.T. (2002). Adsorption – Desorption Of Imidacloprid On Five Tropical Indian Soils. Pesticides Research Journal, **149(1)**, 63-68.

Knopman, D. S. and Voss, C. I. (1987). Behavior of Sensitivities in the One Dimensional Advection – Dispersion Equation: Implication for Parameter Estimation and Sampling Design. Water Resources Research, **23** (2), 253-272.

Laabs, V., Amelung, W., Pinto, A. and Zech, W. (2002). Fate of Pesticides in Tropical Soils of Brazil Under Field Conditions. J. Environmental Quality, **32**, 1455-1463.

Logsdon, S.D., Kaspar, T.C., Meek, D.W. and Prueger, J. H. (2002). Nitrate Leaching as Influenced by Cover Crops in Large Soil Monolith. Agronomy Journal, **94**, 807–814.

Metry, A. A. (1976). Modeling Pollutant Migration In Subsurface Environment. Proceedings Of Epa Conference On Environmental Modeling & Simulation, Usepa, **537**-542.

Mohankumar, M. S. (2005). Mathematical Modeling Of Ground Water And Vadose Zone Flows. Proceedings Of Fourth Dst-Serc School On Mathematical Modeling Of Groundwater Quality And Pollution, Ugc - Center For Advanced Studies In Fluid Mechanics, Department Of Mathematics, Bangalore University, And National Research Institute For Applied Mathematics, Bangalore, India,475-487.

Nouri, J., Mahvi, A. H., Jahed, G.R. and Babaei, A.A., (2008). Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environ. Geo., **55** (6), 1337-1343.

Paramasivam, S., Alva, A. K., Fares, A., and Sajwan, K. S. (2002). Fate of Nitrate and Bromide in an Unsaturated Zone of a Sandy Soil under Citrus Production. J. Environmental Quality, **31**, 671-681.

Pachepsky, Y., Benson, D. and Rawls, W. (2000). Simulating Scale – Dependent Solute Transport In Soils With The Fractional Advective – Dispersive Equation. Soil Science Society Of American Journal, **64**, 1234-1243.

Rudraiah, N. and Vinay, C.V. (2002). Mathematical Modeling Of Groundwater Pollution. Proceeding Of Fourth Dst –Serc School On Mathematical Modeling Of Groundwater Quality And Pollution Ugc – Center For Advanced Studies In Fluid Mechanics, Department Of Mathematics, Bangalore University, And National Research Institute For Applied Mathematics, Bangalore, 359-402.

Schoups G. and Hopmans J. W. (2002). Analytical Model For Vadose Zone Solute Transport With Root Water And Solute Uptake. Vadose Zone Journal **1**, 158-171.

Schwartz, F. and Zhang, H. (2004). Fundamentals Of Groundwater. John Wiley & Sons, New York, 583.

Shahidi Bonjar, G. H.(2007). Potential Hazards of Gasoline Additives in Altering Soil Environment in Favor of Harmful Microorganisms. Int. J. Environ. Res.,1(1), 1-4.

Shukla, M. K., Ellsworth, T. R., Hudson, R. J. and Nielson, D.R. (2003). Effect of Water Flux On Solute Velocity And Dispersion. Soil Science Society Of American Journal, **67**, 449-457.

Thangarajan, M. (2004). Regional Groundwater Modeling Capital Publishing Company, New Delhi, 339.

Vanderbroght, J., Timmerman, A. and Feyen, J. (2000). Solute Transport for Steady State and Transient Flows in Soils with and without Macropores. Soil Science Society of American Journal, **64**, 1305-1317.