

Full Length Research Paper

Atrazine transport and distribution in field soils and comparison of the predictions made by leaching estimation and chemistry model-pesticide (LEACHP) model

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Affluent use of herbicide such as Atrazine especially in corn farms must be supplemented with water and soil resources. This research was conducted in a pilot farm of Chamran University, Faculty of Water Science Engineering, Ahvaz, Iran. This research investigated transmission of the dynamic use of atrazine in various depths of soil in growth period and after growth period. Also, atrazine transmission potentiality and existence from root zone and leaching estimation and chemistry model-pesticide (LEACHP) model of simulating atrazine concentration was evaluated. This research was performed in the form of full stochastically factorial form with three repetitions. So, in the time periods of 30, 60 and 175 days, the remaining atrazine was measured by high-performance liquid chromatography (HPLC) method using soil samples (from depths of 0 to 125 cm in 25 cm layers in four times). Results showed that atrazine concentration in soil decreased with time lapse. For comparison of the observed and predicted data by LEACHP model, ME, MEF, EMSE and CRM statistical index were used. All the data obtained at the end of season for the different statistical index were 2.8, 0.96, 1.4 and 0.66 respectively, and a different depth of soil was obtained for level 2 irrigation. The simulation results show relatively good fitness with the observed data, as such, the LEACHP model could be used for simulation of atrazine movement and its dynamic transmission in soil for farm management.

Key words: Atrazine, high-performance liquid chromatography (HPLC), leaching estimation and chemistry model-pesticide (LEACHP) model, herbicide.

INTRODUCTION

Although pesticides increase crop production (Kalkhoff et al., 1992; Singh and Kanwar, 1991), they could contaminate groundwater resources under poorly managed conditions. Use of agrochemicals improves farming productivity in the world, and their fate in soils is of main concern when applied improperly, as they pose a major threat to water resources (Boivin et al., 2005). Concerns regarding the impacts of pesticide and

herbicide on aquatic species and drinking water sources have increased demands on water quality monitoring programs (Byer et al., 2011). According to reports and estimations in 1993, approximately 5×10^8 kg of toxicants (herbicides and pesticides) are consumed in United State of America and that 75% of it was used in agriculture and 3.4×10^7 kg of these toxicants was atrazine (Aspin, 1994). Atrazine is the most important pollutant of groundwater in many countries (Kovaios et al., 2006). In another study, looking at combined data from 236 Universities corn field trials from 1986 to 2005, atrazine treatments showed an average of 5.7 bushels more per acre than alternative herbicide treatments (Fawcett,

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2008; Bastos and Magan, 2009). Atrazine is increasingly used in corn, sorghum and sugar cane farms for weed control (Moreland et al., 1959). However, the use of herbicides makes farms to be more productive, but when farm management is weak, herbicides will pollute underground water resources (Aspin, 1994). For decreasing ground water pollution potentiality, factors which directly influence degradation and motion dynamic of pesticides must be recognized and processed and management factors must be investigated.

Subsequently, having a full information about motion and dynamic of herbicides in soil is necessary (Weed et al., 1995). This information requires cases like determination of motion size and herbicides concentration in relation to different soils and water. These are applied factors in farm management. As for the decomposition of herbicide in the neighborhood of air and soil after a particular time period, a suitable management method can be used to delay degradation of herbicide to ground water, in other words it can be used to prevent propulsion from the root zone.

The application of a mixture of bentazone and atrazine is a practical approach to enhance the herbicidal effect. These results indicated that biological degradation accounted for the degradation of both herbicides in the soil. When compared with the degradation of the herbicide applied alone, the degradation rates of the herbicides applied in combination in the soils were lower and the lag phase increased (Li et al., 2008). Because of atrazine widespread use, relatively high chemical and biological stability in soils and aquifers, and high leaching potential, atrazine has been detected in surface ground water at high concentration levels (Correia et al., 2007; Guzzella et al., 2006).

Researchers showed that atrazine, notwithstanding its relatively low solubility (about 33 mg l⁻¹), is the cause of most pollution in ground water (Poinike et al., 1989; Wilson et al., 1987). Measure of degradation and seepage of atrazine is a function of soil structure and irrigation or raining intensity in field (Isensee et al., 1990).

Siczek et al. (2008) were to examine leaching of atrazine in tilled and orchard silt loam soils. The experimental objects included: conventionally tilled field (CT) and a 35 year-old apple orchard (OR) with a permanent sward. Atrazine concentration in the leachiest soil was determined by means of HPLC waters. The results indicated potential of management practices for minimizing atrazine leaching.

The decreased dissipation of atrazine with increasing depth in the profile is the result of decreased microbial activity toward atrazine, measured either as total biomass or as populations of atrazine-degrading micro-organisms. The combination of reduced dissipation and low sorption indicates that there is potential for atrazine movement in the subsurface soils (Blume et al., 2004). One of the best and suitable management in field is collection of activities that decrease percolation of atrazine in irrigated farms,

such as using little water when water requirement is low thus, atrazine movement potential and pollution will be decreased (Aspin, 1994). The maximum loss of atrazine in the percolate took place in the soils with the highest organic carbon (OC) level with no effects of tillage practices. These soils had fine texture, and were well structured and aggregated. Intraparticle and intraorganic matter diffusion appear to be responsible for no equilibrium sorption. Delayed sorption in aggregated soils leads to high concentration of atrazine available for leaching (Montoya et al., 2006).

Cost and time limitation restricted farm experiments from the view of the extent and collectivism of its goals. Therefore, it is impossible that field experiments can provide all needed information for performance and development of environment management in each region. So, simulation models are developed with using experiences and field experiments to access more parameters for more suitable management of the farm. Models simulations have different management and hydrological factors on percolation and dynamics of herbicide in various condition of saturated soil. Simulation models with field experiences could be used as a suitable device for management decision (Loague et al., 1995). Simulation models are increasingly used to predict pesticide leaching (Cohen et al., 1995). Computer model and field measurement are used for evaluation of atrazine degradation with different levels of irrigation and atrazine. A lot of pollution transmissions are now available such as PESTAN (Enfield et al., 1982), PRZM (Carsel et al., 1985), GLAMS (Knisel et al., 1989), LEACHP (Hutson and Wagenet, 1992) and SWMS-2D (Simunek et al., 1992).

High-performance liquid chromatography (HPLC) model description

LEACHM (leaching estimation and chemistry model) is a modular package for calculating the one-dimensional water flux and solute movement in vertically layered soils under transient conditions. The latest version is described in detail by Hutson and Wagenet (1992). LEACHM has several component models, each of which describes a different class of chemical. The water flow module is common to all components. In this work, we used LEACHP which simulates pesticide fate and transport. Water flow is modeled with the one-dimensional Richards' equation. The $\theta \pm h$ relationship is described with a two-part function (Hutson and Cass, 1987):

$$K(S_e) = K_s S_e^\lambda (1 - (1 - S_e^{\frac{1}{m}})^m)^2 \quad (1a)$$

$$h = a(\theta_c / \theta_s)^{-b}, \quad h_c > h > -x \quad (1b)$$

Where h is the pressure potential, θ_s the saturated water

content ($m^3 m^{-3}$) and a, b are constants. h_c, θ_c defines the point of intersection of the two curves $h_c = a \left[\frac{2b}{1+2b} \right]^{-b}$ and $\theta_c = \frac{2b\theta_s}{1+2b}$. For the hydraulic conductivity the following equation is available:

$$K(\theta) = K_s \left(\frac{\theta}{\theta_s} \right)^{2b+2+p} \quad (2)$$

Where $K(\theta)$ is the hydraulic conductivity (mm per day), K_s are the hydraulic conductivity at saturation θ_s and p is a pore interaction parameter, alternatively, for the $K-\theta-h$ relationship the following equations are available (Mualem, 1976; Van Genuchten, 1980):

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha|h|)^n]^m} \quad (3)$$

Where θ is the volumetric water content ($m^3 m^{-3}$), h the pressure head (mm), θ_r the residual water content ($m^3 m^{-3}$), and α (mm^{-1}), n (-), and m (-) are empirical parameters.

$$K(S_e) = K_s S_e^\lambda \left(1 - (1 - S_e^m)^m \right)^2 \quad (4)$$

Where S_e is the effective saturation $\lambda, ((\theta - \theta_r) / (\theta_s - \theta_r))$, λ the pore connectivity parameter (-), and m the empirical parameter from Equation (3), the water flow equation is combined with the convection-dispersion equation in LEACHP. Solute sorption to soil can either be described with a linear Equations 5 and 6 or non-linear (Equation 7) isotherm or by two site sorption (Equation 8). For a linear isotherm we have:

$$C_s = K_d \times C_1 \quad (5)$$

Where K_d is the linear distribution coefficient ($dm^3 kg^{-1}$), K_d can vary with depth. For pesticides, K_d values are calculated from the organic carbon partition coefficient K_{oc} and the organic carbon fraction (f_{oc}) as:

$$K_d = K_{oc} \times f_{oc} \quad (6)$$

Non-linear sorption is described with the Freundlich isotherm. Atrazine (6-chloro-N2-ethyl-N4-isopropyl-1, 3, 5-triazine-2, 4-diamine) has relatively low adsorption coefficient with K_{oc} values ranging from 40 to 394 mill/g for atrazine (Giddings et al., 2005):

$$C_s = K_f \times C^{n_f} \quad (7)$$

Where k_f and n_f are constants.

Non-equilibrium linear sorption assumes that a fraction of sites (f) display local chemical equilibrium and a fraction ($1 - f$) is subject to kinetically controlled sorption and desorption. The sorbet concentration is the sum of sorption to the kinetic (s_1) and equilibrium (s_2) sites. Flux density of solute J_a ($mg kg^{-1}$) between the kinetic sites and solution phase C ($mg dm^{-3}$) is assumed to depend upon the current degree of non-equilibrium:

$$J_a = \alpha P_b ((1 - f) K_d C - S_s) \quad (8)$$

Where α is a phase transfer rate coefficient and ρ_b the soil bulk density ($kg dm^{-3}$). The liquid-vapor partition is represented by a modified Henry's law as proposed by Jury et al. (1983). Degradation of pesticides is assumed to follow first-order kinetics. The rate constant may be adjusted for temperature and/or water effects. The temperature correction factor (T_{cf}) at a temperature t ($^{\circ}C$) is calculated as:

$$T_{cf} = Q_{10}^{0.1(t - t_{base})} \quad (9)$$

Where Q_{10} is a constant and t_{base} is the base temperature for which the rate constants are specified in the data file. The water correction factor (W_{cf}) is set to one in the optimum water content range, which is between θ_{max} and θ_{min} . If θ is higher than the optimum, W_{cf} becomes:

$$W_{cf} = W_{cfcat} + \frac{(1 - W_{cfcat})(\theta_s - \theta)}{\theta_s - \theta_{max}} \quad (10)$$

Where W_{cfcat} is the relative rate constant at saturation and θ_s the saturated water content. If the soil moisture is lower than the optimum water content range, the correction factor is:

$$W_{cf} = \frac{MAX(\theta, \theta_{wp}) - \theta_{wp}}{\theta_{min} - \theta_{wp}} \quad (11)$$

The correction factor is zero at wilting point θ_{wp} . Furthermore, uptake of pesticides in the transpiration stream can be included if desired.

MATERIALS AND METHODS

Field information are investigated on the basis of evaluating the study's model and the simulation results obtained. In this research, LEACHP model which is a transport module from LEACHM model, version3, was used (Hutson and Wagenet, 1992). Elaborate input parameters describing hydraulic and solute properties are often lacking, which prevents the proper use of research models like LEACHP (Walker et al., 1995). In order to gain confidence in the

Table 1. Soil properties used for the simulation.

Depth (cm)	Air entry potential (Jkg ⁻¹)	Saturation (sp)%	EC (ds m ⁻¹)	Organic carbon (*10 ² , gg ⁻¹)	Field capacity (m ³ m ⁻³)	PWP (m ³ m ⁻³)	K _{sat} (*10 ⁻⁵ , s ⁻¹)	Bulk density (g cm ⁻³)	B-value
0-25	-3.66	38	7.5	0.35	0.17	0.08	1.86	1.6	3.33
25-50	-2.98	39	4.2	0.31	0.17	0.09	1.68	1.61	3.28
50-75	-3.5	38.1	3.6	0.28	0.18	0.09	1.55	1.55	3.01
75-100	-2.08	38.2	4.5	0.24	0.18	0.07	1.46	1.51	2.85
100-125	-2.66	43.1	7.5	0.22	0.17	0.08	1.73	1.35	3.14
125-150	-3.43	43.5	7.4	0.18	0.17	0.09	1.38	1.4	3.44

model performance, repeated testing of predictions against field data is necessary.

This model has conceptual principles for soil humidity and contaminant transport dynamic simulation. However, LEACHP needs entry parameters such as distribution coefficient, first order degradation rate constant of pesticide, bulk density, organic matter and dispersion length. The overall objective was to collect data for use in formulating best water management practices to minimize atrazine leaching potential in irrigated soil. The soil specific objectives were to use the measured atrazine data to test and evaluate conceptually contaminant transport model. The model involved is LEACHP which use Richard/Convection-Dispersion equations to approximate water and solute dynamics in soils.

Site description

Field experiment was located at Chamran University in pilot farm of Water Science Engineering Faculty, Farming in Ahwaz. The climate at this site is semi-arid with annual mean precipitation of about 250 mm. The soil at the site is silt loam. An automated climate station located close to the study's site recorded the daily weather data. Discretisation of the soil profile and hydraulic parameters are given in Table 1. The study was conducted in pilot farm of Chamran University, Faculty of Water Science Engineering, Ahvaz, Iran (UTM: X=3564212 and Y=5431236). The climate at the site is semi-arid with annual mean precipitation of about 240 mm. The mean pH is 8.10 in the 0 to 25 cm soil layer. The soil profile is deep and well drained. An automated station climate station located Chamran University recorded daily weather data.

Irrigation treatment

Corn is cultivated as furrow and irrigated as surface irrigation. Water requirement is estimated by using evaporation from class (A) pan and irrigation was at constant volume with various intervals on the basis of 7 mm evaporation from pan to end of growth period. Three irrigation treatments were respectively used for irrigation levels I₁, I₂ and I₃, and it was observed that I₁ showed low level of irrigation which was equal to 25% but less than that of normal irrigation (deficit irrigation), level I₂ showed normal irrigation percentage (full irrigation) and level I₃ showed 25% more than that of normal irrigation (excess irrigation).

Used atrazine and soil sampling

Atrazine added to soil five days after the first irrigation and before germination of weeds as three treatments of P₁, P₂ and P₃ are respectively equal to 3.75, 5 and 6.25 kg/ha. Primarily samples of soil are taken from depths of 0 to 120 cm with 20 cm distance (August 11th); second sampling was on the September 11th and January 15th 2010. Complex soil samples were taken from each layer of soil for atrazine analysis. The position of the center of mass of atrazine profiles at different sampling dates was estimated following the procedure used by Zacharias and Heatwole (1994):

$$Z_c = \frac{\sum_{i=1}^n c_i d_i z_i}{\sum_{i=1}^n c_i d_i} \quad (12)$$

Where Z_c is the position of the center of mass of atrazine profile (cm) in which the base point is the soil surface, C_i is atrazine concentration in the ith layer, d_i is the thickness of the layer (cm), and Z_i is the ith depth to the center of the ith layer from the soil surface (cm). The position of the center of mass were used to assess the extent and time course of atrazine leaching in relation to the different amounts of early season and seasonal irrigation used in this study. The position of the center of mass of solute profile is the result of the net balance among infiltration, percolation, solute movement, water and solute redistribution, solute degradation and transformation (if applicable), and plant uptake processes that had occurred in the soil profile at the time of sampling.

Determination of atrazine concentration

Concentration of atrazine in samples were determined by HPLC method. Atrazine was extracted using a solid phase extraction cartridge SCX-Vertical (Phewnil et al., 2010). Briefly, an approximately 100 g of soil was suspended in 99 ml of acetonitrile/water (9:1, v/v), then the standard solution at the amount of 1 ml (0.2 mgml⁻¹ atrazine) was added and the sample was shaken vigorously for 5 min. The samples were then filtered through a paper filter (Whatman GF/C), with the first 5 ml of filtrate being discarded and the following 10 ml being used for analysis. The cartridges were then flushed with 1 column volume of acetic acid (1%), after which 2 ml of acetic acid (1%) were added. A reservoir was placed onto the cartridge with the adaptor prior to use. Subsequently, 5 ml of each sample were then mixed with 25 ml of acetic acid (1%) and poured into the reservoir, stirred and slowly

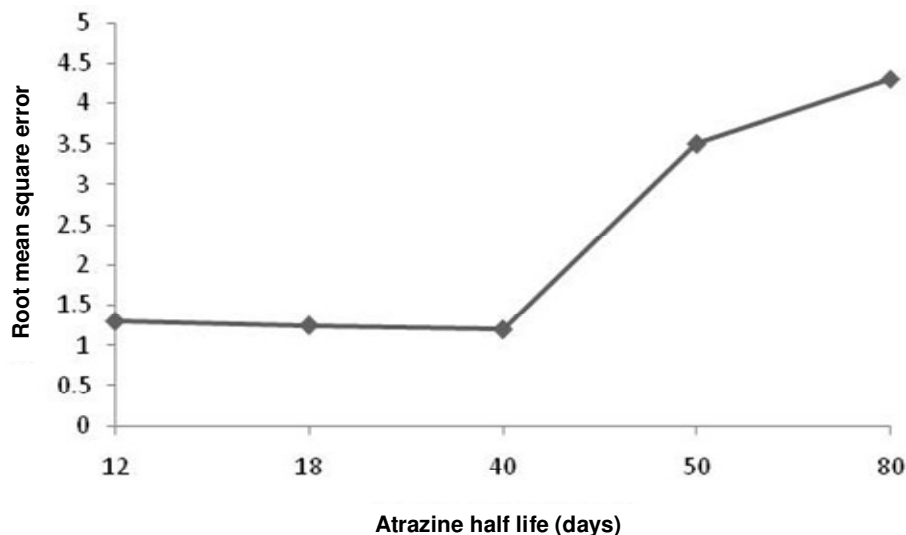


Figure 1. LEACHP response to different atrazine half life values with respect to the field data collected on 11 August 2010.

aspirated through the cartridge. The reservoir was then washed with 2 ml of acetic acid (1%), after which the cartridge was washed with 1 ml of acetonitrile, then 1 column volume of water and finally 1 ml of 0.1 M dipotassium hydrogen phosphate. Between the washing steps, the cartridge was dried briefly for about 15 s under vacuum. The cartridges were then eluted with 2 ml acetonitrile /0.1 M dipotassium hydrogen phosphate (1:1). Finally, the samples were filtered with nylon filter and 2 μ L of each sample was injected into the HPLC.

Calibration of LEACHP Model

Module of water flow in the LEACHP model called LEACHW is related to soil physical parameters such as saturated hydraulic conductivity, air entry value, b-value of Campbell's equation and sorption coefficient of atrazine which is recommended by Wauchap et al., (1992) for field studies is equal to 1001 kg^{-1} . Moreover, atrazine half life is selected 40 days after sensitivity analysis during model calibration (Figure 1). Prediction of the atrazine profile was estimated using the Root Mean Square Error (RMSE) objective function as follows:

$$RMSE = \frac{(\sum_{i=1}^n (P_i - O_i)^2 / n)^{0.5}}{\bar{x}} \quad (13)$$

Where n is the sample size, P is the predicted data using LEACHP model, O is the measured data, \bar{x} is the mean of the measured data, and i is soil layer index. The closer the RMSE value is to zero the better the model prediction. The other indexes for evaluation of model are:

$$\text{Maximum error} \quad ME = \text{Max} |P_i - O_i| \quad (14)$$

$$\text{Modelling Efficiency} \quad MEF = \frac{(\sum (o_i - \bar{o})^2 - \sum (P_i - o_i)^2)}{\sum (o_i - \bar{o})^2} \quad (15)$$

$$\text{Coefficient of residud mass} \quad CRM = \frac{\sum o_i - \sum P_i}{\sum o_i} \quad (16)$$

RESULTS AND DISCUSSION

Estimated maximum density of atrazine from domain and location view is different from measured density estimated and measured. Maximum density of atrazine estimated is generally the same with other estimated densities. Deviations of anticipated quantities are shown by LEACHP model, regardless of the irrigation treatments used with RMSE quantity. The maximum value of difference accrues for 175 days after atrazine was added. It has been shown that standard deviation decreased with lapsing time. Maximum quantity of deviation resulted in first lager (0 to 25) for RMSE. Location of mass center for atrazine in profile for LEACHP model statically increased with lapsing time (Figures 2 to 4).

The model predicted a comparatively higher total amount of atrazine remaining in the soil profile on the first two sampling dates than were measured. The measured amounts of atrazine, however, were under-estimated on the last sampling (Tables 2 and 3). Generally, the measured and predicted atrazine amounts in the soil profile were within one of magnitude.

However, measured Z_c is greater than estimated Z_c in conditions of soil profile because used models atrazine quantity in soil profile was underestimated. For example, this quantity is estimated to be about 42% in LEACHP model in the highest level of irrigation, Z_c of model is about 24%. Generally, it could be said that this model is simulating drained atrazine better in more irrigated conditions.

Model anticipation for Z_c in farm condition is attained in 13.4 to 72.8 cm range. Also, atrazine density in deepest layer of soil (140 to 160 cm) was about zero. Simulation results showed that there is a relationship between quantity of irrigation water and leached atrazine and as such, it can be deduced that this model can show the

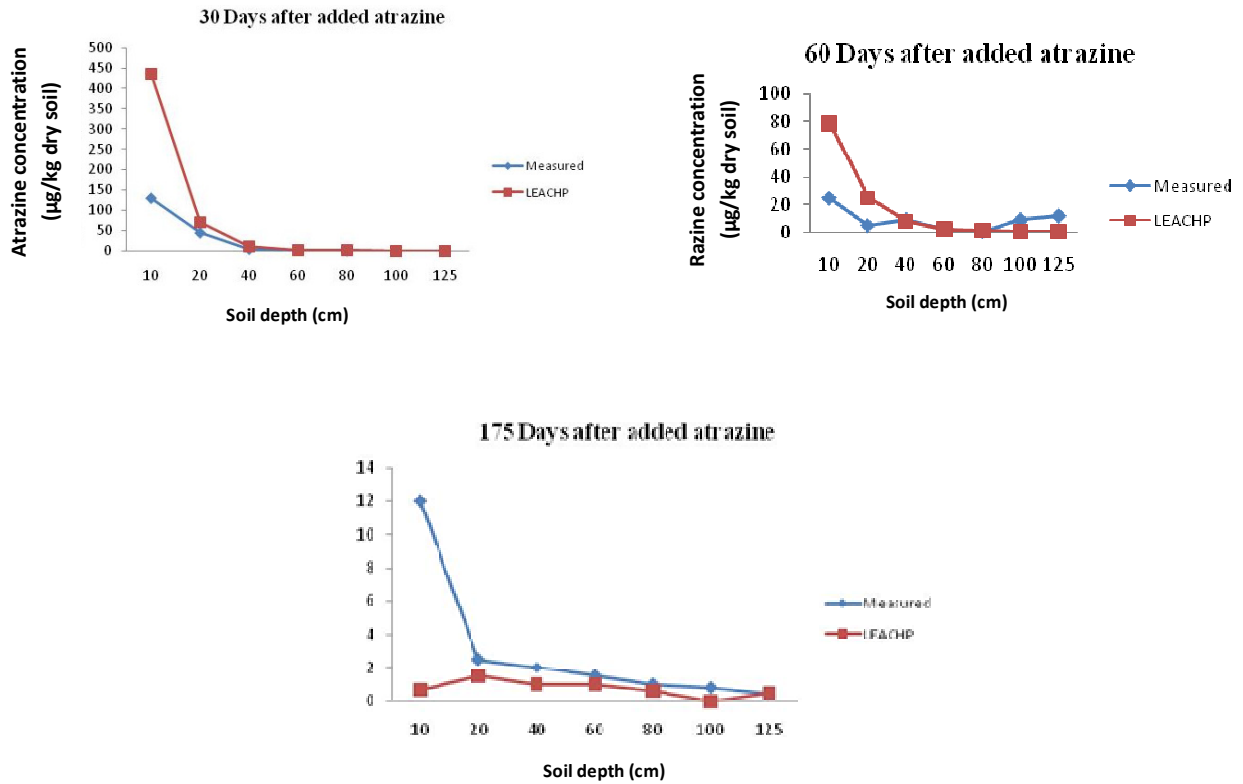


Figure 2. Measured and predicted atrazine profiles at different times of sampling under irrigation level 1, Means days after atrazine application (DAA).

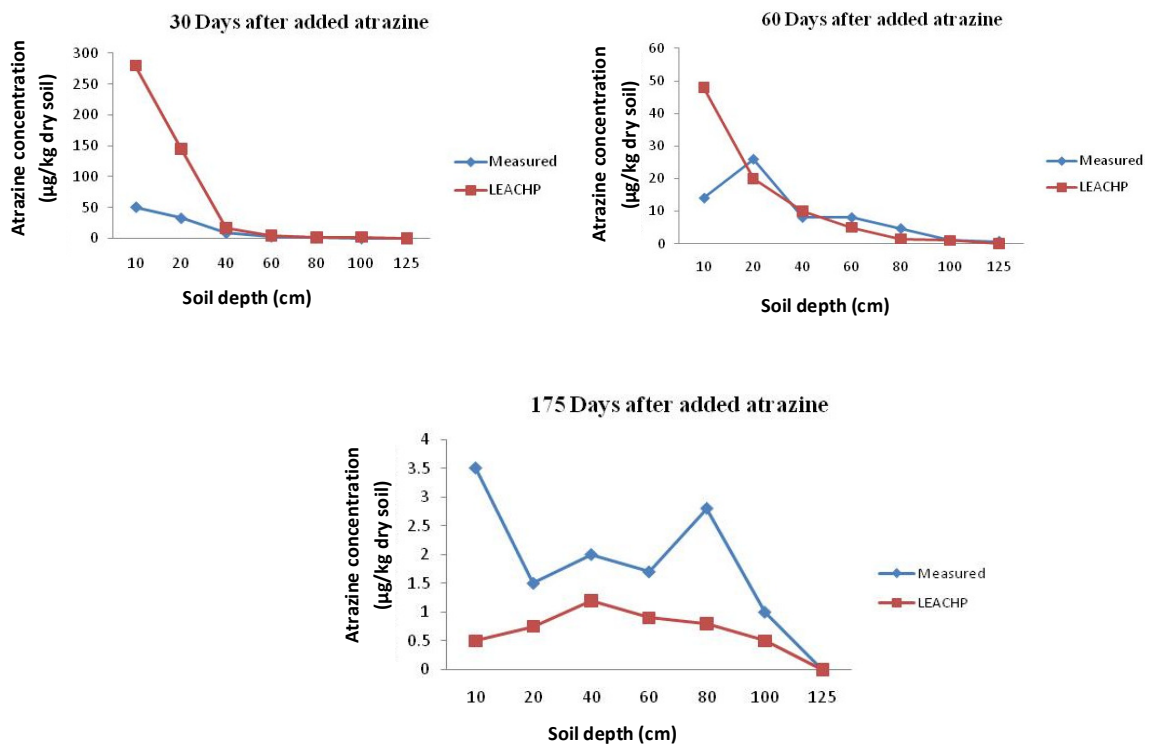


Figure 3. Measured and predicted atrazine profiles at different times of sampling under irrigation level 2, Means days after atrazine application (DAA).

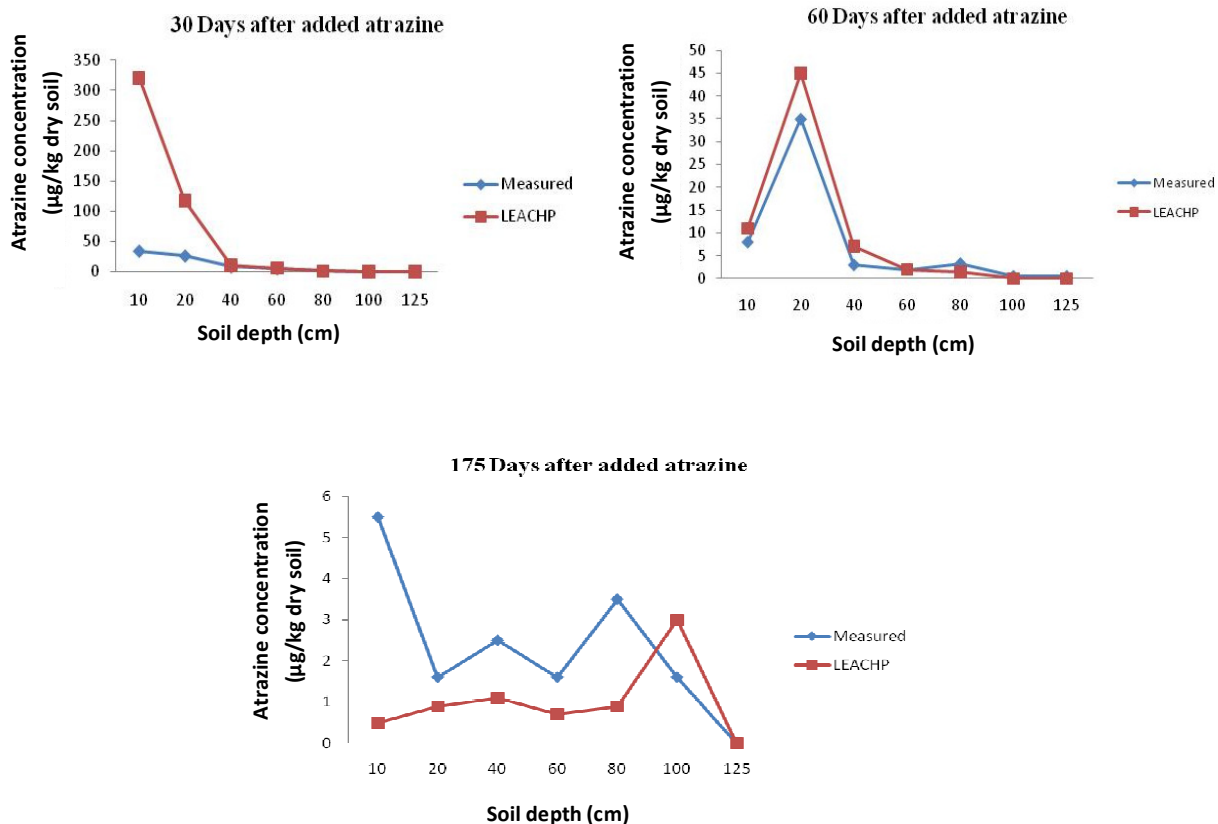


Figure 4. Measured and predicted atrazine profiles at different times of sampling under irrigation level 2, Means days after atrazine application (DAA).

Table 2. Objective function values showing the performance of LEACHP in predicting the measured atrazine profiles RMSE, ME, MEF and CRM values for sampling dates.

Irrigation	Index	Date		
		11-Aug-10	11-Sep-10	15-Jan-11
I ₁	RMSE	4.4	2.54	1.5
	ME	305	54	11.3
	MEF	-0.95	-11.28	0.98
	CRM	-1.83	-0.85	0.74
I ₂	RMSE	7.3	1.32	1.4
	ME	85	31	2.8
	MEF	-12	-5.6	0.96
	CRM	-2.62	-0.38	0.66
I ₃	RMSE	10.73	0.57	0.82
	ME	286	10	3
	MEF	-79	-0.7	0.89
	CRM	-5.15	-0.27	0.63

state of atrazine motion versus irrigation variations. Using an irrigation of about 97 cm with 85% efficiency proved 6 t/ha performance of the product. This performance

efficiency was attained under a suitable programming. Decreasing irrigation in respect to level 1 is causing a reduction of production at MAX state but also reducing

Table 3. Atrazine center of mass positions estimated from the measured and predicted atrazine profiles center of mass (cm) for sampling dates.

Irrigation	Index	Date		
		11-Aug-10	11-Sep-10	15-Jan-11
I ₁	Measured	13.4	31.6	49.3
	LEACHP	8.8	14.3	22.8
I ₂	Measured	22.6	40.5	47.1
	LEACHP	9.1	18.6	27.7
I ₃	Measured	37.6	72.8	63.3
	LEACHP	19.8	29.3	36.1

the depth of atrazine motion. Irrigation reduction which is done by farmers generally does not have a uniform trade but in this condition, atrazine is transmitted beneath the stem region in order for lots of water to enter into the farm, as such the lap times between irrigations will be increased.

LEACHP model measures information in farms underestimating atrazine density in soil profile and also leached atrazine; it may be that this model can very well anticipate atrazine measurement of soil, it should be also noted that LEACHP model can anticipate the growth of leached atrazine in response to addition of irrigation water to the soil which is compatible with farm results. Furthermore, it can be noted that measured atrazine density in soil profile in respect to model measurement was lower which could be because of conceptual trend type and used mechanism for simulation of humidity and solvent dynamics in the soil. With the use of the model results and farm measurements, it can be specified that the quantity of leached atrazine is equal to the quantity of irrigation water after atrazine application.

Conclusions

LEACHP performed well in simulating the trend in the measured atrazine distribution in the soil profile. Also, this model predicted increasing atrazine leaching in response to increasing irrigation levels, which is in line with the results observed from a field experiment. However, LEACHP model underestimated atrazine leaching. Differences in the predicted atrazine profiles and leaching between the model and field experiment due to the different conceptual processes and mechanisms was used by LEACHP for simulating moisture and solute dynamics in the soil.

The conclusion, however, is that this model could be used for preliminary assessment of atrazine leaching, resulting from targeted irrigation management strategies. Measured and simulated atrazine profiles suggest that the extent of atrazine leaching depends on the level of irrigation water applied after atrazine application.

REFERENCES

- Aspin AL (1994). Pesticide industry sales and usage: 1992 and 1993 market estimates. Biological and Economic Analysis Division, Office of Pesticide Programs, Office of Prevention, Pesticides and Toxic Substances.
- Bastos AC, Magan N (2009). Potential for atrazine bioremediation in calcareous clay soil under low water availability conditions. *Int. Biodeter. Biodegrad.* 63(4): 389-394.
- Blume E, Bischoff M, Moorman T, Ronald Turco R (2004). Degradation and Binding of Atrazine in Surface and Subsurface Soils. *Am. Chem. Soc., Section: Agrochem. Bioregul.* 52(24): 7382-7388.
- Boivin A, Cherrier R, Schiavon M (2005). A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere*, 61(5): 668-676.
- Byer JD, Struger J, Sverko E, Klawunn P, Todd A (2011). Spatial and seasonal variations in atrazine surface water concentrations in Ontario (Canada) using ELISA. *J. Chemos.* 82(8): 155-1160.
- Carsel RF, Mulky LA, Lorber MN, Baskin LB (1985). The Pesticide Root Zoon Model (PRZM): A procedure for evaluation pesticide leaching threats to groundwater. *Ecol. Model.* 30: 49-69.
- Cohen SZ, Wauchope RD, Klein AW, Eadsforth CV, Graney R (1995). Offsite transport of pesticides in Water: Mathematical models of pesticide leaching and runoff. *Pure Appl. Chem.* 67(12): 2109-2148.
- Correia FV, Macrae A, Guilherme LRG, Langenbach T (2007). Atrazine sorption and fate in a Ultisol from humid tropical Brazil. *J. Chemos.* 67: 847-854.
- Enfiel CG, Carsel RF, Cohen SZ, Phan T, Walters DM (1982). Approximating pollutant transport to ground water. *Ecol. Model.* 20: 711-722.
- Fawcett RS (2008). Twenty Years of University Corn Yield Data: With and Without Atrazine, North Central Weed Science Society.
- Giddings JM, Anderson TA, Hall JR, Hosmer AJ, Kendall RJ, Richards RP, Solomon KR, Williams WM (2005). Atrazine in North American surface waters: A probabilistic aquatic ecological risk assessment, SETAC, Pensacola, Florida, pp. 32501-3367.
- Guzzella L, Pozzoni F, Giuliani G (2006). Herbicide contamination of groundwater in Northern Italy. *Environ. Pollut.* 142(2): 344-353.
- Hutson JL, Cass A (1987). A retentively function for use in soil-water simulation models. *J. Soil Sci.* 38: 105-113.
- Hutson JL, Wagenet RJ (1992). LEACHM: A process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone. Version 3, Department of Soil, Crop and Atmospheric Sciences Research Series No. 92-3, Cornell University, Ithaca, New York.
- Isensee AR, Nash RG, Helling CS (1990). Effect of conventional versus no-tillage on pesticide leaching to shallow groundwater. *J. Environ. Qual.* 19: 434-440.
- Jury WA, Grover R, Spencer WF, Farmer WJ (1983). Behaviors assessment model for trace organics in Soil. I. Model description. *J. Environ. Qual.* 12: 558-564.
- Kalkhoff SJ, Detroy MG, Cherryholms KL, Kuzniar (1992). Herbicide

- and nitrate variation in alluvium underlying a corn field at a site in Iowa county. 28(6): 1001-1011.
- Knisel WG, Leonard RA, Davis (1989). Southeast Watershed Resource Laboratory, Tifton, GA. GLEAMS User Manual, 25 pp.
- Kovaios ID, Parakeva CA, Koutsoukos PG, Payatakes AC (2006). J. Coll. Interf. Sci. 299: 88-94.
- Li KB, Cheng JT, Wang XF, Zhou Y, Liu WP (2008). Degradation of Herbicides Atrazine and Bentazone Applied Alone and in Combination in Soils. J. Pedos. 18(2): 265-272.
- Montoya JC, Costa JL, Liedl R, Bedmar F, Daniel P (2006). Effects of soil type and tillage practice on atrazine transport through intact soil cores. J. Geoderma, 137: 161-173.
- Moreland DE, Gentner WA, Hilton JL, Hill KC (1959). Studies on the mechanism of action of 2-chloro-4, 6-bis (ethyl-amino)-S-triazine. Plant Physiol. 34: 432-435.
- Mualem Y (1976). A new model for predicting conductivity of unsaturated porous media. Water Resour. Res. 13(4): 773-780.
- Phewnil O, Panichsapatana S, Tungkananuruk N, Pitiyont B (2010). Thai J. Agric. Sci. 43(3): 119-127.
- Siczek A, Kotowska U, Lipiec J, Nosalewicz A (2008). Macro-porosity and leaching of atrazine in tilled and orchard loamy soils. J. Chemos. 70(11): 1973-1978.
- Simunek J, Vogel T, Van Genuchten MT (1992). The SWMS-2D code for simulating water flow and solute transport in variably saturated media.
- Singh P, Kanwar RS (1991). Preferential solute transport through macropores in large undisturbed saturated soil columns. J. Environ. Qual. 20: 295-300.
- Van Genuchten MT (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated Soils. Soil Sci. Soc. Am. J. 44: 892-898.
- Walker A, Calvet R, Del Re AAM, Pestemer W, Hollis J (1995). Evaluation and improvement of Mathematical models of pesticide mobility in soils and assessment of their potential to predict contamination of water systems, Mitt. Bundesanstalt f. Land- und Forstwirtschaft, Berlin-Dahlem, 307: 1-115.
- Weed DAJ, Kanwar RS, Stoltenberg DE, Peiffer RL (1995). Dissipation and distribution on herbicide in soil profile. J. Environ. Qual. 24: 68-79.
- Zacharias S, Heatwole D (1994). Evaluation of GLEAMS and PRZM for predicting pesticide leaching under field conditions. Trans. ASAE 37(2): 439-451.