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Measuring and Simulating 2,4-D Residues in Silty Clay Soil Profile Under Two Water Regimes Using a LEACHP Model

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ABSTRACT-The extensive use of pesticides in agriculture is compromising soil and water quality. One major concern is protecting water resources from contamination. The main objective of this research was measuring 2,4- D in a silty clay soil and simulating temporal transportation of this herbicide in soil using a LEACHP model, in a corn root zone field. 2,4- D was applied at 3.5 kg a.i./ha, followed by two irrigation treatments in a completely randomized design with three replications. 2,4- D concentrations were measured during the growing season by obtaining soil samples from each plot through a 1 m depth. The measured data showed a temporal reduction of 2,4-D concentrations in the soil down to a maximum depth of 40 cm for both irrigation treatments. Total concentration of 2,4 -D in the soil profile 8, 13, 23, 30, 37, and 57 days after application for normal irrigation were 18.5, 16.36, 11.67, 10.47, 8.47 and 3.2 mg kg ^{1}, respectively and deficit irrigation showed 20.2, 16.7, 11.22, 10.05, 8.8 and 7.3 mg kg ^{1}, respectively for the same dates and soil depth. According to our study region, the half life of 2,4- D for 0 10 cm and 10 20 cm of soil depths in a normal irrigation level were 7 and 33 days and in a deficit irrigation level were 9 and 34.65 days, respectively. The statistical parameters including RMSE, CRM and d were used to compare simulated with measured data. These parameters were 0.67, 0.5 and 0.87 for normal irrigation and 0.8, 0.61 and 0.88 for deficit irrigation**.** The LEACHP model simulations were in agreement with actual observations.

Keywords: 2,4-D, Degradation, Pesticides, Irrigation, LEACHP

INTRODUCTION

The extensive use of pesticides in agriculture is compromising soil and water quality. One major concern is protecting water resources from contamination (Younes and Galal-Gorchev, 2000). 2,4-Dichlorophenoxyacetic acid (2,4-D), a related phenoxy compound, was introduced in 1946 with the following phisycochemical properties (Tomlin, 1994) :

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Property	Value
Water solubility	311 mg/litre (pH 1, 25˚C)
Vapour pressure	1.1×10^{-2} Pa (20˚c)
Water partition coefficient	2.58-2.83(pH 1)

This is a selective herbicide used against broad leaf plants in agriculture, in terrestrial and aquatic environments. 2,4-D, with a small K_{oc}, small K_H, and large degradation rate coefficient, is mobile and degrades rapidly, but is only slightly susceptible to loss by volatilization (Jury et al., 1983).

The influence of moisture on the survival, movement and degradation activity of 2,4-D was studied in unsaturated soil columns (Cattaneo et al., 1997). It was shown that more moisture causes more microbial activities, hence increasing the degradation of 2,4-D. There is also evidence that soils with higher organic contents have a significant 2,4-D degradation rate due to increased soil microbial activity (Gaultier et al., 2007). Water does not usually flow continuously down through the soil, and there can be upward movement of water as a result of its evaporation from the soil surface. Such movement will certainly cause the upward movement of any pesticide that has been added to the soil and might lead to an accumulation of the compound near to the soil surface. This process is known as the "wick effect" (Hubbs & Lavy 1990).

Simulation models are used increasingly to predict pesticide leaching. It is important to choose a model that has been validated in more than once, has good user support, requires an amount of data input appropriate for the application, and has a history of producing results acceptable to scientists and regulatory authorities (Cohen et al., 1995).

Deterministic mechanistic models consist of representations of single processes based on physical principles formulated as mathematical equations. The solution of these equations requires a full specification of the boundary conditions of the system in space and time and the initial conditions for each of the variables. These models are comprehensive; simulation results allow insight into the mechanisms and identify sensitive parameters that govern water and solute fluxes in the dynamic soil-water-air system (Schierholz et al., 2000). Elaborate input parameters describing hydraulics of the soil and solute properties are often lacking, preventing proper use of research models such as LEACHP (Summer & Miller, 1996). In order to gain confidence in the model's performance, repeated testing of predictions against field data is necessary. However, accurate measurements of solute concentration distributions are not often available (Rhoades, 1996). As a result, currently used models within the EU registration process have vague validation status (Boesten & Van der Pas, 2000). It is thus unclear how accurately pesticide leaching models reflect solute transport in field studies where a chemical is exposed to all of the dynamic processes that determine its fate. Moreover, models are currently being used to facilitate decision-making by regulatory authorities and the industrial sector. Assurance of quality in such modelling exercise is essential and much work is in progress to evaluate the predictive ability of mathematical models, validate subroutines and improve documentation of models and modelling procedures (Bergstrom & Jarvis, 1994

LEACHM (Leaching Estimation Chemistry Model) was developed over a period of years (the first manual released in 1997). It is a useful tool to model the movement of water and solutes in soils in relation to specific conditions of soil texture and climatic factors (Hutson and Wagenet, 1992). LEACHM is a one dimensional model used for simulating pesticide movement in an unsaturated soil system in the root zone. LEACHM refers to several versions of a simulation model which describes the water regime and the chemistry and transport of solutes in unsaturated or partially saturated soils to a depth of about two meters (Jury et al., 1983). A LEACHP of this model can predict the vertical movement (one dimensional) of a pesticide through soil, if the model parameters for the pesticide are available. It can also predict the volatilization component of a pesticide.

Absorption of water and solutes by plant roots is included in all versions of the model, together with a flexible means of describing precipitation and surface evaporation of water. A heat flow simulation, producing soil temperature profiles, is included in LEACHN and LEACHP, providing the opportunity to adjust rate constants according to both temperature and water content. The development of LEACHM has occurred gradually over the years. The LEACHP model has been tested by several groups using field data studies conducted in the Netherlands at Vredepeel (Summer & Miller, 1996; Boesten & Van der Pas, 2000). The modelling protocol described by Walker et al. (1995) was followed in these studies. In a first step the predictive capability of the LEACHP model was tested on a data set. This situation reflects the use of models in a regulatory context where calibration is generally not done. In a second step the model was calibrated with regard to hydrology, solute transport and pesticide-related parameters and further tested on new results. Five modellers were given a full description of a field experiment carried out in the UK to determine the leaching potential of a novel pesticide. The models LEACHP, PRZM-2 and VARLEACH were then used to predict pesticide concentrations in soil water at 1 m depth and in the soil itself for a 1 m profile, 220 days after application. Agreement with measured results was generally best for LEACHP and worst for VARLEACH (Brown et al., 1996).

Vast and non-scientific use of herbicides such as 2,4-D in agriculture for weed control has caused environmental pollution and contamination of surface and groundwater resources; the objectives of this study are therefore,

1. Carrying out a field study of the temporal concentrations of 2,4-D and their transportation in the root zone profile of the soil.
2. Calibration and evaluation of the LEACHP model for the simulation of 2,4-D transport.

MATERIALS AND METHODS

The study was conducted at the College of agriculture of Shiraz University located about 15 km north of Shiraz, at 1810 m altitude. The analytical grades of 2,4-D, were obtained from Iran Agricultural Research Organization. Some major physical and chemical properties of the soil, such as soil organic matter content (OM) (Darrell & Nelson, 1996), cation exchangeable capacity (CEC) (Vanclooster et al., 2000), soil texture (hydrometer method), electrical conductivity (EC) (Russell, 1995), and saturated hydraulic conductivity (*Ks*) (Guelph method) were determined prior to corn planting (Table 1). Herbicide, 2,4-D, was sprayed on the soil surface with a rate of 3.5 kg a.i./ha and then periodical soil 2,4-D residues were measured 6, 11, 21, 35 and 53 days after application, through a 1 m soil depth with 10 cm increments, before harvesting time.

The experiment was a completely randomized design with three replications and plot sizes of 114 m^2 (12 × 9.5 m). The method of irrigation was a solid set sprinkler with two irrigation treatments of normal and deficit irrigations with depths of 910 and 735 mm, respectively (Table2). Deficit irrigation was applied according to the reduction of irrigation time. Soil temperature was also recorded at 5, 10, 30, 50 and 100 cm depths at the College of Agriculture Weather Station, about 500 m from the experimental site. Based on the soil conditions (such as temperature, moisture content, texture, etc.) at different depths, herbicide behaviour is not constant in the soil profile (Mersie & Foy, 1985). Therefore, the soil depth was divided into 10 cm increments and soil samples were taken periodically with a hand-held soil auger through a one meter depth with a 10 cm increment from each plot, transported to the laboratory and frozen at –20°C.

Table 1. Characteristics of soil in the experimental site[a]

Soil depth (cm)	Texture^b	Sand	Silt	Clay (%)	F.C.^{b}	P.W.P^b	Om (g kg^{-1})	PH^b	CEC^b (cmol kg^{-1})	E C ^{b} (ds m^{-1})	Ks^b × 10^3 (cm h^{-1})	ρ^b :m^{-3})
0-10	SiC	10	44	40	23	8	14.5	7.6	20.8	0.76	203	1.26
10-20	SiC	10.5	42.5	40	23	8	14.6	7.7	21.3	0.57	203	1.43
20-30	SiC	11	41	40	23	8	14.6	7.7	21.8	0.73	47.1	1.43
30-40	SiC	10	42	42	24	11	11.7	7.7	20.8	0.51	47.1	1.43
40-50	SiC	10	40	43	24	11	10.2	7.9	20.82	0.41	20.9	1.43
50-60	SiC	10	38	44	24	11	8.7	7.7	20.84	0.51	20.9	1.43
60-70	SiCL	14	40	36	24	11	6.9	7.4	20.84	0.45	10.2	1.43
70-80	SiCL	14	43	33	24	11	8.5	7.4	20.84	0.45	10.2	1.43
80-90	SiCL	14	46	30	24	11	10.1	--	--	--	4.88	1.43
90-100	SiCL	16	40	34	24	11	5.3	--	--	--	4.88	1.43
100-110	SiCL	16	42	32	--	--	4.6	--	--	--	4.88	--

All parameters are an average of three replications.

[b] FC, field capacity; PWP, permanent wilting point; OM, organic matter; *Ks*, saturated hydraulic conductivity; ρ, soil apparent density; SiC, silty clay and SiCL, silty clay loam

Table 2. Irrigation depth for normal and deficit irrigations during growth season*

Deficit irrigations	Normal irrigations	Date
7 Jun	71	64
15 Jun	98.33	88
22 Jun	72.6	54.4
6 Jul	66.7	46.41
14 Jul	71.3	40.66
20 Jul	54.33	54
31 Jul	94.33	63.33
11 Aug	153.33	96.66
30 Aug	106.66	84.33
7 Sep	96.66	70
23 Sep	105	73.33

***All parameters are an average of three replications**

Extraction of 2,4-D residues

Soil samples were thawed, air-dried at room temperature, and screened through a 1.2 mm sieve for maintaining homogenization of soil to reduce variability of adsorption data. To extract 2,4-D from soil, 50 g of each sample was transferred to a flat bottom flask containing about 100 mL of pure acetone and shook for one hour. The mixture was then transferred to Buchner vacuum funnels and filtered in to a series of vacuum flasks (Pennell et al., 1990). The volume of the collected organic phase was first reduced in a rotary evaporator for about 15min and then rinsed with 5 mL of 99.8% hexane. The recovery was 98%.

Gas Chromatography

A Shimadzu, Model GC-14A system with a 0.22 mm i.d. column capillary with 5% CBP-10 shimalide was calibrated and tested prior to gas chromatography of the samples. A flame ionization detector (FID) was used for the detection of 2,4-D. The injector and detector temperature were set at 200°C and 220°C, respectively. The column temperature was maintained at 50°C for 1 min, and then increased to 200°C with a 10°C min^{-1} rate, held at this temperature for 5 mins, and then with a rate of 5°C min^{-1} raised to 410°C, and held unchanged finally for 10 mins. The Helium carrier gas, hydrogen, and air flow rates were set at 1 mL min^{-1}, 30 mL min^{-1}, and 300 mL min^{-1}, respectively. Twenty-five control injections with various concentrations from 1ppb to 50 ppm implied that, with the setup conditions, the detection limit for 2,4-D was 0.01 mg kg^{-1}.

Model Input and Calibration Process

The data requirements of LEACHP can be broken into four sections as listed in Table 3. This information is used by the subroutines that independently estimate changes in solute movement, P transformations and plant uptake. The processes used to model these changes are discussed below.

Table 3. Input parameters for LEACHM Mode1 Inputs

Model Input	Parameter	source
Soil data	**Initial volumetric water content and organic carbon percentage**	**Measured in the field**
	Hydrological constants for moisture retentivity And hydraulic conductivity and hydrologic conductivity at a specified soi1 matric potential.	**Calculated from a the results of the moisture release curve using regression equations supplied by LEACHM**
Soi1 surface boundary conditions	**Irrigation depth(mm) Evapotranspiration (mm) 2,4-D applications**	**Measured in the field Recorded**
	Soil temperature for each soi1 depth (˚C)	**Measured in the field**
Crop data	**Time of seeding**	**Recorded (start of simulation**
	Crop maturity and harvest dates	**Recorded**
	crop uptake of pesticide	**Is considered 0**
Rate constants	**Distribution coefficient (Kd), degradation rate and molecular diffusion coefficient were calibrated.**	**Values for these are given by the model and were varied during the calibration process**

Statistical Analysis

For testing 2,4-D simulation output, the following statistical parameters were used to compare the simulated data with measured field data:

$$RMSE = \left[\frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n} \right]^{0.5} \times \frac{1}{\overline{O}} \tag{1}$$

$$CRM = \frac{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i}{\sum_{i=1}^{n} O_i} \tag{2}$$

$$d = 1 - \frac{\sum_{i=1}^{n} (P_i - O_i)^2}{\sum_{i=1}^{n} (|p'_i| + |O'_i|)^2} \tag{3}$$

Here $P'_i = P_i - \overline{O}$ and $O'_i = O_i - \overline{O}$

In the above equations, O_i and P_i are measured and simulated 2.4-D concentrations, n is the number of observations and $\bar{O}$ represents the mean measured data values.

RMSE (relative root mean square error) provides the total difference between measured and simulated data proportioned against the mean measured data values. The lower limit for RMSE is zero which occurs when there is no difference between the paired data. Obviously, a small value of RMSE indicates a more accurate simulation. CRM (coefficient of residual mass) is an indication of the consistent errors in the distribution of all simulated values across all measurements with no consideration of the order of measurements. A value of zero for CRM indicates no bias in the distribution of simulated values with respect to the measured values. The index of agreement, *d*, was calculated for assessing the accuracy of the simulation data. The maximum value for *d* is one, which occurs when the simulated values are completely identical to the measured values.

RESULTS AND DISCUSSION

Normal Irrigation

Using the field data, the LEACHP model was calibrated and then applied for 2,4-D simulation in soil. The results of measured and LEACHP simulations of 2,4-D concentrations, are shown in Fig. 1.

On July 20th, 8 days after application, the maximum depth at which 2,4-D was detected, was 30 cm (Fig. 1-a). Although the model could not accurately simulate 2,4-D concentrations in the first layer, simulations in the second and third layers agreed well. For this date the index of agreement (d) was 0.95, RMSE was 0.45 and CRM was -0.26 which signifies good agreement between the measured and simulated data.

The average concentrations of 2,4-D in 0–10 and 10–20 and 20-30 cm soil layers were reduced to 8, 3.5 and 4.86 mg kg^{-1} soil, on August 3rd, due to soil dissipation 13 days after adding 2,4-D (Fig. 1-b). It is noticeable that the total 2,4-D concentration in the soil profile was 18 mg kg^{-1} soil 8 days after its addition. This value reduced to 16.36 mg kg $^{-1}$ of soil 5 days later. Here the prediction of the model in the first and third layers improved; however, there was over simulation in the second layer. Values of *d*, RMSE and CRM were 0.7, 0.42 and -0.27, respectively showing that the simulation was sufficiently accurate (Fig 1-c).

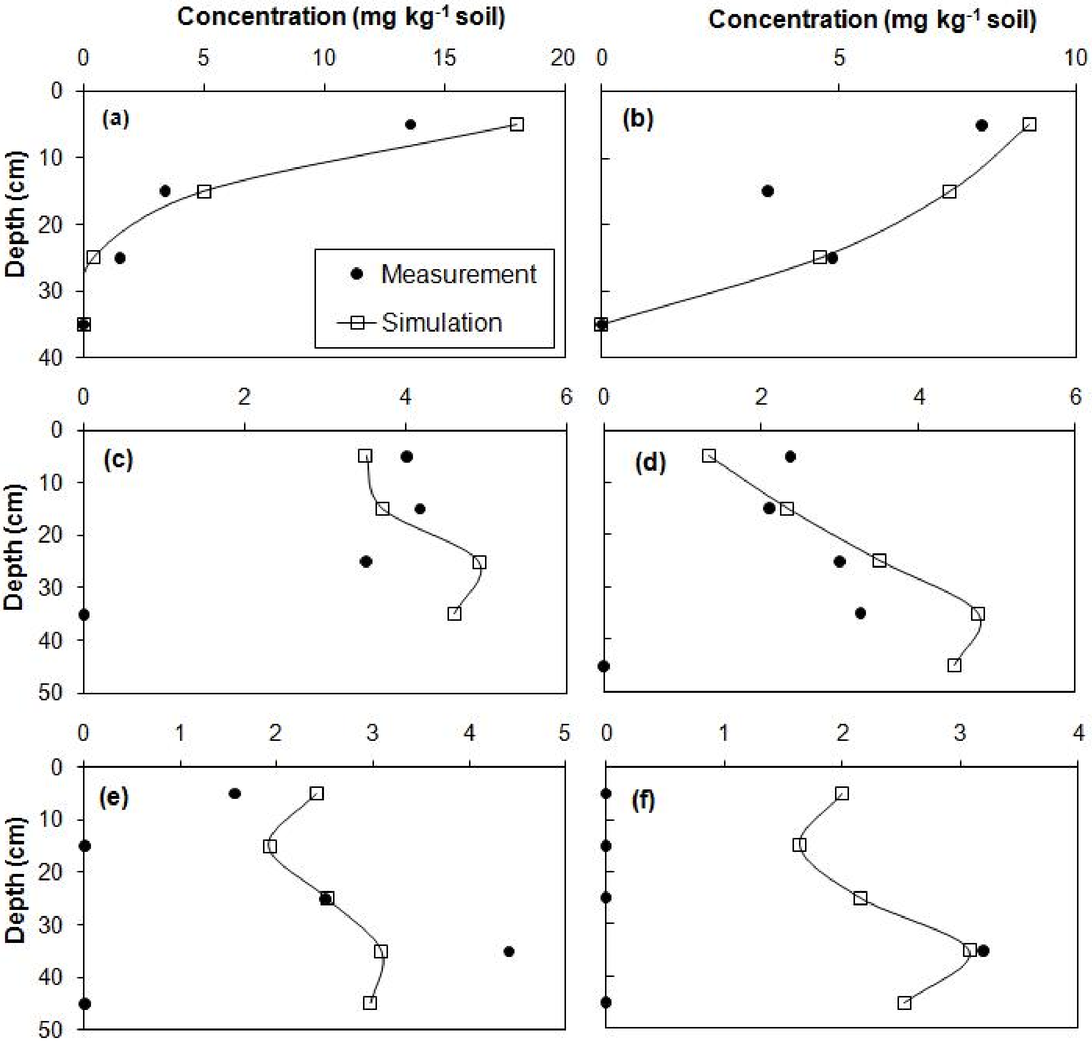

Fig. 1. Measured and LEACHP simulation of 2,4-D in different soil depths for normal irrigation a) 8 days after application b) 13 days after application c) 23 days after application d) 30 days after application e) 37 days after application f) 54 days after application

The total concentration of pesticide was 11.67 mg kg $^{-1}$ soil at that time. The 2,4-D concentration of the first layer reduced by a half compared to 13 days after addition while the concentration of the second layer increased. As soil texture in the upper layer was silty clay, and hydraulic conductivity was low, 2.4-D was only detected through the 30 cm depth of the soil, whereas it was simulated so that 2,4-D could leach to the 4th layer. Based on the calculations, *d*, RMSE and CRM were 0.32, 0.8 and -0.43, respectively. This indicates that statistical parameters were not good enough due to the miscalculation of the model for the fourth layer. Disregarding the fourth layer, *d*, RMSE and CRM for the first three layers were 0.93, 0.2 and 0.03, respectively indicating the good ability of the model to predict the concentrations up to the third layer.

In the present study, 2,4-D leached to the depth of 40 cm, 30 days after application (Fig. 1-d). The total concentration of pesticide was 10.74 at that time. The concentration of the first and second layer reduced to about a half compared to 7 days earlier; however, higher concentrations of the profile leached to the fourth layer. This may be due to the application of 167.2 mm irrigation water on August 11, which was higher than other irrigations due to more corn water demand. The predictions for the first four layers are acceptable. In the fifth layer, the measured value was 0, whereas 4.46 mg kg^{-1} soil was simulated for this layer. The values of d, RMSE and CRM were 0.4, 1 and -0.5, respectively. The simulation of the first four layers agreed well and if the simulation in the fifth layer is discarded *d*, RMSE and CRM are 0.7, 0.33 and 0.01, respectively.

As figure 1-e shows, 37 days after herbicide addition, the total concentrations of pesticide decreased to 8.47 mg kg^{-1} soil. As mentioned, there was no 2,4-D concentration in the second layer 37 days after its addition. The concentration in the first and third layer decreased slightly compared to the thirtieth day; however, herbicide concentration in the fourth layer reached its maximum value at this time. The simulated value in the third layer was exactly the same as the measured one. In general, the values of *d*, RMSE and CRM were 0.35, 1and -0.5, respectively. Ignoring the miscalculation of the fifth layer by the model, these parameters were 0.64, 0.7 and 0.17, respectively which were in good agreement with the measured values.

Finally, fifty four days after application, 2,4-D concentrations in the first four 10 cm layers depth of the soil were 0, 0, 0, 3.2 and 0 mg kg^{-1} soil, respectively (Fig. 1-f). The only place 2,4-D could be detected was the fourth layer which was less than its concentration 37 days after addition. The model was able to predict 2,4-D well only in the fourth layer; however, over-simulation occurred in the other layers. The d, RMSE and CRM were 0.58, 2.5 and -2.5, showing that simulation was not satisfactory.

The ability of the model to simulate decreased as time passed. This might be due to the degradation and transformation processes of the herbicide in the soil which could not be calculated precisely by the model, due to a lack of microbial data.

Deficit irrigation

Fig. 2. shows measured and simulated 2,4-D in the soil profile for different dates between July 20th and September 5th.

As seen in Fig. 2-a, 8 days after 2,4-D addition, the pesticide reached the third layer. Total concentration was 20.2 mg kg^{-1} soil which was 1.7 mg kg^{-1} soil more than the total concentration of 2,4-D at this time for normal irrigation treatment. As mentioned before, less soil moisture causes less microbial activity and therefore 2,4-D degradation decreased (Cattaneo et al., 1997). The best simulation occurred for the second layer. The values found for d, RMSE and CRM were 0.95, 0.64 and -0.26, respectively. These parameters indicate a very good agreement between measured and simulated data.

As figure 2-b demonstrates, 13 days after 2,4-D application, it's concentrations in the first layer reduced to 9.5 mg kg^{-1} soil, the second layer held a concentration of 4 mg kg^{-1} soil and the third contained 3.2 mg kg^{-1} soil. Around 5 mg kg^{-1} soil of the herbicide concentration might leach or be degraded; the third layer had more 2,4-D concentration 5 days after the measurements made on the 8th day. In general, the total concentration of 2,4-D was 17.3 mg kg^{-1} thirteen days after application. It is clear from the data that the simulation of the first and third layers and the maximum depth 2,4-D leached was simulated well. The d, RMSE and CRM were 0.94, 0.48 and -0.3.

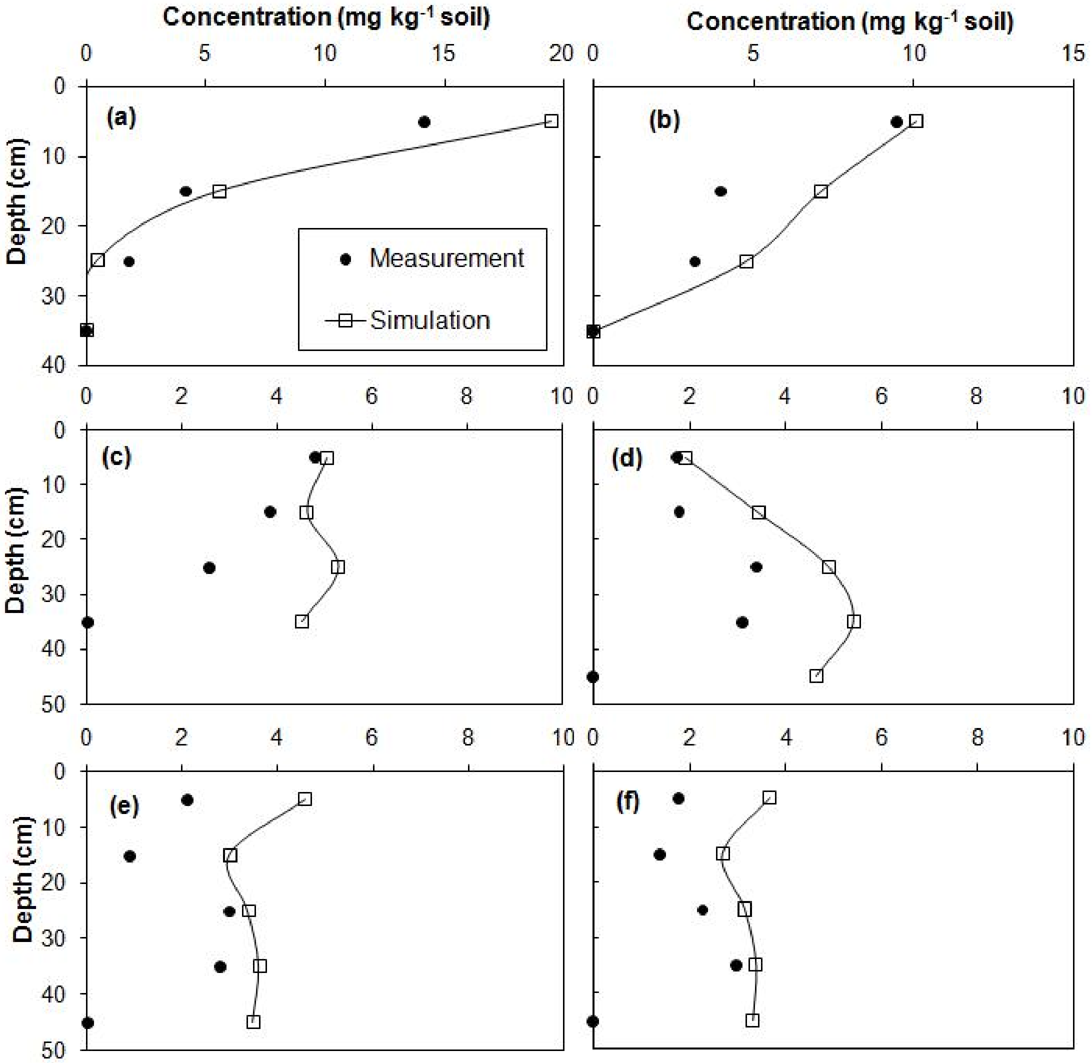

Fig. 2. Measured and LEACHP simulation of 2,4-D in different soil depths for deficit irrigation a) 8 days after application b) 13 days after application c) 23 days after application d) 30 days after application e) 37 days after application f) 54 days after application

Concentrations of 2,4-D could still be detected up to the third layer 23 days after application, whereas the model simulated a value of 4.51 mg kg^{-1} soil for the fourth layer (Fig. 2-c). The simulation of the first layer is very close to the measured one, while the second and third layers were oversimulated. The *d*, RMSE and CRM were 0.47, 1.02 and 0.73, respectively. If the simulation of the fourth layer is not considered, these parameters are 0.42, 0.43 and -0.3 mg kg^{-1}, respectively.

Irrigation was carried out 32 days after application and caused 2,4-D to leach to the fourth layer. The data indicates that simulations of the second, third and fourth layers were very close to those measured. The *d*, RMSE and CRM were 0.34, 1.29 and -0.84, respectively. Ignoring the simulation of the fifth layer, *d*, RMSE and CRM were 0.75, 0.53 and -0.3, respectively (Fig. 2-d).

Fig. 2-e displays 2,4-D concentrations 37 days after application. Total concentration of 2,4-D was 8.8 mg kg^{-1} soil at this time. The 2,4-D concentration of the first layer increased by a small amount compared to 5 days earlier. The reason for the increase of 2,4-D concentration at the 0–10 cm soil depth 37 days after its addition, compared to 32 days after application, was due to the wick effect (Hubbs & Lavy 1990). The best predictions occurred in the third and fourth layers, with *d*, RMSE and CRM 0.62, 1.22, and -1.04, respectively. However, these values were 0.4, 0.76, and -0.65 without considering the fifth layer.

The last measurements were carried out on September 14th (54 days after it addition). The total concentration was 7.33 mg kg^{-1} soil. The wick effect is used to explain the results in the second layer, compared with day 37. Over simulation can be seen in every layer, except the fourth, according to the data (Fig. 2-f). Ignoring the simulation of the fifth layer, d, RMSE and CRM are 0.55, 0.85 and -0.77, respectively.

According to Fig. 1. and 2, and statistical parameters, the simulation of the LEACHP model for deficit irrigation was better than that for normal irrigation, because of less microbial degradation due to less soil moisture.

2,4-D half life

One useful way to express pesticide degradation and their potential comparison in degradation is determining pesticide half-life which can be calculated from the equation below

$$t_{1/2} = \frac{\ln 2}{K}$$

Where, *K* is the first-order degradation rate constant [day^{-1}], and *t* is degradation time (days) for 50% of the pesticide

The half life of 2,4-D in this research for 0-10 cm and 10-20 cm of soil depths for normal irrigation levels were 7.07 and 33 days, respectively and for deficit irrigation levels were 9 and 34.65 days respectively. The degradation half-life of loam soil with 25% moisture content and 8% organic matter in China was 4.6 days (Feng Fu et al., 2009). The degradation rate constant (K) in 0-10 and 10-20 cm of soil depth and normal irrigation was 0.10 and 0.02 day^{-1}, respectively. But for deficit irrigation it was 0.08 and 0.02 day^{-1}, respectively. Therefore, the 2,4-D can be rapidly degraded in the surface soil layer.

CONCLUSIONS

Total concentrations of 2,4-D in the soil profile 8, 13, 23, 30, 37, and 57 days after application were 18.5, 16.36, 11.67, 10.47, 8.47and 3.2 mg kg^{-1} soil for normal treatment and 20.2, 16.7, 11.22, 10.05, 8.8 and 7.3 mg kg^{-1} soil for deficit irrigation respectively.

The values of *d*, RMSE and CRM are shown in tables 4 and 5. The mean of these parameters for all measured and simulated data were 0.87, 0.67 and -0.5, and for deficit irrigation 0.88, 0.8 and -0.61, respectively. In general, according to tables 2 and 3 the 2,4-D concentrations and its transport trend for measured and simulated data agree well especially for the earlier dates after 2,4-D application. The maximum measured leaching depth of 2,4-D was 40 cm with a maximum 2,4-D residue of 4.41 mg kg^{-1} soil. The prediction of the LEACHP model for deficit irrigation was better than for normal irrigation. This is mainly because of reduced moisture in this irrigation regime which reduced microbial activity. As mentioned before less microbial involvement, produces better model simulation results. In general, the accuracy of the LEACHP model in the simulation of 2,4-D residues in the soil profile was medium.

The half life of 2,4-D in deficit irrigation was 27.3% and 5% more than that of normal irrigation in 0-10 cm and 10-20 cm of soil depths, respectively. Therefore, the degradation of 2,4-D in normal irrigation was higher than that of deficit irrigation.

Table 4. Statistical parameters of comparison between measurements and simulations for different dates in normal irrigation treatment

Date	d	RMSE	CRM
July 20th	**0.95**	**0.45**	**-0.26**
July 25th	**0.7**	**0.42**	**-0.27**
August 4th	**0.32**	**0.8**	**-0.43**
August 11th	**0.41**	**1**	**-0.5**
August 18 th	**0.35**	**1**	**-0.52**
September 5 th	**0.58**	**2.9**	**-2.5**
Mean	**0.87**	**0.67**	**-0.5**

Table 5. Statistical parameters of comparison between measurements and simulations for different dates in deficit irrigation treatment

Date	d	RMSE	CRM
July 20th	**0.95**	**0.64**	**0.26-**
July 25th	**0.94**	**0.48**	**0.3-**
August 4th	**0.47**	**1.02**	**0.73-**
August 11th	**0.32**	**1.29**	**0.84-**
August 18 th	**0.62**	**1.22**	**0.04-**
September 5 th	**0.42**	**1.38**	**0.77-**
Mean	**0.88**	**0.8**	**0.61-**

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اندازه گیری و شبیه سازی 2,4-D در نیمرخ خاک سیلتی رسی تحت دو رژیم آبیاری با استفاده از مدل LEACHP

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چکیده- استفاده گسترده از آفت کشها در کشاورزی کیفیت آب و خاک را تحت تاثیر قرار داده و در نتیجه نگرانی در خصوص آلودگی منابع آب و خاک وجود دارد. هدف اصلی این تحقیق اندازه گیری 2,4-D در یک خاک سیلتی رسی و شبیه سازی انتقال این علف کش در خاک بوسیله مدل LEACHP برای گیاه ذرت می باشد. علف کش 2,4-D به مقدار ۳/۵کیلو گرم در هکتار به خاک اضافه شد و تحت دو تیمار آبیاری به صورت طرح کاملا تصادفی با سه تکرار بکار برده شد. غلظت های 2,4-D در طول فصل رشد در نیمرخ خاک تا عمق یک متری به فواصل ۱۰ سانتی متری اندازه گیری گردید. داده های اندازه گیری شد یک کاهش زمانی در غلظت 2,4-D را در خاک تا عمق ۴۰ سانتی متری برای هر دو تیمار آبیاری نشان داد. غلظت کل 2,4-D در نیمرخ خاک در ۸،۱۳،۲۳،۳۰،۳۷،۵۷ روز پس از کاربرد برای تیمار آبیاری کامل بترتیب ۱۸/۵، ۱۶/۳۶،۱۱/۶۷، ۱۰/۴۷، ۸/۴۷، ۳/۲ میلی گرم در کیلو گرم خاک و برای تیمار کم آبیاری بترتیب ۲۰/۲، ۱۶/۷، ۱۱/۲۲، ۱۰/۰۵، ۸/۸۰، ۷/۳۰ میلی گرم در خاک بود. بر اساس این تحقیق نیمه عمر 2,4-D در عمق های ۱۰-۰ و ۲۰-۱۰ سانتی متری خاک در تیمار آبیاری کامل بترتیب ۷ و ۳۳ روز و برای تیمارکم آبیاری بترتیب ۹ و ۳۴/۶۵ روز بود. پارامترهای آماری شامل RMSE ، CRM و d برای مقایسه نتایج داده های اندازه گیری و شبیه سازی مورد استفاده قرارگرفت. این پارامترها در تیمار آبیاری کامل بترتیب ۰/۶۷ ، ۰/۵- و ۰/۸۷ و در تیمار کم آبیاری بترتیب ۰/۸، ۰/۶۱ ، ۰/۸۸ بود. بر اساس نتایج این تحقیق نتایج مدل LEACHP انطباق نسبتا خوبی با داده های اندازه گیری شده داشتند.

واژه های کلیدی: 2,4-D ، آفت کش ها، تجزیه، آبیاری، LEACHP

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