Analysis of 2,4-D residues in soil profile using HYDRUS-1D model

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ABSTRACT- Despite the benefits of herbicides, their persistence in soil can harm other plants in next rotations and contaminate ground water. The main purpose of this research is to simulate 2,4-dichlorophenoxyaceticacid(2,4-D) movement in silty clay loam soil using HYDRUS-1D model in a corn root zone. The maximum contaminant level goal, MCLG, of 2,4-D in water resources is 10 ppb. The 3.5 kg a.i ha^{-1} of 2,4-D was applied to the experimental field under two irrigation treatments including normal and deficit irrigation. The presence of 2,4-D along with soil water content was measured in soil profile at different depths during the growing season at 8, 13, 23, 30, 37 and 57 days after application. Both measured and simulated data showed that 2,4-D concentrations reduced from top to bottom of soil profile, maximum 40 cm in both irrigation treatments. The 2,4-D residues in normal and deficit irrigation were used for calibration and validation of HYDRUS-1D model, respectively. In general, total measured and simulated 2,4-D concentration in normal irrigation treatment were 68.94 and 64.96 mg kg^{-1}and in deficit irrigation treatment were 74.3 and 74.0 mg kg^{-1}, respectively. Statistical parameters including NRMSE, CRM and d were used for comparison of measured and simulated data. These parameters were 0.267, 0.77 and 0.846 for normal irrigation and 0.189, -0.02 and 0.937 for deficit regime, respectively. Therefore, the results showed a good agreement between measured values of herbicide residue and the values simulated using HYDRUS 1D model. The numerical simulations for deficit irrigation regime were more precise than normal irrigation because of less microbial activity due to less soil moisture. The numerical models could not simulate microbial activity with acceptable accuracy.

INTRODUCTION

In recent decades, pesticides have been extensively used in agriculture throughout the world. While chemical materials used for the protection of crops safeguard and improve yields from weeds, they also affect soil and environment health if not properly managed. They are powerful toxicants that are easily absorbed, and they tend to accumulate in soil, plants, foods, ground and surface waters. These effects mainly depend on the active ingredients, application rates, as well as soil properties such as water content, pH and adsorption capacity (Kucharski and Wyszkowska, 2008), on the one hand, and on the other, causing damage to sensitive crops in next crop rotation. Therefore, it is essential to investigate the steps of decomposition, turn and side effects of these compounds in agricultural soils. The most direct way of characterizing the transport of these pollutants is through field monitoring studies and computer simulation models, which provide an efficient and cost-effective alternative that can easily be adapted to many field situations with varying soil types and different land uses (Armstrong et al., 2000; Jarvis et al.,

2000; Pang et al., 2000; Worrall and Kolpin, 2004; Simunek et al., 2005; Köhne et al., 2006; Simunek and Van Genuchten, 2008; Gupta et al., 2012).

During the past 50 years, 2,4-D was one of the most utilized herbicides (Munro et al., 1992), which are used all over the world in agricultural areas (Shen et al., 2005). This herbicide is used widely for broadleaf weed control and will lead to water and soil pollution. The widespread use of 2,4-D in agriculture has caused severe pollution of water and soil (Sparks, 2003; Shukla et al., 2006; Wang et al., 2007). The 2,4-D herbicide belongs to the phenoxyacetic acids class and it could be mobile in aqueous phases because of its acidic carboxyl group (pK$_a$ = 2.8) (Aquino et al., 2007). Therefore, investigation of the distribution and persistence of 2,4-D soil residues is very important.

The usage of models to predict the movement of solutes and pollutants in soil can result in savings in time and costs (Walker, 1987). Over the year, many numerical methods have been used to predict flow and transport process in soil layers. One of the recent

models in this regard is HYDRUS-1D. This model was created and developed to simulate the movement of water, solutes and heat flow in porous media in different moisture conditions. This model describes the movement of water and solute using the equations of Richard and equations, respectively (Simunek et al., 1998).

In recent years, a number of numerical simulation studies have been carried out on different aspects of HYDRUS-1D simulation in transport of pesticide through vegetation (Gupta et al., 2012), study of anion transport (Dousset et al., 2007), pesticide degradation and sorption (Close et al., 2008), equilibrium flow and transport processes through soil (Bernard et al., 2005; Simunek and van Genuchten, 2008), non-equilibrium process investigation (Köhne et al., 2006; Kodesova et al., 2008), and comparison with other models of water movement (Sarmah et al., 2005; Köhne et al., 2009).

The present research was undertaken to measure and simulate the persistence and behavior of 2,4-D under real field conditions in the soil profile. The high solubility of the 2,4-D may suggest that soil water content can be an important factor to influence both movement and degradation of this herbicide in soil profile. Therefore, irrigation water treatments, between the field capacity and wilting point, were considered. The spatial and temporal variations of 2,4-D in soil profile were experimentally determined. Herbicide mobility residues in the soil profile was also simulated using HYDRUS-1D model and the results were compared with the measured concentration. The results of this research would improve our understanding of 2,4-D behavior in the soil profile under real field conditions.

HYDRUS Model

The transport of 2,4-D was numerically simulated using HYDRUS-1D (Simunek et al., 2005), which is an unsaturated soil zone numerical model for analysis of water flow and solute transport. The program numerically solves both the Richards' equation for unsaturated water flow and the Fickian-based advection–dispersion equation for solute transport (Gupta et al., 2012).

In HYDRUS-1D, one-dimensional movement of water in soil described by numerical solution of Richard`s equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[k(\theta)(\frac{\partial h}{\partial x} + \cos \alpha)\right] - S \qquad (1)$$

where θ is volumetric soil water content (L^3L^{-3}), t is time (T), k is the unsaturated soil hydraulic conductivity (LT^{-1}), h is water pressure head (L), α is angle between the flow direction and the vertical axis (for vertical movement of water in soil α=0, for horizontal movement α=90 and 0< α <90 is for other direction.), S is the roots water uptake term ($L^3L^{-3}T^{-1}$) and x is spatial coordinate (L) (positive upward).

In this model, various relationships are defined for description of soil hydraulic properties such as water

retention curve and unsaturated hydraulic conductivity. The most common relationship is the Van Genuchten - Mualem as follows (Van Genuchten, 1980).

$$(h) = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha h)^n]^{\wedge}m} \quad n > 1 \qquad (2)$$

$$k(h) = k_s Se^l \left[1 - \left(1 - Se^{\frac{1}{m}}\right)^m \right]^2 \qquad (3)$$

where θ_r and θ_s are the residual and saturated water content (L^3L^{-3}), k_s is the saturated hydraulic conductivity (L^3T^{-1}), S_e is relative saturation term, l is the pore connectivity parameter, α is reciprocal of the air entry pressure (L^{-1}), n is related to the slope of the retention curve at the inflection point and $m = 1 − 1/n$.

Roots water uptake (S term in equation 1) is determined as the volume of water taken from the soil by plants per unit volume per unit time. In this model, S is based on Feddes relationship and defined as:

$$S(h)= \alpha(h)S_p \qquad (4)$$

where $\alpha(h)$ is water stress function and S_p is water absorption potential.

For solute transport, HYDRUS-1D model considers advective-dispersive transport in the liquid phase as well as diffusion in the gaseous phase. Convective transport involves the passive movement of dissolved constituents with flowing water. Dispersive transport is a result of differential water flow velocities at the pore scale. Displacement of solutes is generally described by the convection-dispersion equation. For one-dimensional vertical transfer in a variably saturated medium where neither adsorption nor degradation occurs, it is expressed as follows:

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) - \frac{\partial(v\theta C)}{\partial z} \qquad (5)$$

where θ is the volumetric water content, C is the solute concentration, t is time, D is the hydrodynamic dispersion coefficient, z is the positive depth measured downward, and v is the average pore water velocity. For a two-region and dual-porosity type solute transport, Eq. 5 becomes

$$\frac{\partial}{\partial t}(\theta_m C_m) + \frac{\partial}{\partial t}(\theta_{im} C_{im}) + \frac{\partial}{\partial t}(f\rho S_m) + \frac{\partial}{\partial t}[(1 - f)\rho S_{im}] = -\frac{\partial}{\partial z}(v\theta_m C_m) - \theta_m \lambda_m C_m - \theta_{im} \lambda_{im} C_{im} \qquad (6)$$

where the subscripts "m" and "im" refer to mobile and immobile regions, respectively; $f = \theta_m \theta^{-1}$ is the fraction of adsorption sites in contact with the mobile liquid; ρ is the soil bulk density; S is the sink term in the flow equation (adsorbed concentration); λ is the first-order degradation constant; and v is the average pore water velocity in the mobile region:

$$v = q\theta_m^{-1} \qquad (7)$$

where q is the water flux. Introducing linear adsorption and assuming uniform water flow in homogenous soil leads to the following equations:

$$(\theta_m + f\rho K_d)\frac{\partial C_m}{\partial t} + [\theta_{im} + (1-f)\rho K_d]\frac{\partial C_{im}}{\partial t} =$$

$$D\theta_m \frac{\partial^2 C_m}{\partial z^2} - v\theta_m \frac{\partial C_m}{\partial z} - \theta_m \lambda_m C_m - \theta_{im}\lambda_{im}C_{im} \qquad (8)$$

where K_d is the distribution coefficient or first-order entrainment (detachment) coefficient. Diffusion transfer of solutes between the two water regions is modeled as a first-order process. First-order degradation is assumed to take place in the immobile region:

$$\theta_{im}\frac{\partial C_{im}}{\partial t} + (1-f)\rho K_d \frac{\partial C_{im}}{\partial t} + \theta_{im}\lambda_{im}C_{im} =$$
$$\alpha(C_m - C_{im}) \qquad (9)$$

where α is the mass transfer coefficient. Combining Eqs. 8 and 9 yields

$$(\theta_m + f\rho K_d)\frac{\partial C_m}{\partial t} = D\theta_m \frac{\partial^2 C_m}{\partial z^2} - v\theta_m \frac{\partial C_m}{\partial z} -$$
$$\theta_m \lambda_m C_m - \alpha(C_m - C_{im}) \qquad (10)$$

This equation describes the solute transport in a two-region flow system considering adsorption and degradation in both mobile and immobile regions (Ladu et al., 2011).

MATERIALS AND METHODS

Field Experiments

The experimental field was located at the Collage of agriculture, Shiraz University, Shiraz, Iran, at 1810 m altitude with mean annual rainfall of 380 mm. The mean, maximum and minimum temperature are 13.5, 22.7 and 4.7^{oC}, respectively. After wheat, corn has the largest area under cultivation in Iran and it is the major crop in the study area.

Corn was planted on May 18, 2008; and the distance between crops and rows were 10 and 75 cm, respectively. The herbicide, 2,4-D, was sprayed on the soil surface with a rate of 3.5 kg a.i. ha^{-1} on July 12, and then periodical soil 2,4-D residues were measured 8, 13, 23, 30, 37 and 54 days after application, through a 1 m soil depth with 10 cm increments, before harvesting time.

The experimental design was a completely randomized design with three replications and plot sizes of 114 m^2 (12 × 9.5 m). 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.

Material and Apparatus

The stock solution of 2,4-D containing 1000 mg L^{-1} was obtained from agricultural ministry of Iran. From this stock solution, 20, 10, 5, 2.5, 1.0, 0.5 and 0.1 mg L^{-1} were prepared by serial dilution. Each solution with three replications was injected into GC and calibration curve was obtained.

Soil Description

Based on the soil conditions (such as soil temperature, soil moisture content, soil texture, etc.) at different depths, herbicide behavior is not constant in the soil profile (Mersie and Foy, 1985). Therefore, before sowing the maize, according to the root depth, 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. Soil samples were transported to the laboratory and frozen at -20^{oC} until they were moved to the laboratory for herbicide's residual concentration analysis. The frozen soil samples at -20^{oC} causes non-significant and long term changes in microbial abundance and activity. It will also reduce the vapor pressure gradient. Therefore, at -20^{oC}, the herbicide concentration will be kept constant until analysis (Zelles et al., 1991; Pesaro et al., 2003). The soil texture was silty clay in depths of 0-60 cm and silty clay loam in 60- 100 cm. The Gulph method was also used for determination of soil hydraulic conductivity (Mohanty et al., 1994). The soil organic matter (OM) was measured by wet oxidation method (Darrel and Nelson, 1996). The physical characteristics of the soil profile are presented in Table1.

Irrigation Treatments

The Potential evapotranspiration was calculated using the Penman-Monteith FAO (Allen et al., 1998), using meteorological station in College of Agriculture. The method of irrigation was a solid set sprinkler with two irrigation treatments of normal and deficit irrigations with depths of 990 and 735 mm, respectively (Table 2). Irrigation water depth in normal irrigation was according to actual evapotranspiration or full irrigation, but in deficit irrigation was according to 26% less than full irrigation. Irrigation water depth in the deficit irrigation was applied according to the reduction in irrigation time.

2,4-D Extraction and Residue Analysis

After the herbicide application, the soil samples were collected on 6, 11, 21, 35 and 53 days after 2,4-D application. 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. The detail of 2,4-D extraction and residue analysis method was explained in Noshadi et al. (2011).

Table 1. Soil physical properties of research area

Depth (cm)	Texture[*]	Particles (%)			ρ_b[*](g cm^{-3})	K_s(cms$^-$)* 10^4	FC[*](gg^{-1})	PWP[*](gg^{-1})	OM[*](gkg^{-1})
		Sand	Silt	Clay					
0-10	SiC	10	44	40	1.26	2.03	23	8	14.5
10-20	SiC	10.5	42.5	40	1.43	2.03	23	8	14.6
20-30	SiC	11	41	40	1.43	0.472	23	8	14.6
30-40	SiC	10	42	42	1.43	0.472	24	11	11.7
40-50	SiC	10	40	43	1.43	0.209	24	11	10.2
50-60	SiC	10	38	44	1.43	0.209	24	11	8.7
60-70	SiCL	14	40	36	1.43	0.102	24	11	6.9
70-80	SiCL	14	43	33	1.43	0.102	24	11	8.5
80-90	SiCL	14	46	30	1.43	0.488	24	11	10.1
90-100	SiCL	16	40	34	1.43	0.488	24	11	5.3

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

Table 2. Irrigation water depth for both treatments during the growth season

Date	Irrigation Water Depth (mm)	
	Normal	Deficit
7 Jun	71.00	64.00
15 Jun	98.33	88.00
22 Jun	72.6	54.40
6 July	66.7	46.41
14 July	71.3	40.66
20 July	54.33	54.00
31 July	94.33	63.33
11 August	153.33	96.66
30 August	106.66	84.33
7 September	96.66	70.00
23 September	105.00	73.33
Total	990.00	735.00

2,4-D Extraction and Residue Analysis

After the herbicide application, the soil samples were collected on 6, 11, 21, 35 and 53 days after 2,4-D application. 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. The detail of 2,4-D extraction and residue analysis method was explained in Noshadi et al. (2011).

Model Input and Calibration Process

According to the measured data and previous studies such as Gupta and et al. (2012), 2,4-D was leached until 50 cm soil depth. Therefore, the 50 cm soil profile is enough for persistence and mobility of 2,4-D. In this research, soil depth was considered to be 60 cm, three layers of 20 cm. Variable soil water flux is prescribed as upper boundary condition. A free drainage boundary condition was considered at the bottom of the soil profile.

The data required for this model are soil characteristics (Table 1), the irrigation water depth (Table 2), evapotranspiration during the growing season which was calculated using weather station data and penman-Monteith FAO equation, amount of applied pesticide to soil and soil boundary condition.

The initial values of constant terms including K_d (partitioning coefficient), dispersivity, diffusion coefficient of water and gas are required for model.

These coefficients were estimated using previous researches and the model manual, then optimal values were obtained during calibration model. Initial values of molecular diffusion coefficient in free water (DIFW) and gas (DIFG) used were 0.58 and 5097.6cm^2.d^{-1}, respectively (Idaho Environmental Quality, 2004). According to soil organic matter, initial values of K_d were between 0.05- 0.28 mg^{-1}.cm^3 (Gupta et al., 2012). Initial values of dispersivity for soils with high clay content were between 0.5-4 cm (Kodesova et al., 2008). The initial concentration of 2,4-D in soil before beginning the experiment was 0.0 ppb. Normal and deficit irrigation treatment data were used for calibration and validation of the model, respectively.

Statistical Analysis For Model Performance

Normalized root mean square error (NRMSE), coefficient of residual mass (CRM) and index of agreement (d) were used for evaluation of model accuracy and assessing the level of agreement between the simulated and measured 2,4-D concentrations.

$$\text{NRMSE} = \left(\frac{\sum_{i=1}^{n}(P_i - O_i)^2}{n}\right)^{0.5} * \frac{100}{\bar{O}} \tag{11}$$

$$\text{CRM} = \frac{\sum_{i=1}^{n} O_i - \sum_{i=1}^{n} P_i}{\sum_{i=1}^{n} O_i} \tag{12}$$

$$d = 1 - \frac{\sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(|P_i'| + |O_i'|)^2} \tag{13}$$

$P_i' = P_i - \bar{O}$ and $O_i' = O_i - \bar{O}$

where O_i and P_i are measured and simulated 2,4-D concentration, n is the number of observations and $\bar{O}$ is the mean measured data values.

NRMSE is a parameter that allows comparing a real deviation between the measured and predicted values. The CRM represents the model trend towards estimating more or less. A positive CRM indicates positive bias in prediction, tendency to overestimate actual values. The index of agreement (d) was used for assessing the accuracy of the simulated data. The maximum value of d is one, which means the simulated and measured values are identical.

RESULTS AND DISCUSSION

In this research, 2,4-D was applied to corn plots under two different irrigation treatments. The experimental results contained the determination of 2,4-D concentrations in soil profile at different depths at a temporal scale to monitor the persistence and mobility of this herbicide. The experimental results were further compared with the simulation of the HYDRUS-1D model.

Normal Irrigation Treatment (Calibration Step)

The HYDRUS-1D model was calibrated using 2,4-D soil residues in normal irrigation treatment. The calibrated parameters are shown in Table (3). Figure 1 represents the comparison between the measured and simulated 2, 4-D concentrations in calibration step.

On July 20th, 8 days after 2,4-D application, the maximum depth of 2,4-D detection was 30 cm (Fig 1-a). The NRMSE, CRM and d were 0.23, -0.21 and 0.7, respectively. The simulated concentration was 21.4% higher than measured concentration. The estimation is considered fair if the NRMSE is greater than 20 and less than 30%, (Jamieson et al., 1991). Therefore, the accuracy of simulation was fair.

The total measured and simulated 2,4-D residues in soil profile at different days after application are shown in Table 4 for normal and deficit irrigation treatments.

Table 3. Calibrated solute transport parameters in normal irrigation data

Depth (cm)	Kd (mg^{-1}.cm3)	Dispersivity (cm)	DIFW (cm^2.day)	DIFG (cm^2.day)
0-20	0.05	3.5	0.58	5100
20-40	0.04	3	0.58	5100
40-60	0.03	0.5	0.58	5100

Table 4. The total measured and simulated 2,4-D concentrations at different days after application

Days after application	2,4-D concentration (mg kg^{-1} soil)			
	normal irrigation		deficit irrigation	
	Measured	Simulated	Measured	Simulated
8	18.05	22.46	20.02	20.29
13	16.36	12.95	16.07	13.51
23	11.67	10.03	11.22	11.82
30	10.74	8.32	10.05	11.33
37	8.47	7.27	8.08	8.85
54	3.02	3.66	7.33	8.02
Total	68.94	64.96	74.3	74

On August 3rd, 13 days after 2,4-D application, the 2,4-D concentration in all layers was decreased (Fig. 1-b). Values of NRMSE, CRM and d were 0.25, -0.2 and 0.88, respectively, showing that simulation was fair.

Total concentration of 2,4-D at this time was 16.36 mg kg^{-1}soil, which has an 11.6% reduction from the previous time (18.5 mg kg^{-1} soil). The simulated concentration was 20.8% less than measured concentration.

At 23 days after adding 2, 4-D, the simulated values were less than measured ones in all layers. The total concentration of 2, 4-D was 11.67 mg kg^{-1} soil, which was 28.7% less than 10 days ago. The total simulated concentrations were 11.5% less than the measured ones. Statistical parameters including NRMSE, CRM and d were 0.3, 0.3 and 0.8, respectively. Therefore, the simulation was not suitable.

Thirty days after 2, 4-D application, the pesticide was found in 40 cm of soil depth (Fig. 1-d) because the irrigation water depth at this time was higher than other irrigations due to more corn water demand. In the top three layers, the concentration of 2, 4-D was reduced but according to the water movement and pesticide movement, there was some 2, 4-D in the fourth layer. Total measured 2, 4-D concentration was 10.74 mg kg^{-1} soil, which was 8% less than 7 days ago. The simulated concentration was 22.5% less than the measured one. The values of NRMSE, CRM and d were 0.26, 0.22 and 0.95, respectively, which represents the good ability of the model prediction.

2, 4-D concentrations reduced in three top layers after 37 days of pesticide addition (Fig. 1-e). However, in the fourth layer, the concentration of 2, 4-D reached its maximum value at this time. The total measured and simulated concentrations of 2, 4-D were 8.47 and 7.27 mg kg^{-1} soil, respectively. Therefore, measured values were 16.5% more than simulated ones. Total measured 2, 4-D concentrations were 21.1% less than 7 days ago. The NRMSE, CRM and d were 0.33, 0.068 and 0.92, respectively, which indicates that the model had an acceptable simulation.

Finally, after 57 days of 2, 4-D application to soil, total measured and simulated concentrations were 3.2 and 3.7 mg kg^{-1} soil, respectively (Fig 1-f). The measured values were 14.5% more than predicted ones. According to the statistical parameters, NRMSE, CRM and d values were 0.21, -0.16 and 0.96; therefore, accuracy of model was very good.

Deficit Irrigation Treatment (Validation step)

Measured and simulated concentrations of 2,4-D at different soil layers in six dates after herbicide application during the corn growing season are provided in Fig. 2.

On July 20th, 8 days after herbicide application, total measured and simulated 2, 4-D concentrations in the soil were 20.20 and 20.29 mg kg^{-1} soil, respectively. The residual of 2, 4-D concentration was 1.7 mg kg^{-1} more than normal irrigation treatment. In general, less soil moisture leads to less microbial activity (Cattaneo et al., 1997). In other words, microbial degradation in high soil moisture is higher than less soil moisture and therefore, 2, 4-D degradation decreased in deficit irrigation treatment. At this time, the herbicide reached the 30 cm of soil depth (Fig.2-a). Concentration of 2, 4-D in the first layer was more than other two layers. The total simulated concentrations were 0.4% more than measured ones. Both the concentrations and their trend

were simulated well using HYDRUS-1D model. Statistical parameters also indicate this fact, because the NRMSE, CRM and d were 0.16, -0.004 and 0.99, respectively.

At 13 days after 2, 4-D addition, pesticide concentration in the top layer reduced. But in the third layer, it increased to 3.2 mg kg^{-1} soil (Fig.2-b). Total residual of measured and simulated 2, 4-D at this time was 16.7 and 13.51 mg kg^{-1} soil, respectively. Therefore, in 5 days, 2.5 mg kg^{-1}soil (17.30%) of the pesticide degraded. The values of NRMSE, CRM and d were 0.26, 0.19 ad 0.9, respectively, which shows the good simulation of this model.

On August 4th, 23 days after herbicide usage, 4.8, 3.85 and 2.57 mg kg^{-1} soil were detected in first, second and third layers of soil, respectively. Total measured and simulated concentration of 2, 4-D were 11.22 and 11.82 mg kg^{-1} soil, respectively. The measured concentrations were 5.1% less than simulated ones. The NRMSE, CRM and d were 0.11, -0.05 and 0.92, respectively, which demonstrates a good agreement between predicted and measured values.

Thirty days after 2, 4-D application to the soil, the residual of pesticide was detected in the 40 cm of soil depth because of high irrigation water depth as mentioned before (Fig. 2-d). The excess water helped the pesticide to move deeper in the soil profile. The measured and simulated 2, 4-D concentrations were 10.05 and 11.33 mg kg^{-1} soil, respectively. Total

simulated concentration was 11.3% higher than the measured one. The values of statistical parameters at this time indicate that model could predict trend and concentrations of 2, 4-D movement very well. The NRMSE, CRM and d were 0.1, -0.12 and 0.92, respectively.

In 37 days after 2, 4-D application, concentration of the herbicide in the top layer increased slightly in comparison to the pervious time (Fig. 2-e). The reasons were volatilization of herbicide and wick effect or upward movement of water and solute (Hubbs and Lavy, 1990). According to the figure and statistical parameters, model prediction was very accurate. The NRMSE, CRM and d were 0.14, -0.005 and 0.95, respectively.

Last measurements were carried out 54 days after herbicide application on September 14th. Total measured and simulated 2, 4-D concentration in the soil profile at this time were 7.33 and 8.2 mg kg^{-1} soil, respectively. Therefore, total measured concentration was 10.6% less than the simulated one. 2, 4-D residue at this time in normal irrigation regime was 3.2 mg kg^{-1} soil. Therefore, 2, 4-D concentration in deficit irrigation was 4.13 mg kg^{-1} soil (129.1%) higher than normal irrigation. Soil moisture leads to this difference between two irrigation treatments because more soil moisture causes more degradation of 2,4-D. The NRMSE, CRM and d were 0.28, -0.11 and 0.89, respectively, which shows a fair simulation of this model.
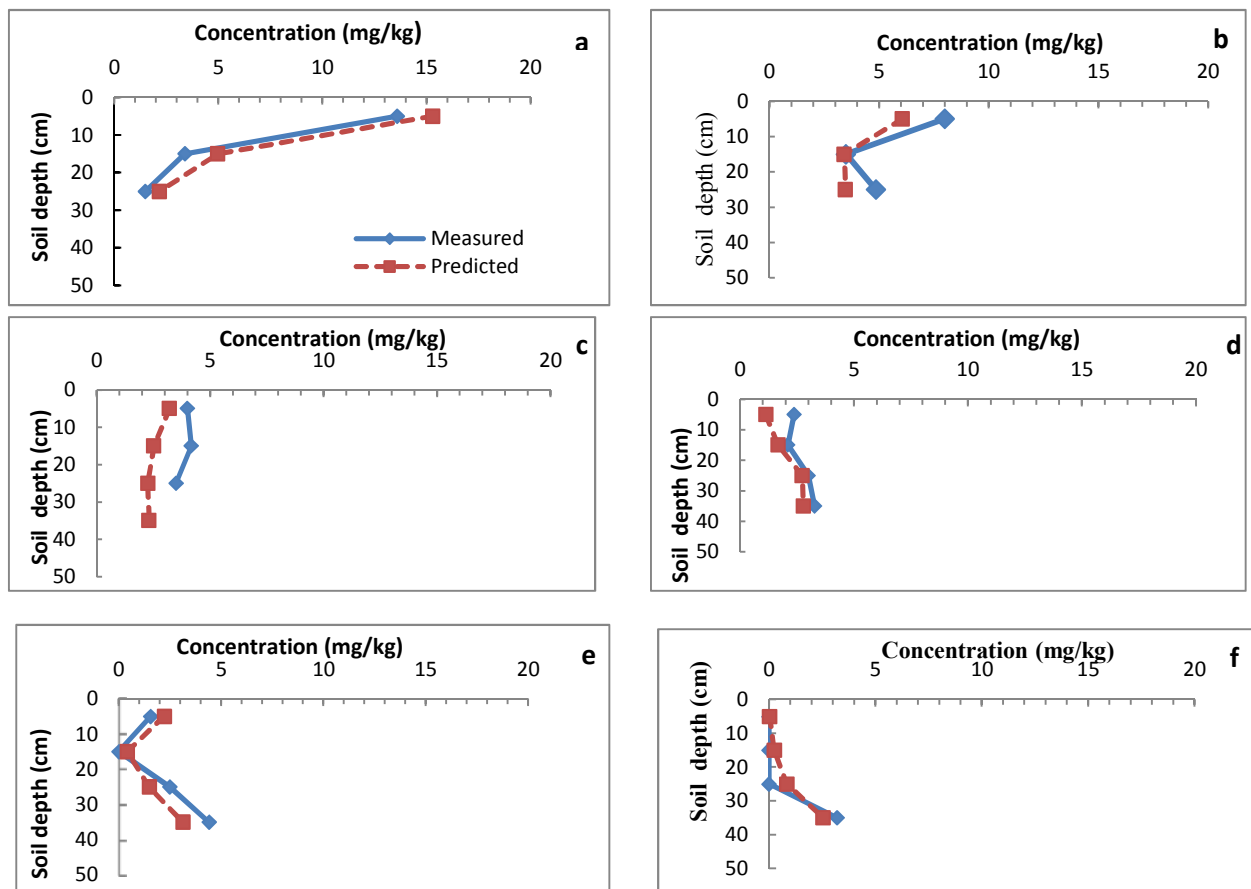

Fig. 1. Measured and simulated 2,4-D concentration using HYDRUS-1D in different soil depths for normal irrigation treatment: a) 8 days after application, b) 13 days after application, c) 23 days after application, d) 30 days after application, e) 37 days after application, f) 54 days after application
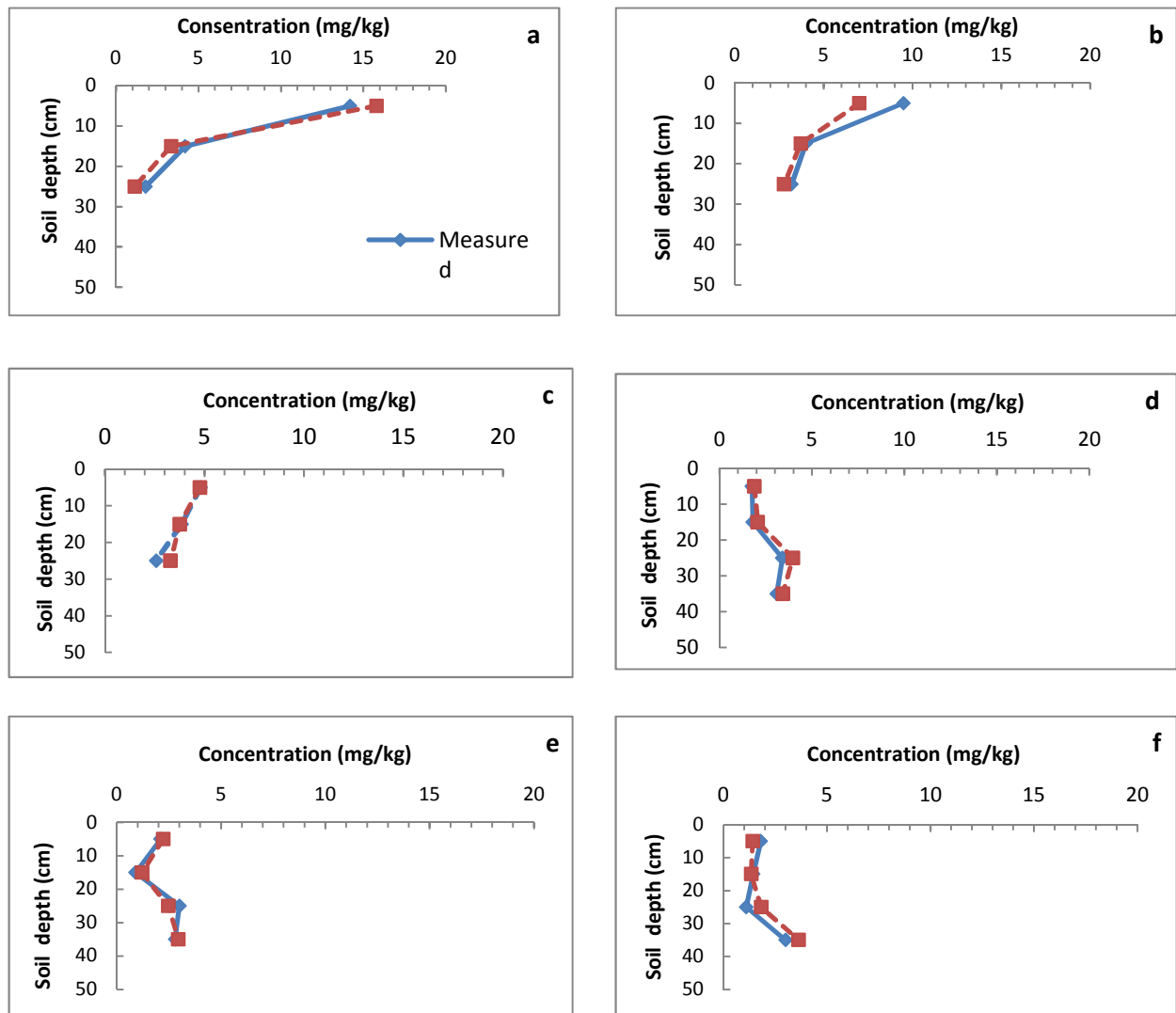
Fig. 2. Measured and simulated 2,4-D concentration using HYDRUS-1D model in different soil depths for deficit irrigation treatment: a) 8 days after application, b) 13 days after application, c) 23 days after application, d) 30 days after application, e) 37 days after application, f) 54 days after application.

It is noticeable that the model prediction was better in deficit treatment because of less microbial activity due to less soil moisture. The numerical models usually could not simulate microbial activity with good accuracy.

CONCLUSIONS

In this research, 2, 4-D was applied to a corn growing plot under two different irrigation treatments and the behavior (persistence and movement) of the herbicide concentrations in soil profile at different depths was determined. Then, the experimental results were compared with the numerical solution of the HYDRUS - 1D model.

In normal irrigation treatment at 8, 13, 23, 30, 37 and 54 days after application, the simulated 2,4-D concentrations were +21.4, -20.8, -11.7, -22.5, -14.2 and +14.4 percent less or more than the measured ones. But in deficit irrigation treatment, the simulated 2,4-D concentrations were +0.4, -19.1, +5.3, +12.7, +0.6 and 11.9 percent less or more than the measured ones. In general, total measured and simulated 2, 4-D concentration in normal irrigation treatment were 68.94 and 64.96 mg kg^{-1} soil and in deficit irrigation treatment were 74.3 and 74.0 mg kg^{-1} soil, respectively. Therefore, the results showed a good agreement between measured values of herbicide residue and the values simulated using HYDRUS 1D model. The numerical simulations for deficit irrigation regime were more precise because of less microbial activity due to less soil moisture. The numerical modeling could not simulate microbial activity with acceptable accuracy.

Mass transport differed under different irrigation treatments but the bulk mass of herbicide remained confined to the top 15 cm of the soil. The mass balance showed that 88.5 and 73.6% of 2, 4- D degraded within 53 days in normal and deficit irrigation treatments, respectively. Since the crop growing period was in

summer, high soil temperature could help the herbicide degradation. Numerical simulation by HYDRUS-1D was found to be a helpful tool towards pesticide mobility and prediction studies.

REFERENCES

Allen, R.G., Pereira, L.S., Raes, D., & Smith, M. (1998). Crop evapotranspiration-Guidelines for computing crop water requirements-FAO Irrigation and drainage paper 56. FAO. Rome 300. D05109.

Aquino, A.J.A.,Tunega, D., Pasalic, H., Haberhauer, G., & Lischka, H. (2007). The thermodynamic stability of hydrogen bonded and cation bridged complexes of humic acid models—A theoretical study. Chemical Physics, 349(1-3), 69-76.

Armstrong, A., Matthews, A., Portwood, A., Leeds Harrison, P., & Jarvis, N. (2000). CRACK-NP: a pesticide leaching model for cracking clay soils. *Agricultural Water Management,* 44, 183-199.

Bernard, H.C., Chopart, P., Legube, J., & Vauclin, B. (2005). Assessment of herbicide leach- ing risk in two tropical soils of Reunion Island (France). *Journal of Environmental Quality*, 34(2), 534-543.

Cattaneo, M., Masson, C., & Greer, C. (1997). The influence of moisture on microbial transport, survival and 2, 4-D biodegradation with a genetically marked Burkholderia cepacia in unsaturated soil columns. *Biodegradation*, 8(2), 87-96 .

Close, M.E., Lee, R., Sarmah, A.K., Pang, L., Dann, R., Magesan, G.N., Watt, J.P.C., & Vincent, K.W. (2008). Pesticide sorption and degradation characteristics in New Zealand soils—a synthesis from seven field. New Zealand Journal of Crop and Horticultural Science, 36, 9-30.

Darrell, W., & Nelson, L.E. (1996). Total carbon, organic carbon, and organic matter. *In Parks D.L. (Ed) Methods of Soil Analysis, SSSA Book Series: 5*, 982–991.

Dousset, S., Thevenot, M., Pot, V., Šimunek, J., & Andreux, F. (2007). Evaluating equilibrium and non-equilibrium transport of bromide and isoproturon in disturbed and undisturbed soil columns. *Journal of Contaminant Hydrology*, 94(3), 261-276 .

Gupta, M., Garg, N., Joshi, H., & Sharma, M. (2012). Persistence and mobility of 2, 4-D in unsaturated soil zone under winter wheat crop in sub-tropical region of India. *Agriculture, Ecosystems & Environment*, 146(1), 60-72 .

Hubbs, G.W., & Lavy, T.L. (1990). Dissipation of norflurazon and other persistent herbicides in soil. *Weed Science*, 38,81-88.

Idaho Environmental Quality.2004.Appendices - Department of Environmental Quality, <http://www. deq. idaho. gov/ media/967306-rem_ 2004_ appendix_ less_ appendix_ m.pdf> .

Jamieson, P.D., Porter, J.R., & Wilson, D.R. (1991). A test of the computer simulation model ARCWHEAT1 on wheat crops grown in New Zealand. *Field Crop. Reserch*, 27, 337–350.

Jarvis, N., Brown, C., Granitza, E. (2000). Sources of error in model predictions of pesticide leaching: a case study using the MACRO model. *Agricultural Water Management,* 44, 247-262.

Kodesova, R., Kocarek, M., Kodes, V., Simunek, J., & Kozak, J. (2008). Impact of soil micromorphological features on water flow and herbicide transport in soils. *Vadose Zone Journal*, 7(2), 798-809 .

Köhne, S., Lennartz,B., Köhne,J.M., & Šimůnek, J.(2006). Bromide transport at a tile-drained field site: Experiment, and one-and two-dimensional equilibrium and non-equilibrium numerical modeling. *Journal of Hydrology*, 321(1), 390-408.

Köhne, J.M., Köhne, S., & Šimůnek, J. (2009). A Review of Model Applications for Structured Soils: a) Pesticide Transport, J. Contam. Hydrol. *Journal of Contaminant Hydrology*, 104, 36–60.

Kucharski, J., & Wyszkowska, J. (2008). Biological properties of soil contaminated with the herbicide Apyros 75 WG. *Journal of Elementology*, 13(3), 357-371.

Ladu, J.L.C., & Zhang, D.R. (2011). Modeling atrazine transport in soil columns with HYDRUS-1D. *Water Science and Engineering*, 4(3), 258-269.

Mersie, W., & Foy, C.L. (1985). Phytotoxicity and Adsorption of Chlorsulfuron as Affected by Soil Properties. *Weed Science,* 33, 564–568.

Mohanty, B.P., Kanwar, R.S., & Everts, C.J. (1994). Comparison of Saturated Hydraulic Conductivity Measurement Methods for a Glacial-Till Soil. *Soil Science Society of America Journal*, 58(3), 672-677.

Munro, I.C., Carlo, G.L., Orr, J.C., Sund, K.G., Wilson, R.M., Kennepohl, E., Lynch, B.S., & Jablinske, M. (1992). A comprehensive, integrated review and evaluation of the scienticts evidence relating to the safety of the herbicide 2,4-D. *International Journal of Toxicology*, 11, 559.

Noshadi, M., Forouharfar, F., Amin, S., Maftoun, M. (2011). Measuring and Simulating 2,4-D Residues in Silty Clay Soil Profile Under Two Water Regimes Using a LEACHP Model. *Journal of Iran Agricultural Research*, 30, 33-46.

Pang, L., Close, M.E., Watt, J.P.C., & Vincent, K.W. (2000). Simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into ground- water using HYDRUS-2D. *Journal of Contaminant Hydrology,* 44, 19- 46.

Pesaro, M., Widmer, F., Nicollier, G., & Zeyer, J. (2003). Effects of freeze-thaw stress during soil storage on microbial communities and methidathion degradation. *Soil Biolojy Biochemi*, 35, 1049-1061.

Sarmah, A.K., Close, M.E., Pang, L., Lee, R., Green, S.R. (2005). Field study of pesticide leaching in a Himatangi sand (Manawatu) and a Kiripaka bouldery clay loam (Northland). 2. Simulation using LEACHM, HYDRUS-1D, GLEAMS, and SPASMO models. *Australian Journal of Soil Research*, 43, 471-489.

Shen, L., Wania, F., Lei, Y.D., Teixeira, C., Muir, D.C.G., & Bidleman, T.F. (2005). Atmospheric distribution and long-range transport behavior of organochlo- rine pesticides in North America. *Environmental Science & Technology*, 39, 409-420.

Shukla, G., Kumar, A., Bhanti, M., Joseph, P., & Taneja, A. (2006). Organochlorine pes- ticide contamination of ground water in the city of Hyderabad. *Environment International* , 32, 244-247.

Simunek, J., Sejna, M., & Van Genuchten, M.T. (1998). The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple

solutes in variably saturated media, version 2.0, US Salinity Laboratory, USDA/ARS, Riverside, CA.

Simunek, J., Sejna, M., & Van Genuchten, M.T. (2005). The HYDRUS-1D software pack- age for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. University of California, Riverside, Research reports, 240.

Simunek, J. & Van Genuchten, M.T. (2008). Modeling nonequilibrium flow and transport processes using HYDRUS. *Vadose Zone Journal*, 7(2), 782-.797.

Sparks, D.L. (2003). Environmental Soil Chemistry. Academic Press.

Van Genuchten, M.T. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, 44 (5), 892–898.

Van Genuchten, M.T., Wierenga, P., & Davidson, J. (1974). Evaluation of kinetic and equilibrium equations for the prediction of pesticide movement through porous media. Soil Sci. Soc. Am. Proc, 38(1), 29-35.

Walker, A. (1987). Evaluation of a simulation model for prediction of herbicide move- ment and persistence in soil. *Weed Research*, 27, 143-152.

Wang, Y., Merkel, B.J., Li, Y., Ye, H., Fu, S., & Ihm, D. (2007). Vulnerability of groundwater in Quaternary aquifers to organic contaminants: a case study in Wuhan City, China. *Environmental Geology,* 53, 479- 484.

Worrall, F., & Kolpin, D.W. (2004). Aquifer vulnerability to pesticide pollutionâ€"combining soil, land-use and aquifer properties with molecular descriptors. *Journal of Hydrology,* 293, 191-204.

Zelles, L., Adrin, P., Bai, Q.Y., Stepperk, K., Adrain, M.V., Fischer, K., Maier, A., & Zigler, A. (1991). Microbial activity merasured in soils stored under different temperature and humidity conditions. *Soil Biology Biochemi*, 23, 955-962.

تجزیه و تحلیل علف کش 2,4-D در نیمرخ خاک با استفاده از مدل HYDRUS-1D

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اطلاعات مقاله	

چکیده- علیـرغم فوایـد بسـیار علـف کشـها، پایـداری آنهـا در خـاک مـی توانـد بـه گیاهـان در کشت هـای بعـدی صـدمه زده و باعـث آلـودگی خـاک و آبهـای زیـر زمینـی گـردد. هـدف اصلـی ایـن تحقیـق شبیـه سـازی حرکـت علـف کـش 2,4-D در یـک خـاک سـیلتی رسـی لـوم بـا اسـتفاده از مـدل HYDRUS-1D در مزرعـه ذرت مـی باشـد. مقـدار ۳/۵ کیلـوگرم در هکتـار 2,4-D خـالص تحـت دو رژیـم کـم آبیـاری و آبیـاری کـامـل بـه خـاک اضـافه شـد و باقیمانـده آن در نیمـرخ خـاک در ۸، ۱۳، ۲۳،۳۰، ۳۷ و ۵۷ روز پـس از کـاربرد انـدازه گیـری گردیـد. داده هـای انـدازه گیـری شـده و شـبیه سـازی شـده نشـان داد کـه غلظتهـای 2,4-D از سـطح بـه عمـق کـاهش یافتـه و در هـر دو رژیـم آبیـاری حـداکثر تـا عمـق ۴۰ سـانتی متـری خـاک نشـت کـرد. مقـادیر باقیمانـده 2,4-D در خـاک در تیمارهـای آبیـاری کامـل و کـم آبیـاری بترتیـب بـرای واسـنجی و اعتبـار سـنجی مـدل HYDRUS-1D اسـتفاده شـد. غلظـت کـل انـدازه گیـری شـده و شـبیه سـازی شـده در نیمـرخ خـاک در رژیـم آبیـاری کامـل بترتیـب ۶۸/۹۴ و ۶۴/۹۶ میلـی گـرم در کیلـو گـرم خـاک و در رژیـم کـم آبیـاری بترتیـب ۷۴/۳ و ۷۴/۰ میلـی گـرم در کیلـو گـرم خـاک بـود. از پارامترهـای آمـاری CRM ,d و NRMSE بـرای مقایسه نتـایج شبیه سـازی و انـدازه گیـری اسـتفاده گردیـد. ایـن پارامترهـا بـرای آبیـاری کامـل بترتیـب ۰/۸۵ ، ۰/ ۲۷ ، ۰/ ۷۷ و بـرای کـم آبیـاری بترتیـب ۰/۹۴، ۰/۱۹ و ۰/۰۲ بـود. بنـابراین نتـایج نشـان داد کـه تطابق خـوبی بـین مقـادیر انـدازه گیـری شـده و شـبیه سـازی شـده توسـط مـدل HYDRUS-1D وجـود داشـت. نتـایج شـبیه سـازی بـرای رژیـم کـم آبیـاری دقیقتـر از آبیـاری کامـل بـود کـه دلیـل آن مـی توانـد فعالیـت کمتـر میکروبـی در خـاک بـه دلیـل کـاهش رطوبـت خـاک در رژیـم کـم آبیـاری باشـد. بـه طـور کلـی مـدلها قـادر بـه شـبیه سـازی دقیـق فعالیـت هـای میکروبـی نیسـتند. بنـابراین در کم آبیاری کـه ایـن فعالیـت کمتـر بـوده اسـت، نتایـج شبیه سازی بهتر شده است.