

TRANSPORT AND FATE OF PESTICIDE IN UNSATURATED NONISOTHERMAL SOIL: EXPERIMENTAL AND NUMERICAL STUDIES FOR BROMOXYNIL OCTANOATE.

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ABSTRACT

Transport of bromoxynil octanoate (3,5-dibromo-4-hydroxy-benzonitrile) and water were studied experimentally and numerically in closed soil columns. Bromoxynil and water content distributions in the soil columns were measured. A numerical model was developed based upon unsteady state movement of water, heat and nonvolatile organic compound (i.e., bromoxynil octanoate) for simulating the measured data. Loamy sand soil was moisturized then packed in sealed PVC columns (0.10m diameter and 0.3m long). The average bulk density of soil columns was 1439 kg/m^3 . The soil had initial water content of $0.113 \text{ m}^3/\text{m}^3$. The top 0.005 m- layer of soil column had 0.000272 mol/l of bromoxynil, while the rest of soil column had zero concentration. The columns were buried vertically within a soil bin such that column surfaces were exposed to natural radiation of Qassim region, Saudi Arabia. Two soil columns lasted for 14 days. Both predicted and measured final soil water contents showed nonlinear distributions and similar trends. The water moved from the upper region (0.05 m thick) toward the cold region at depth 0.1m. The measured and predicted soil water distributions in the lower layer (i.e., 0.1 to 0.3 m) showed small changes. The predicted and measured bromoxynil concentrations behaved similarly in their trend. The upper 0.0- 0.15 m was an active layer for degradation and movement of bromoxynil. The upper 0.0-0.05 m-region possessed lower concentration of bromoxynil while the succeeded region of 0.05 to 0.15 m possessed the highest concentration. Numerical simulation showed that increasing the mean temperature resulted more migration of water and bromoxynil from upper region toward lower region.

انتقال البروموكسينيل أوكسينيل والماء تم دراسته في هذه البحث معمليا ورقميا في أعمدة من التربة مغلقه ، وقد تم قياس توزيع محتوى الماء والبروموكسينيل في هذه الأعمدة . وتم أيضا عمل نموذج رياضي رقمي لوصف حركة الماء والحرارة و المركب العضوي الغير قابل للتطاير بغرض المقارنة مع قيمهم المقاسة . تم ترطيب الرمل الطفي قبل تعبئته في أعمدة الـ PVC أبعادها ٠,٢ متر من حيث القطر و ٠,٣ متر من حيث الطول . وعلى ذلك فقد كانت الكثافة الحجمية المتوسطة في حدود $٠,١١٣ \text{ متر}^3 / \text{متر}^3$. وقد تم تركيز البروموكسينيل (mol/l) $٠,٠٠٠٢٧٢$ في أعلى طبقة من العمود وبسبك مقداره $٠,٠٠٥$ متر بينما كان تركيزه صفرا في باقي العمود . ودفنت الأعمدة رأسيا في صناديق من التربة بحيث تتعرض للإشعاع الطبيعي لمنطقة القصيم بالمملكة العربية السعودية ، وترك عمودين من التربة لمدة ١٤ يوم ثم تم قياس محتوى الماء والذي أظهر توزيعات غير خطية مع تماثل الخصائص لكلا العمودين وتبين تحرك الماء من الطبقة العليا تجاه المنطقة الباردة على عمق $٠,١$ متر . وتبين في المقابل أن قيم التوزيع المقاسة والمحسوبة لماء التربة في الطبقة السفلى بسبك $٠,١ - ٠,٣$ متر أظهرت تغيرا طفيفا . الطبقة العليا بسبك $٠,٠ - ٠,١٥$ متر هي التي تأثرت وشهدت تحرك البروموكسينيل ملموسا ، بينما كانت الطبقة العليا وبسبك $٠,٠ - ٠,١٥$ متر شهدت نقصا في تركيز البروموكسينيل في مقابل زيادة تركيزه في المنطقة التالية بسبك $٠,٠٥ - ٠,١٥$ متر . وقد بينت الدراسة بالمحاكاة الرقمية أن زيادة درجة الحرارة المتوسطة تؤدي إلى زيادة انتقال الماء والبروموكسينيل من الطبقات العليا إلى الطبقات السفلى .

Keywords: bromoxynil octanoate; water movement; pesticide transport; modelling; simulation.

1. INTRODUCTION

Pesticides are widely used in agriculture to control a variety of organisms and weeds that damage crops. More than six hundreds types of agrochemicals are used around the world (Miyake et al., 1999). They provide unquestionable benefit for agricultural production; consequently, low amounts of some residues may persist in the food supply, air, water

and soil. These residues could create potential chronic toxicity and in some cases, acute toxicity (Ekström et al., 1996, Osman and Al-Rehiyani, 2003). Bromoxynil (3,5-dibromo-4-hydroxy-benzonitrile) as the octanoate ester is one of the agrochemicals (herbicide) widely used for controlling broad leaf weeds in cereal crops (Environment Canada, 1986). The bromoxynil was ranked high with respect to potential for groundwater contamination in

an agriculture Canada survey (Agriculture Canada, 1986). In general, the agrochemicals have different fates after their application. Some may be lost to the atmosphere by volatilisation (or evaporation), particularly those have high vapour pressure (Nassar et al., 1999a). Some others can be bounded to the soil components such as clay and organic constituents (Salama et al., 2001). The bromoxynil octanoate is a good reactive with clay and organic components. The sorption coefficient per unit mass of organic carbon in soils (K_{oc}) for bromoxynil octanoate showed a wide variation among studies, possibly reflecting the varying nature of organic materials present in soils. For example, K_{oc} , ranged from 10 (Salama et al., 2001) to 18 Kg/m^3 (Lyman et al., 1990). The bromoxynil octanoate can be degraded or transformed in soils. Biodegradation experiments showed a high mineralization of bromoxynil octanoate (Collins, 1973) in soil. Similarly, the main degradation and transformation pathways of bromoxynil octanoate in soil were mineralization and formation of bound residues (Rosenbrock et al., 2004). It broke down in the environment by photolytic degradation, abiotic hydrolysis and microbial-mediated metabolism under both aerobic and anaerobic conditions. The degradation of bromoxynil is function for several factors. One of these factors is pH. Respective half-lives of 34.1, 11.5, and 1.7 days were reported for Bromoxynil octanoate at pH of 5, 7 and 9. So, the half-life of bromoxynil decreased as soil pH increased. In two field experiments, half-lives were 14 days at a site in California. Bromoxynil has a low persistence in soil. In sandy soil, the half-life is about 10 days (Kidd and James, 1991 and Gordon and Pullin, 2006). Similar results are reported in Canada (Worthing, 1983).

Soil with high-saturated hydraulic conductivity can lead to ground water pollution by the bromoxynil octanoate. (Kookana et al., 1997) studied the sorption coefficient in different Australian soils. They reported that the sorption coefficients for pesticides were much lower in subsoil than in surface soils; in some cases they were negligible in subsoil. This suggests that in such soils, once the pesticide leaches beyond the top 50–100 cm, it can move with the water-front with little retardation through sorption.

Since the agricultural sector is the largest for consuming the bromoxynil octanoate, we need to understand the fate and transport of this herbicide in the soil. Therefore, understanding the mechanisms of movement of the Bromoxynil can lead to better management. According to the literature cited above, bromoxynil movement in soil has rarely been studied experimentally under unsaturated nonisothermal conditions. The research project encompassed greenhouse and theoretical analyses. Therefore, the first objective of this study is to perform

nonisothermal experiments under natural radiation of Al-Qassim region, Saudi Arabia to observe water, and bromoxynil octanoate (non-volatile) transfer in unsaturated soil. Here, we use the Nassar and Horton (1999b) formulation for non-volatile organic chemicals without inclusion of inorganic solute transport and osmotic effects. So, the second objective is to test a model based upon the unsteady state transfer of water, heat and non-volatile organic solute in unsaturated nonisothermal soil conditions against the greenhouse experimental data.

2. MATERIALS AND METHODS

2.1. Experimental

Soil materials were sampled from a surface layer (0.0–0.3 m depth) from the Agriculture and Veterinary Collage farm, Qassim University, Al-Qassim. The soil materials were air-dried and ground to pass a 2-mm sieve. The soil texture was loamy sand (83.96 % sand, 14.82 % clay and 1.22 % silt) materials. In addition, water-characteristic curve was measured for the site soil using pressure plate extractors (Dane and Hopmans, 2002) in a matric potential range 0 to -1500 kPa. Portion of the material was wetted with distilled water to obtain an initial volumetric water content of $0.113 \text{ m}^3/\text{m}^3$. The moistened soil was covered and stored at 20 °C for 2 days. PVC cylinders (0.1-m ID and 0.3-m high) were closed at the bottom ends using epoxy-sealed PVC lids then packed uniformly with the moisturized soil. Two soil columns were packed at an average bulk density of 1439 kg m^{-3} . A volume of 0.5ml of bromoxynil octanoate solution was injected in the top 0.005-m layer of each soil column to obtain $2.72 \times 10^{-7} \text{ mol/m}^3$ in soil solution as an initial concentration. Each soil column was tightly closed at its top end using white plastic then buried vertically within a bare soil field with exposing the upper end to the natural atmosphere of Al-Qassim region on January 11, 2007. The soil temperatures at upper end of soil column were recorded four times a day (6 am, 2, 6 and 12 pm). Mean and the amplitude of the recorded temperature were obtained. The two soil columns were removed and sectioned into seven increments. The length of increments was different. The soil of each increment was divided into two portions: a portion for water content and a portion for bromoxynil octanoate determinations. The soil water contents were determined gravimetrically in each increment. For bromoxynil determination, soil samples were extracted with 20 ml of acetone for 24 hrs in shaker at room temperature then analysed by High Performance Liquid Chromatography (HPLC) (Falqui-Cao et al, 2001). The percentage recoveries for the present study were satisfactory with a range of 90–108% (Schuller et al, 1976).

2.2. Theoretical Analysis

The formulation developed by Nassar and Horton (1999b) for organic volatile chemical was reduced to describe water, heat and bromoxynil octanoate transfer in a soil. The following theory assumes: matric water pressure head, gravity pressure head, temperature and non-volatile organic solute (bromoxynil) concentration gradients are driving forces for water, solute and heat transfers; the organic compounds can be associated with liquid and solid phases of the porous media; the liquid phase is mobile, but the solid phase is immobile; the transfer of organic compounds across liquid/solid is included using equilibrium assumptions at the interfaces, and the degradation of bromoxynil is described by a first-order decay rate. The solute flow based upon the convection-dispersion equation (CDE) was used for describing the bromoxynil flow. The heat flow occurs by conduction and by convection of sensible heat and latent heat. The model can be used to predict spatial and temporal variations of water content, total concentration of non-volatile organic solute and temperature distributions within a porous medium. The finite differences scheme for the partial differential equations of heat, water, and organic solute transfers as described by Nassar et al. (1999a) was used in the model. A brief outline of theory presented below for completeness.

2.2.1. Water flow

The soil water flow equation for transient vertical flow based upon Darcy's law and the continuity equation is:

$$\alpha_1 \frac{\partial \theta}{\partial t} + \alpha_2 \frac{\partial T}{\partial t} = -\Delta_z \left(\frac{q_w}{\rho} \right) \quad (1)$$

where θ is water content ($L^3 L^{-3}$); q_w is the soil water mass flux, ($M/L^2 s$); ρ is the density of soil solution (M/L^3); and α_1 and α_2 are storage terms for water.

2.2.2. Heat flow

The nonsteady-state heat transfer equation in one-dimension can be written as:

$$K_1 \frac{\partial T}{\partial t} + K_2 \frac{\partial \theta}{\partial t} = -\Delta_z q_h \quad (2)$$

where q_h is the net heat flux ($M L^2/L^2 T^3$); T ($^{\circ}C$) is temperature and the coefficients K_1 , and K_2 are storage terms for heat.

2.2.3. Pesticide flow and transformation

The movement of miscible pesticide (i.e., bromoxynil octanoate) through a soil is assumed in the present study to be accomplished by chemical diffusion in the liquid phase in response to an aqueous concentration gradient and convection of the pesticide as the result of water flow in which the pesticide is dissolved. Total organic solute flux is:

$$J_t = J_d + J_c \quad (3)$$

Where J_t is total pesticide flux ($M/L^2 T$), J_d and J_c are diffusion and convection fluxes in the liquid phase, respectively.

The diffusion flux in a soil solution can be obtained from:

$$J_d = -D_p(\theta) \frac{\partial C_l}{\partial z} \quad (4)$$

where $D_p(\theta)$ is the diffusion coefficient of pesticide in porous media, C_l is the concentration in the liquid phase (M/L^3). The diffusion coefficient was described in details Nassar and Horton (1999a) and Lyman et al (1982).

The convective flux of a pesticide is usually represented as:

$$J_c = -\theta D_m(q) \frac{\partial C_l}{\partial z} + q C_l \quad (5)$$

where $D_m(q)$ is the mechanical dispersion coefficient that describes mixing between large and small pores. In the present study, the mechanical dispersion was neglected because the velocity of soil solution is small.

The total steady state solute flux in the liquid phase in a porous media, J_t can be described as:

$$J_t = -\theta D_m(q) \left(\frac{\partial C_l}{\partial z} \right) - D_p(\theta) \frac{\partial C_l}{\partial z} + q C_l \quad (6)$$

The nonsteady-state equation for the pesticide transport

$$\text{can be written as: } \frac{\partial C_t}{\partial t} = -\frac{\partial J_t}{\partial z} \pm \Phi \quad (7)$$

where $C_t = \theta C_l + \rho_b C_s$, is the total pesticide concentration in liquid and sorbed phases (M/L^3), ρ_b is the bulk density of soil (M/L^3), $C_s = K_d C_l$ is the concentration of pesticide in the sorbed phase (M/M), K_d is a partition coefficient (L^3/M), and Φ is sources or sinks of pesticide (such as microbiological degradation) ($M/L^3 T$).

The degradation potential of a given chemical is described with a half-life ($t_{1/2}$) value, assuming first-order rate degradation. The half-life represents the combined influence of degradation in all phases. First-order degradation rate (k_{ref}) is calculated using:

$$k_{ref} = \frac{\ln 2}{t} = \frac{0.693}{t} \quad (8)$$

The half-life, t , for the bromoxynil octanoate is 7 days in the present study. The decay coefficient (Φ) is described as a function of temperature, water content and soil depth (Boesten and van der Linden 1991) as:

$$\Phi = f_T f_\theta f_z k_{ref} \quad (9)$$

where f_T is a factor for the influence of soil temperature, f_θ is reduction factor for the influence of liquid water content, f_z is reduction factor for the influence of the depth, and K_{ref} is decay coefficient

at a reference condition (i.e., those in soil collected from the plow layer at 20 °C and at a matric pressure of -1.0 m).

$$f_T = \exp(\zeta(T - T_o)) \quad (10)$$

where ξ is a function of T

$$f_\theta = \min(l, (\theta / \theta_{ref}))^\beta \quad (11)$$

where β is a constant, and θ_{ref} is the water content at a reference condition. The term f_z is assumed to be unity in the present study.

The partition coefficient, K_d can be estimated as

$$K_d = K_{oc} f_{oc} \quad (12)$$

Where K_{oc} is the organic carbon partition coefficient (L^3/M) and f_{oc} is the organic carbon fraction.

2.2.4. Coupled organic chemical, water, and heat transport

Three partial differential equations (Eqs. 1, 2, and 7) are presented. The equations should be solved simultaneously for understanding the mechanisms of energy and mass transfer in porous media. The equations can be used for describing the spatial and temporal variations of non-volatile organic chemical, water content, and temperature in porous media when the boundary and initial conditions, and the transport parameters are available.

2.2.5. Initial and boundary condition

The initial conditions associated with Eqs. (1), (2), and (7) are given by

$$\begin{aligned} T(z,0) &= T_i, \quad \theta(z,0) = \theta_i, & (0 < z < l), \\ C(z,0) &= C_o, & (0 < z < 0.005 \text{ m}), \\ C_t(z,0) &= 0.0 & (0.005 < z < l), \end{aligned} \quad (13)$$

where l is soil column length (m).

The temperature boundary conditions at upper end of the closed soil columns in Fig. 1 can be described by

$$T(0, t) = T_m + A \left(\sin \frac{2\pi t}{24} \right) \quad t > 0 \quad (14)$$

$$T(l, t) = T_c \quad t > 0 \quad (15)$$

where T_m , and A are the mean and amplitude temperatures at the upper boundary, respectively, and the T_c is temperature at the bottom boundary, respectively. Figure 1 shows the results of calculated diurnal variation of soil temperature based upon the mean and amplitude temperatures. The calculated diurnal temperatures were used as the upper boundary temperatures.

The boundary conditions for water and solute are given in terms of net mass fluxes by

$$(q_l + q_v)(0, t) = 0, \quad n_c(0, t) = 0, \quad q_o(0, t) = 0 \quad t > 0$$

$$(q_w)(l, t) = 0, \quad J_t(l, t) = 0 \quad t > 0 \quad (16)$$

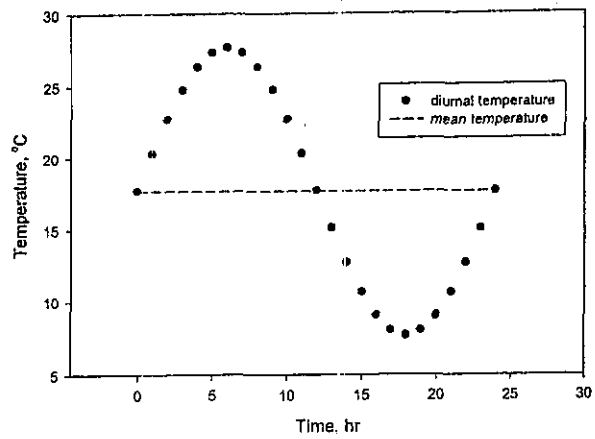


Fig. 1 An average diurnal temperature at the top of soil column.

2.2.6. Soil parameters and characterization

Figure 2 shows the water-characteristic curve for the loamy sand soil used in the present study. The water characteristic curve was described by using Campbell's function (1974) as

$$\psi_m = \psi_e (\theta / \theta_s)^{-b} \quad (17)$$

where b and ψ_e are fitting parameters, and θ_s is saturated volumetric water content. Equation (16) is fitted to the measured θ for determining b and ψ_e . The coefficients of the function, ψ_e and b , are shown in Table (1). The unsaturated hydraulic conductivity, $K(\theta)$, was estimated from knowledge of saturated hydraulic conductivity, K_s as following (Campbell, 1974):

$$K(\theta) = K_s (\theta / \theta_s)^{2b+2} \quad (18)$$

Table 1 shows value for K_s of the loamy sand soil used in the present study.

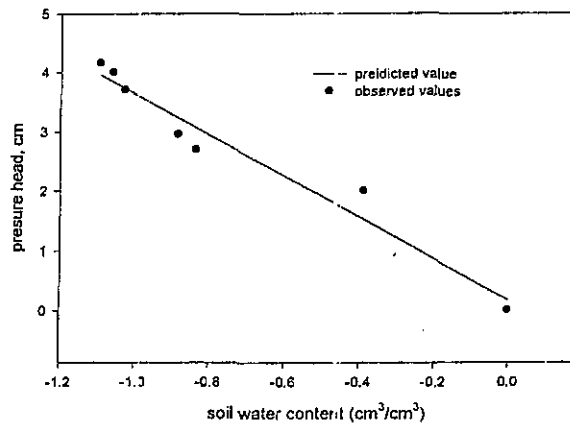


Fig. 2 Soil characteristics curve of loamy sand soil used in the present study.

Table 1. Input characterization data for the presented model.

Parameters	Value
ρ (bulk density) (Mg m^{-3})	1439.5
θ_i (initial water content) ($\text{m}^3 \text{m}^{-3}$)	0.113
θ_s (saturated water content) ($\text{m}^3 \text{m}^{-3}$)	0.459
K_s (m s^{-1})	1.98×10^{-5}
Clay, (%)	14.82
Sand (%)	83.96
Silt (%)	1.22
K_{oc} ($\text{m}^3 \text{kg}^{-1}$)	18
F_{oc} (%)	0.057
K_{ref} (s^{-1})	1.15×10^{-5}
Ψ_c (kPa)	0.15
B	3.46
ζ	0.25
f_0	0
T_m ($^{\circ}\text{C}$)	17.7
A ($^{\circ}\text{C}$)	10.0
T_c ($^{\circ}\text{C}$)	12

3. RESULTS AND DISCUSSION

3.1. Predicted and Measured Soil Water Status

The predicted and measured soil water content distributions in nonisothermal columns are shown in Fig.3. The predicted water content distributions are in agreement to the observed values in their trend. Small amount of water migrated from the upper zone of soil columns toward lower zones. This is expected because small temperature gradients exist beside the limited matric potential gradients. The predicted and observed soil water contents exhibited three distinguished zones. The first zone extended to 0.05-m depth, the second zone was located between 0.05 and 0.10-m depth and the third zone was below 0.10-m depth. The first zone possessed the lowest water content and the second zone possessed the highest water content. It is obvious that water migrated from the upper zone to the second zone. The initiative driving force for water movement is mainly temperature gradient those gradient derived water to migrate from the upper zone in vapour form followed by condensation in the second zone. It is expected that water movement in the upper zone mainly in vapour phase (Nassar et al., 1992). Condensation the water in the second could lead to water movement toward the first and third zone in liquid form under matric potential gradient. Similar results were reported by Nassar et al. (1992) and Al-Salamah (2004). The third zone does not show much water migration since the temperature and matric potential gradient are limited. Several researchers found that temperature gradient has great effect on water flow Globus (1983) and Nassar et al (1992). So, the developed model was used to simulate the water contents under two mean temperatures (15 and 20 $^{\circ}\text{C}$).

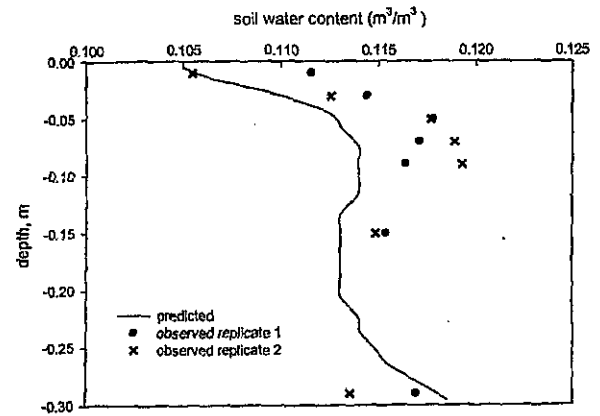


Fig. 3 Observed and predicted soil water contents.

The simulated data are shown in Fig. 4. It is obvious from the simulated soil water distributions that water movement from the upper zone of the soil column increased toward the lower zone as the mean temperature increases. Those increases in water movement are attributed to increasing the water transport coefficients as resulted from the temperature increases. Those coefficients are the soil hydraulic conductivity and thermal water diffusivity (Nassar and Horton, 1997).

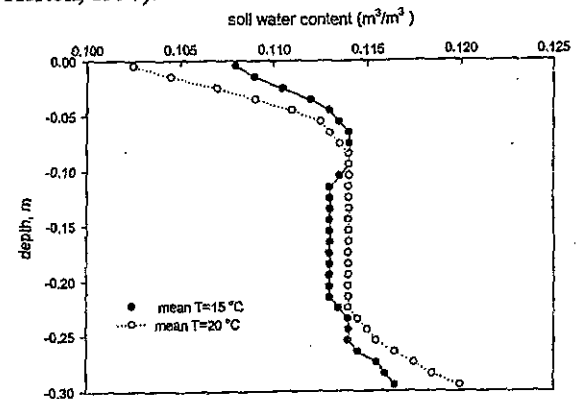


Fig. 4 Predicted soil water content under two different mean temperatures.

3.2 Predicted and Measured Bromoxynil Octanoate Concentration:

Measured and predicted Bromoxynil octanoate concentrations are compared in Fig. 5. The predicted and observed concentrations are similar in their trends. Both show high concentration in the layer 0.05 to 0.10 m. The bromoxynil concentrations decreased in the upper zone (0.05 m depth) then increased in the second zone (0.05 to 0.10 m depth) followed by decreasing in the lower portion of the soil column. Decreasing the bromoxynil concentration in the upper zone could be attributed to its photolytic degradation, abiotic hydrolysis and microbial-mediated metabolism. (Rosenbrock et al., 2004). The upper zone posses high temperature

during the daytime, which increases photolytic degradation for the Bromoxynil. In addition, the initiative concentration of bromoxynil in the upper zone was the highest which drive partially the bromoxynil to move by diffusion mechanism. Under the condition of the present study, mass flow of solute is insignificant because the velocity of liquid water is small. The second zone of the soil column posses the highest concentration of bromoxynil because it has low temperature in comparison with the upper zone.

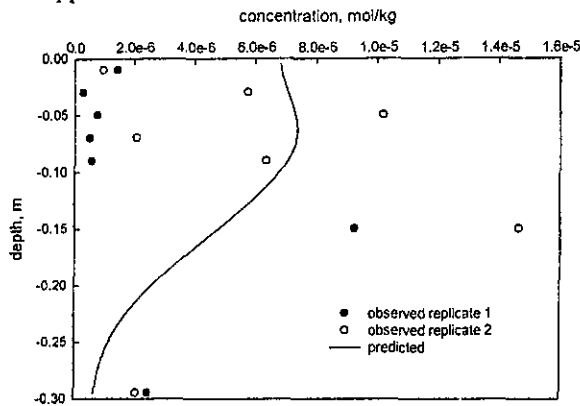


Fig. 5 Observed and predicted bromoxynil octanoate concentration.

Despite that good agreement between the measured and simulated water distributions, there is substantial disagreement between measured and simulated bromoxynil octanoate. One reason for the disagreement could be due to the assumption that degradation of total pesticide obeys first-order kinetics. Similar results were reported by Wagenet et al (1989) for simulation of DBCP (1,2-dibromo-3-chloro-propane). In addition, the distribution coefficient (K_d) of bromoxynil octanoate is high ($18 \text{ m}^3/\text{kg}$). Since the K_d in the present study is high, most of the bromoxynil octanoate exists in the adsorbed phase, which reduces its movement with mass flow of water. The total measured and predicted bromoxynil octanoate concentration means were 4.10018×10^{-6} and 4.38967×10^{-6} mol/Kg of soil, respectively. In comparison with an initial bromoxynil octanoate of 1.89×10^{-4} mol/Kg of soil in the first 0.005 m layer, a great amount of bromoxynil octanoate degraded after 14 days. The favourable fate of a pesticide is a combination of fast degradation and strong adsorption to soil. The most sensitive parameters of pesticide models are related to the sorption and degradation of the compounds to be studied (Autio et al., 2004). Those authors reported that bromoxynil octanoate could be classified as immobile if the sorption coefficient, K_{foc} , calculated from Freundlich's equation, exceeds $5 \text{ m}^3/\text{kg}$.

Effect of soil temperature on the fate of bromoxynil octanoate was studied numerically in the

present study. The calculated concentrations of bromoxynil octanoate are shown in Fig. 6. As the mean temperature increased from 15 to 20 °C, the concentrations decreased in the upper layer drastically. The concentrations of bromoxynil were one order of magnitude greater under mean temperature of 15 °C in comparison to the mean temperature of 20 °C. It is concluded that effect of temperature on the fate of surface applied bromoxynil octanoate must be considered.

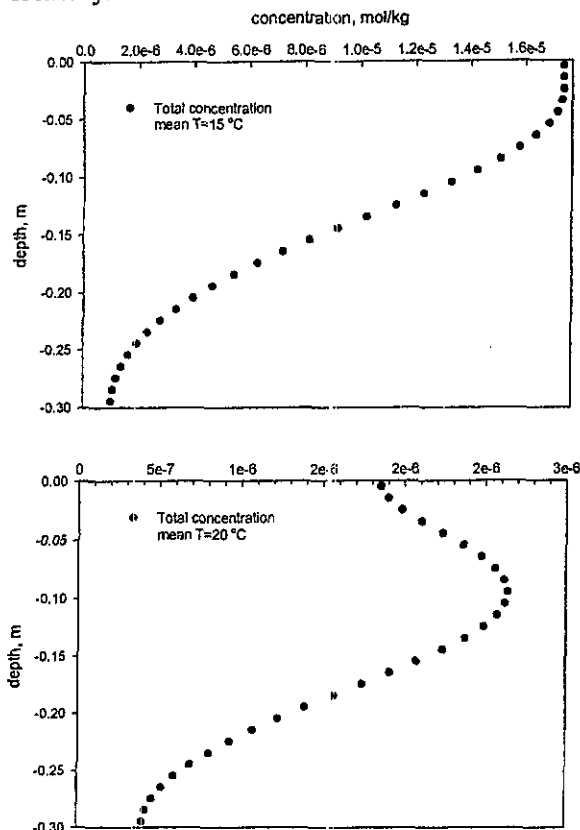


Fig. 6 Predicted bromoxynil octanoate concentrations under two different mean temperatures.

4. CONCLUSIONS

A greenhouse experiment was achieved for monitoring water and bromoxynil octanoate transfer in closed loamy sand soil columns. The soil columns were buried vertically in a bare soil field in Al-Qassium region, KSA. Bromoxynil octanoate solution was added to the upper layer (0.005 m) at experiment initiation. A numerical code was developed based upon the partial diffusion equations of water, heat and non-volatile organic chemicals. The model was used to predict water and bromoxynil octanoate concentrations and compared with measured. The predicted and observed water content trends were in agreement. Also, the predicted and observed bromoxynil octanoate distributions along the soil columns behaved similarly. Temperature has a great impact on water and bromoxynil octanoate movement under the present study

condition. The application of this model may be very useful for the development of remediation strategies to clean soil from bromoxynil octanoate compounds when nonisothermal conditions exist and the degradation and sorption coefficient are measured for the studied site. It should also be useful for monitoring bromoxynil octanoate redistribution at contaminated sites.

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