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APPLICATION OF PHOSPHATE WATER AND SLIME IN AGRICULTURE: INVESTIGATION OF THE MOBILITY OF THE POLLUTANTS USING HYDROLOGIC MODELING

E. DIAMANTOPOULOS[1]
N. DERCAS[1,*]
K.X. SOULIS[1]
S. JELLALI[2]
A. STEFOPOULOU[1]

[1] *Agricultural Hydraulics Laboratory, Agricultural University of Athens 75, Iera Odos str., 11855 Athens, Greece*
[2] *Center of Water Research and Technologies BP273, 8020 Soliman, Tunisia*

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*to whom all correspondence should be addressed:
e-mail: ndercas1@aua.gr

ABSTRACT
The use of phosphate slime or phosphate water in a Mediterranean region (Gafsa, Tunisia) was investigated through hydrologic modeling. The simulations were made using the Hydrus 1D software package for a typical soil in the area of Gafsa (Tunisia). Two main applications were examined: mixing the surface soil with the phosphate slime and irrigating with polluted (phosphate) water or irrigating only with phosphate water. The elements under study were Cd, Cr, Ni, and Sr. The results show that there is no significant risk of groundwater pollution with these elements if the phosphate slime or the phosphate water is used for agricultural purposes. The addition of slime in the upper soil layer retards the mobility of the pollutants. The results also show that the mobility of these elements is highly dependent on the applied irrigation dose. These pollutants need high amounts of water in order to reach great depths. This research was carried out in the framework of the EU project "Integrated water management of Mediterranean phosphate mining and local agricultural systems" (ELMAA).

KEYWORDS: Hydrologic Modeling, Phosphates, Heavy metals, Hydrus 1D.

1. INTRODUCTION

The phosphate industry is a major contributor to the economy of some Mediterranean countries (i.e. Morocco, Jordan, Tunisia). Phosphate industry uses high amounts of water in areas where scarcity and poor quality of water is a main problem. Rock phosphates, which are the raw material of the phosphate industry, carry various chemical elements in mineral forms and in trace amounts, some of which (such as Fe, Zn, Mn, Cu, B and Mo) are necessary for almost all plant organisms on our planet. However, elements such as Cd, Hg, Pb, Ni and Sr, which are also found in rock phosphates, can be toxic in high concentrations.

Because of their low solubility, the movement of heavy metals in soils has generally been considered either as minimal or as practically non-existent (Dowdy and Volk, 1983). Williams *et al*. (1987) found no significant movement of Cd, Cu, Pb and Zn in soils treated with sludge for 8 years. Chang *et al*. (1984) demonstrated that more than 90% of applied heavy metals were found in the surface 15 cm of the soil. Page and Chang (1985) showed that in most cases, trace elements added through different wastes were either retained in the top soil layer or moved only a few centimeters below the treated layer. Navarro-Pedreno *et al*. (2003) concluded that no important displacement or mobility of polluting metals had been found in the calcareous soil examined in their study. However, Schirado *et al*. (1986) discovered that Zn, Ni and Cd migrated from the cultivated soil layer into deeper layers in a silt loam soil due to high annual rainfall. After 14 years of sludge application, Dowdy *et al*. (1991) found a small movement of Cd and Zn down through the soil profile. Dowdy and Volk (1983) demonstrated that the movement of heavy metals in soil could occur in sandy, acid, low-organic matter soil subjected to heavy rainfall or irrigation. Davis *et al.* (1988) carried out a four year experiment without cultivation and where no irrigation was applied and found that Cd, Cr, and Ni moved into the top 10 cm of the profile, with an average of 87% of the metals on the first 5 cm. Legret *et al.* (1988) marked that in a coarse, textured soil, Cr remained in the surface horizon.

Bhumbha and Sencindiver (1989) conducted experiments in Florida showing that phosphate clay could be used as an amendment especially in acid minesoils. Cao *et al*. (2003) accomplished a study regarding the interactions of heavy metals with phosphatic clay, focusing on the sorption and desorption behavior. In the previous study, a desorption and a sorption kinetics experiment were conducted. The accomplishment of the experiments followed a field demonstration of Lead immobilization in contaminated soil after application of phosphorous amendments. The results indicate that phosphatic clay has a potential to immobilize heavy metals in contaminated soils, sediments, wastes and wastewater due to a high capacity to adsorb and retain metals. Singh *et al.* (2006) used the phosphatic clay as an effective sorbent for Pb immobilization from aqueous effluents. The clay used in the particular study was obtained from Phosphate Mining Company, White Springs, FL, USA.

The European project ELMAA aims to reduce tensions on water resources around phosphate mines at regional scale. The main activity of the ELMAA project consists in investigating the possibility to use phosphate slimes and phosphate water (slime and water from phosphate washing process) for agricultural use. One major concern is the risk of groundwater pollution. For this reason various field and laboratory experiments were carried out. Also, the Hydrus 1D software (Simunek *et al*., 1998) was applied in order to examine the soil and water pollution risk from slimes or phosphate water utilization under various scenarios. The model was applied in the region of Gafsa, which is located 350 km south of Tunis, close to the north-eastern part of the Sahara desert and it represents the most important phosphate area of Tunisia. The area is characterized by a Mediterranean arid climate and the groundwater available in shallow and deeper aquifers constitutes its main water resource. The application of the model was mainly based on data concerning the soil characteristics for Gafsa, data from the column experiments carried out by the Center of Water Research and Technologies (CERTE, Tunisia), climatic data from the experiment area and data from the international literature.

2. METHODOLOGY

2.1. Hydrus 1d

The Hydrus 1D is a software package for simulating water, heat and solute movement in one-dimensional variably saturated media. The software consists of the Hydrus computer program, and the Hydrus 1D interactive graphics-based user interface. The Hydrus program numerically solves the Richards equation for variably saturated water flow and advection-dispersion type equations for heat and solute transport. The governing flow and transport equations are solved numerically using Galerkin-type linear finite element schemes.

The Richards equation for one-dimensional unsaturated flow is given by:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left[K\left(\frac{\partial H}{\partial z} + \cos a\right)\right] - S \qquad (1)$$

where H is the water pressure head [L], θ is the volumetric water content [L^3L^{-3}], t is time [T], z is the spatial coordinate [L] (positive upward), S is the sink term [$L^3L^{-3}T^{-1}$], α is the angle between the flow direction and the vertical axis (i.e., $\alpha = 0^0$ for vertical flow, 90^0 for horizontal flow, and $0^0 < \alpha < 90^0$ for inclined flow), and K is the unsaturated hydraulic conductivity function [LT^{-1}] given by:

$$K(H,z) = K_S(z)K_r(H,z) \qquad (2)$$

where K_r is the relative hydraulic conductivity [dimensionless] and K_s the saturated hydraulic conductivity [LT^{-1}].

In order to incorporate the soil layers into the Hydrus software, the Van Genuchten (1980) model was used:

$$\theta(H) = \theta_r + \frac{\theta_s - \theta_r}{(1+(\alpha \cdot H)^n)^m} \quad Se = \frac{\theta(H) - \theta_r}{\theta_s - \theta_r} \tag{3}$$

$$K(Se) = K_s Se^{0.5}\left(1 - \left[1 - Se^{n/(n-1)}\right]^m\right)^2 \text{ where } m = 1 - \frac{1}{n} \tag{4}$$

The parameters θ_r, θ_s are residual and saturated water content respectively (L^3L^{-3}), α (> 0, in L^{-1}) is related to the inverse of the air entry pressure, n (> 1) is a dimensionless measure of the pore-size distribution and Se is effective saturation (dimensionless).

The sink term, S, is defined as the volume of water removed from a unit volume of soil per unit time due to plant water uptake. Feddes *et al.* (1978) defined S as

$$S(H) = a(H)S_p \tag{5}$$

where the root-water uptake water stress response function $a(H)$ is a prescribed dimensionless function (Figure 1) of the soil water pressure head ($0 \leq a \leq 1$), and S_p the potential water uptake rate [$L^3L^{-3}T^{-1}$]. Figure 1 gives a schematic of the stress response function as used by Feddes *et al*. (1978). It must be noted, that water uptake is assumed to be zero close to saturation (i.e., wetter than some arbitrary "anaerobiosis point", H_1). For $H<H_4$ (the wilting point pressure head), water uptake is also assumed to be zero. Water uptake is considered optimal between pressure heads H_2 and H_3, whereas for pressure head between H_3 and H_4 (or H_1 and H_2), water uptake decreases (or increases) linearly with H. The variable S_p in equation 5 is equal to the water uptake rate during periods of no water stress when $a(H)=1$.

The required parameters for the Feddes model incorporating in Hydrus are:

P_0: Value of the pressure head, below which roots start to extract water from the soil (H_1 of the Feddes model).
P_{Opt}: Value of the pressure head, below which roots extract water at the maximum possible rate (H_2 of the Feddes model).
P_{2H}: Value of the limiting pressure head, below which roots can no longer extract water at the maximum rate (H_3 of the Feddes model for a high potential transpiration rate of r_{2H}).
P_{2L}: As above, but for a low potential transpiration rate of r_{2L}.
P_3: Value of the pressure head, below which root water uptake ceases (H_4 of the Feddes model, usually taken at the wilting point).
r_{2H}: Potential transpiration rate (high) [LT^{-1}].
r_{2L}: Potential transpiration rate (low) [LT^{-1}].

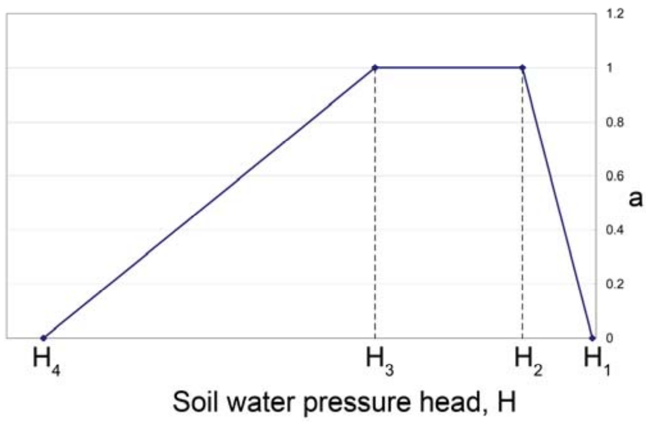


Figure 1. Schematic of the plant water stress response function, *a(H)*, as used by Feddes *et al*. (1978)

Hydrus can implement both equilibrium and non-equilibrium solute transport. In this study, the transport of the elements was assumed as an equilibrium transport. One-dimensional transport of a sorbing solute through a homogeneous soil at constant water content is described here using the convection-dispersion equation (Lapidus and Amundson, 1952):

$$\rho \frac{\partial S_a}{\partial t} + \theta \frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z} \quad (6)$$

where t is time [T], z is the depth of the soil profile [L], ρ is the soil bulk density (ML^{-3}), θ is the soil water content ($L^3\ L^{-3}$), D is the dispersion coefficient ($L^2\ T^{-1}$), q is the volumetric water flux density ($L\ T^{-1}$) or simply the water flow velocity in the z-direction. The flow velocity q is referred to as Darcy's flux (cm h^{-1}). The dispersion coefficient D is given by:

$$\theta D = \lambda |q| \quad (7)$$

where $|q|$ is the absolute value of Darcian velocity [LT^{-1}] and λ is the longitudinal dispersivity. Generally, this value is obtained experimentally by performing a non reactive tracer experiment at the same flow velocity and measuring its breakthrough curve in the column effluent. The convection-dispersion equation for a non-reactive solute is:

$$\theta \frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - q \frac{\partial C}{\partial z} \quad (8)$$

The implementation of the elements' retention by the soil was made using the Freundlich isotherm equation:

$$S_a = K_f C^b \quad (9)$$

where S_a is the weight adsorbed per unit weight of adsorbent (MM^{-1}), C is the concentration of the element in the solution (ML^{-3}), K_f is a distribution coefficient (L^3M^{-1}) and b is a dimensionless variable.

3. IMPLEMENTATION

The mobility of the elements under study was tested with two main investigations. First the effect of slime addition (one time addition) in the first 10 cm was examined (investigation I). In this investigation we assumed also irrigation with polluted water. The second investigation tested a scenario with no addition of slimes but we examined only irrigation with polluted (phosphate) water (investigation II) under the natural soil profile. The soil profile modeled for the two investigations can be seen in Figure 2.

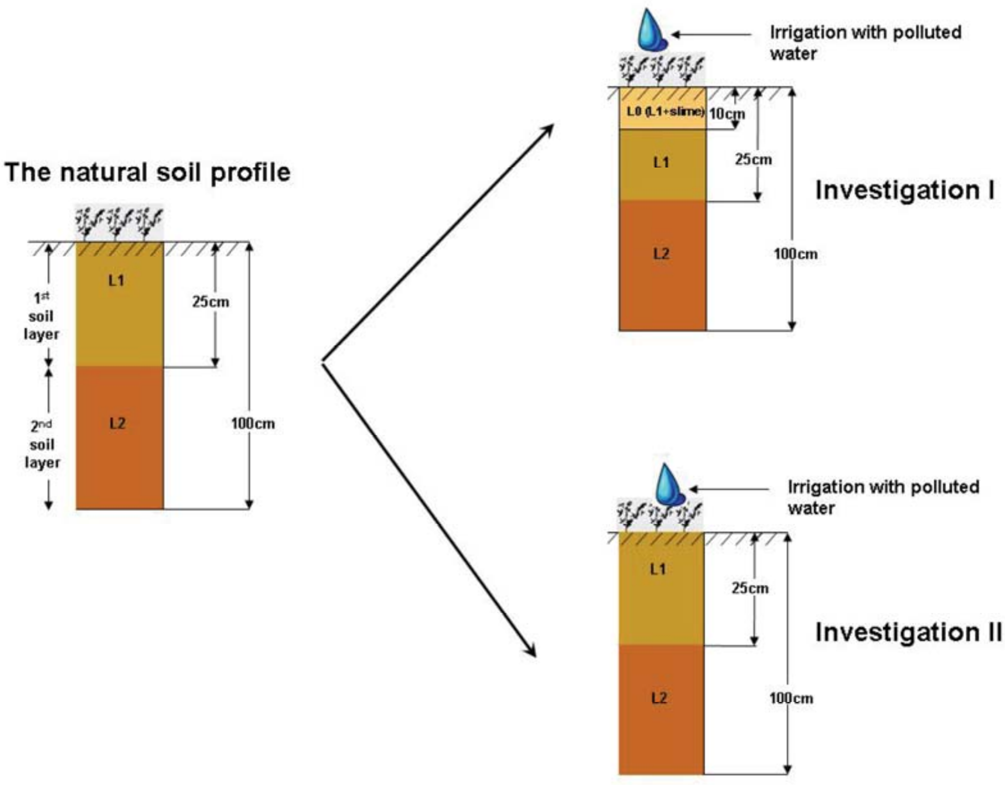


Figure 2. The physical problem for investigation I & II

3.1. Investigation I & II

Investigation I consists mainly in examining the transport of the elements under study in the case of slime addition in the top 10 cm while investigation II examines the effect of irrigation with polluted water without slime addition (Figure 2).

For investigation I the soil profile consists of three layers. The first layer called *L0* (0-10cm) is artificially created by a mixture of slime with the surface layer L1. The second layer *L1* is located from 10 to 25cm and the third *L2* from 25 to 100cm. For investigation II the modeled soil profile consisted only of the soil layers *L1* and *L2*. The percentage of Sand, Silt and Clay along with the chemical properties of the soil profile were determined by CERTE and can be seen in Tables 1 and 2, respectively.

Table 1. Sand, Silt and Clay percentage of the soil profile

Layer	**Sand (%)**	**Silt (%)**	**Clay (%)**
L0 (*L1*+slime) *(0 – 10 cm)*	40	30	30
L1 *(10 – 25 cm)*	82	10	8
L2 *(25 – 100 cm)*	42	33	25

Table 2. Chemical properties of the soil profile

Layer	**Total Carbon (%)**	**Organic Matter (%)**	**pH**	**Salinity (g l^{-1})**
L0 (*L1*+slime) *(0 – 10 cm)*	1.10	1.90	7.75	0.70
L1 *(10 – 25 cm)*	0.86	1.48	7.75	0.5
L2 *(25 – 100 cm)*	0.74	1.27	7.69	1.3

The soil parameters (θ_r, θ_s, α, n, K_s in equations 3 and 4) were determined for each soil texture with Rosetta Lite Version 1.1 (Schaap *et al.*, 2001). Table 3 shows the values of the abovementioned parameters incorporated in the Hydrus setup.

For both investigations the irrigation method of basins was examined, which is the typical irrigation method in these regions. Two different irrigation scenarios were simulated. The first was a typical irrigation covering 100% of the crops water needs with an irrigation dose of 84 mm representing regular irrigation. The second irrigation scenario covers 70% of the crops water needs and the irrigation dose was 58.8 mm representing deficit irrigation.

In addition it was assumed a mature barley plantation and a mature pasture plantation for the two irrigation scenarios. The required parameters for the root water uptake model (Feddes model) can be seen in Table 4 for the two plantations respectively.

Table 3. Values of van Genuchten model (1980)

Layer	α (cm^{-1})	**n** (-)	θ_s (cm^3 cm^{-3})	θ_r (cm^3 cm^{-3})	K_s (cm h^{-1})
L0 (*L1*+slime) *(0 – 10 cm)*	0.016	1.380	0.420	0.077	0.237
L1 *(10 – 25 cm)*	0.036	1.736	0.374	0.047	4.314
L2 *(25 – 100 cm)*	0.014	1.423	0.411	0.070	0.300

Table 4. Root water uptake model parameters for barley and pasture

Plant Water Uptakes parameters	Barley	Pasture
P_0 (cm)	-10	-10
P_{Opt} (cm)	-25	-25
P_{2H} (cm)	-400	-200
P_{2L} (cm)	-500	-800
P_3 (cm)	-8000	-8000
r_{2H} (cm day^{-1})	0.5	0.5
r_{2L} (cm day^{-1})	0.1	0.1

As a boundary condition on the top of the soil profile, for the water flow problem, the "Atmospheric boundary condition with surface layer" was used. This type of boundary condition requires information concerning potential evapotranspiration, precipitation, and irrigation. Figure 3 shows 10 years of rainfall and evapotranspiration data used in both investigations. The meteorological data were obtained at the meteorological station placed in the region under study (Metlaoui). In general, the average yearly rainfall for the region under study (data of 10 years), was 93.6 mm, ranging from 32 mm to 198 mm. The maximum daily rainfall was 36 mm. The calculated average yearly ET_0 was 1594 mm, ranging from 1483 mm to 1752 mm. The maximum ET_0 rate was 8.6 mm day^{-1} and the minimum 1.5 mm day^{-1}. In order to determine accurately the irrigation schedule for a 50-year period, a special Excel VBA application was developed, accomplishing the following steps:

- Effective rainfall evaluation
- Daily ET_0 calculation using the FAO Penmann-Monteith method.
- Evaluation of the daily values of the Crop Coefficients (K_c).
- Calculation of the daily Potential Evapotranspiration rate for each crop.
- Estimation of soil water deficit.
- Estimation of irrigation date.

As a boundary condition in the bottom of the soil profile the "free drainage" type was selected. The initial condition for the water flow was an initially dry soil (H_{in}= -400 cm).

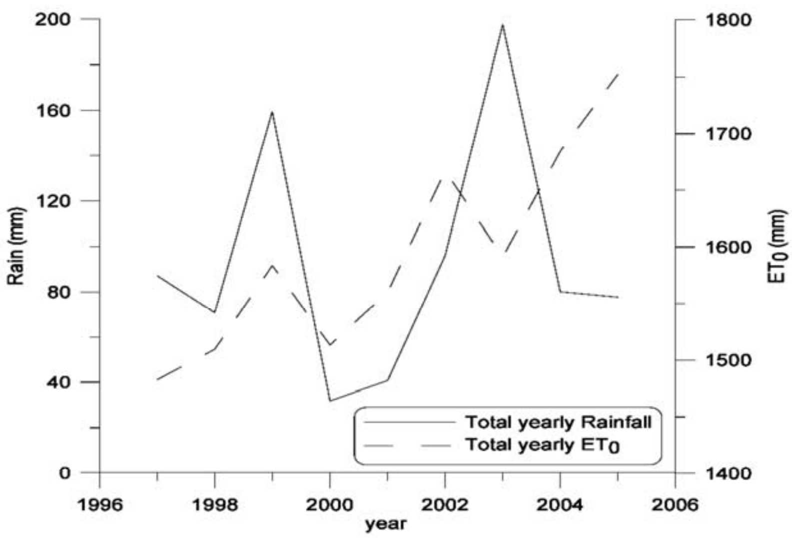


Figure 3. 10 years rainfall and evapotranspiration data used for investigation I&II

In both investigations the mobility of Cd, Cr, Ni and Sr was studied. The parameters of K_f and b used in Equation 9 were determined according to Buchter *et al.* (1989) for Cd, Cr and Ni (Selim and Amacher, 1997) and from Hsu *et al*. (1994) for Sr (Table 5). The value of longitudinal dispersivity λ was estimated experimentally for each soil layer by performing a non reactive tracer experiment at the same flow velocity and measuring its breakthrough curve in the column effluent and it was found equal to 0.59 cm for layer *L0* (layer *L1*+slime), 0.64 cm for layer *L1* and 4.3 cm for layer *L2*. The upper boundary condition for the element transport problem was:

$$-\theta D \frac{\partial C}{\partial z} + q_0 c = q_0 c_0 \qquad (11)$$

where q_0 represents the fluid flux and c_0 is the concentration of the incoming fluid [ML^{-3}]. The concentration in irrigation water c_0 for each element can be seen in Table 6. The boundary condition at the bottom (z=100 cm) of the soil profile was the zero gradient:

$$\frac{\partial C}{\partial z} = 0 \text{, for any } t \geq 0 \qquad (10)$$

The initial concentration of the elements under study for each soil layer can be seen in Table 7.

Table 5. Solute transport parameters for Cd, Cr, Ni and Sr

Layer		Studied Elements			
		Cd	Cr	Ni	Sr
L0 (*L1*+slime)	K_f	59.3	11.2	36.1	164
	b	0.74	0.501	0.741	1.04
L1	K_f	14.4	8.47	8.43	34.1
	b	0.78	0.521	0.741	1.00
L2	K_f	59.3	11.2	36.1	164
	b	0.74	0.501	0.741	1.04

Table 6. Concentration of the under study elements in irrigation water

	Cd	Cr	Ni	Sr
Concentration in irrigation water c_0 (mg l^{-1})	0.04	0.07	0.01	10.2

Table 7. Initial concentration in mg kg^{-1} for each soil layer and for each element

Layer	Studied Elements concentrations (mg kg^{-1})			
	Cd	Cr	Ni	Sr
L0 * (*L1*+slime)	8.9	32.0	10.3	55.9
L1	1.06	12	5.36	2.68
L2	1.06	12	5.36	2.68

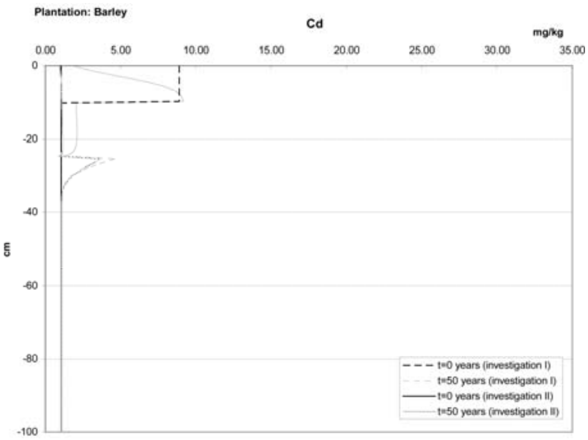
* Only in investigation I

4. RESULTS AND DISCUSSION

Figures 4a, b, c, d show soil concentration profiles for Cd, Cr, Ni and Sr, for both investigations and for the barley plantation. In these figures we can see soil concentration profiles for the initial condition (*t* = 0 years) and for the final simulation time (*t* = 50 years) for both investigations. In investigation I we assumed slime addition in the first 10 cm and for this reason the initial concentration at the top 10 cm in investigation I is different from investigation II. Comparing the elements under study it is obvious that for both investigations the elements reached almost the same depth. The most mobile element was Cr, which reached 100 cm after 50 years, and Cd was the less mobile (around 35 cm). In the case of Sr (Figure 4d), a high amount of the element was found in irrigation water. Comparing the two investigations in Figure 4d, it can be seen that both investigations reached almost 50 cm but the second investigation gave higher element concentration in the soil layer *L2*. This means that more element concentration reached the layer

L2 in investigation II. On the contrary, the total mass of the element was greater in investigation I (high initial concentration in layer *L0* due to slime addition). So, we can conclude that the addition of slime retards the movement of these elements.

(a)



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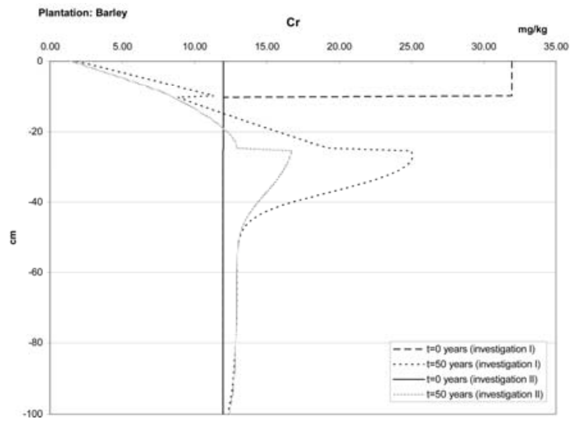

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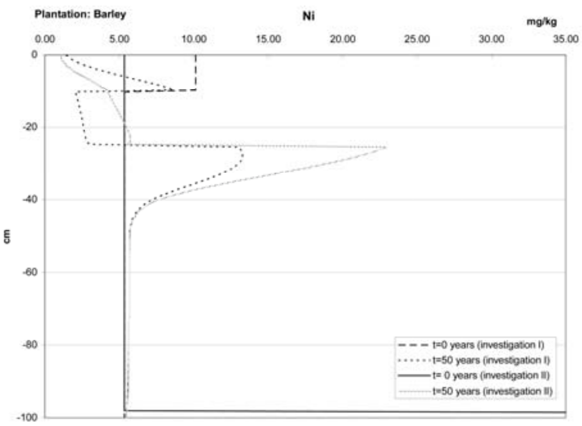

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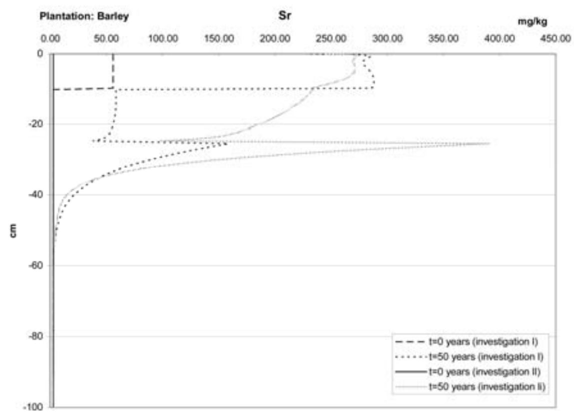

Figure 4. Soil concentration profiles for (a) Cd, (b) Cr, (c) Ni and (d) Sr after 50 years for the two investigations and for the Barley plantation (in the initial condition for the depth 10 to 100 cm the element concentration for Investigation I and II are the same)

Figures 5 a, b, c and d show concentration profile after 50 years for Cd, Cr, Ni and Sr, for both investigations but for the pasture plantation. Again, Cr was the most mobile and Cd the less mobile element. Comparing Figures 4 and 5, it is obvious that all the elements reached greater depths in the case of pasture plantation. Barley generally needs less water than pasture (the average yearly irrigation water application in this study was 580 mm for Barley and 1180 mm for pasture).

Figures 6 a and b show Cd and Cr concentration profiles for investigation I after 50 years for regular and deficit irrigation and for the barley plantation. Figures 7a and b show the same profiles but for the pasture plantation.

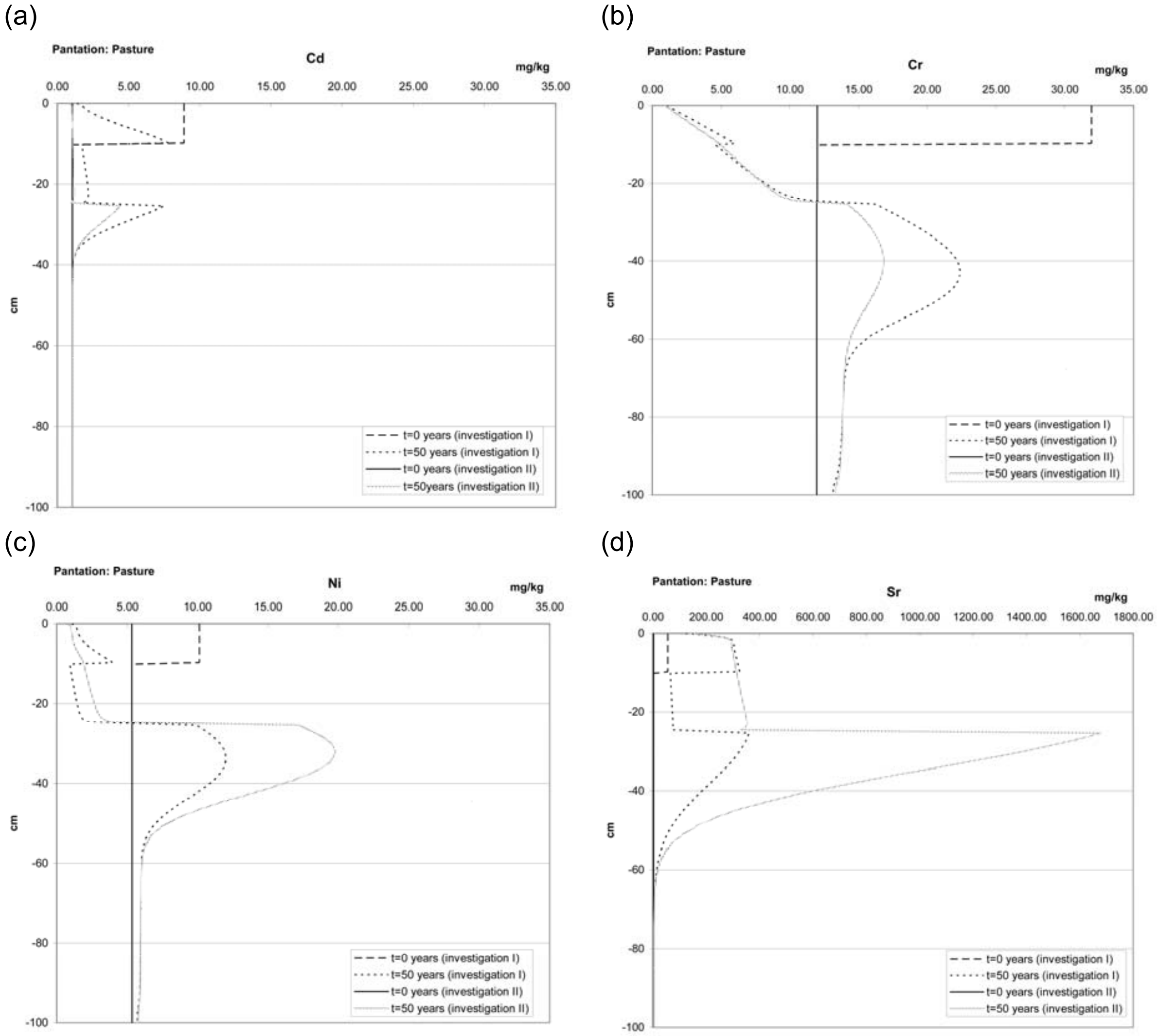

Figure 5. Soil concentration profiles for (a) Cd, (b) Cr, (c) Ni and (d) Sr after 50 years for the two investigations and for the Pasture plantation (in the initial condition for the depth 10 to 100 cm the element concentration for Investigation I and II are the same).

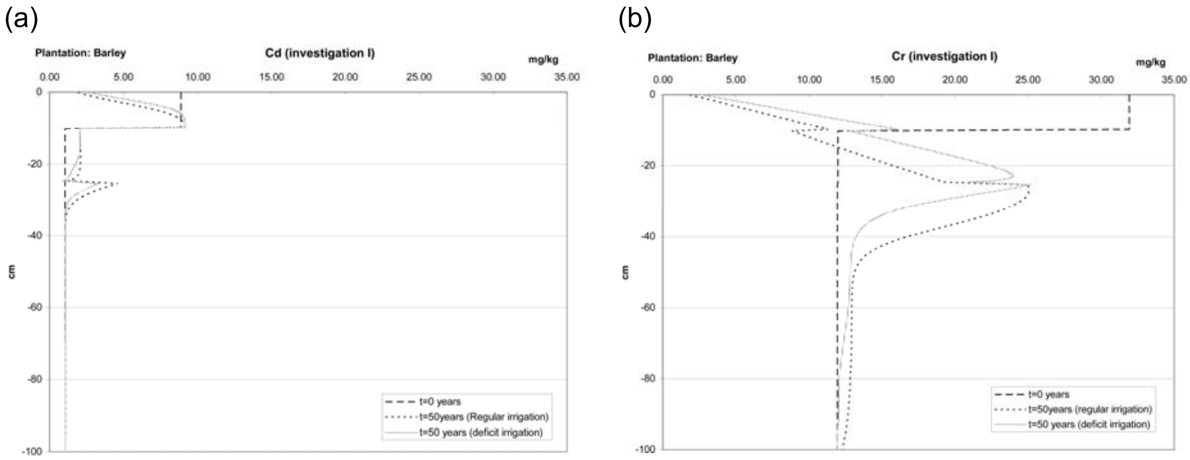

Figure 6. Soil concentration profiles for (a) Cd and (b) Cr after 50 years for investigation I, for the two irrigation scenarios and for the Barley plantation.

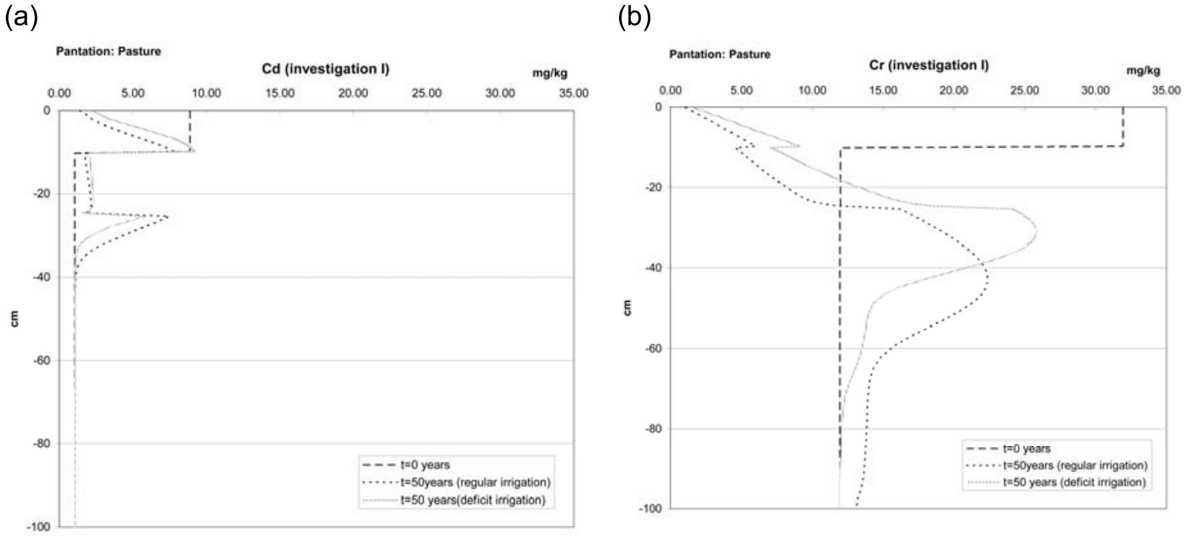

Figure 7. Soil concentration profiles for (a) Cd and (b) Cr after 50 years for investigation I, for the two irrigation scenarios and for the Pasture plantation.

The results show that in the case of deficit irrigation the elements were less mobile than in the case of regular irrigation. Also, in the case of pasture the differences between regular and deficit irrigation were greater than in the case of barley. These results are due to the higher irrigation applied in the case of pasture. They show that the mobility of these elements is highly dependent on the applied irrigation dose. High application of irrigation water increases the elements depth and decreases the maximum concentration value for the upper layer *L0*. In the case of regular irrigation higher amount of the elements reached the layer *L2* and so the concentration in layer *L2* was greater in the case of regular irrigation, except Figure 7b (in the upper limit of layer *L2*) in which the concentration was greater in the case of deficit irrigation. This is due to the fact that an important quantity of water (regular irrigation for pasture) transported the very mobile Cr in the deeper layers and decreased the concentration of the element in the upper limit of layer *L2*.

The mobility of the elements under study follows the relationship below:

- Cr>Sr>Ni>Cd for both investigations and for both irrigation scenarios.

This conclusion is strongly dependent on the Freundlich isotherms (Equation 9) used in this study. The parameters describing these isotherms correspond to soils with similar characteristics (pH, organic matter content, percentage of Sand, Silt, Clay, etc) provided by Selim and Amacher (1997) and by Hsu *et al*. (1994) for Sr. The soil under investigation have pH greater than 7. These conditions favor the low mobility of the elements under investigation.

In general, the results show that there is no significant risk of polluting the aquifer if the phosphate slime or the phosphate water is used for agricultural purposes. On the contrary, the mobility of these elements in the case of preferential flow must be examined. Hydrus can also implement preferential flow into numerical simulations. Further research must be carried out in this direction.

5. CONCLUSIONS

The use of phosphate slime or phosphate water in a typical soil of Gafsa area (Tunisia) for agricultural use was examined. The simulations were made with the use of the Hydrus 1D software package. The elements under study were Cd, Cr, Ni and Sr. The results show that there is no significant risk of polluting the groundwater with these elements. The results also show that the mobility of these elements is highly dependent on the applied irrigation dose. These pollutants need high amounts of water in order to reach great depths. Moreover, slime addition retards the movement of these elements. Field experiments in the region under study, simulations for a longer period and the existence of preferential flow must be investigated in future work in order to use safely the phosphate slime or the phosphate water for agricultural purposes.

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