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Application of Hydrus -1D Model to Simulate the Transport of some Selected Heavy Metals in Paddy Soil in Thanh Trì, Hanoi

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Abstract: Application of fertilizers and pesticides or using waste water for irrigation can result in an accumulation of heavy metals (HM) in cultivation areas. Under flooding condition of the paddy soils, HM can be leached and result in a potential risk for groundwater. In this study, Hydrus – 1D was applied to simulate the infiltration of Cu, Pb and Zn in paddy soils (in Huu Hoa, Dai Ang and Ta Thanh Oai communes, Thanh Tri district, Hanoi) in the time span from 1 to 720 days. Simulations were based on input data of the soils: texture, bulk density, Freundlich constants (K_f and β), head pressure as 20 cm ± 10 cm and assummed concentrations of the HM in irrigated water as 0.5 mmol Cu cm^{-3}, 0.1 mmol Pb cm^{-3} and 0.75 mmol Zn cm^{-3}.

Leaching rates of the HM were observed to decrease in the order: Zn > Cu > Pb. Under constant flooded conditions at a water table of 20 cm, Cu, Pb and Zn were estimated to reach 1 m deep in the soil domain within 193, 312 and 450 days, respectively. At water layers of 10 and 30 cm, the leaching rate of HM increase or decrease 17%, respectively. Speciation experiments revealed that Zn transport might be affected by the presence of Fe-, Al-oxides, while the factor prohibiting the leaching rate of Cu was soil organic matter. Pb showed a strong dependence on both Fe-, Al-oxides and organic matter. These results reinforce the necessity of using transport models to improve predictions of HM transport and more efficient remediation of contaminated aquifers. Uncertainties in modeling arise as several parameters in the simulation can be determined only with significant errors. However, Hydrus-1D is a suitable tool for simulation of the transport of HM in paddy soil.

Keywords: Hydrus-1D, simulation, transport, heavy metal, paddy soil.

1. Introduction

The accumulation of HM e.g. Cu, Pb and Zn in surface soils by application of fertilizers and using domestic wastewater for irrigation has been reported in many studies [1-3]. HM can be leached from the topsoil which results in a contamination in the subsoil or groundwater pollution. Recently, many numerical models can be used to simulate the transport of pollutants in general or the leaching of HM in soil in particular. These are helpful tools to generalize the fate or behavior of pollutants in soils. There are a number of models coded to

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simulate the transport of pollutants from surface layer into soils, e.g.Hydrus-1D, PADDY, RICEWQ, DynA. Two models, PADDY and RICEWQ, have been used to simulate the concentration of organic pollutants in water and sediment [4] and the dynamic and mobility of pesticides in paddy soils [5]. However hydrological parameters and meteorological conditions e.g. rainfall and evaporation have not been included as input data in these both models [6]. Hydrus-1D model introduced by Šimůnek*et al.* (1998) was used to simulate infiltration and the one - dimensional transport of solutes with various boundary conditions, so that it might also be applied for flooded condition [7]. This work applies Hydrus-1D model to simulate the movement of Cu, Pb and Zn in the paddy soils in Thanh Tri, Hanoi as a case study.

2. Materials and Methods

2.1. Materials

Simulation of the HM transport was performed for three soil profiles at the cultivation areas in Dai Ang Huu Hoa and Ta Thanh Oai commune, Thanh Tri, Hanoi. For each soil profile, samples were collected at the depth of 0 ÷ 25, 25 ÷ 50, 50 ÷ 75 and 75 ÷ 100 cm, air - dried, homogenized and passed through 2mm-sieve. Some physicochemical properties of soil samples were presented in Table 1.

Table 1. Some physicochemical properties of studied soil samples

Location	Depth	pH_{KCl}	OM content	Fe_2O_3	Al_2O_3	Texture(%)			Bulk density
	cm	_	%C	%	%	Clay	Silt	Sand	g/cm^3
Dai Ang	0 - 25	6.11	2.60	5.99	15.49	23.3	61.3	15.4	1.34
	25 - 50	6.11	1.80	4.79	11.19	11.2	33.3	55.5	1.53
	50 - 75	6.08	2.00	5.83	14.63	19.2	52.1	28.7	1.39
	75 - 100	6.07	2.00	4.23	15.34	25.1	42.3	32.6	1.36
Huu Hoa	0 - 25	6.45	2.70	9.12	10.04	30.7	43.1	26.2	1.32
	25 - 50	6.89	1.60	7.99	17.52	29.2	22.3	48.5	1.37
	50 - 75	6.91	1.60	8.14	18.07	27.3	52.4	20.3	1.32
	75 - 100	6.63	1.30	7.83	17.68	29.5	42.2	28.3	1.33
Ta Thanh Oai	0 - 25	6.89	2.53	5.43	17.52	25.2	51.1	23.7	1.34
	25 - 50	7.12	1.45	9.26	18.82	20.6	35.3	44.1	1.43
	50 - 75	7.08	1.03	6.55	22.94	25.7	50.8	23.5	1.34
	75 - 100	6.64	1.03	4.95	21.83	28.5	43.6	27.9	1.33

The samples have neutral reaction with pH values change from 6.07 to 7.12 (exchanged with KCl 1M, 1/5 w/v). Determination of organic matter (OM) by Walkley-Black method showed that C (%) were 1.03 ÷ 2.60. By complexon method, Al_2O_3 and Fe_2O_3 determined to be 11.19 ÷ 22.94% and 4.23 ÷ 9.26%, respectively. Results of XRD (PHILIPS X-ray spectrometer PW2404) revealed that illite, kaolinite and chlorite are major soil clays in these samples.

2.2. Methods

2.2.1. Determination of Freundlich adsorption coefficient

The interaction between HM in liquid phase and solid phase can be expressed in the equation: $Q_s = K_F C_e^{\beta}$ (1)

Where Q_s denotes the amount of solute sorbed under equilibrium conditions (mmol kg^{-1}); C_e is the concentration in the equilibrium solution (mmol L^{-1}); K_F represents an affinity constant ($L^{\beta}mmol^{1-\beta}$ kg^{-1}); The regression β provides the relative saturation of the adsorption sites.

Freundlich constants (K_F and β) were determined from HM adsorption experiments. These experiments were conducted as follows: 2g sample was mixed with 20 mL solution in concentration of 3 – 15 mmol L^{-1} for Cu and Zn; 4 – 18 mmol L^{-1} for Pb (ratio of 1:10) in a centrifuge tube as described method elsewhere [8-11]. The metal solutions were prepared from nitrate salts. Solution – soil systems were shaken for 2h, kept overnight and then centrifuged at 3000 r.p.m. HM (Cu, Pb, Zn) were determined by atomic absorption spectroscopy (AAS) method (Perkin Elmer AA 800). Freundlich coefficient (K_F and β) were calculated from the linear form of the Freundlich equation (1).

2.2.2. Flow and transport modeling

Water flow and reactive transport of HM was modeled using the finite-element model Hydrus-1D which was introduced by Šimůnek et al. (1998) and since that time has been used in more than hundred studies and is still further developed. In Hydrus-1D, water flow is described by the Richards equation. The temporal change of solute concentration in the liquid phase, c (M L^{-3}), and in the sorbed phase, S (M M^{-1}), is described with the convection–dispersion equation:

$$\frac{\partial \theta c}{\partial t} + \frac{\partial \rho S}{\partial t} = \frac{\partial}{\partial X}\left(\theta D \frac{\partial c}{\partial X}\right) - \frac{\partial q c}{\partial X} \qquad (2)$$

In which: c is HM concentration in solution (M L^{-3}), S the amount of adsorded HM (M M^{-1}), θ (L^3 L^{-3}) denotes the volumetric water content, ρ (M L^{-3}) the soil bulk density, D (L^2 T^{-1}) the dispersion coefficient for the liquid phase, q(L T^{-1}) the volumetric water flux density, t (T) time and X (L) is the spatial dimension. The correlation between HM concentration in the liquid phase and HM amount adsorbed on the solid phase is expressed in Freundlich equation.

The movement of HM was simulated for a 1m deep soil domain in the time span up to 720 days. The lower boundary condition was a seepage face and the upper was a constant head pressure (resulted by a water layer of 20 cm built up on the field). Other soil physicochemical properties (in Table 1 and Table 2) are also used as input data for simulation. The concentration values of Cu, Pb, Zn were setup in corresponding to the actual concentration of the wastewater used for irrigation 0.5, 0.1 and 0.75 mmol cm^{-3}, respectively. The simulation of Cu, Pb, Zn concentration in the soil solution at different observation nodes N1, N2, N3, N4 represented for the depth of 25 cm, 50 cm, 75 cm, 100 cm respectively, and the different times T1, T2, T3, T4 represented for 180, 360, 540, 720 days, respectively.

3. Results and discussions

3.1. Adsorption of heavy metal

The results of adsorption experiments allowed to establish the Freundlich adsorption isotherms representing the relationship between the HM-adsorbed amount on the solid phase (Q_s) and the concentration of HM in the equilibrium solutions (C_e). By converting the Freundlich equation to linear forms, Freundlich constants were determined and used for comparison of the adsorption capacity of HM (Table 2).

Table 2. Freundlich constant K_F and β for heavy metal of the different soil layers

Location	Depth (cm)	Cu		Pb		Zn	
		K_F	β	K_F	β	K_F	β
Dai Ang	0 – 25	19.21	0.32	23.83	0.58	16.44	0.21
	25 – 50	18.16	0.29	21.29	0.59	13.14	0.24
	50 – 75	18.93	0.31	20.79	0.54	15.86	0.25
	75 – 100	18.02	0.33	20.15	0.60	16.19	0.31
Huu Hoa	0 – 25	23.69	0.45	24.08	0.69	17.03	0.34
	25 – 50	20.54	0.42	22.07	0.65	16.64	0.32
	50 – 75	21.65	0.44	24.82	0.62	16.84	0.27
	75 – 100	22.62	0.39	21.89	0.59	16.78	0.33
Ta Thanh Oai	0 – 25	20.14	0.40	24.70	0.60	16.90	0.39
	25 – 50	20.10	0.38	24.50	0.63	17.40	0.39
	50 – 75	19.40	0.40	23.80	0.60	18.85	0.29
	75 – 100	19.40	0.39	22.70	0.61	17.83	0.30

The results showed that K_F constant for Pb was highest followed by Cu and Zn (Table 2). The adsorption capacity of HM decreased in the order: Pb > Cu > Zn. This inferred that it takes longer time for Pb to transport from the surface to 1m deep in the soil domain as compared to Cu and Zn. The β< 1 for all samples and HM suggested a decreasing energy of sorption with increasing saturation of the exchange sites.

The K_F coefficient showed a high dependence on soil properties. High K_F coefficients were found for Cu in the soil samples with large amount of organic matter, and those for Zn in the samples with high total amount of Al_2O_3 and Fe_2O_3. This can be explained that Cu was strongly absorbed by organic matter while Zn was strongly associated with Al-, Fe-oxides. Factors affecting the adsorption capacity for Pb were not be clarified in this work.

3.2. Simulation of heavy metal transport

The simulation shows that among the elements under the investigation, Zn is preferentially leached into the soil domain in comparison with Cu and Pb (Figure 1-3). At all observation nodes, Zn appears earliest. At the bottom the the 1 m deep soil domain, concentration of Pb^{2+}, $Cu^{2+}$and Zn^{2+}increased after 450, 312 and 193 days, respectively. This can also be seen from the figures (1-3) that the change of HM concentrations were along the depth of the soil domain in which Zn and Cu have broader curves as compared to Pb. Because Pb was trapped in the upper soil layer, it would have potential to contaminate the topsoil, while Zn and Cu showed a higher potential to contaminate groundwater.

Leaching rate of HM showed a strong dependence on soil properties. The layer 0 ÷ 50 cm with relatively high organic matter and clay contents tends to accumulate HM and prohibits leaching. Steep curves at N1 and N2 indicate a low dispersity for HM, whereas the broader curves of N3 and N4 suggest higher dispersities for all HM at layers > 50 cm. This is agreement with the findings from Nguyen et al. [8], Le et al. (2000) [12] and Wang et al. (2003) [13]. In these studies, Zn was reported to have a higher mobility in comparison with Cu and Pb.

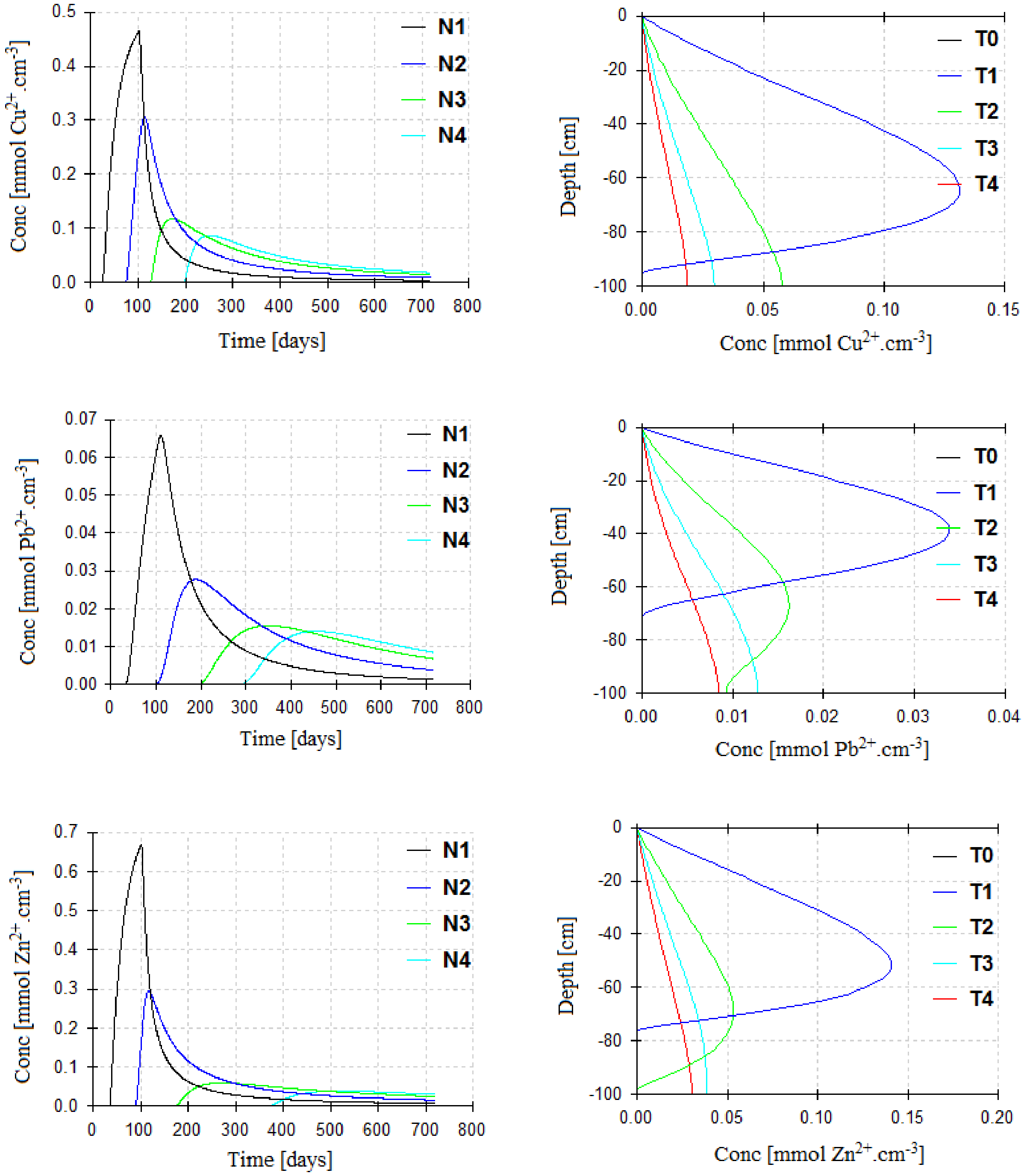

Figure 1. Simulation of HM concentrations in the soil solution at different observation nodes for Dai Ang soil profile.

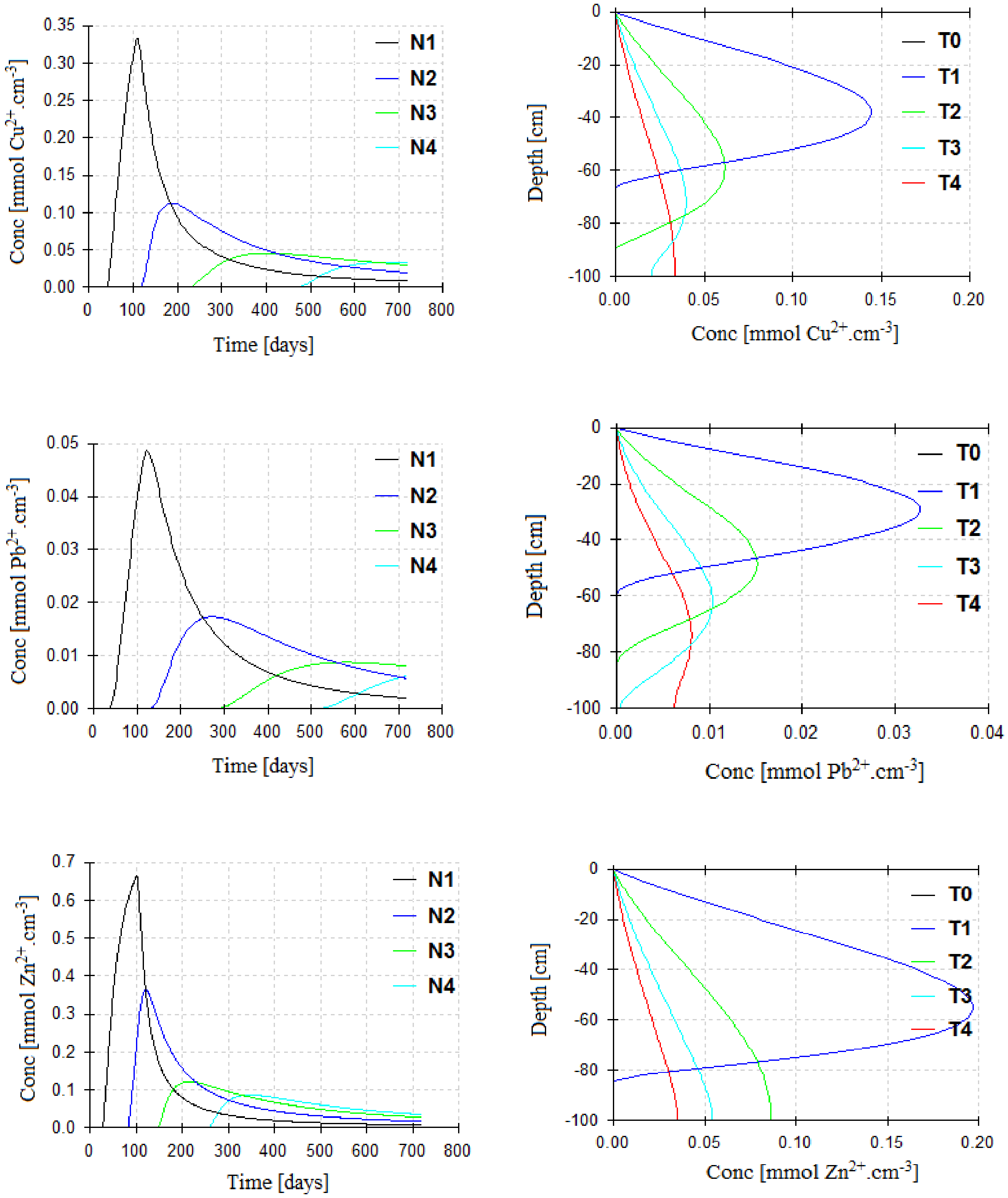

Figure 2. Simulation of HM concentrations in the soil solution at different observation nodes for Huu Hoa soil profile.

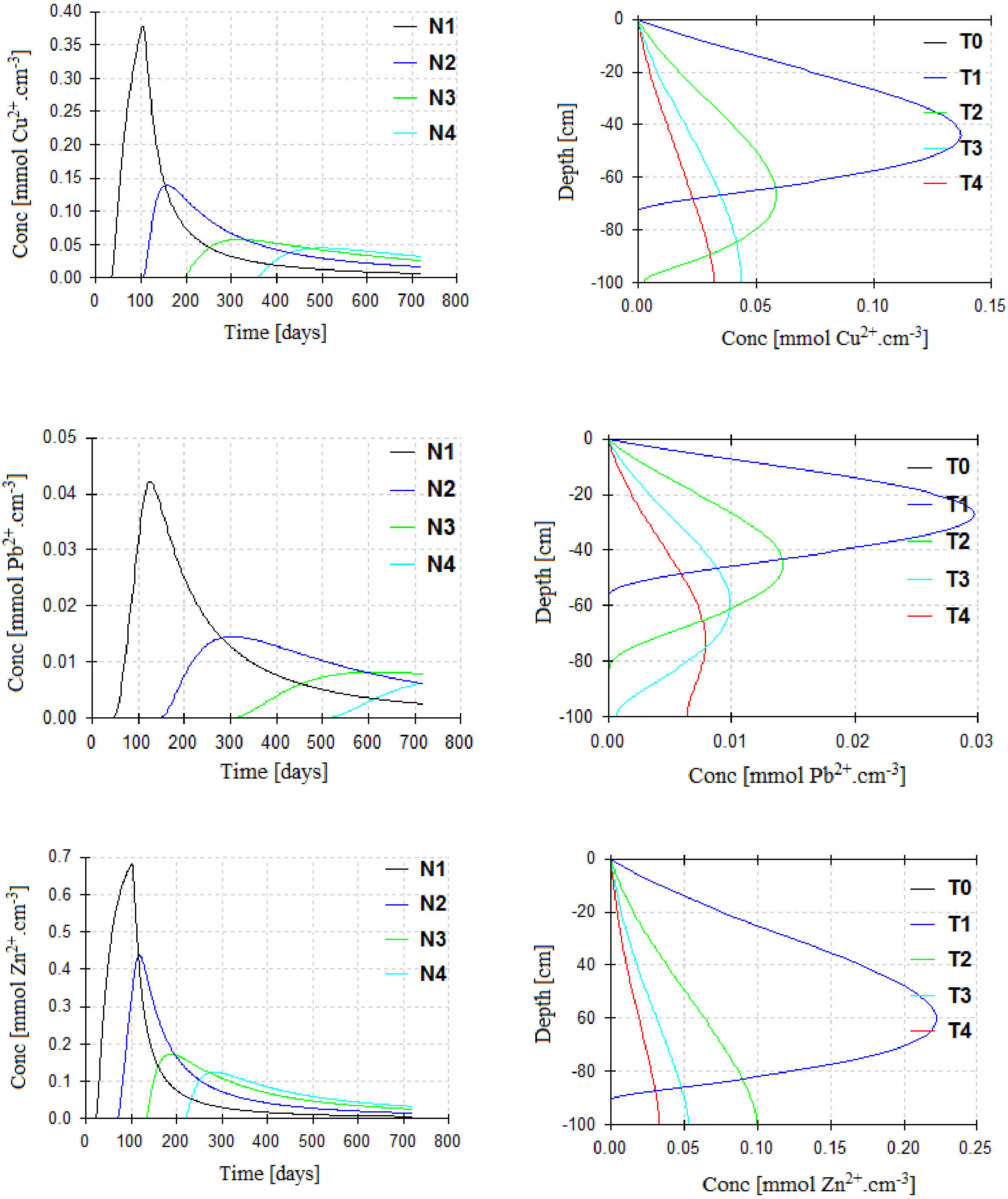

Figure 3. Simulation of HM concentrations in the soil solution at different observation nodes for Ta Thanh Oai soil profile.

3.3. Uncertainties in modeling

A change of surface water layer influences the head pressure and can influence the leaching rate of HM as a consequence. An increase of the water table can accelerate HM transport, whereas low leaching rate of HM can be resulted due to a decrease of water layer. With the water layer increased or decreased 10 cm, corresponding leaching rates of ± 17% were obtained.

The appearance of the preferential flows (resulted by the presence of "soil cracks" e.g. in dry season, activities of the soil fauna or root growths) may have certain effects. The preferential flow can accelerate the movement of HM to the deeper layer. In addition, HM can be absorbed on soil colloids, so that the mobility of soil colloids (clay minerals) is a factor accelerating the transport of sorbed ions [[8]]. The decomposition of organic matter and the decomposition of inorganic minerals are likely to increase HM concentrations in soil solution. In contrast, the formation and the accumulation of organic matter can retain HM and reduce the leaching rate and increase the infiltration time of HM in soils.

4. Conclusion

Factors affecting the movement of HM include: soil physical properties (texture, bulk density), adsorption coefficients (K_F) and head pressure caused by the water layer on the surface of profile. The K_F coefficient showed a high dependence on soil chemical properties. The high K_F coefficients were found for Cu in the soil samples with large amount of organic matter.Similarly, high K_F coefficients were found for Zn in the samples with high total amount of Al_2O_3 and Fe_2O_3. Pb showed a strong correlation with both organic matter and Al_2O_3 and Fe_2O_3 oxides.

With a water layer of 20 cm, Pb^{2+}, Cu^{2+} and Zn^{2+} reached the bottom of the soil domain after 450, 312 and 193 days, respectively. A change of water layer can affect the transport of HM. With a change of the water of ± 10 cm, corresponding leaching rates of HM were ± 17%. These results reinforce the necessity of using transport models to improve predictions of HM transport and more efficient remediation of contaminates aquifers. On the other hand, influence of parameter uncertainties and modeling imponderability upon the simulation results should also be considered in further studies.

References

[1] Chu, A.D., Nguyen, N.M., Pham, V.A., Khuong, M.P., Nguyen, M.K., 2012. Investigation on accumulation of heavy metals (Cu, Pb and Zn) in cultivated soils of the Thanh Tri district, Hanoi. VNU Journal of Science, Natural Science and Technology, 28, 26-32 (in Vietnamese)

[2] Nguyen, M.K., Pham, Q.H., Ingrid Öborn, 2007. Nutrient flows in small-scale peri-urban vegetable farming systems in Southeast Asia - A case study in Hanoi. Agriculture, Ecosystems and Environment, 122, 192-200.

[3] Nguyen,. M.K, Pham,Q.H, Ingrid Öborn, 2006. Element balance as a tool to assess the potential risk contamination for soil environment – A case study of heavy metal balance in peri-urban agriculture of Hanoi city. Vietnam Soil Science, 26, 112-118 (in Vietnamese)

[4] Infantino A., Pereira T., Ferrari C., Cerejeira M.J., Guardo A.D., 2008. Calibration and validation of a dynamic water model in agricultural scenarios. Chemosphere 70, 1298-1308.

[5] Christen E.W., Chung S.O., Quayle W., 2006. Simulating the fate of molinate in rice paddies using the RiceWQ model. Agri. Water Manage. 85, 38-46.

[6] Inao K., Kitamura Y., 1999. Pesticide paddy field model (Paddy) for predicting pesticide concentrations in water and soil in paddy fields. Pest. Sci. 55, 36-42.

[7] Šimůnek, J., Sejna, M., van Genuchten, M.Th., 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, IGWMC-TPS-70, International Ground Wate rModeling Center, Colorado School of Mines, Golden.

[8] Nguyen N.M., Dultz S., Kasbohm J. (2009). "Simulation of retention and transport of copper, lead and zinc in a paddy soil of the Red River Delta, Vietnam", Agriculture, Ecosystems and Environment ,129, pp 8–16.

[9] Wan Zuhairi, W.Y. 2003a. Sorption capacity on lead, copper and zinc by clay soils from South Wales, United Kingdom. Journal of Environmental Geology, 45(2), 236 - 242.

[10] Wan Zuhairi, W.Y. 2003b. Heavy Metal Sorption Capabilities of some Soil Samples from Active Landfill Sites in Selangor. Geological Society of Malaysia Bulletin, 46, 295-297.

[11] Wan Zuhairi W.Y. 2004. Natural sorption capability of heavy metals: Granitic residual soil from Broga and marine clay from Sg. Besar Selangor. Geological Society of Malaysia Bulletin, 48, 13-16.

[12] Le, D., Pham, V.K., Le, B.V.B., Duong, T.O., 2000. Preliminary study on adsorption capacity and diffusion rate of heavy metals in Red River alluvial soil at Trung Van commune, Tu Liem district, Hanoi. In: Proceedings of the Second Scientific Conference, University of Science on Environmental Science. Vietnam National University Publishing House-2000, p. 152. (in Vietnamese)

[13] Wang, C.X., Mo, Z., Wang, H., Wang, Z.J., Cao, Z.H., 2003. The transportation, time-dependent distribution of heavy metals in paddy crops. Chemosphere 50, 717–723.

Ứng dụng mô hình Hydrus - 1D mô phỏng sự dịch chuyển của một số kim loại nặng trong đất lúa huyện Thanh Trì, Hà Nội

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Tóm tắt: Sử dụng phân bón, thuốc bảo vệ thực vật hay dùng nước thải để tưới có thể dẫn đến sự tích lũy các kim loại nặng (KLN) trong đất canh tác. Dưới điều kiện ngập nước (ví dụ: canh tác lúa), các KLN có thể tồn tại ở dạng tự do (ion) và là một trong những nguy cơ tiềm ẩn gây ô nhiễm nước ngầm khi bị rửa trôi. Nghiên cứu này ứng dụng mô hình HYDRUS – 1D để mô phỏng sự di chuyển của Cu, Pb và Zn theo chiều sâu trong khoảng thời gian 720 ngày, và áp dụng cho phẫu diện đất lúa tại xã Hữu Hòa, Đại Áng và Tả Thanh Oai, huyện Thanh Trì, Hà Nội. Dữ liệu đầu vào để chạy mô hình bao gồm: thành phần cơ giới, dung trọng, hệ số hấp phụ đẳng nhiệt Freundlich (K_F và β), áp suất thủy tĩnh và nồng độ các ion kim loại.

Kết quả mô phỏng với phần mềm Hydrus-1D cho thấy, tốc độ di chuyển của kim loại nặng giảm theo thứ tự: Zn > Cu > Pb. Thời gian để Zn, Cu và Pb và di chuyển qua tầng đất mặt với chiều sâu 1m lần lượt là 193, 312 và 450 ngày. Khi lớp nước trên bề mặt tăng thêm hoặc giảm đi 10 cm, tốc độ di chuyển sẽ tăng hoặc giảm tương ứng là 17%. Tốc độ di chuyển của Zn^{2+} bị chi phối bởi sự có mặt của các oxit sắt nhôm, trong khi đó Cu^{2+} chịu tác động của thành phần hữu cơ đất. Ion Pb^{2+} bị hấp phụ mạnh bởi cả oxit sắt nhôm và chất hữu cơ. Kết quả nghiên cứu cho thấy nguy cơ tiềm ẩn ô nhiễm nước ngầm bởi sự di chuyển của các KLN từ lớp đất mặt. Một số yếu tố có thể ảnh hưởng đến việc đánh giá khả năng di chuyển của kim loại nặng trong điều kiện thực như: áp suất thủy tĩnh, sự hút thu của cây trồng, dòng chảy ưu thế, phân bón,... sẽ được đề cập đến trong các nghiên cứu tiếp theo.

Từ khóa: Hydrus-1D, mô phỏng, di chuyển, kim loại nặng, đất lúa.