Simulation of Herbicide Transport in an Alluvial Plain

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Abstract: Herbicide transport through the vadose zone was studied in the Upper Rhône River Valley (South-West Switzerland). The herbicides atrazine and isoproturon were applied to instrumented field plots and the concentrations reaching the groundwater were measured. The solute transport is closely linked to precipitation. Following the first heavy rainfall after the application, the chemicals are quickly transported through the vadose zone and reach the groundwater in a short time. The transport experiments were simulated with the mechanistic deterministic model HYDRUS-1D. The mobile-immobile water concept was used to account for the rapid transport. In the study area, the shallow groundwater influences considerably the water conditions in the unsaturated zone; in such cases the use of a one-dimensional model to simulate the water flow and the chemical transport in the vadose zone is difficult because of problems in defining the lower boundary condition. Groundwater flow is typically three-dimensional and therefore, a saturated - unsaturated 3-D model or the coupling of an unsaturated 1-D model to a 3-D saturated model would be more appropriate. Nevertheless, HYDRUS-1D allowed to describe qualitatively some observations and to confirm the assumption that accelerated flow occurs on the experimental plots.

Keywords: herbicide transport; groundwater contamination; water and transport modeling

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1. INTRODUCTION

The contamination of groundwater (GW) by pesticides has become an increasing problem throughout the last decades. Pesticides that are ineffectively retained or rapidly transported through the unsaturated zone may reach the GW. The transport of pesticides in the unsaturated zone depends on the physico-chemical characteristics of the substance, on the intensity and frequency of its application, on the soil properties, and on regional characteristics such as climate and hydrogeology. Heavy rainfall may transport chemicals deep into the vadose zone, especially in highly porous or fractured soils [Flury et al., 1998]. Shallow GW tables are especially vulnerable for such pesticide contamination [Flury, 1996].

Transport experiments may be carried out using different techniques at several scales. In order to analyse the experiments, numerical models are often used. Within the last decades several models have been developed to simulate the water flow and solute transport in agricultural environments [Wauchope et al., 2003], some of them account for physical non-equilibrium processes [Simunek et al., 2003].

Mechanistic models that account for physical non-equilibrium have recently been divided into two groups: dual-porosity and dual-permeability models [Simunek et al., 2003]. Both groups divide the soil into two separate pore domains. While dual-porosity models assume that water in the matrix domain is stagnant, dual-permeability models allow for water flow in both, the macropores and the micro (matrix) pores [Simunek et al., 2003]. Dual-permeability models are frequently used to describe flow and transport in fractured or structured media displaying shrinkage cracks, earthworm channels, root cracks, or heterogeneous soil textures [e.g., Larsson and Jarvis, 1999]. In dual-porosity models the water flow is restricted to one flow domain (inter-aggregate pores), while the matrix domain (intra-aggregate pores) retains and stores water, but does not permit convective flow. An exchange between the pore regions is described as a first-order process. This mobile-immobile water concept [MIM; Van

Genuchten and Wierenga, 1976] is often used to describe solute transport processes in aggregated porous media [Vanderborght et al., 1997].

This paper describes the simulation of transport experiments carried out in the Rhone River Valley between Martigny and Charrat (Switzerland). Two herbicides and a tracer were applied to instrumented field plots and the concentrations reaching the groundwater were measured. The model HYDRUS-1D was chosen for the simulations and a dual-porosity approach was used to simulate the observed transport. The simulations aimed at explaining the dominant processes involved in pesticide transport towards the shallow GW table.

2. MATERIALS AND METHODS

Experimental plots (2,50 m x 1,60 m) were instrumented in April 2001 with TDR probes and tensiometers between the soil surface and 1 m depth. Additionally, 2.5 m deep stainless steel piezometers and a rain gauge were installed. Two herbicides and Iodide (tracer) were applied to the bare soil surface on May 24, 2002. During the following months, groundwater samples were collected using a peristaltic pump. The samples were analysed for their solute concentration using HPLC.

The soil at the experimental site is a rather homogeneous silt loam with low organic carbon and clay contents. Because the solutes reached the shallow GW table (1.4-2 m depth) surprisingly quick, a dual-porosity model was used to simulate the accelerated transport. Moreover, evaporation in the valley is strong and varies considerably within a day; therefore, an hourly time step had to be considered for the simulation of the strong capillary rise and quick flux changes derived from the experiments.

Water flow and solute transport were simulated with HYDRUS-1D, a mechanistic deterministic model. It uses Richard's equation for water flow and the Convection-Dispersion Equation for solute transport. The model allows for dual-porosity calculations using the MIM-concept. Boundary conditions like evaporation and rainfall can be introduced at an hourly time step.

3. OBSERVATIONS

Figure 1 shows the herbicide concentration in the GW during the summer 2002 and the water table depth. Hardly any chemicals were found in the GW during the first two weeks without rainfall after the application (Fig. 1). After the first heavy precipitation on June 5, a sudden peak was observed. The concentrations decreased during the following dry period and a second concentration peak appeared as a consequence of rainfall at the end of June (49 mm). A third attenuated concentration peak was observed in mid July. The concentration development of the two herbicides is very similar. Moreover, the tracer iodide was transported as quickly as the herbicides (Fig. 2) indicating that adsorption does not play a predominant role in this soil.

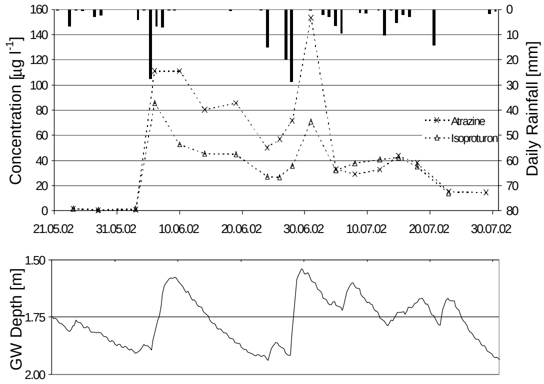

Figure 1: Herbicide concentration in GW, daily rainfall, and depth of the GW table

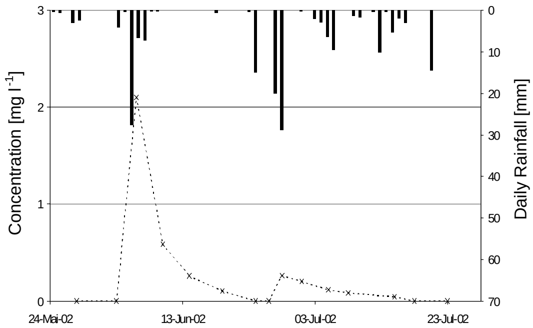

Figure 2: Iodide concentration in the GW and daily rainfall

4. NUMERICAL MODELING

The experiment has been simulated with the mechanistic deterministic model HYDRUS-1D [Simunek et al., 1998]. The aim of the simulations was to define the processes involved in pesticide transport and, if possible, to predict the fate of chemicals applied at the soil surface.

4.1 Water Flow Simulations

The model domain is one-dimensional, extending from the soil surface to a depth of 2.5 m. At the beginning of a simulation, the lower part of the profile is water saturated and the pressure head at the bottom node is specified as the height of the water column. From the water table to the soil surface the profile is supposed to be at hydraulic equilibrium. At the upper boundary, atmospheric conditions with possible surface ponding were imposed. Hourly potential evapotranspiration rates (Penman-Monteith) were calculated based on data from nearby weather stations and specified together with hourly measured rainfall as a time variable boundary condition. At the lower boundary, two basically different conditions were considered: i) a variable pressure head boundary condition (approach 1), where the GW level was specified as pressure head on the bottom node at an hourly time step; thus, water is allowed to enter and leave the profile through the lower boundary, ii) a zero flux boundary condition (approach 2), where no water can enter or leave the profile at the lower boundary; the GW level is calculated by the model.

The soil profile was assumed to consist of one uniform soil layer; the parameters of the soil water retention function [van Genuchten, 1980] were estimated from the field measurements using the code RETC [van Genuchten et al., 1994]. The parameters of the hydraulic conductivity function (Ks, l) were determined by inverse modeling on pressure heads and/or on GW levels. In order to implement the MIM concept, a value of the immobile water fraction had to be defined. Because the model considers that immobile water cannot evaporate, the lowest measured value of the water content (0.28 $cm^3\ cm^{-3}$) was taken as the immobile water content.

The simulation started at the end of March 2002, roughly two month before the chemical application and ended in late August 2002. Figure 3 shows the measured and simulated pressure heads at 10 and 90 cm depth in the unsaturated zone for approach 1 (A1) and approach 2 (A2). The observed pressure heads at both depths are well reproduced when using approach 1. Approach 2 matches the data less well, especially at 10 cm where the observed pressure heads are significantly underestimated. The GW level changes, however, are relatively well predicted in approach 2 (Fig. 4).

The cumulative evaporation was calculated for both approaches and additionally, for approach 1 the cumulative water flow at the lower boundary was considered (Fig. 5). In approach 1, the simulated actual evaporation (Act. E, A1; Fig. 5) is close to the potential evapotranspiration (Pot. ET). At the bottom water continuously enters the profile (Bot. In, A1). When using approach 2, the actual evaporation (Act. E, A2) accounts for only 50 % of the potential evapotranspiration.

Analysis of the instantaneous fluxes shows only little drainage of rainwater to the GW with approach 1; the observed GW level rise is not a consequence of percolating water, but of the inflow of water through the lower boundary. This is not consistent with the observations that show rapid herbicide transport towards the GW during rainfall events. Therefore, approach 2 was used for the transport simulations.

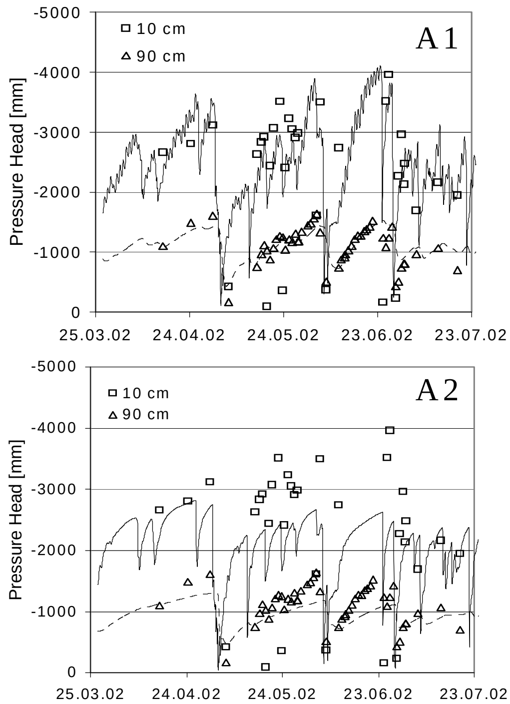

Figure 3: Measured (points) and simulated (lines) pressure heads at 10 and 90 cm depth for approaches A1 and A2

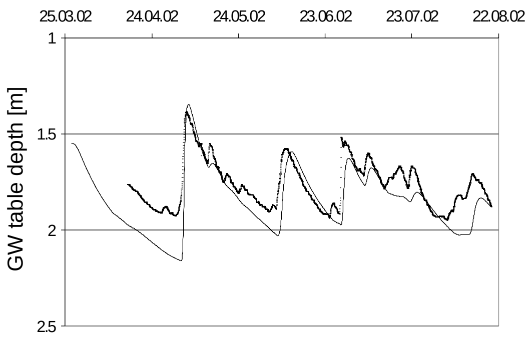

Figure 4: Measured (points) and simulated (line) GW table depth in approach 2

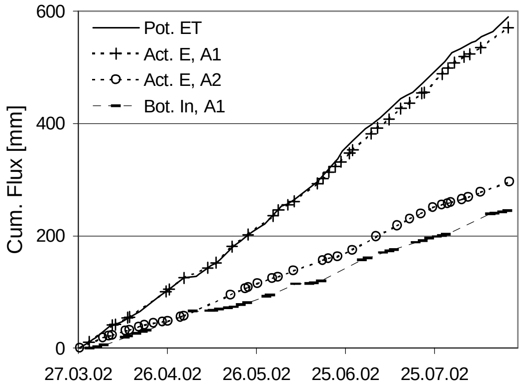

Figure 5: Cumulative boundary fluxes : Pot. ET=potential evapotranspiration; Act. E, A1=actual evaporation, approach 1; Act. E, A2=actual evaporation, approach 2; Bot. In, A1=inflow at lower boundary, approach 1.

4.2 Transport Simulations

The transport parameters were either measured directly in the laboratory (distribution coefficient, degradation constant) or assessed by roughly adjusting the simulations to the available concentration data (dispersivity, mass transfer coefficient, fraction of adsorption sites in contact with the mobile liquid). Initially, the soil profile was free of chemicals. At the upper boundary, a concentration flux condition was imposed and the herbicides were introduced with the first rainfall after the application. At the lower boundary, a zero gradient condition was chosen. The GW concentrations were calculated as an average over the water column.

Figure 6 shows observed and simulated atrazine concentrations in the GW. A first small peak is predicted in early June, but its relative intensity is significantly underestimated compared to the observed value. The shape of the second and third concentration peaks are rather well reproduced, although the third simulated peak occurs slightly earlier than observed. A sensitivity analysis shows that both, the immobile water content and the dispersivity, have a considerable influence on the herbicide transport and consequently, on the concentrations in the GW. For the simulation presented in Fig. 6 a dispersivity value as high as 1000 mm was assumed. This value is clearly exaggerated and must be considered as a lumped parameter accounting for the quick transfer of the solutes through the vadose zone. The immobile water content was set to 0.28 cm^3 cm^{-3}, the maximum possible value, as it represents the lowest measured water content. In spite of this, the model underestimates the concentrations in the GW and simulates a very small first concentration peak.

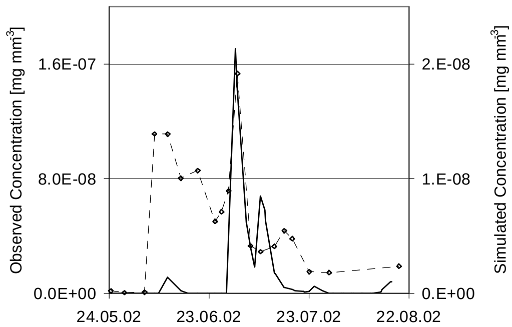

Figure 6: Observed (points) and simulated (line) atrazine concentration in the GW

5. DISCUSSION

The experimental results have shown that the herbicide transport is closely linked to precipitation. The applied solutes are rapidly transported towards the GW after the first heavy rainfall subsequent to the application. The rapidity of the transport is surprising bearing in mind that the soil is not visibly structured. A dual-porosity model was therefore chosen to simulate the observed GW concentrations.

For the hydraulic simulations, two different lower boundary conditions were considered.

When assuming a variable pressure head lower boundary condition (A1), the strong evaporation is well reproduced. The GW level rise subsequent to precipitation, however, is caused entirely by an inflow of water through the lower boundary and not by rainwater percolation; this is not consistent with the rapid transport of the herbicides observed after rainfall events.

On the other hand, when no inflow of water is assumed at the bottom boundary (A 2), the evapotranspiration is significantly underestimated.

Therefore, it is difficult to define precisely the lower boundary condition. Either the model is too unrestricted resulting in unreasonable water fluxes at the bottom node or the soil column is considered isolated and excluded from the regional water flow.

The transport of the chemicals as observed in the field experiment was extremely quick. In order to account for this rapidity, a high dispersivity value together with a great immobile water content were assumed. Still, the simulations were not satisfactory and the concentration peak observed in the GW were only roughly reproduced.

6. CONCLUSIONS

In conclusion, the model HYDRUS-1D is badly adapted for predicting herbicide transport in the specific context of the study area because of two principal problems :

The shallow GW and the high evaporation rate influence considerably the water conditions in the unsaturated zone; therefore, a correct simulation of the water flow depends to a great extend on a realistic definition of the lower boundary condition. When using a one-dimensional model, however, the boundary conditions cannot be correctly defined. The problem could probably be solved by using a three-dimensional saturated-unsaturated model or an unsaturated 1-D model coupled to a 3-D saturated model.

Even with the MIM concept, it is difficult to reproduce the extremely rapid transport observed after rainfall events. Dual-permeability models might be more appropriate to reproduce the rapid transport. This conclusion is somewhat surprising as the soil appears to be homogeneous without cracks or earthworm burrows. The simulation results indicate that even in a rather homogeneous soil significantly accelerated flow may occur.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

Flury, M., Experimental evidence of transport of pesticides through field soils - a review, *Journal of Environmental Quality*, 25 (1), 25-45, 1996.

Flury, M; Jury, W.A. and E.J. Kladivko, Field-scale solute transport in the vadose zone: experimental observations and interpretation, in: Magdi Selim, H. (ed.), Physical nonequilibrium in soils: modeling and application, *Ann Arbor Press*, 349-369, 1998.

Larsson, M.H. and N. J. Jarvis, Evaluation of a dual-porosity model to predict field-scale solute transport in a macroporous soil, *Journal of Hydrology*, 215, 153-171, 1999.

Simunek, J.; Sejna, M. and M.Th. Van Genuchten, 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, 1998.

Simunek, J.; Jarvis, N.; van Genuchten, M. Th. and A. Gärdenäs, Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone, *Journal of Hydrology*, 272, 14-35, 2003.

Vanderborght, J.; Mallants, D.; Vanclooster, M. and J. Feyen, Parameter uncertainty in the mobile-immobile solute transport model, *Journal of Hydrology*, 190(1), 75-101, 1997.

Van Genuchten, M. T. and P. J. Wierenga, Mass transfer studies in sorbing porous media. I. Analytical solutions, *Soil Science Society of America Journal*, 40, 473-480, 1976.

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

Van Genuchten, M.Th; Leij, F.J.; Yates, S.R. and W. B. Williams, RETC, Code for quantifying the hydraulic functions of unsaturated soils. US Salinity Laboratory, USDA/ARS, Riverside, CA, 1994.

Wauchope, R.D.; Lajpat, R.A.; Jeffrey, G. A.; Bingner, R.; Lowrance, R.; Van Genuchten, M.T. and L.D. Adams, Software for pest-management science: Computer models and databases from the United States Department of Agriculture, Agricultural Reserach Service, *Pest Management Science,* 59, 691-698, 2003.