

# One-dimensional Transport Model on Column Scale. Case study: Fluvisols Developed on Zagreb Quaternary Aquifer

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## Abstract

*The subject of this study is Fluvisol developed on the floodplain of Sava River. Goal of the study is one-dimensional transport model on column scale. The purpose of the study is better understanding of sorption and migration of selected trace elements through the soil column.*

*Two undisturbed soil samples for each of two best developed horizons of Fluvisols (AC and C) at Kosnica water capture site (800 m from right bank of Sava River) were collected. Soil samples were installed in Plexiglas columns and irrigated continuously by metal (Pb, Zn, Cd) solution using peristaltic pump. Samples of the leachate are being collected continuously and analyzed using atomic absorption spectrometry (AAS) for determination of lead, zinc and cadmium concentrations once every two weeks. The experiment will end when concentrations of analysed metals in leachate become same as in the initial metal solution. At the end of the test, the column samples will be cut into 10 mm slices. Such soil samples will be treated by aqua regia solution and analyzed to reveal concentrations and vertical distributions of selected trace elements.*

*Hydrus 1D software is used for modelling. Transport model shown in this paper is first version of model which will be modified after the completion of column test. Results of this model reveal time period for sampling solution at the end of outlet from column.*

**Keywords:** *Fluvisol, Zagreb Quaternary aquifer, trace elements, column test, Hydrus 1D, transport model, sorption, dispersivity*

## Introduction

The subject of this study is Fluvisol developed on the floodplain of Sava River. Fluvisol (AC profile) is found on alluvial plains, river fans and valleys (1). In the Zagreb aquifer area, this type of soils have humus-accumulative horizon which is mainly mollic and noncalcareous, developed by pedogenetic processes from rendzine on marls and Holocene deposits. Texture of this soil is silty-clay to clay-loam and mainly loamy, on marls and Holocene deposits, respectively. The structure is granular and very stable. This soil is very porous and permeable, with good characteristics for agricultural cultivation (2).

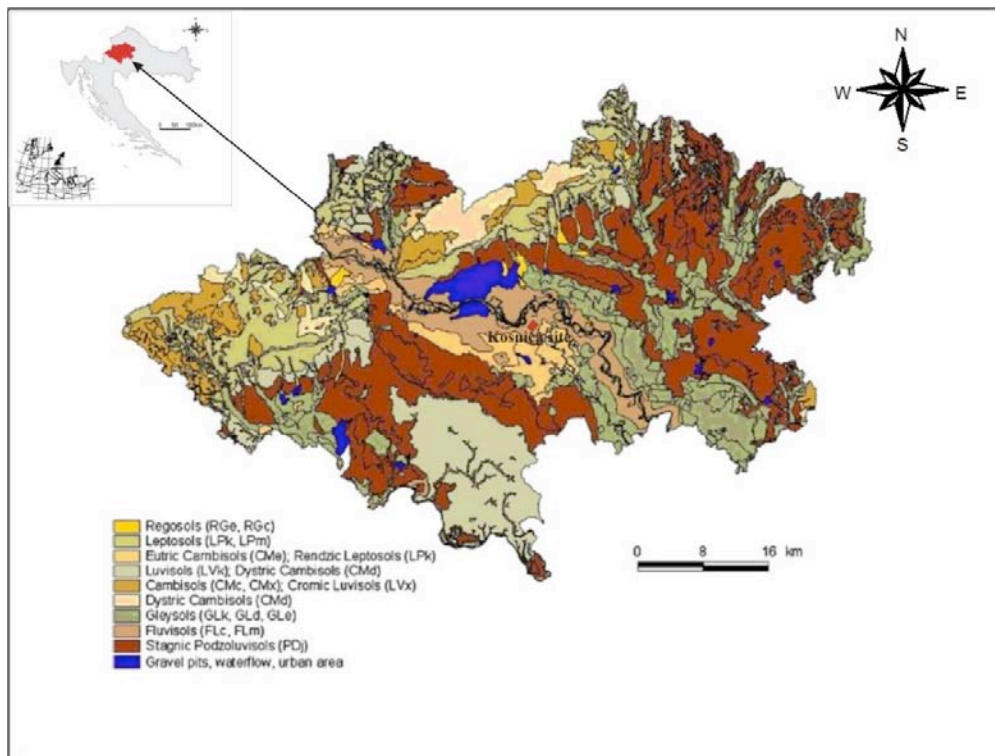
Numerous studies of vertical movement and distribution of metals through soil column have been made (3, 4, 5, 6, 7, 8).

This study aims to apply Hydrus-1D model for estimating solute transport through soil column in laboratory conditions.

## Materials and methods

### Case study description

Area of investigation is situated in northwest Croatia (Fig. 1). The broader area (Fig. 1) consists of a large alluvial plain bordered in the north and northwest by a mountain range, Mt Žumberak and Mt Medvednica. The region is characterized by large variability in lithology, pedological features and land use.



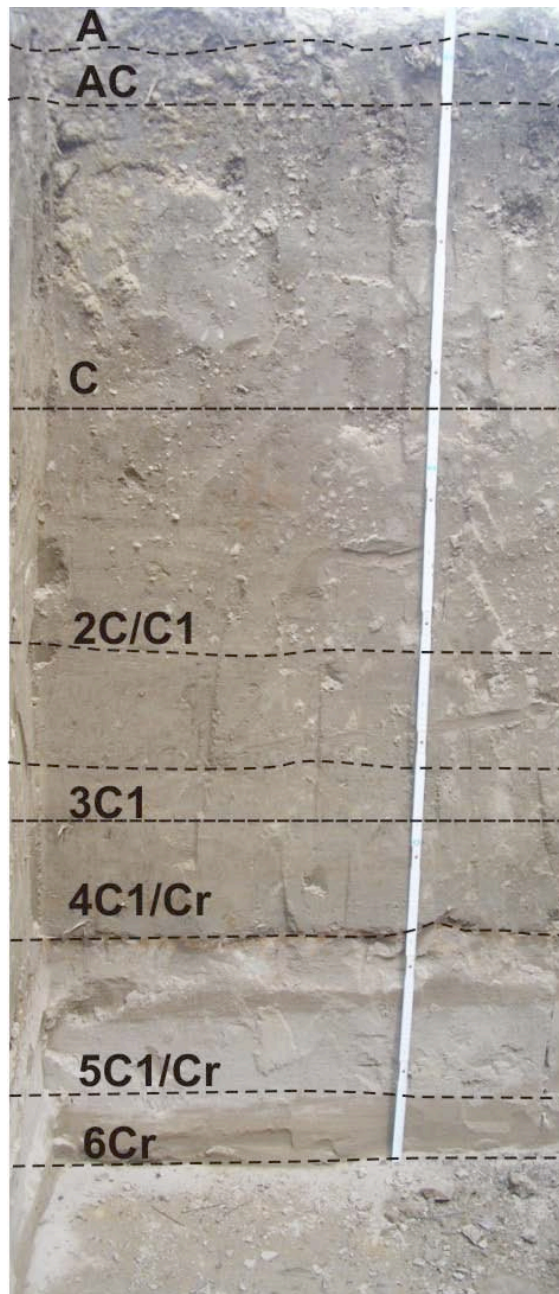
**Figure 1.** Pedological map of Zagreb and Zagreb county area (9). Simplified by (10).

The large heterogeneity of the parent material, combined with the climate and geomorphology of the broader region of Zagreb, has caused the development of a wide variety of soil types (Fig. 1). The floodplain soils are result of the material eroded from the geological units present in the catchment basin, i.e. its mineralogical and chemical compositions as well as the textural properties of the sediments, which are result of the dynamic of the Sava River flow and its solid transportation. Hydromorphic soils prevail in the Sava River valley, where the recent deposits form fluvial terraces (9). Molic Fluvisols, Calcaric Fluvisols, Eutric Cambisols, Eutric and Calcic Gleysols are developed on the Holocene deposits. In the area of Pleistocene terraces, Stagnic Podzoluvisols prevail on the plateau, whereas Stagnic Podzoluvisols and Glayic Podzoluvisols are prevalent on the slopes.

The Zagreb aquifer encompasses predominantly three pedologic units: Fluvisols, Stagnic Podzoluvisols (Pseudogley) and Eutric Cambisols, developed on Holocene deposits (Fig. 1) (9).

#### **Soil Samples and Analytical Methods**

This study was conducted in Kosnica village, about 8 km from Zagreb, capital of Croatia. Investigated profile (Fig. 1) (45°46' N; 16°05' E) is situated about 800 m from right bank of Sava River at Kosnica water capture site where Fluvisol type of soil is developed. The following soil horizons were recognized: O; A; AC; C; 2C/C1; 3 C1; 4C1/Cr; 5C1/Cr and 6Cr (Fig. 2). Soil is silty to sandy in texture.



**Figure 2.** Soil horizons, depth of profile 215 cm.

Two undisturbed soil samples for each of two best developed horizons (AC and C) of soil profile (Fig. 2) were sampled with soil sampling apparatus which consists of stainless steel cylinders (height 25 cm, volume 1963 cm<sup>3</sup>) and plastic tubes placed in inner diameter of cylinder. Two replicates of soil samples were taken from depth of 19–68 cm (AC) and 68–110 cm (C).

Separately, undisturbed and disturbed samples of investigated horizons are taken for laboratory analyses. Undisturbed samples were analyzed for bulk density, porosity, water capacity, air capacity, and sediment density while on disturbed samples grain size distribution were conducted. Total porosity was calculated using the bulk density of undisturbed samples and the average particle density as  $n = 1 - (\rho_b/G_s)$  where  $\rho_b$  is the bulk density and  $G_s$  is the soil density. The soil particle size distribution was determined by wet sieving and sedimentation. Analysed and calculated parameters are used in model.

## Column test

Column tracer experiments are being performed in order to determine the transport parameters: longitudinal dispersion coefficient and sorption coefficient for two main soil horizons (each horizon has two replicates).

The experiments are being carried out in four different Plexiglas cylindrical columns (25 cm in length; 5 cm in inner diameters) vertically placed. The soil column apparatus consists of the soil column; a column support structure; a pressure pump unit and a storage tank. At the top and bottom of the column, filter papers are placed to prevent finest grains from flowing out of the column and to support the soil. Experiments are being conducted at a room temperature of  $20 \pm 2$  °C. Sample are uniformly packed in a soil column and saturated with water carefully from the bottom side of column.

### *Dispersivity test*

The tracer solution ( $\text{CaCl}_2$ ) is being pumped into the column inlet at a constant flow rate. The most essential point in tracer experiment is calculation of tracer mass. For calculation of tracer mass water volume ( $V_w$ ) and detection limit of the tracer were established. Water volume was calculated using following equation (11):

$$V_w = \pi \times r^2 \times L \times n \quad [1]$$

where  $V_w$  is the water volume ( $\text{m}^3$ ),  $L$  is length (m) of cylinders and  $r$  is radius (m) of cylinders.

Mass of tracer ( $\text{CaCl}_2$ ) was calculated with the following equation (11):

$$M = 15 \times C_b \times V_w \times n \quad [2]$$

where  $M$  is mass of tracer (g),  $C_b$  is the detection limit of measurement method for salt tracer ( $\text{mg l}^{-1}$ ) used (in this investigation, it is ion chromatography and detection limit is  $0.67 \text{ mg l}^{-1}$ ) and  $n$  is porosity (%).

Calculated mass of tracer is 9.5 g.

Percolated solution samples are being collected from the beginning ( $t=0$ ) of the experiment in equal intervals and tracer concentration is being analyzed using ion chromatography. The experiment will be conducted until concentration in the final sample reaches the initial  $\text{CaCl}_2$  concentration.

Breakthrough curves of chloride concentration will be used for determination of longitudinal dispersion coefficient.

### *Sorption experiment*

After calcium chloride application soil columns will be irrigated by metal solutions prepared from  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$  and  $\text{CdCl}_2$ . The concentration of these potentially toxic metals in the feed solution is  $1 \text{ mg cm}^{-3}$ . As the columns are made of Plexiglas, metals adsorption on column walls is insignificant. Samples of the leachate with metals will be collected continuously and analyzed using atomic absorption spectrometry (AAS) for determination of lead, zinc and cadmium concentrations, once every week. The experiment will be ended when concentrations of analysed metals in leachate become same as in the initial metal solution. At the end of the test, the column samples will be cut into 10 mm slices. Such soil samples will be treated by aqua regia solution and analyzed to reveal concentrations and vertical distributions of selected trace elements which left bound to the soil.

## Mathematical models and their analytical and numerical solutions

Water flow in unsaturated zone is based on the following equation often referred to as the Richard's equation (12):

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z} \left[ K(h) \left( \frac{\partial h}{\partial z} + 1 \right) \right] - S \quad [3]$$

Where:  $z$  is the vertical coordinate positive upward from water table (m),  $t$  is time (s),  $h$  is the pressure head (m),  $\theta$  is the water content ( $\text{cm}^3 \text{cm}^{-3}$ ),  $S$  is a sink term representing root water uptake ( $1 \text{ s}^{-1}$ ), and  $K(h)$  is the unsaturated hydraulic conductivity function, often given as the product of the relative

hydraulic conductivity,  $K_r$  (dimensionless), and the saturated hydraulic conductivity,  $K_s$  ( $\text{ms}^{-1}$ ). Richard's equation, Eq. [3], will be solved numerically for one-dimensional water flow.

Advection, dispersion and sorption are main processes of solute transport in unsaturated zone. Solute transport is described using the advection–dispersion and reaction equation in the following form:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s}{\partial t} = \frac{\partial}{\partial z} \left( \theta D \frac{\partial c}{\partial z} \right) - \frac{\partial qc}{\partial z} - \Phi \quad [4]$$

Where:  $c$  is the solution concentration ( $\text{mg l}^{-1}$ ),  $s$  is the sorbed concentration ( $\text{mg mg}^{-1}$ ),  $D$  is the dispersion coefficient accounting for hydrodynamic dispersion ( $\text{m}^2 \text{s}^{-1}$ ),  $q$  is the volumetric fluid flux density ( $\text{ms}^{-1}$ ), and  $\Phi$  is rate constants representing reactions ( $\text{mg m}^{-3} \text{s}^{-1}$ ).

Sorbed concentration ( $s$ ) will be obtained from following equation:

$$s = K_d c \quad [5]$$

Where:  $K_d$  is the distribution coefficient ( $\text{ml g}^{-1}$ ).

Dispersion coefficient ( $D$ ) will be determined analytically also, with following equation (13):

$$\theta D = \lambda |q| + \theta D_d \tau \quad [6]$$

Where:  $\lambda$  is the longitudinal dispersivity (m),  $D_d$  is molecular diffusion ( $\text{m}^2 \text{l}^{-1}$ ) and  $\tau$  is tortuosity factor (dimensionless).

Volumetric fluid flux density ( $q$ ) will be determined using Darcy- Buckingham law (14) as:

$$q = -K(h) \frac{\partial h}{\partial z} \quad [7]$$

Tortuosity factor ( $\tau$ ) which depends on water content will be determined with following equation:

$$\tau = \frac{\theta^{7/3}}{\theta^2} \quad [8]$$

The reaction term  $\Phi$  of Eq. [4] may represent various chemical or biological reactions that lead to a loss or gain of chemical in the soil system, such as radionuclide decay, biological degradation, and dissolution (15). These reactions, in analytical and numerical models, are most commonly expressed using first-order reaction rates as follows:

$$\phi = - \frac{d[A]}{dt} \quad [9]$$

Where:  $A$  is the concentration of the chemical of interest.

The conceptual models for each of these processes are typically written in terms of partial differential equations and then solved numerically by Hydrus 1D software.

### Flow and transport modelling

For the simulation of water and solute transport in a 50 cm deep soil domain, the lower boundary condition was a seepage face and the upper was a constant flux. This flux is calculated from Eq. [7], and it is  $50 \text{ cm day}^{-1}$ . Hydrus-1D provides other options for the lower boundary condition such as constant head pressure, constant flux and free drainage. However, the seepage face was chosen because this type of boundary condition is often applied to laboratory soil columns when the bottom of the soil column is exposed to the atmosphere. The model was run for 10 days. Values of the longitudinal dispersivity typically range from about 1 cm to 2 cm for packed laboratory columns (15). Longitudinal dispersivities were taken from literature (15), and it is 1 cm for upper and lower part of column. Values of the adsorption isotherm coefficient,  $K_d$  values were taken from literature (16) for the time being, later it will be taken from the column experiments results.

## Results and discussion

### Soil characteristics

The physical characteristics of the investigated soil profiles are summarized in Table 1.

**Table 1.** Physical characteristics of investigated soils

Soil horizons	Depth (cm)	Water capacity (% vol.)	Air capacity (% vol.)	Bulk density (g/dm <sup>3</sup> )	Sediment density (g/dm <sup>3</sup> )	Porosity (%)	Sand (%)	Silt (%)	Clay (%)
AC	19-68	41,57	6,81	1,36	2,63	48,38	13,79	76,69	9,52
C	68-110	39,89	7,50	1,39	2,63	47,39	56,33	38,23	5,44

Air capacity is higher in the upper part of soil profile, while bulk density has opposite trend. All soil horizons are porous and have medium water retention capacity.

Hydraulic parameters of two soil horizons were calculated from bulk density and grain size analysis using Rosetta Lite software program (17) and listed in Table 2.

**Table 2.** Hydraulic parameters of the different soil horizons

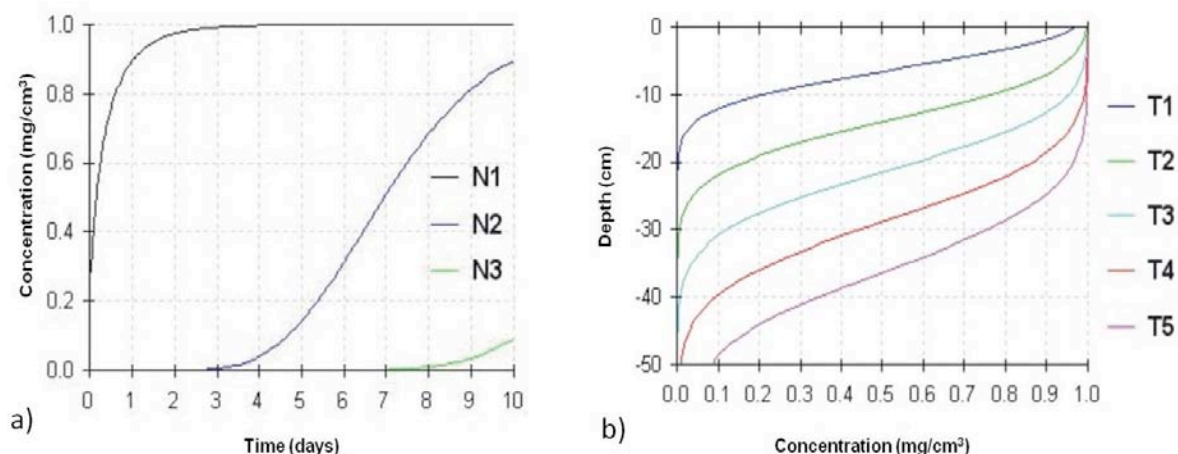
Depth (cm)	Qr	Qs	$\alpha$ (m <sup>-1</sup> )	n	Ks (cm day <sup>-1</sup> )
0-25	0.0683	0.5153	0.0040	1.7651	169.11
25-50	0.0414	0.4651	0.0116	1.4780	215.90

Solute transports from the topsoil to subsoil were provided by the model at three observation nodes (N1: 0 cm; N2: 25 cm; N3: 50 cm depth). Top of the soil column (0 cm) represent top of AC soil horizon (19 cm).

### Preliminary modelling results

Several of the parameters used in the simulation of solute transport can be determined only with great uncertainties for the time being. While a soil hydraulic model property for water flow is established, solute parameters are only predicted. Exact values will be known after completion of column experiment. Figure 3 represent outcome of the preliminary model. Solute concentration at the observation node one (soil surface), raising from 0 mg cm<sup>-3</sup> to 1 mg cm<sup>-3</sup> at the soil surface (Fig. 3a) in one day. Metals in solution come to 25 cm after three days, while at 50 cm (bottom of the soil column) after ten days. Figure 3b shows diagram of solute concentration versus depth in different time periods. The final time of simulation is ten days, and diagram shows concentration every two days. Solute concentration falls from 1 mg cm<sup>-3</sup> to from 0 mg cm<sup>-3</sup> after two days at 20 cm depth. The final time shows that concentration is constant for first 20 cm, after that curve became steep and falls to 0.1 mg cm<sup>-3</sup> at 50 cm depth. This preliminary model shows that multi component solution made of Cd, Zn and Pb elements will came relatively fast from top to bottom of modelled soil column. Soil hydraulic parameters are suitable for fast solution transport.





**Figure 3.** Simulation of Cd, Pb and Zn concentration in the soil solution at (a) different observation nodes (N1: 0 cm; N2: 25 cm; N3: 50 cm depth) and (b) different times (T1: 2 days; T2: 4 days; T3: 6 days; T4: 8 days T5: 10 days).

## Conclusions

In order to better understand transport parameters such as dispersivity and sorption, conceptual model for solute transport at column scale was made. Two undisturbed soil samples for each of two best developed horizons of Fluvisols (AC and C) at Kosnica water capture site (800 m from right bank of Sava River) were collected. Undisturbed soil samples were installed in the columns. Preliminary model was simulated. Results of this model reveal time period for sampling solution at the end of column outlet. The influence of parameter uncertainties against simulation results should also be considered for future works. Therefore sorption and dispersivity experiments are necessary to provide realistic results obtained from the model.

**Acknowledgments:** The work was carried out as part of the GENESIS project on groundwater systems (<http://www.thegenesisproject.eu>) financed by the European Commission 7FP contract 226536 and Croatian Ministry of Science, Education and Sport (no. 195-1953068-2704 to G.D.).

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