

BUILDING CONCEPTUAL AND MATHEMATICAL MODEL FOR WATER FLOW AND SOLUTE TRANSPORT IN THE UNSATURATED ZONE AT KOSNICA SITE

IZRADA KONCEPTUALNOG I MATEMATIČKOG MODELA TOKA VODE I TRANSPORTA ONEČIŠĆIVALA U NESATURIRANOJ ZONI NA PODRUČJU KOSNICE

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Abstract

Conceptual model of flow and solute transport in unsaturated zone at Kosnica site, which is the basis for modeling pollution migration through the unsaturated zone to groundwater, is set up. The main characteristics of the unsaturated zone of the Kosnica site are described. Detailed description of investigated profile of unsaturated zone, with all necessary analytical results performed and used in building of conceptual models, is presented. Experiments that are in progress and processes which are modeled are stated. Monitoring of parameters necessary for calibration of models is presented. The ultimate goal of research is risk assessment of groundwater contamination at Kosnica site that has its source in or on unsaturated zone.

Sažetak

U radu je postavljen konceptualni model toka i transporta otopina u nesaturiranoj zoni na lokaciji Kosnica, kao temelj modeliranja transporta onečišćivala kroz nesaturiranu zonu do podzemne vode. Opisane su glavne karakteristike nesaturirane zone lokacije Kosnica. Prikazan je detaljan opis istraživanih profila s analitičkim rezultatima korištenim pri izradi konceptualnog modela. Eksperimenti koji su u tijeku i procesi koji se simuliraju su utvrđeni. Prikazan je monitoring parametara potrebnih za kalibraciju modela. Krajnji cilj istraživanja je utvrđivanje rizika od onečišćenja podzemne vode na lokalitetu Kosnica čiji je izvor u ili na nesaturiranoj zoni.

Introduction

Developments of industry and fast growth of the City of Zagreb have considerably affected groundwater quality of the Zagreb aquifer system (Nakić et al., 2011). It is therefore necessary to investigate the leaching of pollutants from different points of view (e.g. leaky sewerage, the city landfill, agriculture, illegal waste depositories and illegal gravel pits) and diffuse sources (e.g. traffic, airborne deposition) through the unsaturated zone. The unsaturated zone is typically defined to extend from land surface to the underlying water table or saturated zone within porous media (Tindall and Kunkel, 1998).

Numerous studies of lateral and vertical potentially toxic metal distribution in soils have been made in the area of Zagreb and Zagreb County (Namjesnik, 1994; Miko et al., 2001; Romić, 2002; Romić and Romić, 2003; Romić et al., 2004, 2005; Halamić and Miko, 2009; Solitto et al., 2010). These studies show elevated concentration of potentially toxic metals in topsoils, as well as increase of cadmium, iron, manganese, and nickel with depth.

Romić & Romić (2003) emphasized that the distribution of trace elements in soils of investigated area is primarily controlled by: (a) geology, (b) industrial impact (traffic, heating plants, chemical industry and airports) and (c) external factors (some trace elements are brought

by the Sava River, which has been exposed to intensive pollution by mining, industries and towns in its upper course). A portion of trace metals is introduced by wind, blown from the industrial region of north Italy (Antonić and Legović, 1999).

The aim of this study is development of conceptual model of water flow and solute transport, taking into consideration various scenarios. Conceptual model is descriptive model of a system based on qualitative assumptions about its elements, their interrelationships, and system boundaries. Conceptual model of water flow and solute transport through unsaturated zone at Kosnica site is developed for three main purposes: (1) to provide an overview of the current state of scientific understanding; (2) to identify those variables that have the largest effects on outcomes and set up field investigation and data collection plan; (3) to be used in 1D numerical simulations of contaminant transport (numerical models of the system are based on the same set of concepts as conceptual models, but describe the behavior of the system in a quantitative manner).

Understanding how water and solutes move through the unsaturated zone is necessary to make effective remedial action decisions where contaminants were spilled or leaked at the ground surface or were buried in shallow land-disposal sites.

Area description

Location

The broader region is characterized by large variability in lithology, pedological features and land use. Investigated area consists of a large alluvial plain bordered in the north by a mountain range Mt Medvednica. Alluvial plain has two marked geomorphological features: raised sealed terrace of the Sava, and so called second river, i.e. Holocene terrace. Investigative profile is located about eight hundred meters from the right bank of Sava river ($45^{\circ}46' N$; $16^{\circ}05' E$) (Figure 1), in second zone of sanitary protection of the water abstraction site Kosnica.

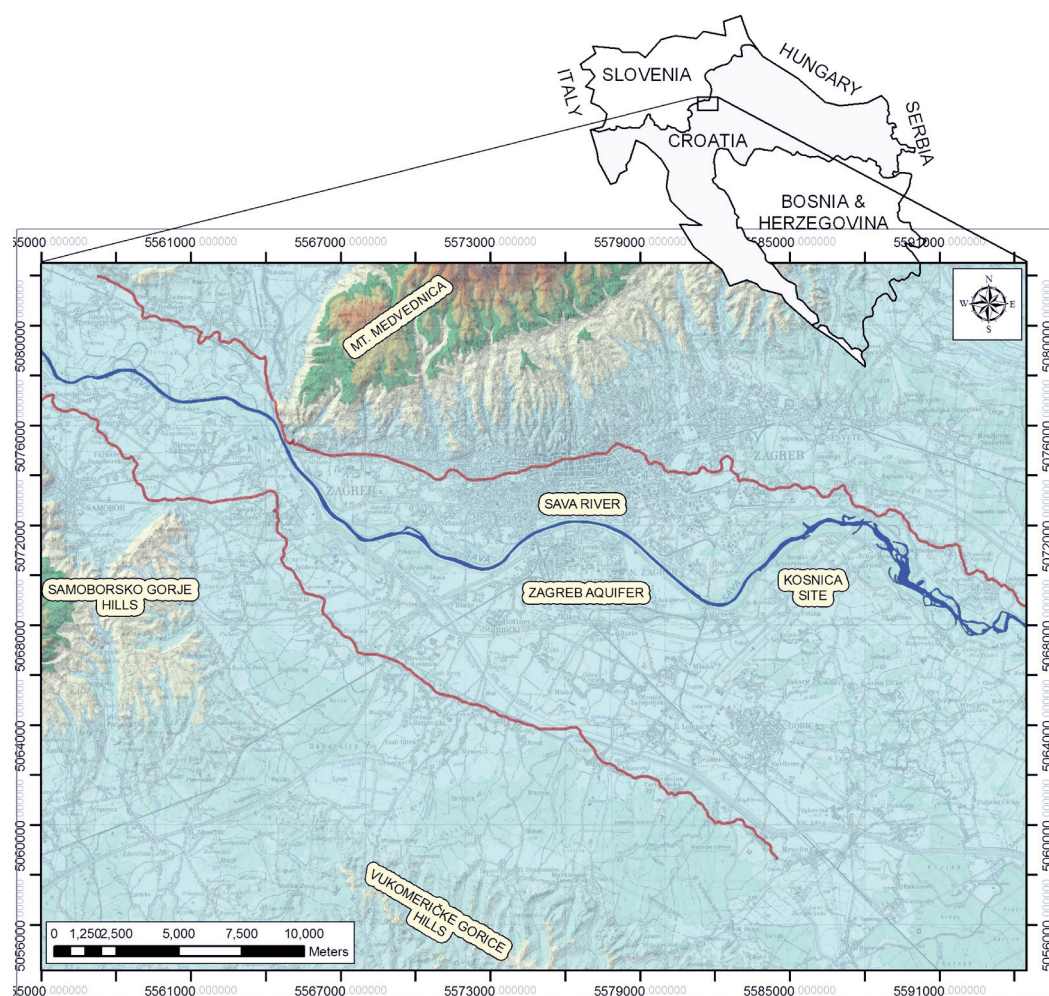


Figure 1. Geographical position of Zagreb aquifer system (red line – aquifer boundaries) with Kosnica Site

Slika 1. Geografski položaj Zagrebačkog vodonosnika (crvena crta – granice vodonosnika) sa lokalitetom Kosnica

Geology

Shallow unconfined Zagreb aquifer and its unsaturated zone is represented mainly by unconsolidated Quaternary sediments (Figure 2). Lower Pleistocene deposits are predominantly composed of clayey silts/silty clays with sporadic lenses and interbeds of gravelly-sands, up to thickness of few decimeters (Velić and Durn, 1993). While the lower and middle part of Middle Pleistocene unit is predominantly composed of sands, the upper part comprises silt and clay sized material (Velić and Durn, 1993; Velić and Saftić, 1996). The Upper Pleistocene unit is characterized by frequent lateral changes of gravels, sands, silts and clays. The Holocene is composed of gravels and sands in which limestone cobbles prevail.

Unsaturated zone

The thickness of unsaturated zone in Zagreb area varies from 8 meters in NW part to 2 meters in SE part (Figure 3). The upper part of this zone is composed mainly of silty to sandy material, while the lower part consists of gravels. In some parts this material was intersected with clay layers. Predominantly three pedologic units develop

ped on these sediments: Fluvisols, Stagnic Podzoluvisols (Pseudogley) and Eutric Cambisols (Sollitto et al., 2010).

At the Kosnica site, lower part of profile (Figure 4) consists of gravels with sand component, while upper part is dominated by gravels with silty to sandy material. Pebbles are mainly rounded and oval in shape. Sands reveal different granulation, from gravelly to silty sands. In some places, these sediments are red to black in color. Fluvisols is developed of the top of unsaturated zone profile.

Texture of this type of soils is mainly loamy, in some parts clayey with loam. Structure of this type of soils is mainly granular.

Methods

The conceptual model which is result of this paper integrates the current understanding of the stratigraphy, hydrology, ground-water movement, meteorological data and geochemistry of soil and sediments in the model area, as well as data obtained during this study which were missing. Data used for developing the conceptual model were obtained from numerous reports published during the past 20 years, including ground-water modelling studies, geochemical and stratigraphic research.

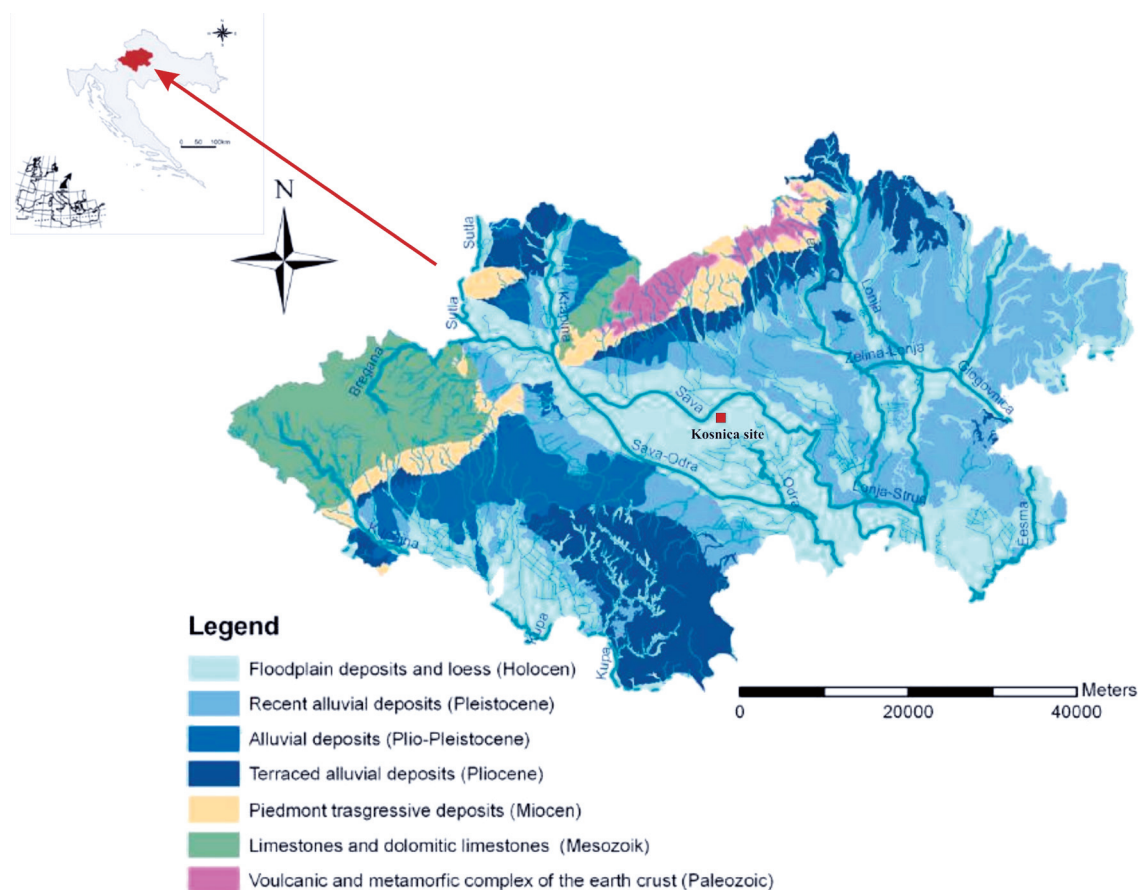


Figure 2. Simplified geological and geomorphological map of Zagreb area (according to Sollitto et al. 2010)

Slika 2. Pojednostavljena geološka i geomorfološka karta Zagrebačkog područja (Prema: Sollitto i dr. 2010)

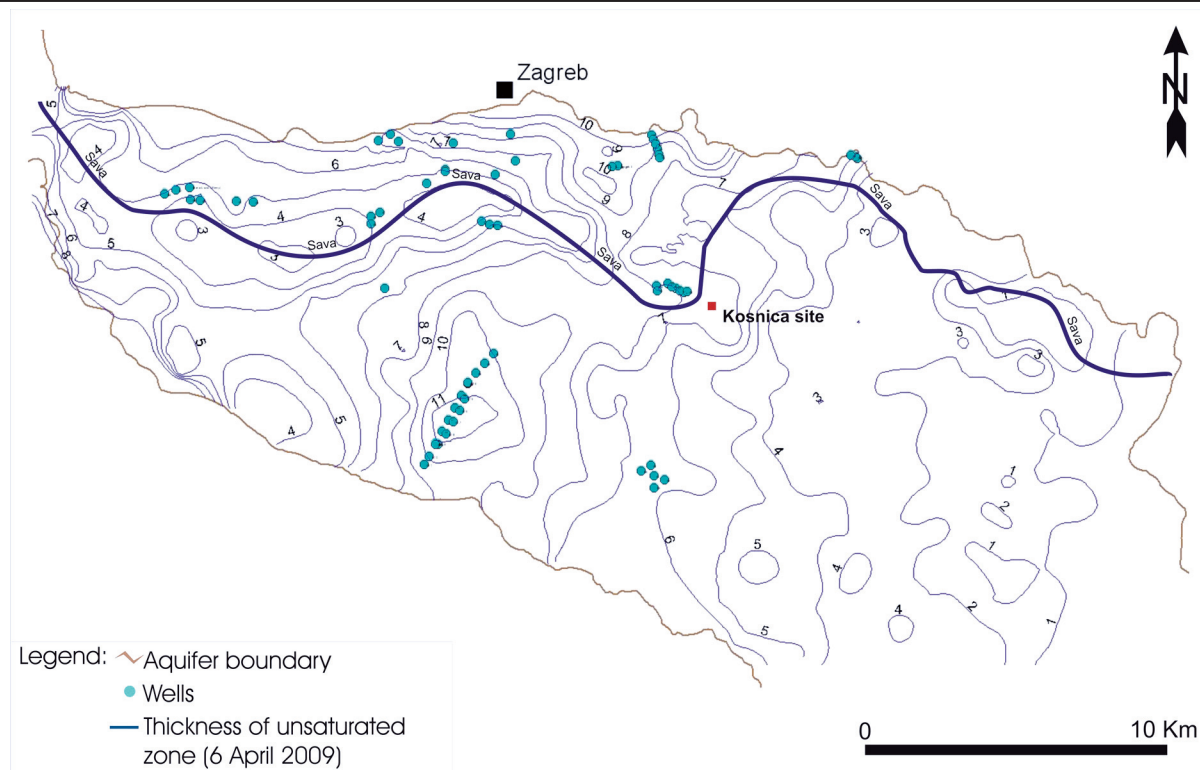


Figure 3. Isopach map of unsaturated zone
Slika 3. Karta izopaha nesaturirane zone

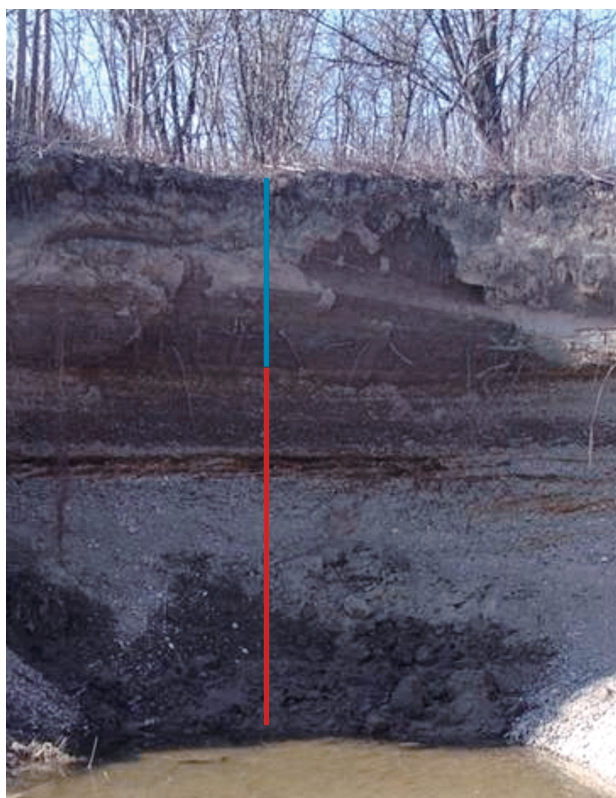


Figure 4. Unsaturated zone profile. Legend: Blue label – soil (approx. 2 m); red label - gravels and sands (approx. 3.5 m)
Slika 4. Vertikalni profil nesaturirane zone. Legenda: plava linija – tlo (cca. 2 m), crvena linija – šljunci i pijesci (cca. 3,5 m)

Data obtained during this study include physical and chemical characteristics of soil and sediments (grain size distribution, electrical conductivity, pH, sorption parameters, soil water tension, water content, etc.) acquired by field and laboratory measurements. Although a large quantity of data were available for developing the conceptual model, there were several limitations with these data. These data limitations included uneven spatial distribution, both spatially and vertically and scaling-compatibility issues involving the application of small-scale measurements to a large-scale study.

Results

Parameters

Grain size analysis, pH and electrical conductivity are measured on disturbed samples to define profile hydraulic and chemical parameters. Soil pH increases while electrical conductivity generally decreases with depth (Figure 5).

Disturbed samples from Kosnica profile are taken for grain size analyses. The soil particle size distribution was determined by wet sieving and sedimentation. Grain size analyses of samples taken from Kosnica profile (Figure 4) are represented in Table 1.

Separately, undisturbed and disturbed samples of investigated horizons are taken from pedological burrow for laboratory analyses. Undisturbed samples were analyzed for bulk density, porosity, water capacity, air capacity, and

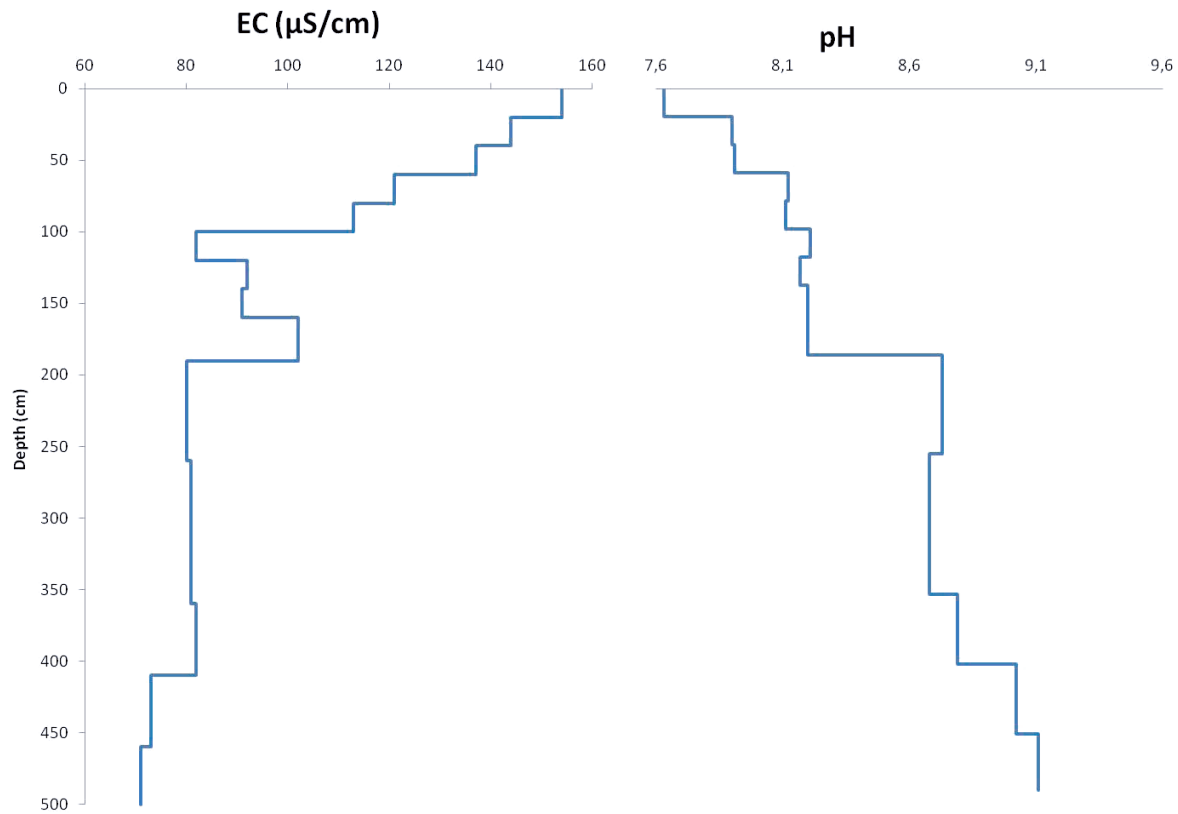


Figure 5. Distribution of electrical conductivity (EC) and pH through profile

Slika 5. Distribucija električne vodljivosti i pH kroz profil

Table 1. Grain size analysis results from Kosnica profile

Tablica 1. Rezultati granulometrijske analize s profila Kosnica

Depth (cm)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)
0-20	0.46	25.96	55.08	18.50
20-40	0.12	27.24	49.19	17.14
40-60	0.05	23.64	56.29	20.02
60-80	0.00	20.99	64.19	14.83
80-100	0.00	26.10	70.60	3.30
100-120	0.00	59.92	34.75	5.59
120-140	0.00	48.58	41.88	9.53
140-160	0.00	42.10	48.12	9.77
160-190	0.00	32.73	57.49	9.79
190-260	68.15	29.34	2.34	0.17
260-360	76.86	20.00	1.43	1.71
360-410	78.16	18.37	1.79	1.68
410-460	90.28	7.32	1.11	1.29
460-500	78.24	20.09	0.79	0.88

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 ρ_b is the

bulk density and G_s is the soil density. The soil particle size distribution was determined by wet sieving and sedimentation. Physical properties of soil horizons taken from pedological burrow are represented in Table 2.

Table 2. Physical properties of soil horizons taken from pedological burrow**Tablica 2.** Fizikalna svojstva horizonata tla iz pedološke jame

Soil horizons	Depth (cm)	Water capacity (% vol.)	Air capacity (% vol.)	Bulk density (g/dm ³)	Sediment density (g/dm ³)	Porosity (%)
A	0-19	44.56	14.70	1.04	2.54	59.26
AC	19-68	41.57	6.81	1.36	2.63	48.38
C	68-110	39.89	7.50	1.39	2.63	47.39
2C/C1	110-140	38.53	10.43	1.37	2.69	48.96
4Cl/Cr	140-190	42.06	4.11	1.41	2.62	46.17
5Cl/Cr	190-215	41.27	5.47	1.43	2.69	46.74

Flow parameters

Hydraulic conductivity, water tension and water content are flow parameters used for water flow in unsaturated zone. Hydraulic conductivity (K) is usually determined in three ways: 1) using grain size analysis of samples from the profile and empiric formulas, 2) by Guelph permeameter measurements in the field for each horizon of the profile, 3) by constant-head (for coarse sediments such as gravels and sands) and falling-head (for fine sediments as silts and clays) permeameter apparatus in the laboratory. Hydraulic conductivity (K) was in this study determined using grain size analysis of samples from the pedological burrow (Table 3) using empiric formulas (Van Genuchten, 1980) and it varied from 26.3 to 47.6 cm/day.

Determination of hydraulic conductivity using Guelph permeameter as well as constant-head and falling-head permeameter is currently in progress and the results will be used for comparison of gained values of hydraulic conductivity.

Water content (θ) is determined from bulk density analysis results using Rosetta Lite software (Schaap et al., 2001), and varies from 15 to 46%. Root water uptake (S) is parameter which is dependent on plant covers and will be taken from literature (Feddes et al., 1978; Van Genuchten, 1987).

Monitoring of parameters such as water content, electrical conductivity, soil water tension and concentrations of metals in percolating water is necessary for calibration of models. Therefore, field measurement instruments are installed on the investigative profile. Due to loose sediment in the lower part of the profile which cause collapse of the profile, and due to security of the equipment, pedological burrow in the proximity of the profile was excavated (Figure 6). Two instruments for each parameter, namely water content, electrical conductivity and soil water tension are installed at two different depths. Water content (soil moisture) is being measured using *Time domain reflectometry* (TDR) equipment; electrical conductivity (EC) using EC-probes (Figure 6a) and soil water tension using tensiometers (Figure 6b).

Table 3. Grain size analysis results from pedological burrow**Tablica 3.** Rezultati granulometrijske analize iz pedološke jame

Soil horizons	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Hydraulic conductivity (cm/day)
A	0-19	24.56	65.27	10.17	30.27
AC	19-68	13.79	76.69	9.52	36.15
C	68-110	56.33	38.23	5.44	47.57
2C/C1	110-140	43.29	47.43	9.28	26.28
4Cl/Cr	140-190	37.21	50.50	12.29	27.13
5Cl/Cr	190-215	55.62	38.45	5.93	43.54

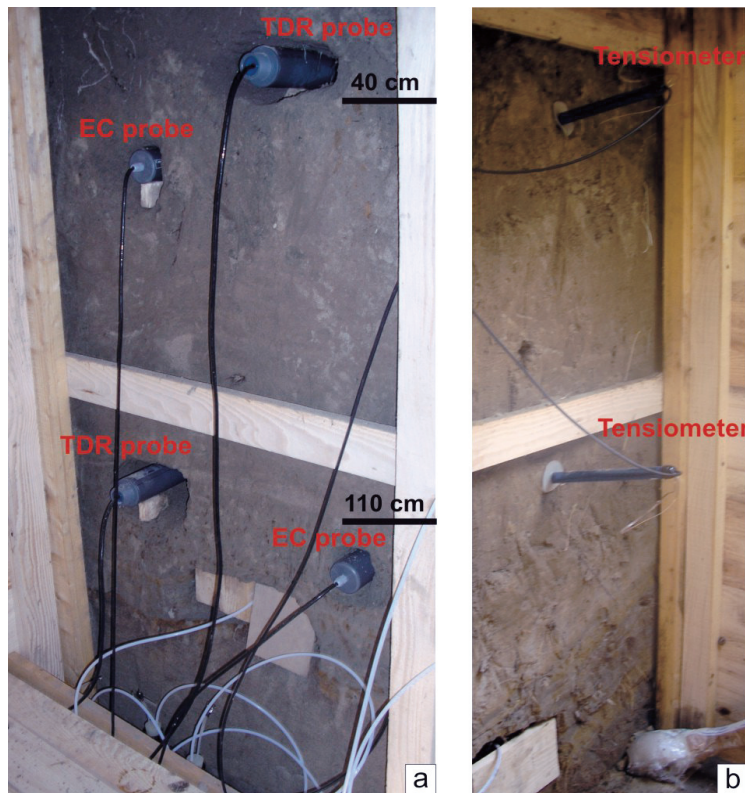


Figure 6. a) Investigative pedological burrow with TDR probes and EC-probes; b) tensiometers
Slika 6. a) Istražna pedološka jama sa TDR-sondama i EC-sondama; b) tenziometri

Water content depends on weather conditions (varies from 16% in lower part to 38% in upper part of pedological burrow) (Figure 7a). Results of soil water tension vary

from 11000 Pa in upper part to 14000 Pa in lower part of pedological burrow (Figure 7b).

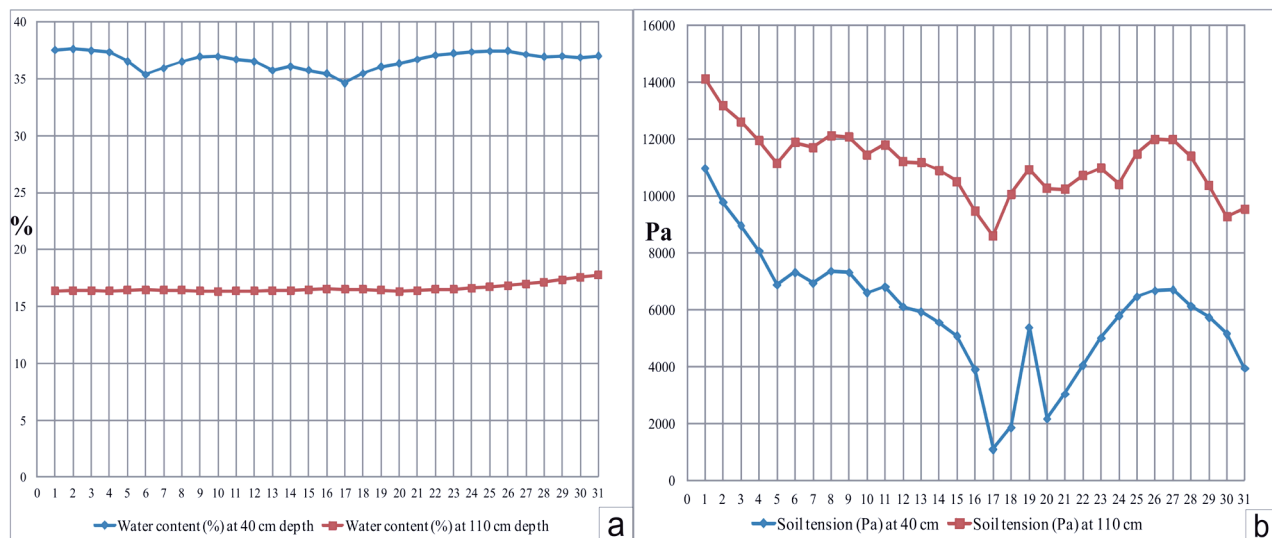


Figure 7. a) Diagram of water content for period of one month (December 2011). The blue line show measurements of water content at 40 cm depth, while red line show measurements at 110 cm depth; b) diagram of soil water tension for period of one month (December 2011). The blue line show measurements of soil water tension at 40 cm depth, while red line shows measurements at 110 cm depth

Slika 7. a) Dijagram sadržaja vode za period od jednog mjeseca (Prosinac 2011). Plava crta označava mjerenja sadržaja vode na dubini od 40 cm, crvena crta označava mjerenja na dubini od 110 cm; b) dijagram matričnog potencijala tla za period od jednog mjeseca (Prosinac 2011). Plava crta označava mjerenja matričnog potencijala tla na dubini od 40 cm, crvena crta označava mjerenja na dubini od 110 cm

Transport parameters

Batch sorption experiment. The batch sorption experiment at laboratory scale was conducted to determine the relationship between adsorbent and adsorbate. In this study, the sorption parameters (distribution coefficient, K_d; Freundlich K_f) of Cd, Pb and Zn in six different soil samples taken from pedological burrow was studied by means of batch tests.

The test was performed with multi element solutions of Cd, Pb and Zn at constant temperature (24 ± 1°C) in the laboratory condition. All soils were air-dried and sieved through a 2-mm sieve. For this purpose, 0.5 g of air-dried soils was put into 50 mL plastic tubes and 50 mL of a solution with initial concentrations of 10, 20, 30, 40, 50 mg/l, containing potentially toxic metal (e.g. Cd) was added to establish linearity of the sorption process. Closed plastic tubes was shaken 24 h to ensure sufficient time for solid-liquid equilibrium to be reached. The initial and final solutions were analyzed using flame atomic absorption (instrument Perkin Elmer AAnalyst 700) to determine potentially toxic metal concentration before and after the batch experiment.

In order to obtain the sorption capacity, the amount of ions adsorbed per unit mass of adsorbent \bar{S}_i (in milligrams of metal ions per gram of adsorbent) was calculated with the following equation:

$$\bar{S}_i = \frac{(C_i - C_{aqi}) \times V_i}{W} \quad (1)$$

where \bar{S}_i is the amount of metal removed from solution (mg/g) of the i-th sample; C_i is the concentration of metal in the solution of the i-th sample before mixing with soil (mg/l); C_{aqi} is the equilibrium concentration of contaminant left in the solution of the i-th sample after the experiment (mg/l); V_i is the solution volume of the i-th sample (dm³), and W is the weight of air-dried soil of the i-th sample (g). The equilibrium concentrations C_{aqi} were analyzed using flame atomic absorption (instrument Perkin Elmer AAnalyst 700). The amount of metal removed from solution (\bar{S}_i) is then plotted with the equilibrium concentration (C_{aqi}) to determine the sorption response curves (i.e., sorption isotherms). There are three isotherm models that have been widely used to represent the response curves; linear, Freundlich, and Langmuir models. The constants (the linear value K_d; Freundlich values K_f, a) derived from these isotherms were calculated and are shown in Table 4, together with the corresponding correlation coefficients. As results of multicomponents batch experiments carried out, for Cd, Pb and Zn the sorption process was described by the Freundlich isotherm models (Table 4). The linear model for Pb was suited better only in A horizon.

Table 4. Isotherm parameters for selected potentially toxic elements (K_d, distribution coefficient; K_f, Freundlich sorption constant; R², correlation coefficient; a, Freundlich exponent).

Tablica 4. Parametri izoterma za odabrane potencijalno toksične elemente (K_d, distribucijski koeficijent; K_f, Freundlich-ova sorpcijska konstanta; R², korelacijski koeficijent; a, Freundlich-ov eksponent).

Metal	Soil horizon	Freundlich isotherm			Linear isotherm	
		a	K _f (l/kg)	R ²	K _d (l/kg)	R ²
Cd	A	0.759	172	0.98		
	AC	0.392	366	0.99		
	C	0.250	404	0.97		
	2C/Cl	0.297	392	0.98		
	4Cl/Cr	0.322	376	0.98		
	5Cl/Cr	0.293	375	0.96		
Pb	A				99	0.9998
	AC	0.538	272	0.99		
	C	0.527	282	0.99		
	2C/Cl	0.531	280	0.99		
	4Cl/Cr	0.526	284	0.99		
	5Cl/Cr	0.528	283	0.99		
Zn	A	0.851	137	0.99		
	AC	0.417	357	0.99		
	C	0.377	327	0.96		
	2C/Cl	0.378	355	0.97		
	4Cl/Cr	0.389	356	0.99		
	5Cl/Cr	0.390	336	0.98		

Sorbed concentration (s) can be obtained from following equation (only in case of linear isotherm):

$$s = K_d c \quad (2)$$

Where: K_d is the distribution coefficient (ml/g), and c is concentration (mg/l).

Dispersion experiment. The dispersion experiment at field scale will be used for determination of transport parameters, namely longitudinal dispersion coefficient. Tracer (CaCl_2) will be used for determination of longitudinal dispersion coefficient. The sorption potential of calcium chloride is relatively low, and its suitability has been demonstrated in the unsaturated zone (Seuntjens et al., 2001; Akhtar M.S. et al., 2003; Heilig et al., 2003; Dišli, E., 2010). The plot area for tracer application is 4.5 m². All vegetation will be removed from the research area and the surface will be leveled. 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 (Leibundgut et al., 2009):

$$V_w = \pi \times r^2 \times L \times n \quad (3)$$

where V_w is the water volume (m³), L is length (m) from surface to lowest placed lysimeter in pedological burrow, r is radius (m) of surface area on the top of pedological burrow and n is porosity.

Mass of tracer (CaCl_2) was calculated with the following equation:

$$M = 15 \times C_b \times V_w \times n \quad (4)$$

where M is mass of tracer (g), C_b is the detection limit of measurement method for salt tracer (mg/l) used (in this investigation, it is ion chromatography and detection limit is 0.67 mg/l).

Over a period of 15 min a tracer cocktail of 1 L CaCl_2 -solution (45 g CaCl_2) will be spread on the soil surface followed by 200 L of pure water for flushing.

Concentrations of tracer (CaCl_2) in percolating water will be analyzed in leachate, after occasional sampling by suction lysimeters, installed at four different depths.

Mathematical and numerical model

Water flow equation. Water flow in unsaturated zone is based on the following equation often referred to as the Richard's equation (Richards, 1931):

$$\frac{\partial \theta(h)}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] - S \quad (5)$$

Where: z is the vertical coordinate positive upward from water table (m), t is time (s), h is the pressure head (m), θ is the water content (cm³/cm³), S is a sink term representing root water uptake (1/s), 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 (m/s). Richard's equation, Eq. (5), will be solved numerically for one-dimensional water flow. Period (t) of modeling will be set on one year.

Transport equation. Advection, dispersion and sorption are processes of solute transport which will be modeled in unsaturated zone. Solute transport is described using the advection–dispersion equation with sorption in the following form:

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s}{\partial t} = \frac{\partial}{\partial z} \left(\theta D \frac{\partial c}{\partial z} \right) - \frac{\partial q}{\partial z} - \Phi \quad (6)$$

Where: c is the solution concentration (mg/l), s is the sorbed concentration (mg/g), D is the dispersion coefficient accounting for hydrodynamic dispersion (m²/s), q is the volumetric fluid flux density (m/s), and Φ is rate constants representing reactions (mg/m³s).

The reaction term Φ of Eq. (6) 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 (Šimůnek and Van Genuchten, 2006). In analytical and numerical models these reactions are most commonly expressed using first-order reaction rates as follows:

$$\phi = - \frac{d[A]}{dt} \quad (7)$$

In this research reaction terms will be left out and only sorption processes will be modeled.

Boundary conditions. The boundaries define the hydraulic conditions at the boundary layer or system (Bačani and Posavec, 2011). Determination of flow boundaries was based on detailed field analysis of investigative profile. The model domain is delineated by the atmospheric conditions (precipitation and evaporation) on the upper boundary, known hydraulic head as boundary condition on the bottom of profile (variable pressure head) and no flow boundary conditions on the left and right domain margins (Figure 8). Average value for precipitation is 843.7 mm/year, while for evaporation is 740 mm/year (Bačani, 2006).

Atmospheric condition permits water to build up on the surface. The height of the surface water layer increases due to precipitation and reduces because of infiltration and evaporation (Šimůnek et al., 1998). Variable pressure head represents boundary condition which is controlled by water table.

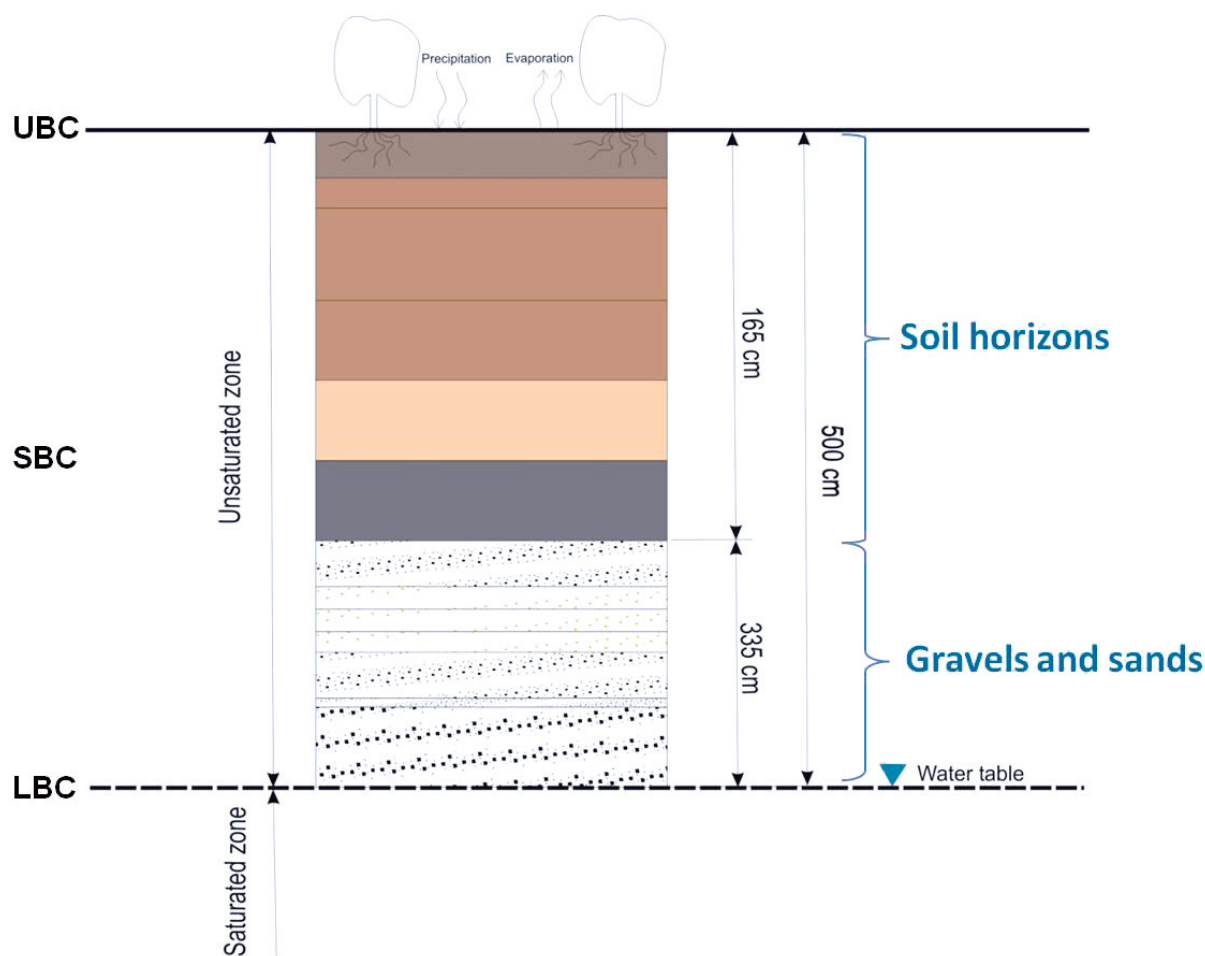


Figure 8. Sketch of profile Kosnica with boundaries conditions for water flow and solute transport modeling in unsaturated zone. Legend: UBC-upper boundary condition; SBC-side boundary condition; LBC-lower boundary condition

Slika 8. Skica profila Kosnica s graničnim uvjetima za modeliranje toka vode i transporta otopina u nesaturiranoj zoni. Legenda: UBC-gornji granični uvjet; SBC-bočni granični uvjet; LBC-donji granični uvjet

The model domain is delineated by the concentration flux on the upper boundary, zero concentrations gradient on the lower boundary conditions, and no concentration flux boundary conditions on the left and right domain margins (Figure 8).

Numerical solution of the flow and solute transport equation (finite element scheme). The governing flow and transport equations are solved numerically with Hydrus 1D software (Šimůnek et al., 1998) using Galerkin-type linear finite element schemes. The Galerkin finite element method was used to solve the solute and heat transport equations subject to appropriate initial and boundary conditions.

Conclusions

In order to define conceptual model for water flow and solute transport in unsaturated zone at Kosnica site, vertical profile of unsaturated zone and pedological burrow were excavated. Complete descriptions of profile as well as mi-

nerological, geochemical and sedimentological analyses of soil horizons and sediment layers were made. Equipments for monitoring of physical soil parameters and suction lysimeters were installed. Monitoring data with resolution of 2 hours have been collected for ten months. All till now obtained results were the basis for setting field and laboratory experiments for determination of solute transport parameters, namely dispersivity and sorption. According to sorption of Cd, Pb and Zn, from the multicomponent batch experiments that followed different trends shows that Pb had a slightly higher affinity for sorption on these soil textures than Cd and Zn. The study is still ongoing, and results are intended to be used in risk assessment of groundwater contamination at Kosnica site.

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