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VPLIV AGREGACIJE POROZNEGA MEDIJA NA PRENOS NITRATA IN AMONIJA V ZEMELJSKIH KOLONAH
THE INFLUENCE OF POROUS MEDIA AGGREGATION ON THE NITRATE AND AMMONIUM TRANSPORT IN SOIL COLUMNS

Vesna ZUPANC, Miran VESELIČ, Peter CEPUDER

V enodimenzionalnih kolonah smo preučevali prenos tekočine z drugo mešajočo tekočino v nasičenih pogojih. Kot sledilo za opazovanje obnašanja dušika v procesih prenosa, smo uporabili dušično gnojilo (mešanica amonijske (NH_4^+) in nitratne (NO_3^-) oblike dušika). Za premikajočo tekočino smo uporabili destilirano vodo. Med izvajanjem poskusov so se pogoji v kolonah, napolnjenih z medijem frakcije tal < 2 mm spremenili. Izbrana velikost agregatnih delcev je imela vpliv na obnašanje sledila. Krivulje prehoda NO_3^- so bile v primerjavi s krivuljami prehoda NH_4^+ simetrične oblike pri vseh velikostih agregatnih delcev. Krivulje prehoda NH_4^+ so dobile simetrično obliko pri večjih delcih od 0.63 do 2 mm in od 2 do 4 mm. Največji vpliv na prenos NH_4^+ je imela sposobnost fiksacije NH_4^+ na negativne površine delcev.
Ključne besede: *kolonski poskusi, porozen medij, velikost delcev, nitrat, amonij*

The displacement of one fluid by another miscible fluid under saturated conditions and at different average flow velocities in one – dimensional soil columns was studied. For the tracer solute, nitrogen fertilizer (combination of ammonium (NH_4^+) and nitrate (NO_3^-) form of nitrogen) was used to observe the behavior of the nitrogen in the transport processes. For the displacing fluid, distilled water was used. In the course of the experiments, conditions in soil columns with < 2 mm soil fraction were altered. The size of the chosen aggregates influenced the behavior of the tracer. Breakthrough curves of NO_3^- were compared to the NH_4^+ breakthrough curves symmetrical with all aggregate sizes. The BTC of the NH_4^+ obtained a clear shape with the larger aggregate sizes 0.63–2 mm and 2–4 mm. The greatest influence on the NH_4^+ transport had the ability of the NH_4^+ to fixate on the negatively charged particle surfaces.
Key words: *column experiments, porous media, aggregate size, nitrate, ammonium*

1. UVOD

Kakovost podtalnice je lahko ogrožena zaradi različnih onesnažil, zatorej je poznavanje in razumevanje procesov prenosa, kot so sorpcija, disperzija in difuzija nujno in pomembno. Prisotnost nitratov (NO_3^-) v podzemnih vodah je posledica številnih dejavnikov. Eden glavnih dejavnikov onesnaževanja je neprimeren način kmetovanja.

Dušik je bistvena sestavina rastlinskih gnojil in igra pomembno vlogo pri povečevanju količine in kakovosti pridelka

1. INTRODUCTION

Groundwater quality can be compromised by many different contaminants; therefore, it is imperative to understand the importance of transport mechanisms such as sorption, dispersion, and diffusion. The widespread appearance of nitrate (NO_3^-) in ground water is a consequence of a number of factors. Unsuitable agricultural practices are one of the main pollution sources.

Nitrogen is an integral component of many essential plant nutrients and plays important roles in increasing crop yields and crop quality (Brady, 1998). The human mediated

(Brady, 1998). Vnos reaktivnega dušika v nitratni (NO_3^-) in amonijski obliki (NH_4^+) z gnojenjem je najbolj učinkovita metoda za povečanje rastlinske proizvodnje. Vendar ima odvečni dušik, uporabljen za gnojenje, nedvomno okoljevarstvene posledice na globalni, regionalni in lokalni ravni, kot npr. onesnaženje površinskih in podzemnih voda z NO_3^- (Brady, 1998).

Kationska narava NH_4^+ omogoča retenzijo NH_4^+ - N na talnih koloidih v izmenljivi obliki, tako so ioni v tej obliki učinkovito zaščiteni pred izpiranjem s pronicujočo vodo (Nommik & Vahtras, 1982). Med talne koloide uvrščamo glinene minerale, organske snovi ali okside mangana in železa ter so večinoma negativno nabiti.V nasprotju z NH_4^+ ioni, se NO_3^- ioni ne vežejo na negativno nabite koloide, ki prevladujejo v večini tal. Zatorej se NO_3^- ioni prosto gibljejo navzdol z odtekajočo vodo in so tako zlahka sprani iz tal. Te izgube NO_3^- povzročijo širše resne okoljske težave in hkrati zmanjšajo produktivnost ekosistema (Brady, 1998). V svetovnem merilu izpiranje NO_3^- iz tal še vedno predstavlja izgubo okrog 19 odstotkov celotnega dušika, ki se uporabi za gnojenje (Lin et al., 2001). Kljub pomembnosti problematike pa je razumevanje izpiranja NO_3^- iz različnih tipov tal še vedno pomanjkljivo (Hansen et al., 2000).

Pri študiju spiranja NO_3^- iz tal in procesov v tleh se pogosto uporabljajo kolonski poskusi. Iz praktičnih razlogov je težko izpeljati poljske poskuse na regionalni ravni pod normalnimi pogoji toka, mogoče pa je oceniti relativni transport reaktivnih in nereaktivnih snovi v laboratorijskih poskusih. V Sloveniji smo jih uporabili pri raziskavah vpliva vrste gnojila in tipa tal na koncentracijo in izotopsko sestavo NO_3^- v perkolatu z ^{15}N (Pintar et al., 1998; Lojen et al., 1999; Pintar, 2001), ki so sledile študijam izvora onesnaženja podtalnice z NO_3^- na Apaškem polju, s pomočjo stabilnih izotopov. Poskus izpiranja je potrdil, da za izluževanje NO_3^- iz tal ni pomembna le vrsta gnojila, pač pa tudi substrata. Podatki, ki jih pridobimo iz takih poskusov, lahko v praksi pojasnijo pretekla gibanja onesnažil v podtalnici ter so v pomoč pri napovedi prenosa snovi.

introduction of reactive nitrogen such as nitrate (NO_3^-) and ammonium (NH_4^+) for fertilization, has been recognized as the most effective method for increasing food production. However, excess nitrogen used in fertilization has undoubtedly resulted in various global, regional and local environmental problems such as the NO_3^- pollution of ground and surface waters (Brady, 1998).

The cationic nature of NH_4^+ permits the retention of NH_4^+ - N by soil colloids in exchangeable form, and in this form, the ions are effectively protected against leaching by percolating waters (Nommik & Vahtras, 1982). Soil colloids are clay minerals, organic substances or manganese or iron oxides and are mostly negatively charged. In contrast to NH_4^+ ions, NO_3^- ions are not adsorbed by the negatively charged colloids that dominate most soils. Therefore, NO_3^- ions move downward freely with percolating water, and are thus readily leached from the soil. Such NO_3^- leaching losses not only cause several serious environmental problems, but also reduce ecosystem productivity (Brady, 1998). Of the total amount of applied fertilizers worldwide, 19% is lost to NO_3^- leaching (Lin et al., 2001). In spite of the importance of the issue, a major deficiency in our understanding of NO_3^- leaching form various soil types persists (Hansen et al., 2000).

For the NO_3^- leaching and transport processes, research column experiments are often used. Due to practical constraints, it is difficult to conduct field tests at regional scales under normal flow conditions; however, it is feasible to gauge the relative transport of reactive and non-reactive solutes at the laboratory scale. Column experiments have been used for he research of the influence of different fertilizer and soil types on NO_3^- concentration and isotopic composition in effluent with ^{15}N (Pintar et al., 1998; Lojen et al., 1999; Pintar, 2001), which followed the research on the source of NO_3^- groundwater pollution in the Apače valley using stable isotopes. The experiment showed that for NO_3^- leaching, not only the type of fertilizer applied, but that substrate type was also important. On a practical level, data obtained from such tests can elucidate past contaminant movement in groundwater, and may also assist in transport prediction.

Z uporabo mešanih sledil različnih fizikalnih in kemičnih lastnosti lahko ločimo različne parametre prenosa snovi in tako zagotovimo edino mogočo rešitev za uporabne enačbe. Kemična in fizikalna sredstva prenosa snovi so pod vplivom porozne narave medija. Večina zemljin je strukturiranih, vsebujejo agregate ali pore različnih velikosti. V tem primeru se gibanje vode ne more opisati s posamezno povprečno hitrostjo toka, ker voda znotraj večjih por teče znatno hitreje kot v manjših porah. Vodo, ki se nahaja v majhnih porah znotraj gostih agregatov, lahko označimo kot efektivno stoječo. Snovi bodo skozi večje pore migrirale s premikanjem vode (konvekcija), medtem ko difuzija snovi v stagnirajočo raztopino povzroči zaostanek.

Ta fenomen pripisujemo fizikalnemu neravnovesju ali neravnovesju prenosa (Brusseau & Rao, 1990). Ta povzroči asimetrično krivuljo prehoda za nereaktivne kemikalije: do začetnega prehoda snovi pride hitreje, celoten prehod snovi pa traja precej dalj, kot bi pričakovali v primeru homogenih tal. Ta pojav, ki se lahko označi kot razvlečen prehod, je bil opažen v študijah prenosa snovi v različnih tipih strukturiranih medijev, kot so agregirane in razpoklinske zemljine, zemljine z makroporami, kanali korenin in kanali zemeljskih črvov ter v zemljinah s prostorskimi razlikami v hidravlični prevodnosti tal (Brusseau & Rao, 1990).

Razvlečeni prehodi krivulj prehoda so posledica nihanj hitrosti fluida porozne snovi, povzročene zaradi zamašenih por. Blokada ustij por povzroči visoke hitrosti v preferenčnih poteh, kar vodi v zgodnji prehod snovi. Območja s slabo prepustnostjo zakasnijo prehod snovi, kar poveča nagib krivulj prehoda (Bouhroum & Civan, 1994).

By using multiple tracers of differing physical and chemical characteristics, the various transport parameters can be separated, and thus provide a unique solution of the applicable governing equations. The chemical and physical means of transport are influenced by the porous nature of the media. Most soils are structured; they contain aggregates or pores with a range of sizes. The water movement cannot be described by one average flow velocity because soil water flows significantly faster in larger pores than in smaller pores. The soil water that is located in the small pores inside aggregates might even be considered effectively stagnant. The solute will migrate along with the movement of the water through the large pores (convection), while diffusion into the stagnant solution causes retardation.

This phenomenon is referred to as physical non-equilibrium or transport non-equilibrium (Brusseau & Rao, 1990). It causes an asymmetrical breakthrough curve for non-reacting chemicals: initial breakthrough occurs faster, and complete breakthrough takes much longer. That would be expected in the case of a homogeneous soil. This effect, also named 'tailing', has been observed in transport studies with different types of structured media, such as aggregated and fractured soils; soils with macropores, root channels or earth worm channels and soils with spatial variation in hydraulic conductivity (Brusseau & Rao, 1990).

Long tails in BTCs are a result of the velocity fluctuations induced by particle clogging. The blockage of pore necks, which induces higher velocity in preferential flow pathways, leads to early solute penetration; whereas the low permeability zones which delay the rate of the solute transport increase the skewness of the BTCs (Bouhroum & Civan, 1994).

2. MATERIALI IN METODA DELA

V enodimenzionalnih kolonah smo preučevali prenos tekočine z drugo mešajočo tekočino v nasičenih pogojih. Kot sledilo za opazovanje obnašanja dušika v procesih prenosa je bilo uporabljeno dušično gnojilo (mešanica amonijske NH_4^+ in nitratne NO_3^- oblike dušika) v ekvivalentu 100 kg N/ha. Za premikajočo tekočino smo uporabili destilirano vodo (ISO 3696:1987).

Krivulje prehoda za sledilno raztopino (C_o) so izmerjene za dve hitrosti vode porozne snovi. Dve hitrosti sta določeni z različnima ravnema vodnih tankov. Na podlagi teksturne klasifikacije, dostopne na Inštitutu za hidravliko in upravljanje z vodami v kmetijstvu, sta bili določeni dve lokaciji za zbiranje vzorcev tal (preglednica 1). Vzorec tal s poskusnega polja Univerze za agronomske znanosti na Dunaju pri Gross–Enzersdorfu (GE), v bližini Dunaja, je bil vzet iz globine 0 do 25 cm, vzorec tal s poskusnega polja Univerze za agronomske znanosti na Dunaju pri Pyhra (P) pa iz globine 15 cm.

2. MATERIALS AND METHOD

The displacement of one fluid by another miscible fluid under saturated conditions in one – dimensional soil columns was studied. For the tracer nitrate, fertiliser in the equivalent of 100 kg N/ha (combination of ammonium NH_4^+ and the nitrate form NO_3^- of nitrogen) was used to observe the behavior of the nitrogen in the transport processes, and for displacing the fluid distilled water.

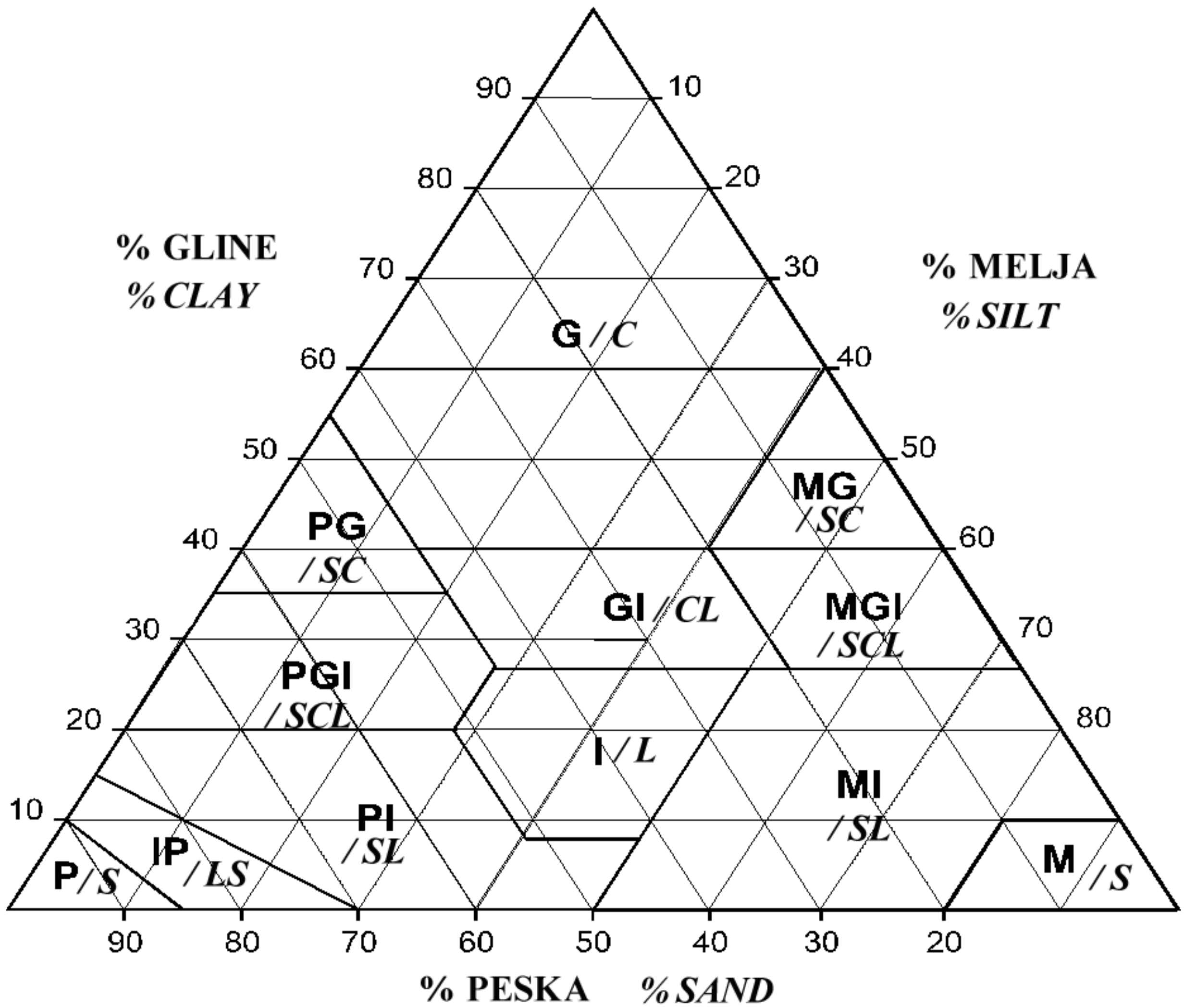
The breakthrough curves for the tracer solute C_o) were measured for two pore water velocities. The two water velocities were determined by the different water tank levels. Based upon the textural classification available at the Institute for Hydraulics and Rural Water Management, two locations were identified for soil sample collection (Table 1). Soil from the experimental station of the University of Agricultural Sciences, Vienna, at Gross – Enzersdorf (GE), near Vienna, was collected from a depth of 0 – 25 cm, and soil from the experimental site of the University of Agricultural Sciences, Vienna, at Pyhra (P), was collected up to a depth of 15 cm.

Preglednica 1. Teksturna klasifikacija vzorcev tal P < 2 mm in GE < 2 mm.
Table 1. Textural classification of P < 2 mm and GE < 2 mm samples.

	Prod **Gravel** **>2 mm**	Pesek **Sand** **2–0,06 mm**	Melj **Silt** **0,06–0,002 mm**	Glina **Clay** **>2 μm**	Teksturni razred (Slika 1) ***Textural classification (Figure 1)***
P < 2 mm	0	34	45	21	Ilovica / *Loam*
GE < 2 mm	0	20	55	25	Meljasta ilovica / S*ilty loam*

Vzorci tal so bili v laboratoriju posušeni s pomočjo električnih ventilatorjev. Večje grude tal smo previdno ločili in odstranili gramoz. Prav tako smo odstranili kamne in korenine. Preostali vzorec smo presejali skozi sita velikosti 4 mm, 2 mm, 1 mm in 0.63 mm. Drug material (npr. manjši ostanki korenin), ki je prodrl skozi sita, smo izločili. Na presejanih talnih vzorcih so bile narejene analize za teksturo tal (slika 1), pH tal, električno prevodnost kot tudi za organski ogljik, humus in celokupen dušik (preglednica 2).

The soil was dried, carefully disintegrated and the gravel, stones and roots were removed. The remaining soil was sieved through 4 mm, 2 mm, 1 mm and 0.63 mm sieves, and all the material passing through was collected separately (i.e. smaller root residues) and removed. For the sieved soil sample particle size analysis (Figure 1), soil pH and electrical conductivity were determined, as well as organic carbon, humus and the total nitrogen composition (Table 2).



Slika 1. Teksturni trikotnik po USDA klasifikaciji (Vrščaj, 2001)
Figure 1. Texture triangle after USDA classification (Vrščaj, 2001)

Preglednica 2. Kemične lastnosti in mineraloška struktura celokupnih vzorcev.
Table 2. Chemical properties and mineralogical structure of bulk samples.

	P < 2 mm	**GE 0,63–2 mm**	**GE 2–4 mm**
MINERALOŠKA STRUKTURA CELOKUPNIH VZORCEV ***MINERALOGICAL STRUCTURE OF BULK SAMPLES***			
% Kremen / *% Quartz*	60	59	55
% Silikatni sloji / *% Silicate layers*	31	0	0
% Sljud / *% Feldspars*	9	5	2
% Kalcit / *% Calcite*	0	19	17
% Dolomit / *% Dolomite*	0	17	25
KEMIJSKE LASTNOSTI / *CHEMICAL PROPERTIES*			
pH	6.4	8.27	8.89
Električna prevodnost (μS/cm) *Electrical conductivity (μS/cm)*		0.3	0.32
Organski ogljik / *Organic carbon*	1.24	0.777	0.456
Humus	2.138	1.34	0.785
Skupni dušik / *Total nitrogen*	15	10	5
TEKSTURA (po USDA klasifikaciji)	Ilovica	Pesek	Prod
TEXTURE (after USDA classification)	*Loam*	*Sand*	*Gravel*

Kot sledilo je bilo uporabljeno mešano dušično gnojilo amonij nitrat (komercialno ime Nitramoncal/NAC, proizvaja AgroLinz, Avstrija, 27% N-NO_3, 27% N-NH_4), ki je v vodi zelo topen. Z agronomskega stališča je odlično gnojilo. Zagotavlja enake količine NH_4^+ in NO_3^- oblike dušika, kar je fiziološka prednost pri prehrani rastlin (Follet, 1989).

Za kemično analizo perkolata je bila za določitev NH_4^+ uporabljena metoda z indofenolom. NH_4^+ oksidira s pomočjo aktivnega klora v kloramin. Reakcija se pojavi ob oksidaciji fenola v chinonchloramin, ki se v alkalnih snoveh veže z drugimi fenoli v zeleno obarvan indofenol. Koncentracijo indofenola lahko fotometrično ugotovimo pri 660 nm.

Za določitev NO_3^- je bila uporabljena metoda po Navonnu. NO_3^- adsorbira UV-svetlobo v kislem mediju. Valovna dolžina svetlobe, uporabljene pri tej metodi je 210 nm. Ker pa pride do adsorpcije nekaterih drugih organskih substanc, kot npr. huminske kisline

As a tracer, ammonium nitrate (commercial name Nitramoncal/NAC, produced by AgroLinz, Austria, 27% N-NO_3, 27% N-NH_4) was used. It is highly soluble in water. From an agronomic standpoint it is an excellent fertilizer. It provides equal amounts of NH_4^+ and the NO_3^- form of N, which may be a physiological advantage in the nutrition of crops (Follet, 1989).

For the chemical determination of NH_4^+ in the effluent, the indophenol method was used. NH_4^+ oxidizes through active chlor to chloramin. The reaction occurs in the presence of phenol under the oxidation to chinonchloramin, which, in an alkaline media, bonds with other phenol to a green colored indophenol. The concentration of indophenol can be photometrically determined at 660 nm.

For NO_3^- determination, the method belonging to Navonne was used. NO_3^- adsorbs UV light in an acidic medium. The wavelength used with this method is 210 nm. Because some of the organic substances, such as the humic acids, also adsorb at the same pri isti valovni dolžini, moramo izvesti dve meritvi. Pri drugem merjenju izmerimo količino motečih substanc. Zaznavo koncentracije NO_3^- ovirajo bakreni svinčeni delci, ki jih pred drugo meritvijo čez noč dodamo vzorcu. Perkolat je bil vzorčen z avtomatičim vzorčevalnikom.

Spodnji del kolone je bil zaprt z zamaškom iz pleksi stekla. Kolono smo pazljivo napolnili s posameznimi vnosi po 100 g vzorca tal. Vzorec tal znotraj kolone smo enakomerno porazdelili, s fino paličico smo ga premešali, da bi odstranili sloje, ki bi se lahko oblikovali ob posameznih vnosih v kolono. Kolone smo nato udarili po vseh štirih smereh na zunanji strani, da bi zagotovili homogenost posamezne kolone. Kolono smo zaprli s čepom iz pleksi stekla. Na vsakem koncu kolone iz pleksi stekla smo namestili fin najlonski filter, ki je preprečeval izgubo vzorca tal med poskusom (slika 2).

Težo dela iz pleksi stekla, težo in volumen suhega in nasičenega vzorca tal smo določili gravimetrično za vsako kolono, da bi lahko izračunali poroznost, suhi obseg gostote in vsebnost vlage v tleh (preglednica 3).

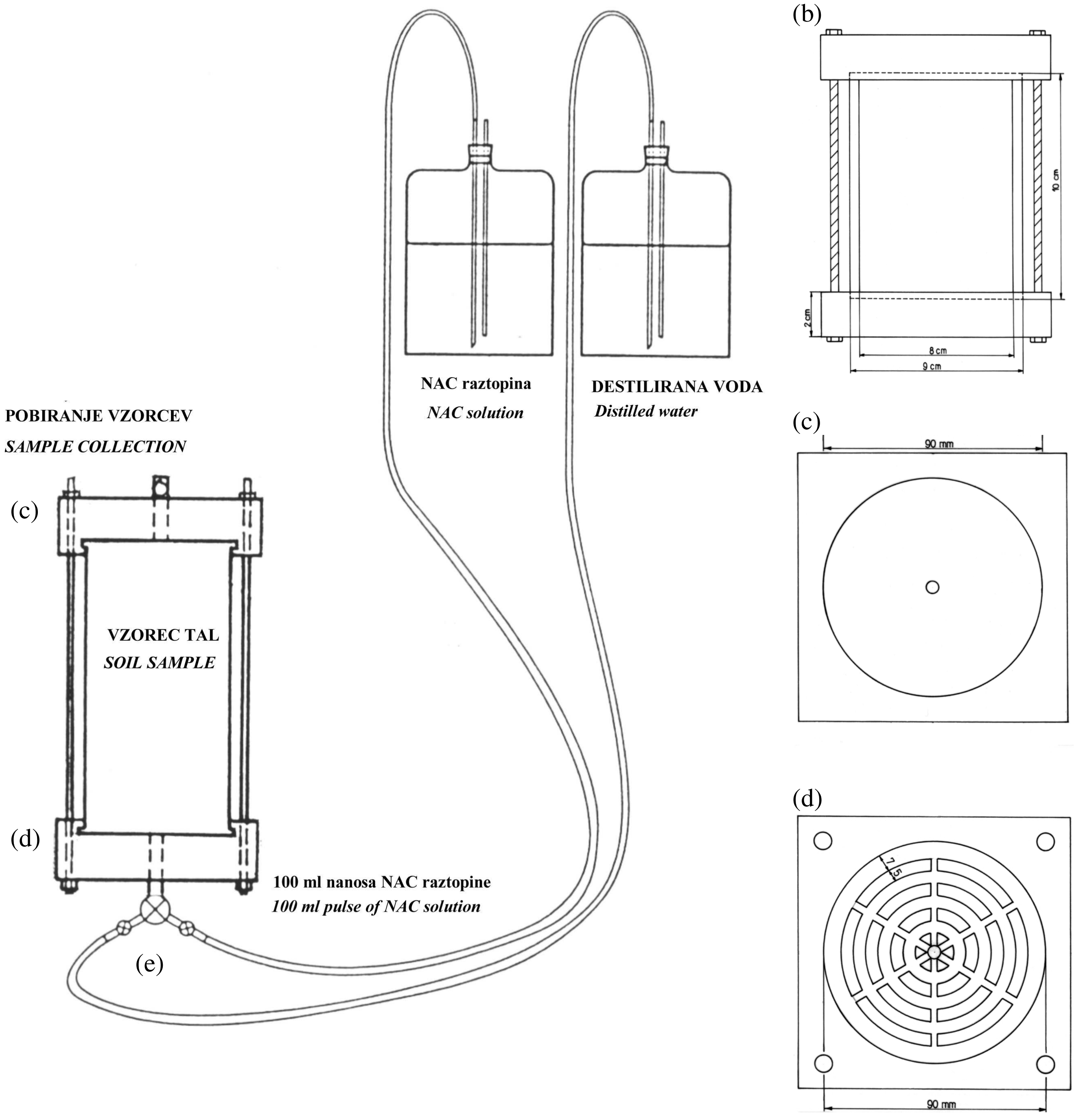
Kolono z vzorcem tal smo počasi od spodaj nasičili z destilirano vodo v času 24 ur. Najprej smo dovolili, da se je voda znotraj kolone dvignila s pomočjo kapilarnega dviga, nato pa smo pri vstopu počasi dvigovali pritisk, dokler ni pričela pritekati tekočina pri izhodni cevki. V tistem trenutku smo kolono stehtali, da bi ugotovili volumen vode v koloni.

wavelength, two measurements were needed. The second time, only the disturbing substances were measured. The registration of the NO_3^- concentration was hampered by adding coppered zinc granulates to the probe overnight. The effluent solution was collected with an automatic sample changer.

One end of the column was enclosed with a Plexiglas end cap. The column was carefully packed by dropping 100 g of soil into the column each time. The soil inside the column was spread uniformly and stirred with a very fine rod to remove any layers which might have formed each time the soil was dropped inside the column. To ensure that media inside the column remained homogenous, the column was also tapped from all four directions on the outer side. The column was closed by a Plexiglas end cap, and a fine nylon filter was placed to prevent soil sample loss during the experiment (Figure 2).

The weight of the Plexiglas assembly, and dry and saturated soil weight and volume were determined gravimetrically for each column, in order to calculate porosity, dry bulk density and the moisture content of the soil (Table 3).

The soil column was slowly saturated from the bottom with distilled water for 24 hours. Initially the water was allowed to rise inside the column by capillary rise, and later the head at the inlet was slowly raised until the solution started appearing from the outlet. At this moment the soil column was weighed to determine the water content of the column.



Slika 2. (a) Oprema in postavitev poskusa. (b) Stranski ris valjaste prozorne kolone iz pleksi stekla (10 cm dolžine, 9 cm zunanji premer, 8 cm notranji premer), tloris pokrova pri vtoku (d) in iztoku (c), (e) menjalna točka.
Figure 2. (a) Experiment equipment and installation. (b) Side plan of the cylindrical transparent Plexiglas column (10 cm length, 9 cm outer diameter; 8 cm inner diameter), (c) ground plan of the inlet and (d) outlet cover; (e) switching point.

Po doseženem ravnotežju smo poskuse pričeli z nižjo hitrostjo vode porozne snovi. Po določitvi pritiska za dano hitrost vode porozne snovi smo vhodno cev preusmerili (t = 0) v rezervoar s tekočino za premeščanje, tj. destilirano vodo (slika 2, e). Iz rezervoarja na vstopnem koncu smo koloni dodali 100 ml vodne raztopine dušičnega gnojila (NAC) in nato to raztopino spodrinili z destilirano vodo. Avtomatični izmenjalec vzorcev je zbiral perkolat ob določenih časovnih intervalih v majhne plastične lonce (max 80 ml). Vse poskuse smo izvajali pri stalni temperaturi 20° C ± 1° C.

The experiments started with the lowest pore water velocity after reached equilibrium. After establishing the head for a given pore water velocity, the input line was changed (t = 0) to the reservoir containing the displacing solute, i.e. distilled water (Figure 2, e). From a reservoir at the input end, a volume of 100 ml of an aqueous solution of nitrogen fertilizer (NAC) was added to the column, and then the solution was displaced by distilled water. The automatic sample changer collected the effluent at fixed time intervals in small plastic bottles (max 80 ml). All the experiments were conducted at a constant temperature of 20°C ± 1°C.

Preglednica 3. Podatki za zemeljske kolone.
Table 3. Soil column data.

	Specifična gostota tal (g/cm^3) *Bulk density (g/cm^3)*	**Poroznost** *%* *Porosity %*	**Volumska vsebnost vode θ** *Volume Wetness θ*	**Povprečni tok (ml/h)** *Average flow (ml/h)*	**Hitrost vode porozne snovi (cm/h)** *Pore water velocity (cm/h)*	**Darcy-jeva hitrost (cm)** *Darcy's velocity (cm)*	***Re* število** ***Re* number**	***K* (začetni) (cm/sec)** *K (start) (cm/sec)* **x 10^{-5}**	***K* (končni) (cm/sec)** *K (end) (cm/sec)* **x 10^{-5}**
	< 2 mm								
1	1.49	0.44	0.42	15.66	0.74	0.3	0.2	1.15	1.04
				19.26	0.91	0.4	0.2	1.28	1.17
2	1.48	0.44	0.39	20.1	1.03	0.4	0.2	1.59	1.41
				30.1	1.54	0.6	0.3	2.03	1.77
	0.63–2 mm								
1	1.55	0.41	0.42	36.5	1.74	0.7	0.4	5.93	
				46.73	2.20	0.9	0.5	4.69	
2	1.55	0.42	0.41	36.5	1.75	0.7	0.4	5.76	
				54	2.62	1.1	0.5	6.78	
	2–4 mm								
2	1.57	0.44	0.39	175.4	5.87	3.5	1.7	74.6	
				186.8	6.30	3.7	1.9	73.7	

Da bi preverili veljavnost Darcyevega zakona, na podlagi katerega smo izračunali hitrosti vode porozne snovi in hidravlično prevodnost vzorca v zemeljski koloni, smo določili tudi Reynoldsovo število (*Re*). *Re* za porozen medij smo izračunali po formuli:

Pore water velocity and hydraulic conductivity were calculated based on Darcy's law. To gauge the Darcy's law validity for this experiment, Reynolds number for flow through porous media was determined:

$$\mathrm{Re} = \frac{q \cdot d}{v} \tag{1}$$

kjer je q specifični pretok (cm/sek), d reprezentativna dimenzija zrn (cm) ter v kinematična vsiskoznost tekočine (cm^2/sek) (preglednica 3).

Tako rekoč v vseh primerih, kjer je *Re*, izračunano na podlagi povrečnega premera zrn med 1 in 10, je Darcyev zakon veljaven. Pri večjih *Re* pride do tranzicijske cone. Na spodnjem delu je prehod iz laminarnega režima, kjer prevladujejo sile viskoznosti, do drugega območja laminarnega režima, kjer prevladujejo sile inercije. V zgornjem koncu tranzicijske cone je postopen prehod do območja turbulentega toka. Nekateri avtorji navajajo kot zgornjo mejo za laminarni tok vrednost *Re* 100 (Bear, 1988).

3. REZULTATI Z DISKUSIJO

Predmet te raziskave so bili laboratorijski sledilni poskusi, pod nasičenimi pogoji v kolonah (dolžine 10 cm), s tremi različnimi frakcijami talnih delcev (vzorec tal P < 2 mm, vzorec tal GE 0.63–2 mm in 2–4 mm). Kot sledilo je bilo uporabljeno mešano dušično gnojilo Nitratamoncal (NAC), v količini, ekvivalentni nanosu 100 kg N/ha. Namen laboratorijskega eksperimentalnega dela je bil ugotoviti obnašanje dušika v obliki nitratnega (NO_3^-) in amonijevega iona (NH_4^+), v odvisnosti od teksture tal.

3.1 PREPUSTNOST

Pred začetkom poskusa so bili določeni poroznost, specifična gostota tal in hidravlična prevodnost (Preglednica 3). Med poskusom so se v kolonah z vzorcem tal P < 2 mm po vnosu sledilne raztopine pogoji spremenili, zato smo po končanem poskusu vnovič določili hidravlično prevodnost (Slika 3). Sprememba je nastala kot posledica nenamernega stranskega učinka, ob odprtju vtoka na atmosferski pritisk (to je bilo opazno tudi pri poskusih na večjih talnih frakcijah) in kot posledica spremembe prepustnosti kolone zaradi rabe sledila.

where q is the specific discharge (cm/sec), d, the representative dimension of the grains (cm), and v, the kinematic viscosity of the fluid (cm^2/sec) (Table 3).

In practically all cases, Darcy's law is valid as long as the *Re* based on the average grain diameter does not exceed some value between 1 and 10. As *Re* increases, we observe the transition zone. At the lower end of this zone we have the passage from the laminar regime, where viscous forces are predominant, to another laminar regime, where inertial forces govern the flow. At the upper end of the transition zone we have a gradual passage to the turbulent flow. Some authors suggest *Re* 100 for the upper limit of the laminar flow regime (Bear, 1988).

3. RESULTS AND DISCUSSION

The subject of this study were laboratory trace experiments under saturated conditions in soil columns (length 10 cm) with three various soil aggregates (soil sample P < 2 mm, and soil sample GE 0.63–2 mm and 2–4 mm). As a tracer, mixed nitrogen fertilizer Nitratamoncal (NAC) in the equivalent of 100 kg N/ha was used. The purpose of the laboratory experimental work on the soil columns with various soil fractions was to determine the behavior of nitrogen in the form of the nitrate ion (NO_3^-), and the ammonium ion (NH_4^+), in relationship to the soil texture.

3.1 PERMEABILITY

Before the experiment, porosity, bulk density and hydraulic conductivity were determined (Table 3). In the course of the experiments, column conditions with the P < 2 mm sample were altered after the tracer solute application; therefore, hydraulic conductivity was determined again after the experiment (Figure 3). The change occurred, firstly, due to the unintentional side effect of opening the inlet to the atmospheric pressure (as well noted with coarser fractions), and, secondly, due to the changes in column permeability caused by the use of the tracer.

Nepredviden učinek spiranja sledila z destilirano vodo je bila občutno zmanjšana prepustnost kolone. Za prvotno izbrani tip tal se sledilni poskusi niso posrečili, ker se je prepustnost v kolonah z vzorcem tal GE frakcije < 2 mm zmanjšala, preden je kolono prešel NO_3^- del sledila. Zmanjšana prepustnost je lahko posledica interakcije med NH_4^+ kationi sledila ter glinene frakcije tal. Vnos sledila v kolono lahko povzroči zmanjšano debelino difuznega dvojnega sloja okoli glinenih delcev (Luckner & Schestakow, 1991), kar koloidne agregate stabilizira. Vendar se zaradi spiranja sledila z destilirano vodo koncentracija kationov hitro zmanjša. To povzroči nenaden obrat v debelini difuznega dvojnega sloja. Povečan dvojni sloj lahko zmanjša permeabilnost zaradi dveh pojavov:

- nabrekanja frakcije glinenih mineralov,
- destabilizacije koloidnih agregatov.

Prvi pojav pomeni povečano razdaljo med prilegajočimi glinenimi delci zaradi povečanih elekričnih odbojnih sil in je torej reverzibilen pojav.

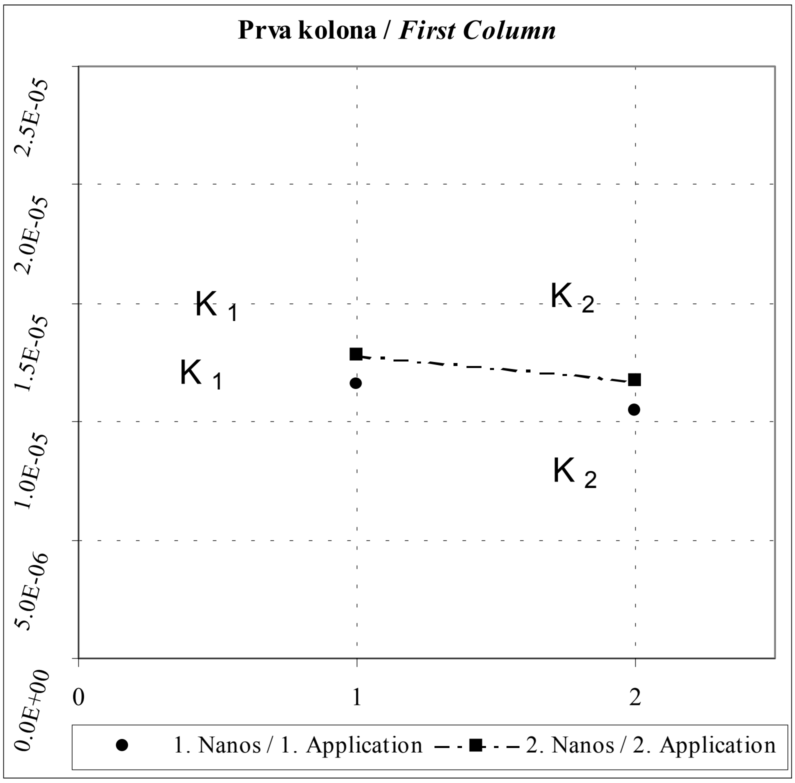
Drugi pojav pomeni razpad koloidnih glinenih agregatov zaradi povečanih odbojnih sil. Stabilnejši koloidni glineni delci postanejo mobilni in migrirajo skozi pore tal, dokler ne zaprejo mejnih por oziroma so izprani iz kolone. Ta proces je ireverzibilen. Do premeščanja delcev pa je verjetno prišlo tudi zaradi neprimerno izbranih hidravličnih gradientov za izbran tip tal.

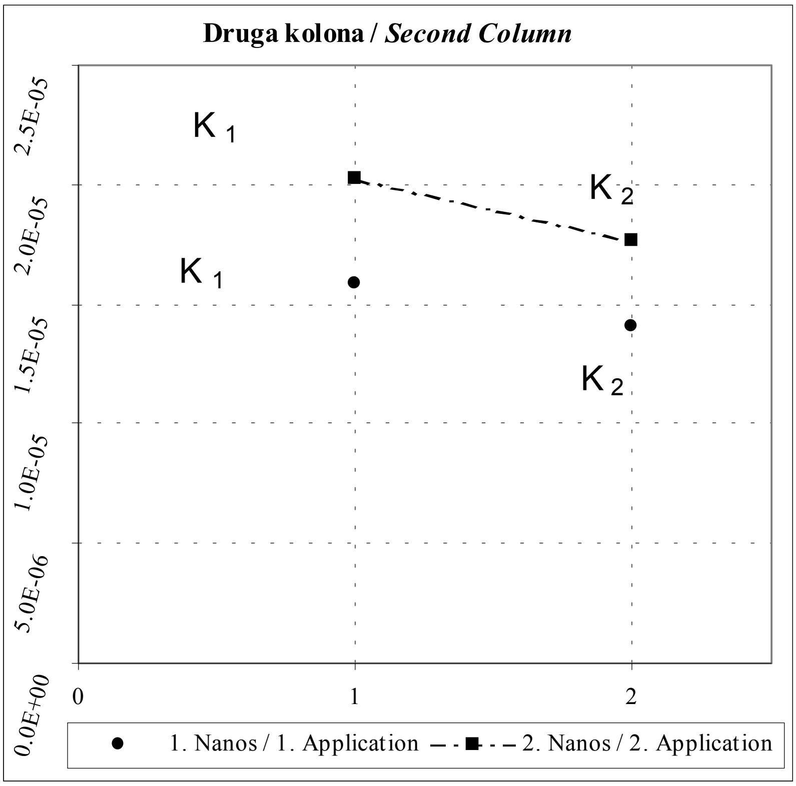
The unintentional side effect of the flushing with distilled water was a significant reduction in column permeability. Experiments on the originally chosen GE < 2 mm soil samples failed because the permeability was reduced before the NO_3^- part of the tracer came through the column. The reduced permeability may have been due to interactions between the NH_4^+ cations of the tracer and the clay fraction of the soil. The introduction of the tracer to the column may cause a decrease in the thickness of the diffuse double layer around the clay particles (Luckner & Schestakow, 1991), stabilizing the colloidal aggregates. However, when fresh water is used to flush the column, the cation concentration is suddenly reduced. This causes an abrupt reversal of the change in the thickness of the diffuse double layer. And the increasing double layer reduces the permeability via two mechanisms:

- swelling of the clay fraction,
- destabilization of the colloidal aggregates.

The first mechanism involves an increased distance between adjacent clay particles due to the increased electrical repulsive forces, and is, therefore, reversible.

The second mechanism involves colloidal clay aggregates breaking up due to the increased repulsive forces. The more stable colloidal clay particles become mobile and migrate through the soil pores until they clog pore restrictions or are washed out of the column. This process is irreversible. It is possible that the particle transport also occurred due to the inappropriate hydraulic gradients.





Slika 3. Sprememba koeficienta hidravlične prevodnosti pri poskusih na kolonah P < 2 mm. Vrednosti koeficienta hidravlične prevodnosti so se spremenile pri drugem poskusu na talnih kolonah P < 2 mm.
Figure 3. Hydraulic conductivity coefficient values of P < 2 mm soil column experiments Coefficient of hydraulic conductivity values changed with the second tracer experiment on the P < 2 mm soil columns.

3.2 VPLIV MIKROORGANIZMOV

Pojavi se vprašanje, ali je bil vpliv mikroorganizmov pri opisani nastavitvi poskusa odločilen na obliko dobljenih krivulj prehoda pri NO_3^- in NH_4^+. Poskus je bil izvajan pod nasičenimi pogoji, zatorej predvidevamo, da anoksičnih con ni bilo. Vzorec tal, uporabljen v poskusu, je bil pred pakiranjem toplotno tretiran (sušen na 105°C za 24 ur), pri katerem je prišlo verjetno do uničenja mikroorganizmov skoraj v celoti. Predvidevamo lahko, da je bil vpliv mirkoorganizmov na obliko krivulj prehoda minimalen.

3.3 VPLIV VELIKOSTI DELCEV

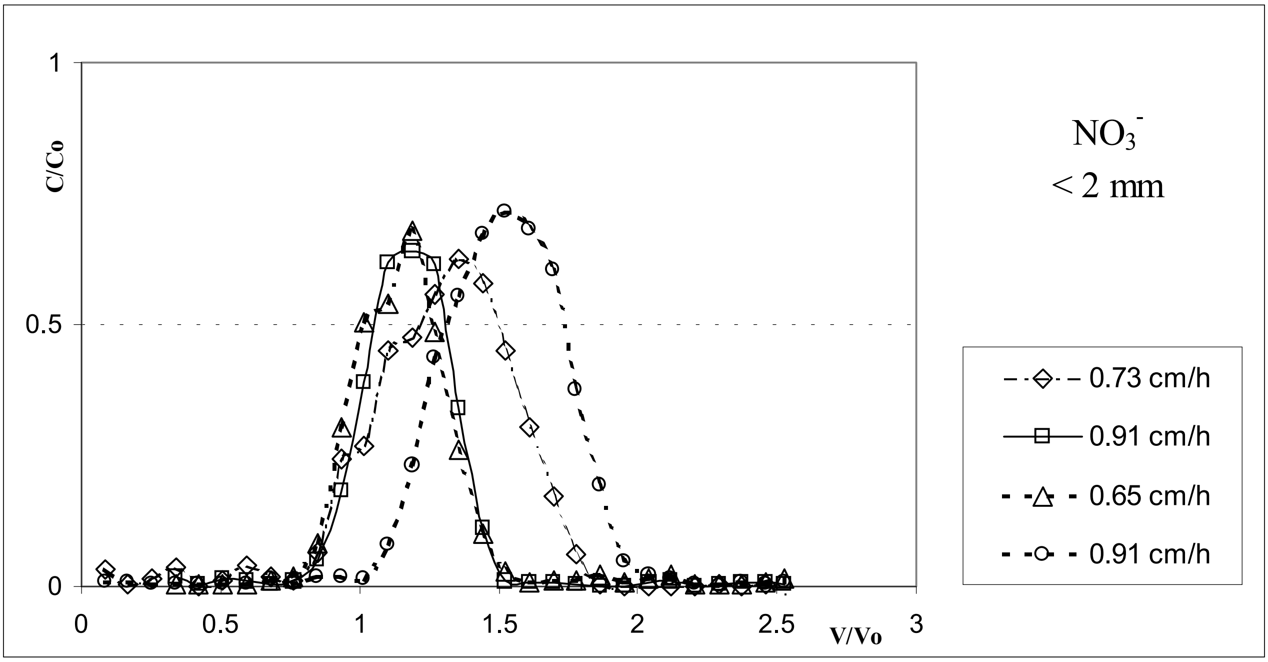
Krivulje prehoda pri NO_3^- so bile v primerjavi s krivuljami prehoda pri NH_4^+ pri vseh velikostih agregatnih delcev simetrične (slike 4 – 9).

3.3 INFLUENCE OF MICROORGANISMS

The question was what was the influence of microorganisms on the shape of the obtained breakthrough curves for NO_3^- and NH_4^+ from the described experiment. The experiment was conducted under saturated conditions; therefore, the presence of anoxic zones was highly unlikely. The soil sample used in the experiment was dried at 105°C for 24 hours; during this time, the extermination of microrganisms occurred. It can be presumed that the influence of microrganisms on the shape of the breakthrough curves is minimal.

3.3 INFLUENCE OF AGGREGATE SIZE

Breakthrough curves of NO_3^- were symmetrical with all aggregate sizes; the NH_4^+ breakthrough curves were not (Figures 4 – 9).



Slika 4. Krivulja prehoda za nitratni ion (NO_3^-) pri hipnem nanosu sledila na medij velikosti P < 2 mm.

Figure 4. Nitrate ion (NO_3^-) *BTCs for pulse tracer application on P < 2 mm media*

V primeru večjih frakcij (večje hitrosti toka) je prišlo do premika krivulj prehoda proti manjši vrednosti relativnega volumna perkolata porozne snovi (V/V_o). Vpliv na obliko krivulje ima hitrost, s katero potuje sledilo skozi porozni prostor. Vrednosti *Re* števila (preglednica 3) kažejo na to, da je bil med poskusom v kolonah laminarni režim toka. Mogoč je tudi delni vpliv prejšnjega poskusa in spremenjene strukture znotraj kolon, vendar menimo, da pri frakcijah 0.63 do 2 in 2 do 4 mm ta vpliv ni bil velik.

Pri večjih hitrostih je postal jasen rep – razvlečen desni del krivulj prehoda (sliki 5 in 6). Oblika krivulj prehoda NO_3^- grobih frakcij (sliki 5 in 6) odraža vpliv nihanja hitrosti tekočine v poroznem prostoru, nastalih zaradi preferenčnih poti skozi makropore.

Razvlečena oblika krivulj prehoda se pojavi pri debelo zrnatih tleh (prisotnost makropor) ali tleh, spiranih v zasičenih pogojih (van Genuchten, 1981; Bouhroum & Civan, 1994). Ta pojav je opisal Selim s sod. (1987) za Mg^+ in Ca^{2+} na 1 do 2 in 4 do 5 mm velikih agregatih, pri hitrosti vode porozne snovi 2 cm/h. Li & Ghodrati (1997) sta pri študiju modelov za preferenčne poti pri kontrolni krivulji prehoda za NO_3^- dobila še bolj ostro obliko krivulje prehoda na silikatnem pesku pri hitrosti vode porozne snovi 17 cm/h (max C/C_o = 0.35).

Pri prehodu NH_4^+ je imela največji vpliv sposobnost fiksacije NH_4^+ na negativno nabit difuzni sloj vode okoli glinenih mineralov agregatnega medija, kar je imelo tudi učinek na permeabilnost vzorca v koloni (Poglavje 3.1). Nejasna oblika krivulj prehoda na vzorcu tal do 2 mm je posledica fiksacije NH_4^+ na mineralne delce (slika 7). Krivulje prehoda pri NH_4^+ so dobile jasno obliko pri večjih agregatnih delcih, velikosti GE 0.63 do 2 in 2 do 4 mm (sliki 8 in 9).

Pri predstavljenih poskusih smo uporabili prodne in peščeno ilovnate frakcije. Predvidevamo, da je uporabljeni vzorec, kljub odstranitvi frakcije < 0.063 mm, vseboval zelo majhno količino frakcije, ki vsebuje glinene minerale.

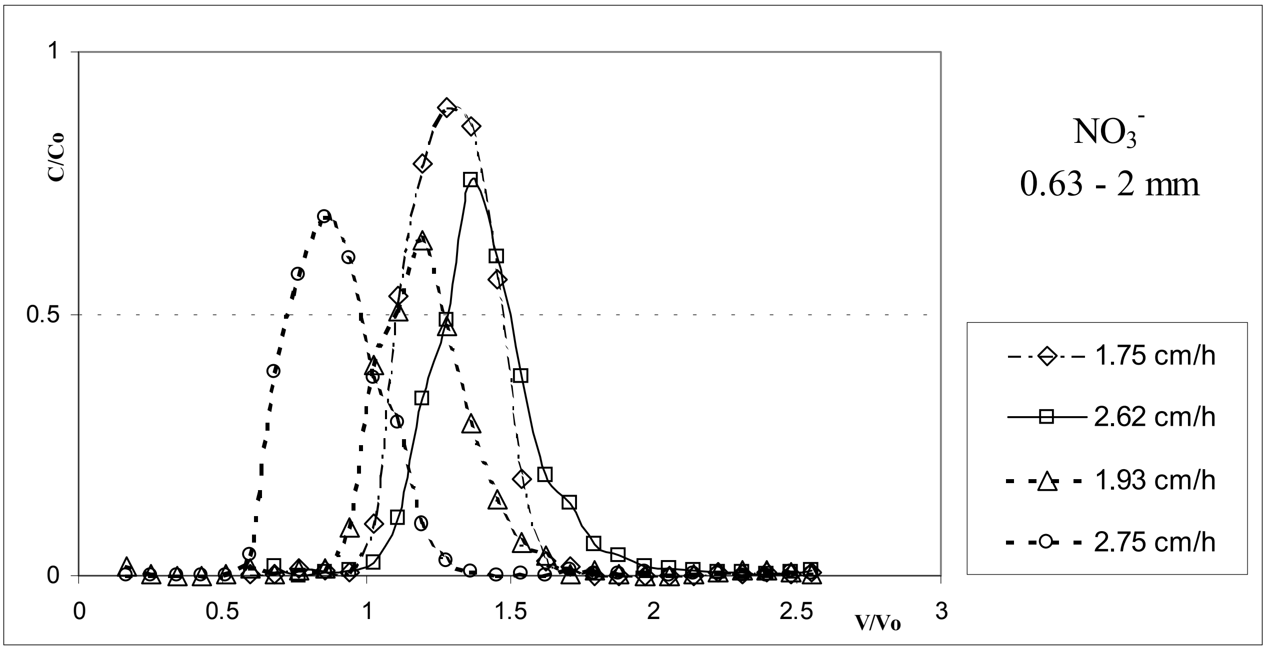
In the case of larger fractions (higher flow velocities), the shift of the BTC toward a smaller relative pore water volume (V/V_o) occurred. The velocity with which the tracer traveled through porous media had some influence on the shape of the curve. *Re* number values (Table 3) support the laminar flow regime during the soil column experiment. A partial influence of the previous experiment was also possible, due to the changed structure inside the column, but it is our opinion that this influence was not significant.

With higher pore water velocities, the tailing became clear (Figures 5 and 6). The shape of the NO_3^- BTCs of the coarser aggregates (Figure 5 and 6) reflects velocity fluctuations in the porous media due to the preferential flowpaths forming from the macropores.

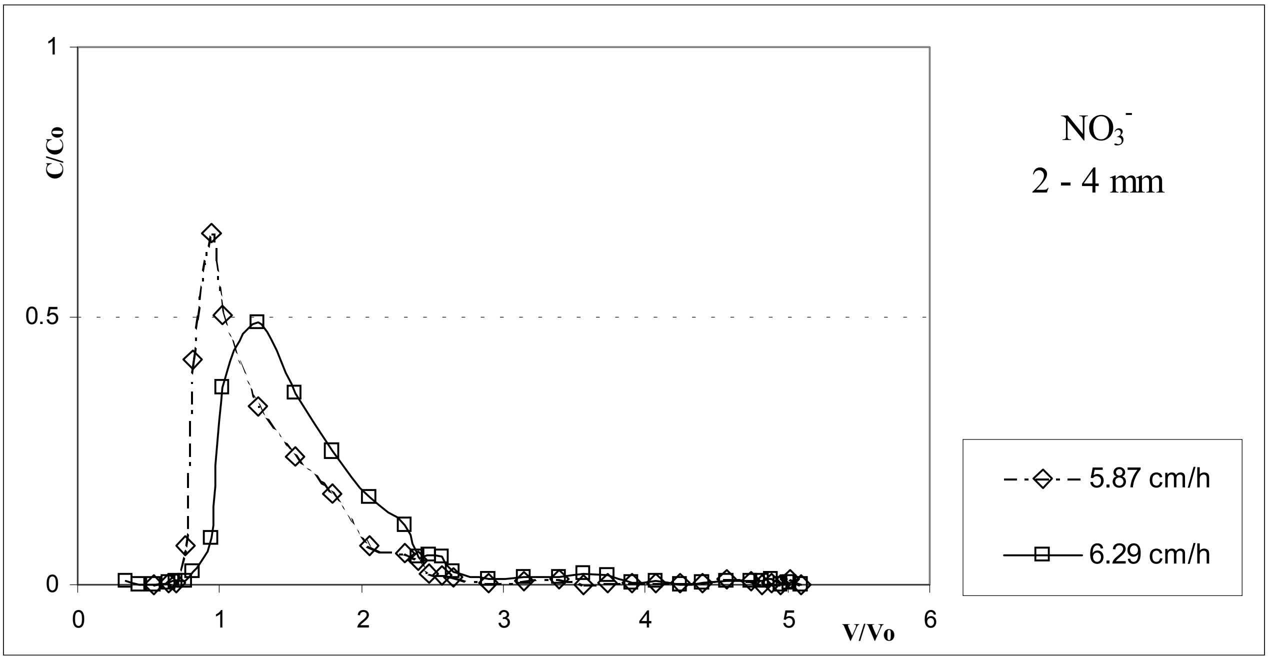
Extreme tailing is expected when cracked soils or soils containing macropores are leached under saturated conditions (van Genuchten, 1981, Bouhroum & Civan, 1994). The phenomena was described by Selim et al., (1987), with Mg^+ and Ca^{2+} BTCs on 1–2 and 4–5 mm aggregate sizes of pore water velocity 2 cm/h. Li & Ghodrati (1997) studied preferential flow paths and obtained an even sharper shape of the BTC for NO_3^- on silica sand with a pore water velocity of 17 cm/h (max C/C_o = 0.35).

The ability of NH_4^+ to fixate onto the negative charged diffuse water layer had the greatest influence on the breakthrough of NH_4^+, which also affected the permeability of the soil sample in the column (Chapter 3.1). The unclear shape of the NH_4^+ BTCs on the P < 2 mm soil samples is due to the NH_4^+ fixation on the clay minerals (Figure 7). The BTC of NH obtained a clear shape with larger aggregate sizes GE 0.63–2 and 2–4 mm (Figures 8 and 9).

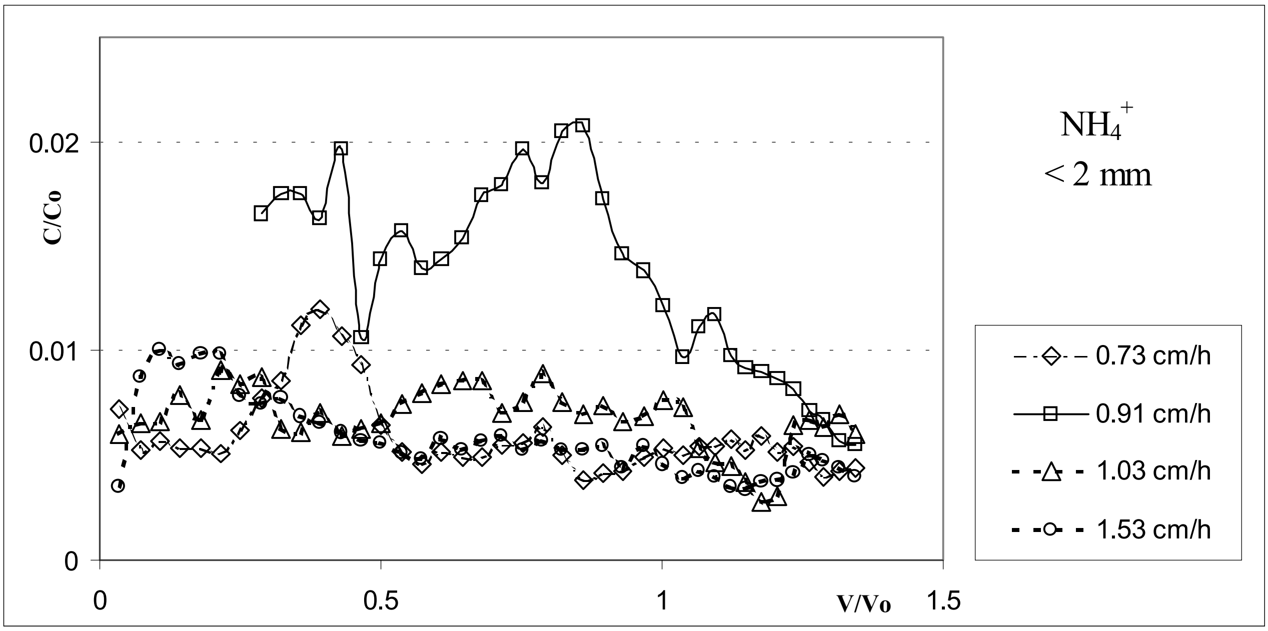
In the presented experiments, the gravel fraction of the loamy sand type of soil was used. We presume that the coarse soil samples, in spite of removal of the < 0.063 fraction, still contained a small part of the fraction which includes clay minerals.



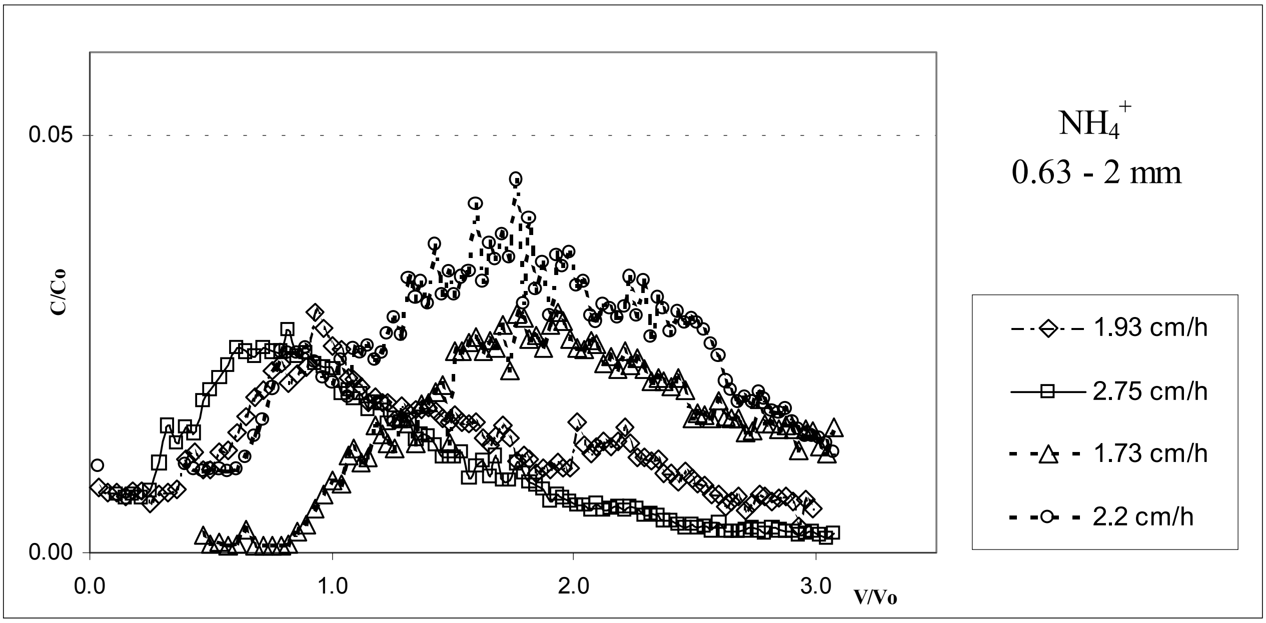
Slika 5. Krivulja prehoda za nitratni ion (NO_3^-) pri hipnem nanosu sledila na medij velikosti GE 0.63 do 2 mm.
Figure 5. Nitrate ion (NO_3^-) *BTCs for pulse tracer application on GE 0.63–2 mm media.*



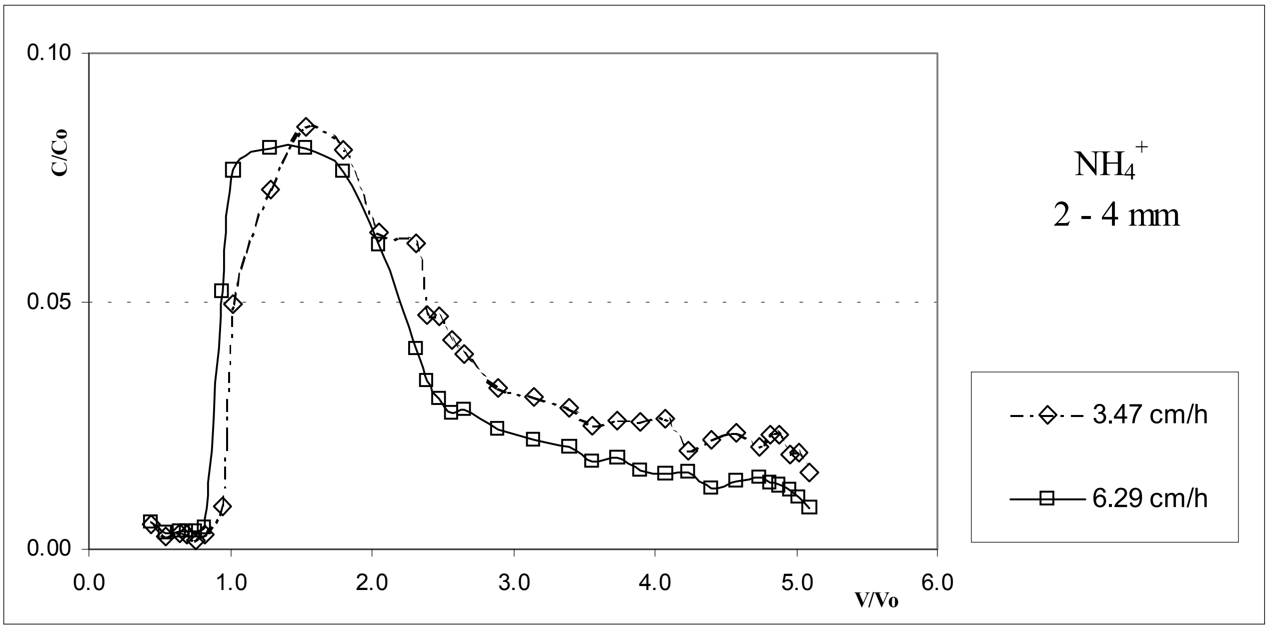
Slika 6. Krivulja prehoda za nitratni ion (NO_3^-) pri hipnem nanosu sledila na medij velikosti GE 2 do 4 mm.
Figure 6. Nitrate ion (NO_3^-) *BTCs for pulse tracer application on GE 2–4 mm media.*



Slika 7. Krivulja prehoda za amonijev ion (NH_4^+) za hipni nanos sledila na medij P < 2 mm.
Figure 7. Ammonium ion (NH_4^+) BTCs for pulse tracer application on P < 2 mm media.



Slika 8. Krivulja prehoda za amonijev ion (NH_4^+) za hipni nanos sledila na medij GE 0.63–2 mm.
Figure 8. Ammonium ion (NH_4^+) BTCs for pulse tracer application on GE 0.63–2 mm media.



Slika 9. Krivulja prehoda za amonijev ion (NH_4^+) za hipni nanos sledila na medij GE 2–4 mm.
Figure 9. Ammonium ion (NH_4^+) *BTCs for pulse tracer application on GE 2–4 mm media.*

Glineni minerali močno vplivajo na prenos kationov, še posebej NH_4^+ iona. Ta ima visoko sposobnost adsorpcije na trdne površine prodnatih delcev. Zatorej bi bilo zanimivo videti stopnjo zadržanega NH_4^+ na predhodno z NH_4^+ zasičenem mediju, da bi videli stopnjo prehoda NH_4^+ pri prevelikih vložkih NH_4^+ - N. Zadrževanje – fiksacija NH_4^+ in imobilizacija sta zelo kompleksna problema. Kolonski poskusi, predstavljeni v tem delu, niso pokrili vseh vidikov, ki vplivajo na prenos NH_4^+.

Clay minerals strongly influence cation transport, especially NH_4^+, the latter having the capacity to adsorb on the surface of gravel parts. It would be interesting to compare NH_4^+ mass recovery from previously NH_4^+ saturated media in order to observe the NH_4^+ breakthrough with excess NH_4^+ - N input. The detention – fixation of NH_4^+ and immobilization is a very complex problem. Soil column experiments do not cover all the aspects that influence the transport of NH_4^+.

4. ZAKLJUČKI

Med poskusom so se v kolonah z vzorcem tal < 2 mm pogoji spremenili. Vzroki so nenameren stranski učinek ob odprtju vtoka na atmosferski pritisk, sprememba prepustnosti kolone zaradi uporabe NH_4^+ sledila in spiranja z destilirano vodo. Pogoji v < 2 mm koloni so se med poskusom spremenili tudi zaradi nepravilno izbranih hidravličnih gradientov.

4. CONCLUSIONS

In the course of the experiments, the conditions in < 2 mm soil columns were altered. The causes were the unintentional side effect of opening the inlet section to atmospheric pressure, changes in the column permeability caused by the use of the NH_4^+ tracer, and rinsing with distilled water. Conditions in the < 2 mm soil columns were also changed during the experiment due to improper hydraulic gradients.

Velikost talnih delcev je imela vpliv na obnašanje sledila. Krivulje prehoda pri NO_3^- so bile v primerjavi s krivuljami prehoda pri NH_4^+ pri vseh velikostih agregatnih delcev simetrične. V primeru večjih frakcij in večje hitrosti toka je prišlo do premika krivulj prehoda proti manjši vrednosti relativnega volumna perkolata porozne snovi (V/V_o), razvlečen desni del krivulj prehoda je postal jasen. Pri večjih agregatnih delcih, velikosti 0.63 do 2 in 2 do 4 mm so pri NH_4^+ krivulje prehoda dobile jasno obliko.

The size of the chosen aggregates influenced the behavior of the tracer. Breakthrough curves of NO_3^- were compared to the NH_4^+ breakthrough curves and were symmetrical with all aggregate sizes. In the case of larger fractions (higher flow velocities), the shift of the BTC toward smaller relative pore water volume (V/V_o) occurred. The BTC of the NH_4^+ achieved a clear shape with the larger aggregate sizes of 0.63–2 and 2–4 mm.

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OZNAKE - *SYMBOLS*

C	(mg/l)	Koncentracija raztopine	*Solution concentration*
C_0	(mg/l)	Začetna koncentracija	*Initial concentration*
V	(cm^3)	Volumen pretečeni	*Volume*
V_o	(cm^3)	Celotni volumen perkolata porozne snovi v eksperimentalni koloni	*Total pore volume of the experimental column*
q	(cm/sek)	Specifični pretok	*Specific discharge*
d	(cm)	Reprezentativna dimenzija zrn	*Representative dimension of the grains*
v	(cm^2/sek)	Kinematična viskoznost tekočine	*Kinematic viscosity of the fluid*
	USDA	Urad za agronomijo Združenih držav	*United States Department of Agriculture*