Nitrate and Ammonium Transport in Aggregated Porous Media

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Abstract

The subject of this study were laboratory trace experiments in 1D soil columns with three various soil aggregates. For the solute nitrate fertiliser and for the displacing fluid distilled water was used. The measured breakthrough curves (BTCs) were used to calculate the transport parameters of 1D equilibrium and non-equilibrium transport models using inverse modelling technique. The size of the chosen aggregates influenced the behaviour of the tracer. Compared to the ammonium breakthrough curves the BTCs of nitrate were symmetrical with all aggregate sizes. BTCs of ammonium obtained clear shape with bigger aggregate sizes. The biggest influence on the nitrate retention had GE 0,63-2 mm fraction (50-70 % mass recovery). The biggest influence on the ammonium transport had its ability to fixate. Computer simulation of BTCs of bigger aggregates was successful with the non-equilibrium model.

Zusammenfassung

Das Studienthema waren Tracerexperimente in 1D Bodensäulen, gefüllt mit drei verschiedenen Bodenaggregaten. Stickstoffdünger wurde als Tracer benützt und destilliertes Wasser als verdrängende Flüssigkeit. Gemessene Durchbruchskurven wurden für Transportparameterberechnungen von 1D Gleichgewichts- und Nichtgleichgewichtsprozessen benützt. Die Bodenaggregatgröße beeinflusste die Formen der Stofftransport- sowie Durchbruchskurven. Nitratdurchbruchskurven waren bei allen Bodenaggregatgrößen symmetrisch, Ammoniumdurchbruchskurven aber erst bei größeren Bodenaggregaten. Den größten Einfluss auf Nitratzurückhaltung hatte die GE 0,63-2 mm Fraktion (50-70 % Massenrückgewinnung). Den größten Einfluss auf den Ammoniumtransport hatte dessen fixierende Wirkung.

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. 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. On a practical level, data obtained from such tests can elucidate past contaminant movement in groundwater and also may assist in transport prediction. 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 porosity nature of the media.

The subject of this study were laboratory trace experiments in soil columns (length 10 cm) with three various soil aggregates (soil sample P < 2 mm, soil sample GE 0,63-2 mm and 2-4 mm). As a tracer mixed nitrogen fertiliser Nitramoncal in equivalent of 100 kg N/ha was used. Purpose of the laboratory experimental work on the soil columns with various soil fractions was to determine behaviour of nitrogen in form of nitrate (NO_3^- - N) and ammonium (NH_4^+ - N) in relationship to the soil texture. Transport parameters were determined using the computer simulation model developed by USSL, Riverside (van GENUCHTEN et al., 1981). Solute transport through soils is a major process for leaching of salts from soil profile, contamination of groundwater, plant nutrient uptake and water renovation. It has become evident that by investigating these mechanisms we may better predict contaminant migration in the subsurface.

Breakthrough curves of nitrate were compared to the ammonium breakthrough curves symmetrical with all aggregate sizes. In case of bigger fractions (higher flow velocities) the shift of the BTC towards smaller relative pore water volume (V/V_o) occurred. With higher pore water velocities tailing became clear. Extreme tailing will be expected if cracked soils or soils containing macropores are leached under saturated conditions. The phenomena were 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. The velocity with which the tracer travels through porous media has some influence on the shape of the curve. LI and GHODRATI (1997) studied preferential flow paths and obtained 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 to fixate onto the negative charged diffuse water layer had the greatest influence on its breakthrough. BTC of ammonium got clear shape with bigger aggregate sizes, 0,63-2 and 2-4 mm.

The amount of detained nitrate was 8 - 20 % of the initial input with < 2 mm. Obtained values mean big amount of detained nitrate considering the fact that nitrate served as a conservative tracer. The amount of detained nitrate is higher compared to the values obtained by LI and GHODRATI (1997) on experiments with silica sand where they noted < 5 % detained nitrate. The amount of detained nitrate can be explained by capture of

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the tracer in dead-end pores of aggregate media. A high percentage of detained nitrate in the soil columns P < 2 mm (8-20 %) is presumed to be the result of nitrate detention in dead-end pores due to the insufficient rinsing.

The biggest influence on the nitrate retention had GE 0,63-2 mm fraction, where 30-50 % of the total mass was preserved. In soil columns with GE 2-4 mm sample nitrate had the shortest breakthrough time, where 5-18 % of nitrate was detained.

The level of detained ammonium is 78-93 % of the initial mass input for the aggregate size < 2 mm and 60-80 % for the aggregate size 0,63-2 and 2-4 mm. Ammonium was equally detained for both aggregate sizes 0,63-2 and 2-4 mm. The influence of the initial concentration input on the transport and fixation of ammonium was shown. At the first application of the third experiment on the aggregate size 0,63-2 mm almost double concentration came through the column in less than five hours (70 % mass recovery), which is faster than the breakthrough time of the previous first applications of the first two experiments. The shift of the curve to the left is caused by change of the concentration rather than by hydrodynamic and geometric aspects of the flow regime (KUTILEK and NIELSEN, 1994). With this application fast breakthrough of high concentration occurred. High initial concentration of ammonium can have an influence on decreased level of NH_4^+ fixation (NOMMIK and VAHTRAS, 1982). Second application needed 20 hours to breakthrough, which is twice or three times as much as it was needed for the second application of the first two experiments. Mass recovery is 49 %. This experiment results lead to the conclusion that high concentration of ammonium have quick breakthrough. Breakthrough delay of the second application

occurred due to the ammonium fixation on the free places of soil particles.

Overrated doses of ammonium to the coarse textured soils cause that the ammonium deeper moves into the soil profile. Nutrients stored under the effective root depth are unavailable for the plant uptake and are potential pollution source at the same time. Fixated ammonium stores in soil profile and is thus included in N circle in soil. Through nitrification it is gradually transformed in more mobile nitrate which later leaches into the groundwater (FOLLET, 1989).

The second part of this study was the simulation of the measured data and the estimation of the transport parameters with the non-linear curve fitting computer program CFITIM (VAN GENUCHTEN, 1981). Simulations for equilibrium and non-equilibrium transport model were made. Experimentally obtained breakthrough curves for nitrate from soil columns packed with small aggregates P < 2 mm were well described with both linear and physical non-equilibrium model. Experimentally obtained breakthrough curves for nitrate from soil columns packed with GE 0,63-2 mm and 2-4 mm aggregate size were almost perfectly described with physical non-equilibrium model, however the linear model failed to describe solute transport in most cases. Parameter estimation with help of curve-fitting often led to the convergence or no convergence occurred - dependent on the initial parameter estimation. Obtained values of the non-dimensional parameters were physically unrealistic in some cases .

Original transport parameter calculation showed influence of the aggregate size on the size of the mobile phase and its relationship to water flow. Mobile water phase of P < 2 mm soil sample decreased with water flow. Mobile water phase of GE 0,63-2 mm and GE 2-4 mm soil sample generally increased with aggregate

size and flow. Immobile water phase of GE 0,63-2 mm and GE 2-4 mm aggregate size soil columns generally increased along with the size of both aggregate size and flux. Computer simulation with non-equilibrium model gave satisfactory results. Retardation coefficient changed with aggregate size, less with the increase of pore water velocity. Comparison of dispersion coefficient values of nitrate and ammonium with respect to pore water velocity showed no linear relationship. For precise original parameter determination direct measurement of parameters as mobile water fraction q_m would be necessary.

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