

NITRATES TRANSPORT COMPARISON THROUGH TWO DIFFERENT SOIL PROFILES IN THE EASTERN SLOVAKIA LOWLAND LYSIMETRIC STATION

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Nitrates belong to the major nutrient required for plant growth and they are generally very well soluble in water often used as fertilizers in agriculture. The higher values of nitrates concentration will occur in the case of large amounts use of fertilizer in intensive agriculture, pipe damage or damaged drainage near wells. The fertilization reduction could be one of this problem solution for health protection, environmental and economic reasons. In our study, the spectrophotometric determination of nitrates concentration in 5 times over-fertilized soil in lysimeters localized in the Eastern Slovakia Lowland showed nitrates leaching in the 40 cm layer of sandy soil, while in the silty-loam soil profile nitrates were not detected. The main goal of the experimental work was to show different nitrates leaching through two types of soil profile differing in hydraulic soil properties. Low retention capacity and high hydraulic conductivity of sandy soil (locality Poľany) were favourable for nitrate leaching in comparison with higher retention and conductivity of silty-loam soil (locality Vysoká nad Uhom) under relatively low precipitation events in the studied period from April 29th to May 28th 2019.

KEY WORDS: nitrates, spectrophotometry, lysimeter, precipitation

Introduction

With a population increase in the world and industrial development, the amount of harmful waste substances, which leak out to the surface and groundwater, grows. Drinking water represents only about 3% of the total amount of water on Earth with a decreasing tendency. Criteria for the quality of drinking water for human consumption are laid down by the applicable legislation in every country. Healthy drinking water is assessed and controlled by drinking water quality indicators and their limits. Billions of people have no drinking water available, especially in India, China or states in Africa. Slovakia (Fig. 1), the main object of our research activity, a small country located in the middle of Europe, belongs to countries with good quality and quantity of drinking water.

Groundwater represents the most important source of drinking water in Slovakia. The largest amount of groundwater is bound to the quaternary sediments of the Danube area with the most important water management area in Central Europe – the Rye Island. Groundwater monitoring probes and river basins observation network could be visible on the Slovak website www.shmu.sk. The Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources (the Nitrates Directive) was accepted in 1991. Based on

water quality protection across Europe nitrates use from agricultural sources has to prevent polluting ground and surface waters. The council directive contributed to promoting the use of good farming practices. Nevertheless, there are sources of water pollution, so it is necessary to search methods for water purification, decontamination and reasonably separate, reduce and remove harmful substances. Nitrates, used as soil fertilizers in agriculture, belong to the frequent substances that cause pollution of water (Bibi et al., 2016). The most commonly used nitrate fertilizers are calcium nitrates ($\text{Ca}(\text{NO}_3)_2$), potassium nitrates (KNO_3) or ammonium nitrates (NH_4NO_3) (Kant and Kafkafi, 2013). In the case of nitrogen fertilizers applications, incorrect use may often occur, with nitrates being able to reach groundwater or other water sources when overdosed (Bibi et al., 2016). Nitrates pose a threat to human health, especially for the sensitive organisms of infants, because higher concentrations (over 10 mg l^{-1}) can lead to methemoglobinaemia, i.e. to the inability of haemoglobin to transfer oxygen, leading to suffocation (Kim-Shapiro et al., 2005; Greer and Shannon, 2005; Knobloch et al., 2000). Nitrates are converted into more toxic nitrite by the bacterial activity in the human body. Nitrates and nitrites are involved as precursors to the formation of highly active carcinogenic substances that increase the risk of gastrointestinal cancer diseases of the gastrointestinal system and bladder. The literature



Fig. 1. The map of Slovakia in the middle of Europe (marked yellow).

also mentions the relationship of nitrites to the incidence of tumour diseases of the lymphatic system (Bruning-Fann and Kaneene, 1993; Forman, 1989; Magee and Barnes, 1967; Bogovski and Bogovski, 1981; Mirvish, et al., 1987). For these reasons, it is necessary to monitor the concentration of nitrates in water sources, especially those intended for human consumption. In 1993 Pekárová and Miklánek studied spatial distribution and concentrations trend change of nitrate-based on trend analysis in five sub-basins of the Ondava River in the Slovakia basin for 25-years-time series 1968/69–1992/93. Important differences were found if nitrate concentrations derived from daily samples were compared to those estimated from regular monthly samplings of the hydrometeorological network (Pekárová and Miklánek, 1993). In 2002 an ecologic study of nitrate in municipal drinking water and cancer incidence in Trnava district, Slovakia was published. These ecologic data supported the hypothesis that there is a positive association between nitrate in drinking water and non-Hodgkin lymphoma and colorectal cancer (Gulis, et al., 2002). Variation of nitrates in runoff from mountain and rural areas was studied by Holko et al. in 2006. Water samples collected at the outlet of the mountain part had lower concentrations of nitrates than the samples collected downstream in the rural area. The differences were smaller during the summer. The highest concentrations of nitrates and the highest differences among the uninhabited and inhabited areas were observed at the time of snowmelt (Holko et al., 2006). The next study of irrigation effect on nitrates movement in soil and risk of subsoil contamination has shown that movements of nitrates in irrigated and non-irrigated fields differed significantly mainly during the early stages of the vegetation period. Applied irrigation was not the reason for nitrates penetration

below the root zone under the soil (Nováková and Nágel, 2009). To facilitate the detection, determination and monitoring of nitrates, many strategies have been developed. Various techniques and their limitations have been summarized in several papers (Moorcroft et al., 2001; Moo et al., 2016; Wang et al., 2017; Ciulu et al., 2018). Spectroscopic methods are by far the most widely used for nitrates determination due to the excellent limits of detection obtained, rapidity, sensitivity and the simplicity of the protocols. Based on this, a spectrophotometric UV-VIS method was used for our investigations of nitrates concentration in small volumes of water collected from lysimeters localized in Petrovce nad Laborcom situated in the eastern part of Slovakia operated by the Institute of Hydrology Slovak Academy of Sciences – Research Base for Lowland Hydrology. Lysimeters represent very convenient tools for this study thanks to the possibility to obtain water samples, which flowed through the given soil. Also, actual evapotranspiration using the balance equation can be calculated (Matusek et al., 2017). The most frequently used grass fertilizer, containing highly effective water-soluble nitrates, was applied to fertilize selected soil monoliths in lysimeters. Transport processes depend on soil type, the size of soil microparticles in a porous environment, plant cover of soil, irrigation, precipitation or season. From these factors, we focused on the study of soil type, precipitation and evapotranspiration effect on nitrate movement through the soil profile. In this way, the main aim of the work was to determine the capacity of the soil with grassy cover in the given season at specific sampling time intervals to bind and consume applied nitrates for the vegetation growth needs. We have found, that increasing the nitrate sorption capacity of the soil has the potential to reduce nitrate leaching to groundwater.

Material and methods

Lysimeters description

Lysimeter station in Petrovce nad Laborcom (Umwelt-Geräte-Technik, GmbH., Germany) was built in 2014 and was put into full operation in spring 2015. The geographical position is 48°45'19''N and 21°54'48''E; 117 m a.s.l. The Station consists of five cylindrical weighable lysimeters and a meteorological station. The whole station is powered by solar panels. The specific surface area of each lysimeter is 1 m², the height is 2.5 m and the total mass is about 5000–5300 kg. Lysimeters are equipped with UMP (i.e. *Unit with Moisture Probe*) probes (for measuring volumetric moisture, temperature and electric conductivity of soil), tensiometers and suction probes (for water sampling). The sensitivity of the weighing system is 10 g. The vegetation cover is grass, maintained by mowing at 12 cm (Matusek et al., 2017). Soil monoliths (undisturbed soil blocks) represent five different types of soils from various locations in the region. Lysimeters no. 1 with silty-loam soil (locality Vysoká nad Uhom) and no. 3 with sandy soil (locality Poľany) were selected for our study of transport processes of nitrates in standard and overdosed fertilized soil. It should be noted that the groundwater level for lysimeter no. 3 is constant and maintained at the depth of 1 m under the soil surface and lysimeter no. 1 is equipped by free drainage.

Fertilization and sampling

Fertilization and sampling were performed at the lysimeter station of the Research Base for Lowland Hydrology Institute of Hydrology, Slovak Academy of Sciences, localized in Petrovce nad Laborcom in the Eastern Slovakia Lowland. Standard used fertilizer "Kristalon" (producer AGRO CS a.s. the Czech Republic, originating in the Netherlands), containing highly effective water-soluble nitrates was diluted in water to achieve the standard and overdosed concentration of nitrates and applied on selected soil placed in lysimeter no. 1 and 3 during the vegetation period from the beginning of April to the end of May 2019 with average temperature 10°C in April and 15.2°C in May. The water samples were collected to identify nitrates transport processes from 3 different depths (40, 100 and 160 cm). Before fertilization for the study of the solute movement, the non-fertilised water sample was taken as a starting solution.

Spectrophotometric determination of nitrates concentration

The Hach Lange DR6000 is the most advanced laboratory UV-VIS spectrophotometer for water quality testing. It offers high-speed spectral scanning. For the determination of NO₃[−] concentration, we used the LCK-340 cuvette test from the Hach Lange Company for the concentration range of nitrates 22–155 mg l^{−1}. For lower concentrations of nitrates (1.0–60.0 mg l^{−1}) LCK-339 cuvette test was used. Both LCK tests are based on

the reaction of NO₃[−] anions with 2,6-dimethylphenol in an aqueous solution containing sulfuric and phosphoric acid. First, water sampled from lysimeters was pipetted slowly to cuvette according to the procedure outlined in the instruction manual for the given LCK test. Then, the cuvette was closed and inverted a few times until no more streaks can be seen. Measurement of absorbance ran one-time at automatically set wavelength ~ 370 nm and the final concentration was subtracted from the display. During the sampling from lysimeters, the direct concentration of nitrates and nitrites was also determined using a portable field spectrophotometer-pHotoFlex pH. Reaction cell test with the program no. 314 was applied for NO₃[−] determination (concentration range 1–133 mg l^{−1}) and reagent test with the program no. 334 for NO₂[−] (concentration range 0.007–0.985 mg l^{−1}) determination. Reaction tests contained a mixture of organic and inorganic compounds with chronotropic reagents, which changed the colour of the solution with intensity according to the nitrates concentration in the added sample.

Results and discussion

To determination the concentration of nitrates transported through the soil, we focused on taken of aqueous samples from lysimeters (no. 1 and 3) with two different soil type monoliths localized in Petrovce nad Laborcom in the Eastern Slovakia Lowland. These lysimeters were chosen for our experiment thanks to the suitable water afflux and built-in suction probes to collect water. As a first step, the standard amount (recommended by the producer) of commercially used grass fertilizer was weighed and dissolved in water. The precise concentration of NO₃[−] anions was determined by the LCK 340 test with the final value of 200.5 mg l^{−1}. Before fertilization, initial water samples were taken from three different depths (40, 100 and 160 cm) with final values below the detection limit of the LCK 339 test. This means that during the selected period there was no detected residual amount of nitrates from the nitrogen cycle in the soil or from the precipitation. After standard fertilization, the next four spectrophotometric measurements were realized on samples taken in daily intervals at the beginning of April, but the NO₃[−] concentrations did not exceed the lowest detection limit of the LCK test for determination of NO₃[−] concentration despite the occurrence of rain, which is supposed to accelerate the movement of nitrates into the lower soil layers. Most probably the whole amount of added NO₃[−] anions in the form of fertilizer was up-taken by grass for growth needs in started vegetation period (Fig. 2).

Therefore, we added approx. 5 times the recommended fertilizer amount to achieve the transport of nitrates to the lower layers of the soil. The final concentration of NO₃[−] anions in the dissolved aqueous solution of fertilizer was 1120 mg l^{−1}. Before the second fertilization of soil in lysimeter no. 1 and 3, initial water samples were taken from three different depths (40, 100 and 160 cm) with final values below the detection limit of the nitrate test. An increase in concentration detected using portable



Fig. 2. The photography of grass cover on lysimeters localized in Petrovce nad Laborcom in the Eastern Slovakia Lowland at the beginning of the vegetation period (3th April 2019).

field pHotoFlex pH device and laboratory LCK test was observed from the second day after fertilization only at the depth 40 cm in the lysimeter no. 3 containing sandy soil monolith (Fig. 3). Nitrates were not detected in the greater depth, i.e. did not achieve the groundwater level, which is 1 m under the surface of lysimeter no. 3. The observed difference between the determination of NO_3^- concentration using pHotoFlex pH and LCK tests in the graph (Fig. 3) can be related most probably by the difference between chemical principles of methods (various reagents, interference). At depths 100 and 160 cm in lysimeter no. 3 and in all depths of lysimeter no. 1, the NO_3^- concentration did not exceed the lowest detection limit of the used method. Because the grass cover and the meteorological conditions were the same for both lysimeters, it should be highlighted that the better sorption capacity of lysimeter no. 1 was caused by the different soil type. The silty-loam soil profile is characterized by a finer texture compared to the sandy soil profile, which results in much lower hydraulic conductivity values. The finer soil texture and hence the higher proportion of the silt and clay fractions in the silty-loam soil results in an incomparably higher specific surface area. We assume, that both, the lower hydraulic conductivity and higher specific surface of the soil profile in lysimeter no. 1, are responsible for its lower content and slower-moving of nitrates. Due to the fact, that precipitation, irrigation and evapotranspiration measured with an hourly step of a lysimeter no. 3 belong to factors affecting the nitrates concentration, we added these factors into the graph (Fig. 3). We can conclude, that heavy irrigation (contained fertilizer) together with significant precipitation during the first days of our experiment caused rapid movement of NO_3^- to the lower depth of the soil (Fig. 3).

In general, applied fertilizer, containing NO_3^- anions,

undergoes various processes before becoming available for plants within the natural nitrogen cycle in the soil. Besides the most important grass uptake, we taking into account the binding of NO_3^- anions to soil particles, immobilization and mineralization in the soil organic matter, leaching to lower soil depths and transformation to NO_2^- anions. The excess of NO_2^- anions is measurable before its chemical transformation. Similarly, as nitrates, nitrites can also negatively affect human health when exceeding the limit set by the applicable legislation, i.e. 0.5 mg l^{-1} in the European Union and for infants 0.1 mg l^{-1} . For this reason, we determined also the possible presence of NO_2^- anions using a portable field spectrophotometer – pHotoFlex pH (Fig. 4).

For depths 100 and 160 cm in lysimeter no. 3 and in all depths of lysimeter no. 1, the NO_2^- concentration did not exceed the lowest detection limit 0.007 mg l^{-1} of the used method. Fig. 4 represents results from determination NO_2^- concentration from 40 cm depth of lysimeter no. 3. We observed an increase of NO_2^- concentration at the end of the experiment only, but recommended limits were not exceeded. Fig. 5 represents the photography of the grass cover after the experiment as visible evidence that the grass cover was not "burned" by excessive fertilization.

It should be noted that irrigation, grass cover and meteorological conditions (precipitation, global radiation, wind speed, air temperature) were the same for both lysimeters. The main difference should come from the various components of soil monoliths, hydraulic conductivity and specific surface of soil particles. A low retention capacity and a high hydraulic conductivity of sandy soil may be favourable for nitrate leaching in comparison with higher retention and conductivity of silty-loam soil. Therefore our findings at the experimental site indicate a low ability of nitrates

movement to the groundwater during the vegetation period after fertilization of silty-loam soil. An increased risk of nitrates movement below the soil root zone can be expected for increased fertilizers doses during winter periods when soil is wet, and after heavy rains, if fertilization is performed in the early spring times. Plant cover can eliminate this risk nevertheless the deep penetration of nitrates during the vegetation period depends highly on precipitations. For generalization, it is

necessary to continue with monitoring studies of water balance.

The basic hydrophysical characteristics of the studied object used for nitrates transport were collected in the latest study within Research Base for Lowland Hydrology work and monitoring. Here similarly under the same meteorological conditions for both soil types, water balance components in 2018 differ due to variations in soil profiles. Measurements using

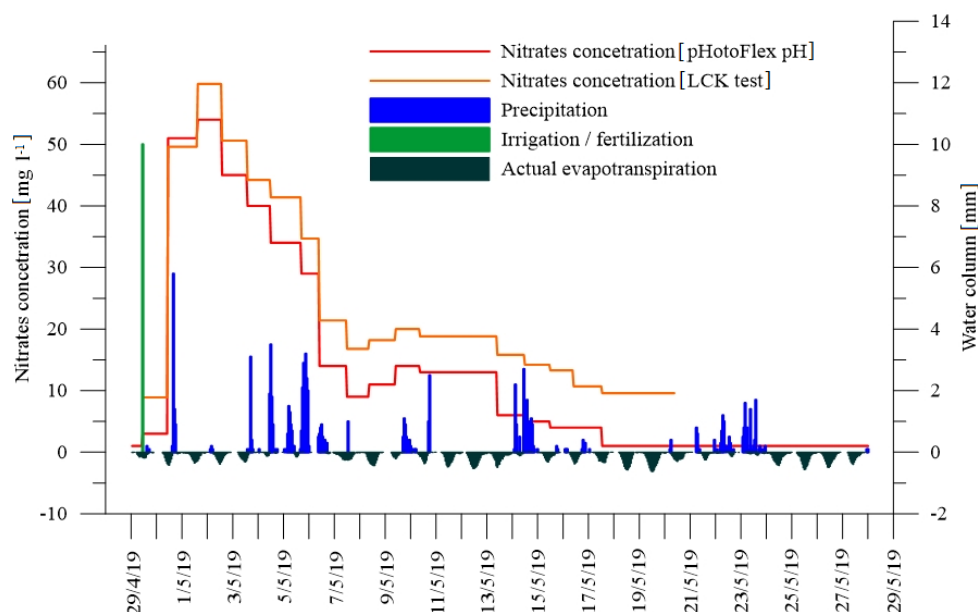


Fig. 3. The time course of nitrates concentration determined by portable field pHotoFlex pH device (red course) and LCK laboratory test (orange course) from lysimeter no. 3 in the 40 cm depth. Blue columns represent precipitation, green column illustrated water content after initiated irrigation/fertilization and dark green columns actual evapotranspiration.

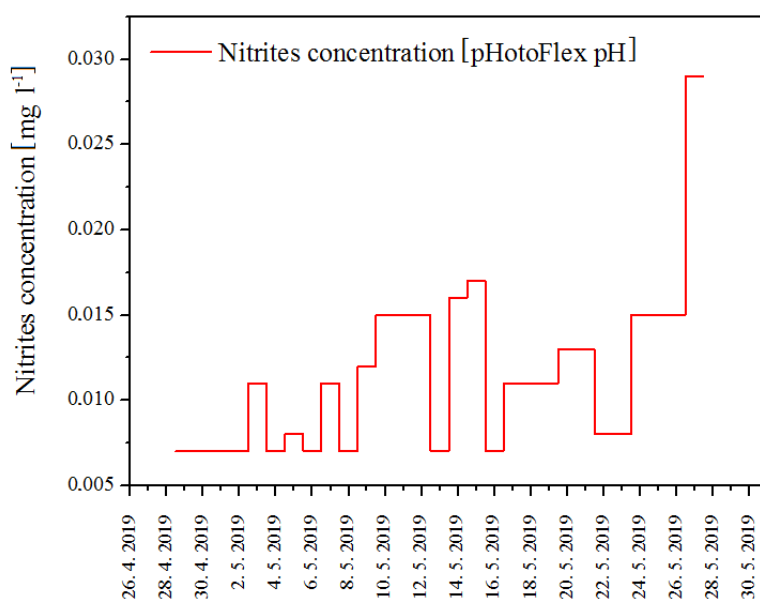


Fig. 4. The time course of nitrites concentration determined by portable field pHotoFlex pH.



Fig. 5. The photography of grass cover on lysimeters localized in Petrovce nad Laborcom in the Eastern Slovakia Lowland at the end of experiment (27th May 2019).

hydrometer measurement method for particle-size analysis up to 1 m depth has shown the followed soil hydrometer measurement method for particle-size analysis up to 1 m depth has shown the followed soil profile composed of sandy loam surface, deeper horizons of loamy sand continued by pure sand from Poľany source. Soil collected from Vysoká nad Uhom locality was relatively homogeneous and consists of silt loam. Soil water retention curves, obtained by pressure plate extractor, confirmed greater heterogeneity of sandy soil (Poľany) compared to the profile from Vysoká nad Uhom. Saturated hydraulic conductivities were: 12, 430 and 470 cm day⁻¹ for the Poľany soil profile and 10, 35 and 32 cm day⁻¹ for the soil profile from Vysoká nad Uhom. The volumetric moisture content in the studied the year 2018 in the soil profile from locality Vysoká nad Uhom reached the level of the field capacity and in the soil profile from locality Poľany, field capacity was even exceeded (Tall and Pavelková, 2020).

In this work, we have demonstrated that the nitrates movement should be affected by the type, size and composition of the soil particles, which have absorbed and leached nitrates differently. We take into account that some difference can come from various transformation processes of nitrates in the natural nitrogen cycle in selected soil monoliths (bacterial metabolism). Except for bacteria use of nitrates in metabolic processes, chemical soil composition could affect nitrates content in the soil environment. One of the essential elements for plant growth is iron. Muradova and co-workers showed that Fe⁰ can reduce nitrates thanks to redox potential. They indicated the pH value can be a helpful factor in nitrates reduction (Muradova et al., 2016). This investigation could partially explain the small detected nitrates amounts in sandy soil (in 40 cm depth) and non-detectable nitrates amounts in silty-loam profile (in all depths). Thus, nitrates remaining in relatively dry soils could be exposed to other redox-active iron compounds or other reactive components. Unfortunately, our experiment cannot distinguish loss of nitrates during

the chemical transformation from the contribution of the nitrates movement and leaching. From the major observation, we have point on, that the 5 times higher nitrates concentration, as recommended fertilization, did not cause the nitrates to leach into the groundwater in the selected soils under specific meteorological conditions probably as the effect of good sorption capacity in both soils. With this experiment, we would like to point out that with a further increase in the concentration of added nitrates by over-fertilization, groundwater can be contaminated in combination with rich precipitation. Lysimeters are a suitable tool for studying the transport processes of various other ions, electrolytes, nutrients, substances, heavy metals, radionuclides, drugs, etc., which can reach and contaminate the groundwater source. Similar studies are necessary to determine the maximum limit concentration of substances that enter the soil while not reaching groundwater levels. The study of transport processes using lysimeters can also inspire the development of separation technology to prevent the leaching of harmful substances into groundwater.

Conclusion

The investigation of the nitrates movements through the soil monoliths was performed at the lysimeter station of the Hydrological Research Base, Institute of Hydrology, Slovak Academy of Sciences, localized in Petrovce nad Laborcom in the Eastern Slovakia Lowland. By simply spectroscopic measuring the nitrate concentration we have shown in our work that soil monoliths varying in type, size and grain composition of soil particles affect the nitrates movement differently. The main reason is associated with hydraulic conductivity and specific surface of soil particles. Our results suggest that the natural precipitation and irrigation exhibit a low risk of nitrates penetration to the groundwater during the vegetation period under standard and overdosed fertilization. It was shown

a significant nitrate content decrease during the vegetation period probably due to the nitrates uptake by grass and good sorption capacity of the soil. These findings are valid for the soils with the hydraulic properties closely resembling those at the experimental site. We suggest that lysimeters represent a suitable model tool for the study of transport processes not only nitrates and nitrites useful mainly in agriculture but also other nutrients or vice-versa pollutants important for environmental research.

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