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Impact of fertilization on water resources in karst, example of research field site Sinji Vrh

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ABSTRACT

A research field site (RFS) was established at Sinji Vrh in the western part of Slovenia in order to study flow and solute (particularly pollutant) transport in fractured and karstified rocks, with a focus on the unsaturated zone. RFS consists of surface set-up and a research tunnel, 15 m below the surface. Agrometeorological station was installed on the RFS. A special construction (1.5 m long segments) for collecting water seeping from the ceiling of the research tunnel was developed. At the research field site Sinji Vrh fertilizer application experiments were performed for estimation of impact of fertilization on water resources. Results of the fertiliser application experiments have shown that a thin autochtonous soil cover on karstic rock is insufficient to retain nitrate and prevent pollution of groundwater.

Key words: karstic rock, nitrate pollution, agricultural pollution, unsaturated zone, water resources

IZVLEČEK

VPLIV GNOJENJA NA VODNE VIRE NA KRASU, RAZISKOVALNI POLIGON SINJI VRH

Terenski eksperimentalni poligon na Sinjem vrhu v zahodni Sloveniji je bilo urejeno za raziskave toka vode in prenosa snovi (predvsem onesnažil) v kraško - razpoklinskih kamninah, s poudarkom na nezasičeni coni. Terenski eksperimentalni poligon sestavljata površinski in podzemni del – predor 15 m pod površjem. Nad raziskovalnim rovom je bila nameščena agrometeorološka postaja. V raziskovalnem predoru je bilo nameščeno posebno ogrodje v 1.5 m dolgih segmentih za vzorčenje prenikle vode. Na terenskem eksperimentalnem poligonu je bil izveden poskus z mineralnimi gnojili z namenom ocenit vpliv gnojenja na vodne vire. Rezultati so pokazali, da je tanek sloj avtohotnih tal na površini kraške kamnine nezadostna zaščita pred onesnaževanjem podzemnih voda z nitrati.

Ključne besede: kraška kamnina, onesnaževanje z nitrati, onesnaževanje v kmetijstvu, nezasičena cona, vodni viri

1 INTRODUCTION

Fractured and karstified rocks are very heterogeneous and complex in terms of their geometry and void topology. This results in parameter variability and large uncertainties reflecting complicated hydraulic, mechanical, thermal, and chemical processes. Therefore, detailed studies of these processes have to be performed on a macro scale at instrumented research field sites (Čenčur Curk, 1997, 2001). Such a site was established at Sinji Vrh in the western part of Slovenia (Figure 1). The main goal of the research field site at Sinji Vrh (RFS Sinji Vrh) was the study of flow and solute (particularly pollutant) transport in fractured and karstified rocks, with a focus on the unsaturated zone.

In hydrogeological systems of karstified aquifers, the unsaturated zone above the water table has

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physical and chemical retention properties which provide a potential natural protection zone for karstic groundwater. Simulation of fertilisation on meadow at this research field site was performed in order to study the behaviour of nitrates and their percolation through karstic soil and underlying unsaturated zone of karstified rock.

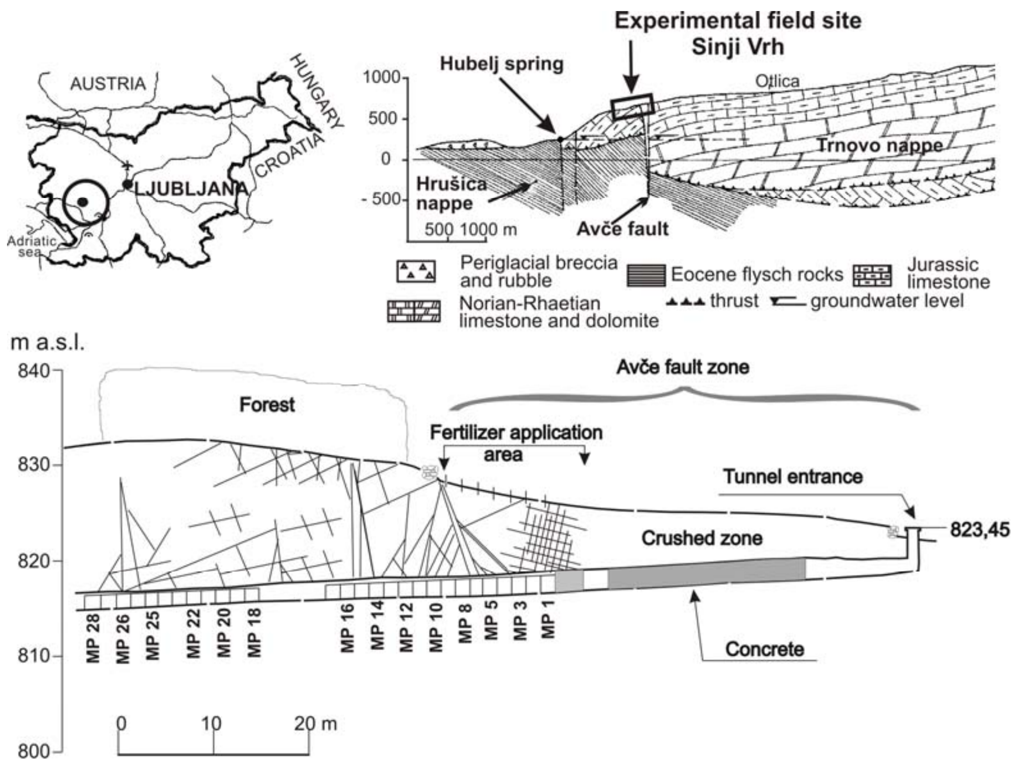

Figure 1: Location of the research field site Sinji Vrh (RFS Sinji Vrh) with a geological cross-section of Trnovo plateau (Janež, 1997, Veselič and Čenčur Curk 2001)

2 MATERIALS AND METHODS

2.1 Research field site Sinji Vrh

RFS Sinji Vrh is located in the western part of Slovenia (Figure 1) at the edge of the Trnovski Gozd plateau (mean altitude of 900 m a.s.l), which is an over thrust (Trnovo nappe) of carbonate rock over impermeable Eocene flysch rocks (turbidites sediments, mainly changing of marble and sandstone). This area is composed of Jurassic limestone, which passes laterally into crystalline dolomite. This territory is crossed by the sub vertical Avče fault with a Dinaric direction (NW-SE), resulting in crushed and fractured rock. The geological profile of the Trnovski Gozd plateau is presented in Figure 1 (Janež, 1997).

The groundwater horizon lies extremely deep and appears on the surface at the lowest point of the impermeable flysh border in karstic spring Hubelj. Average annual precipitation in the catchment is roughly 2450 mm. In this region mainly thin (10-50 cm) carbonate soil types are found. They have low water retention capacities facilitating fast infiltration rates (Matičič, 1997).

The research field site in the unsaturated zone of fractured and karstified rock presents a 340 m long artificial tunnel, 5 to 25 meters below the surface (Figure 1). The surface is covered with grassland and small beech forests which usually cover outcrops. The unsaturated fractured and karstified limestone has a negligible matrix porosity and very high fracture density with some larger conduits (Čenčur Curk and Veselič 1999).

An agrometeorological station (Figure 2) has been installed on the surface, where precipitation, evaporation, air temperature, air moisture, wind speed and direction (both at two levels) are continuously measured. It is located near the tunnel entrance at a height of 825 m above sea level.

On the grassland, an area of 150 m^2 was used for a fertiliser application experiment (Figure 2). The grassland close to the tunnel entrance is cut twice a year and used for livestock feed; there are no other crop and irrigation practices. Suction cups were installed at two levels (depth of 15 and 45 cm) in the karstic soil above the tunnel. For these experiments a special water collecting structure was made and installed in the tunnel. Each sampling segment consists of metal girders across which a plastic sheet is tightened. Special funnels were made to collect water in narrow sampling containers (Figure 3). The water seeping from the ceiling of the tunnel is gathered in 28 segments (each 1.5 m long); each has a total collecting surface of 2.2 m^2 (Figure 1 and 3).

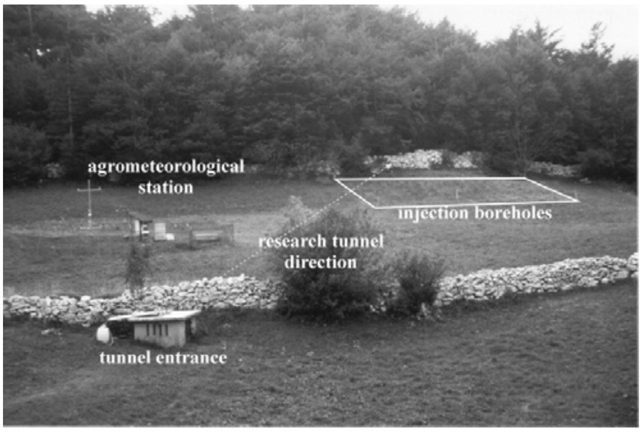

Figure 2: Agrometeorological station and area where fertiliser was applied (rectangle) on the research field site Sinji Vrh

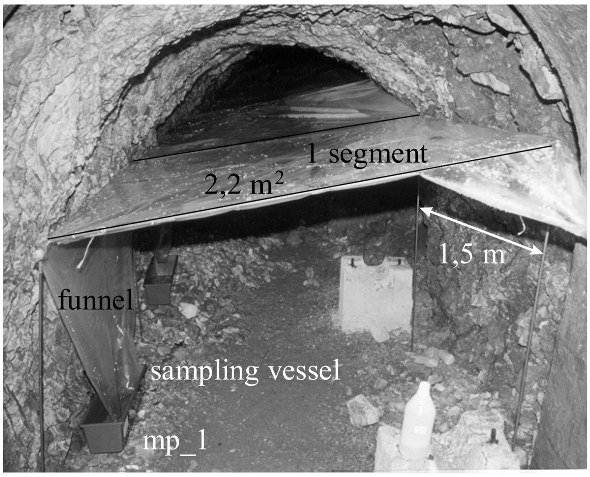

Figure 3: Construction for collecting water samples in the tunnel

2.2 Soil parameters

Standard soil parameters and hydraulic functions were determined at the Biotechnical Faculty, Agronomy Department. The 0.2 – 1 m thick soil is a typical karstic pocket soil (calcaric brown soil), very similar to a rendzina but with characteristic deeper pockets extended along weak zones like fractures in the underlying rock (Figure 4). In a 0.7 m deep soil profile the Ah-horizon has a thickness of 0.15 m, and the B-horizon 0.55 m. In the latter a horizon with more roots and higher organic content (Brz1) can be distinguished (Table 1). The soil has a middle value of cationic exchange capacity, since the soil particles bound only 25 – 35 meq $100g^{-1}$ of soil. On the sorptive part of the soil particles 15 – 25 meq bases $100g^{-1}$ of soil are bound. The V-ratio is higher than 50 %; therefore the soil is eutric and saturated with bases.

Figure 4: Soil profile at the RFS Sinji Vrh

Table 1: Results of soil profile analysis on the research field site Sinji Vrh

Parameter	Soil horizon	A horizon	Brz1	Brz
	Unit / Depth	0-15 cm	15-33 cm	33-70 cm
pH in 0.1M KCl	-	5.6	7.1	7.6
P_2O_5	mg $P2O_5$ $100g^{-1}$ soil	4.5	1.8	1.1
K_2O	mg K2O $100g^{-1}$ soil	10.7	10.4	8.4
N – total	%	0.42	0.15	0.08
Humus	%	7.04	2.51	1.19
H+	meq $100g^{-1}$ soil	17.81	7.5	2.81
K+	meq $100g^{-1}$ soil	0.26	0.25	0.20
Ca++	meq $100g^{-1}$ soil	12.68	24.32	22.38
Mg++	meq $100g^{-1}$ soil	3.41	1.46	0.98
S	meq $100g^{-1}$ soil	16.39	26.07	23.59
T	meq $100g^{-1}$ soil	34.2	33.57	26.40
V	%	47.9	77.7	89.4
sand	%	17.1	12	25.2
silt	%	34.3	16.6	14.7
clay	%	48.6	71.4	60.1
texture class	-	SC-C	C	C

meq = miliequivalent; S = total sum of bases, T = sorption capacity, V = S/T, SC = silty clay, G = clay

Before the first fertiliser application experiment soil samples were taken from two different depths and analysed on nitrate and ammonium nitrogen. In depth of 10-20 cm there was 6.5 mg N-NO3 kg^{-} 1 soil and 9.6 mg N-NH3 kg-1 soil, whereas in depth of 30-40 cm there was 7.8 mg N-NO3 $kg^{-}1$ soil and 5.1 mg N-NH3 $kg^{-}1$ soil. Isotopic composition (δ15N) of soil water was not determined due to small amount of sampled water.

Soil samples were taken in two depths (10 – 20 cm and 30 – 40 cm) for analysis of nitrate and ammonium nitrogen (Table 2).

Table 2: Nitrate and ammonium concentrations in soil samples at two depths

Depth (cm)	mg N-NO_3 in kg soil	mg NO_3 in kg soil	mg NH_4 in kg soil	mg N-NH_4 in kg soil
10-20	6.5	28.6	12.4	9.63
30-40	7.8	21.5	6.5	5.05

The soil samples were taken for determination of the hydraulic functions of the soil in two depths: 30 cm and 60 cm (Figure 5). The pF curves are very similar and differ only for some mass % at low-tension conditions. The data demonstrates that the water retention capacity of the soil at the research field site is relatively low. Soil samples were also taken for determination of hydraulic conductivity. The hydraulic conductivity of these soil samples varies from 9E-4 to 1.25 cm min^{-1}; the average value is 0.4 cm min^{-1}.

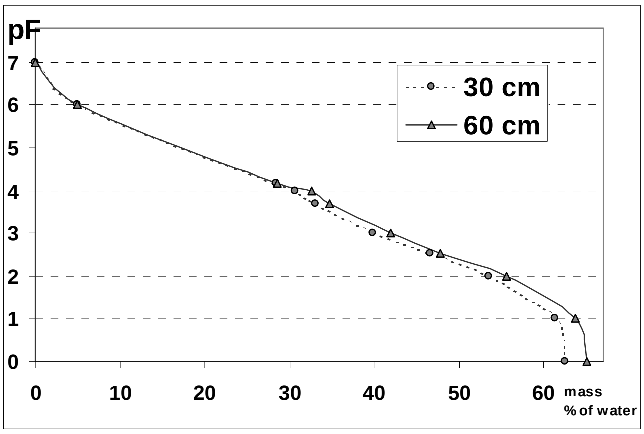

Figure 5: pF curves for the soil depths of 30 and 60 cm

2.3 Fertilizer application experiments

Three fertiliser application experiments were performed at the research field site Sinji Vrh. For all experiments the mineral fertilizer KAN (calcium ammonium nitrate) was used in accordance with appropriate agricultural practice. KAN was selected, because this is widely used mineral fertilizer in Slovenia. For the meadow with mowing twice a year, a norm for application rate is 40 kg N ha^{-1}, therefore 0.6 kg N is needed for 150 m^2 of test area (Figure 2). Regarding 28% N portion in KAN, 2.25 kg of that fertilizer is needed.

In-situ measurements of temperature, pH, Eh and electrical conductivity of seepage water in the research tunnel were performed weekly or after each rain event, whereas samples for chemical and isotopic composition were taken in case of higher electrical conductivity values. Nitrate ion and nitrite ion concentrations were determined with portable WTW photometer MPM 3000 (Institute of Mining, Geotechnology and Environment) with detection limit for nitrate 4,4 mg L^{-1} and 0,16 mg L^{-1} for nitrite. Nitrogen isotope 15N was determined at the Institute Josef Stefan.

3 RESULTS OF FERTILISER APPLICATION EXPERIMENTS

In the first fertiliser application experiment (experiment G1) increased nitrate concentration was detected in water samples of almost all sampling points after approximately 30-35 days (Figure 6), which was five days after the heavy rain (4-July; 51.7 mm), followed by more or less constant rain (Čenčur Curk et al. 2000, Veselič et al. 2001). The first precipitation event (Figure 6) caused dissolution of the fertiliser and transported it into the soil zone. The highest nitrate concentration (15.1 mg L^{-1}) appeared at the measuring point MP5 (Figure 6); δ15N value of total dissolved N was 0.2 ‰, which refers to mineral fertiliser. It should be noted that for MP5 nitrate concentration before fertilizer application was 16.5 mg L^{-1}, which is higher than the nitrate peak after the fertiliser application. δ15N value after the application was +3.1 ‰, therefore we can assume that there were extensive mineralization processes in the soil because of vegetation. In MP2 the nitrate concentration before the application was even higher: 58.93 mg L^{-1}, but afterwards there was not enough water for analyse. Samples could be taken only after 11th August, when nitrate concentration was very low (5.05 mg L^{-1}). Previous tracer experiments and structural mapping identified this sampling point as a fast channel with the potential to permit large contaminant fluxes. Natural background unsaturated zone concentrations measured in springtime, which are dominated by mineralization processes in the soil, were higher than the observed unsaturated zone nitrate concentrations following fertiliser application.

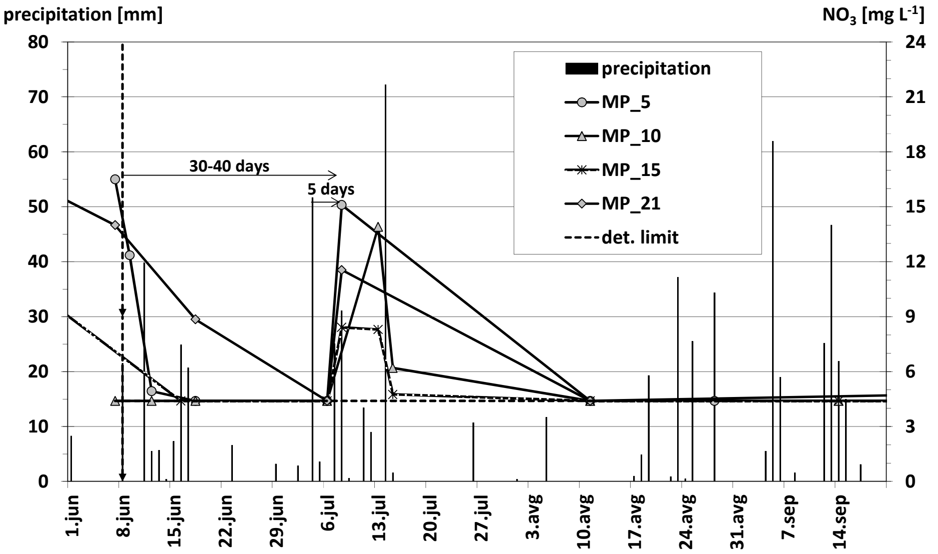

Figure 6: Precipitation events (mm) and nitrate concentrations (mg L^{-1}) (detection limit: 4.4 mg L^{-1}) in sampling points MP5, MP10, MP15 and MP21 for experiment G1 (dashed vertical arrow presents fertiliser application date on 8 June)

The second fertiliser application experiment (G2) was performed in order to obtain further information on nitrate percolation through the soil cover. For this reason, suction cups were installed in the soil and isotope analysis was carried out on water obtained from multiple sampling points (MP2, MP5, MP10 and MP21 in Figure 7). The nitrate appeared one week after one very large precipitation event (68.8 mm; 21-Sept.), about 22 days after fertiliser was applied. Since the isotope composition of the synthetic fertilizer KAN is about 0 ‰, the isotope data δ15N (Figure 7) confirmed that the nitrate source was the fertiliser applied on the meadow in experiment G2 (Čenčur Curk et al. 2000). The nitrate transport along the fast channel at measuring point MP5 showed the first breakthrough of nitrate after 8 days. In some measuring points another flush of the nitrate was detected (MP21 and MP10). After another very large precipitation event in the following spring (1-March; 85.1 mm) the nitrate was flushed again, which released nitrate previously retained in micro fractures of the unsaturated zone (MP2 in Figure 7).

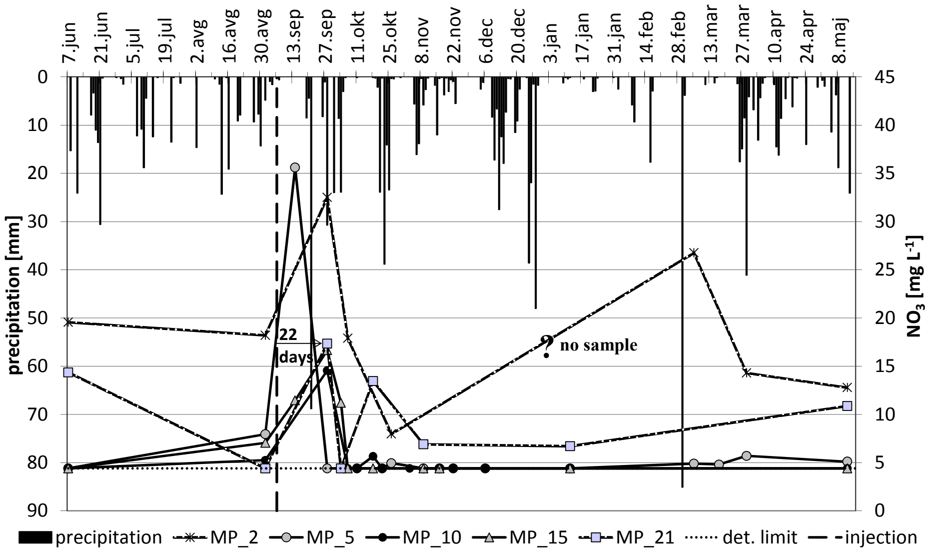

Figure 7: Precipitation events (mm) and nitrate concentrations (mg L^{-1}) (dashed horizontal line: detection limit at 4.4 mg/L) in sampling points MP2, MP5, MP10, MP15 and MP21 for experiment G2

The third fertiliser application experiment (G3) was performed on 8th August. Measuring position MP2 had slightly higher nitrate concentration on 18th September, but this cannot be attributed to fertilization, because there was no precipitation before 15th September and the precipitation event between 15th and 17th September only dissolved the applied fertilizer. On 26th October (57 days after fertiliser application) nitrate concentration in MP2 was extremely high (116.6 mg L^{-1}). δ15N value was 0.5 ‰ (Table 2), which means that this high concentration of nitrate can be result of fertilization. Even δ15N values at MP5 were at the beginning lower and then rose again. The first increase of nitrate concentration on 26th October (7.0 mg L^{-1}) cannot be attributed with certainty to fertilization, because in that time there was not enough water for the isotopic analysis of nitrogen. The next concentration increase on 13th November (9.1 mg L^{-1}) was probably due to fertilization (δ15N = + 0.2 ‰).

Table 2: Nitrate concentrations (mg L^{-1}) and nitrogen isotope composition (‰) in sampling points MP2, MP5, MP10 and MP15 for experiment G3

	MP2		MP5		MP10		MP15	
Date	NO_3^- [mg L^{-1}l]	$\delta^{15}N$ [‰]	NO_3^- [mg L^{-1}l]	$\delta^{15}N$ [‰]	NO_3^- [mg L^{-1}l]	$\delta^{15}N$ [‰]	NO_3^- [mg L^{-1}l]	$\delta^{15}N$ [‰]
31.8.			1.7	11.4	1.7	-4.1	2.1	-0.5
18.9.	23.8	-1.2	1.3	8.8	5.3	3.2	3.0	0.9
6.10.	15.6	0.8	0.6	2.5	4.7	3.0	2.3	-2.1
9.10.			1.3	0.9			7.2	-2.3
11.10.								
26.10.	116.6	-0.5	7.0		86.3		11.8	
2.11.					48.8		19.9	
13.11.			9.1	0.2	48.4		19.3	
15.11.			3.4		47.9		26.5	
17.11.			3.0	-1.5	37.7	0.4	23.3	
20.11.			1.6	2.6	27.1		18.4	
23.11.	0.6	-0.8	0.8	4.0	0.0	-1.1	0.2	4.5
25.11.	2.2	-0.1	0.7	4.4	0.0	1.4	0.2	
27.11.	3.7		0.6	5.5	0.1	2.5	0.3	1.9
29.11.	5.2		0.7	3.6	0.1	-3.8	0.3	-3.9
6.12.			0.8	2.9	0.5	-1.9	0.7	-6.0
13.12.	2.6	-0.9	0.7		0.1		0.5	0.4
4.1.	2.8	0.4	1.1	6.2	0.3		0.4	-0.2

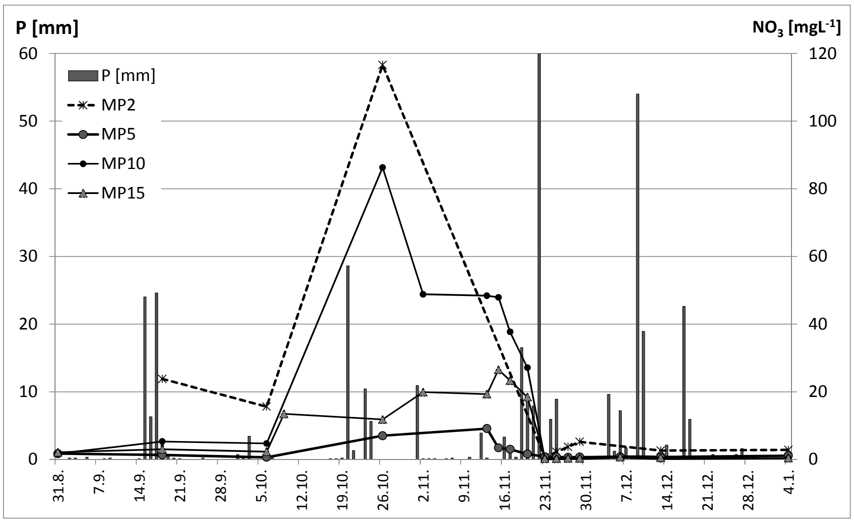

Figure 8: Precipitation events (mm) and nitrate concentrations (mg L^{-1}) (dashed horizontal line: detection limit at 4.4 mg/L) in sampling points MP2, MP5, MP10, MP15 and MP21 for experiment G3

4 CONCLUSIONS

Fractured and karstified rocks are highly heterogeneous and complex, therefore knowledge of the rock structure is of paramount significance for predicting flow and transport. The transport of pollutants depends on i) saturation rate of the soil and unsaturated zone, ii) on precipitation events and iii) on the presence of channels and interconnected fracture networks. Pollution remains in the soil and in fractures of the upper part of the unsaturated zone and is flushed by subsequent large precipitation events which can occur several months or years afterwards. The degree of flushing is highly dependent on the antecedent moisture conditions within the unsaturated zone.

Results of the fertiliser application experiments have shown that a thin autochthonous soil cover on karstic rock is insufficient to retain nitrate and prevent pollution of groundwater. In most cases the maximum nitrate concentrations were lower than natural background values and the drinking water limit. Therefore the usage of fertilisers should be in accordance with strictly defined standards. Further detailed studies on this aspect are needed within the frame of the research into karstic aquifer vulnerability. Additional experiments with an emphasis on biogeochemical transformations (e.g. measurement of nitrogen gas, N_2O, soil nitrogen compounds, dissolved nitrogen compounds and their isotopic composition, and microbiological processes) is planned in order to better understand the behaviour of nitrate in soil and the unsaturated zone.

5 ACKNOWLEDGEMENTS

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