EGU General Assembly 2020, 4th – 8st May 2020

SORPTION AND DEGRADATION OF PHARMACEUTICALS IN THE UNSATURATED ZONE

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1. INTRODUCTION

The vulnerability of the aquifer is directly related to the hydraulic and transport characteristics of the unsaturated zone and properties of the pollutants. The properties of emerging organic pollutants in the unsaturated zone are still not well known.

Transport parameters of selected organic pollutants through aquifer were determined by **COMBINED TRACING EXPERIEMNT (Lysimeter Selniška dobrava):**

- ***Deuterium:*** determination of transport characteristics of coarse gravel unsaturated zones.
- ***Propyphenazone, caffeine and carbamazepine (pharmaceuticals):*** determination of transport parameters.

2. TRACING EXPERIMENT

Site characteristics:

- Coarse gravel deposit: 50 m thick
- Groundwater table at depth: 25 to 37 m
- Saturated layer: 7-14 m thick
- Hydraulic conductivity of the gravel: $5 \cdot 10^{-3}$ m/s
- Vegetation covering: mixed forest
- Soil type: district cambisol
- Climate: moderate continental
- Average yearly precipitation: 1200 - 1300 mm
- Average yearly air temperature: 8 - 12 ˚C

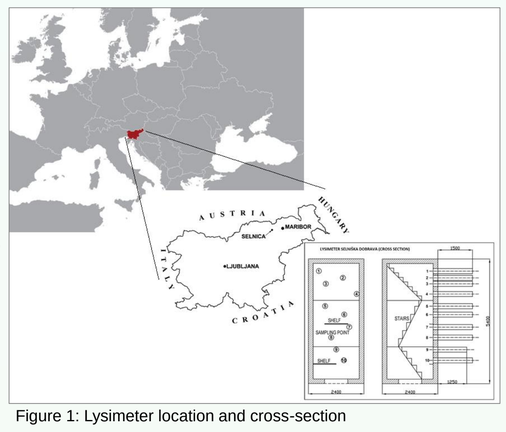

Figure 1: Lysimeter location and cross-section

Lysimeter set up:

- Dimensions: 2 x 2 m, 5 m deep, with walls 0.2 m
- Sampling points: 10, from JV-1 to JV-10
- Sampling system: gravitational, drainage
- system
- Drains: stainless steel drains, 10 x 10 cm profiles,
- 1.7 m long, with inverse inner perforated profiles (5 x 5 cm)
- Water collection system: 400 ml glass bottles and collecting containers

Tracing experiment:

- April 2010 - January 2012
- 1945 ml D_2O (50%)
- 1000 g Propyphenazone
- 100 g (99%) Carbamazepine
- 500 g Caffeine
- Injection area 9.5 m^2
- Irrigated water 55 mm
- 231 samples


Figure 2: Tracing experiment

3. HYDRUS model

Based on shape of deuterium tracer breakthrough curves it was concluded that total flow (Q_{tot}) is consisting of two components; dispersive flow (Q_{dis}) and preferential flow (Q_{pref}):

$$Q_{tot} = x_1 \cdot Q_{dis} + x_2 \cdot Q_{pref},$$

where $x_1 + x_2 = 1$ representing shares of each flow components respectively.

Data for the model:

- Precipitation measurements in model were used from measurement station Maribor (meteo.arso.gov.si).
- Evapotranspiration was calculated by Penman-Monteith equation from meteorological data for every day.
- Hydraulic Model: Single porosity model (van Genuchten-Mualem); no hysteresis (van Genuchten, 1980):

$$\begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{[1 + [1 + |ah|^n]^m]} & h < 0 \\ \theta_s & h \geq 0 \end{cases}$$

$$K(h) = K_s S_e \left[1 - \left(1 - S_e^{1/m}\right)^m\right]^2$$

$$m = 1 - \frac{1}{n}, n > 1$$

- Upper boundary Condition: Atmospheric BC with surface Run off (Cauchy boundary condition).
- Lower boundary condition: Free Drainage.
- Model efficiency: Nash-Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970).
- Sorption: Linear sorption coefficient (Kd); Degradation: 1st order constant degradation (μ).

4. RESULTS

Estimated soil parameters

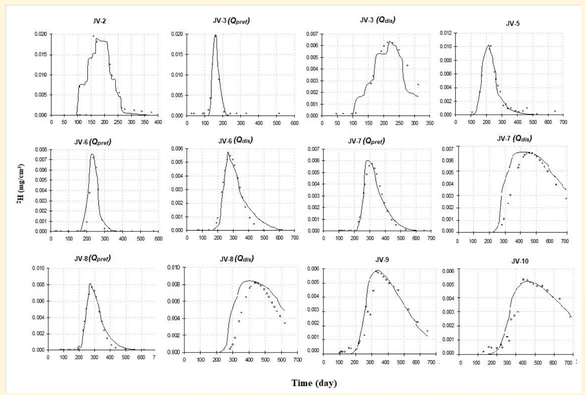

Figure 3: Inverse models of deuterium in HYDRUS-1D (observed values (circles) and simulated values (lines)

Table 1: Optimized UZ hydraulic and transport parameters for deuterium in lyzimeter

Sampling point		θs	α	n	Ks (m/s)	λ	NSE (%)
JV-2		0.38	0.03	1.35	$9.65 \cdot 10^{-4}$	8	82
JV-3	Q_{pref}	0.43	0.03	1.25	$5.98 \cdot 10^{-3}$	4	97
JV-3	Q_{dis}	0.48	0.03	1.38	$4.03 \cdot 10^{-4}$	15	97
JV-5		0.40	0.03	1.31	$4.65 \cdot 10^{-3}$	20	96
JV-6	Q_{pref}	0.42	0.03	1.32	$5.05 \cdot 10^{-3}$	7	92
JV-6	Q_{dis}	0.44	0.03	1.32	$2.70 \cdot 10^{-3}$	12	97
JV-7	Q_{pref}	0.45	0.03	1.33	$3.48 \cdot 10^{-3}$	9	93
JV-7	Q_{dis}	0.49	0.03	1.30	$1.52 \cdot 10^{-3}$	20	94
JV-8	Q_{pref}	0.44	0.03	1.33	$4.08 \cdot 10^{-3}$	10	98
JV-8	Q_{dis}	0.51	0.03	1.35	$2.20 \cdot 10^{-3}$	20	83
JV-9		0.49	0.03	1.30	$4.63 \cdot 10^{-3}$	35	91
JV-10		0.51	0.03	1.30	$4.63 \cdot 10^{-3}$	52	93

Estimated soil hydraulic properties:
- θr (residual volumetric water content): 0
- θs (saturated volumetric water content): 0.38 - 0.51
- α (inverse of the capillary fringe thickness): 0.027 - 0.03 (1/cm)
- n (shape parameter): 1.25 - 1.38
- l (tortuosity parameter): 0.5 (Mualem (1976)
- Ks (saturated hydraulic conductivity): $4.03 \cdot 10^{-4}$ - $5.9 \cdot 10^{-3}$ (m/s)
- α_L (longitudinal dispersivity): 4 to 52 (cm)
- NSE (Nash-Sutcliffe efficiency): 0.82 - 0.98

Transport parameters of selected pharmaceuticals

Propyphenazone:

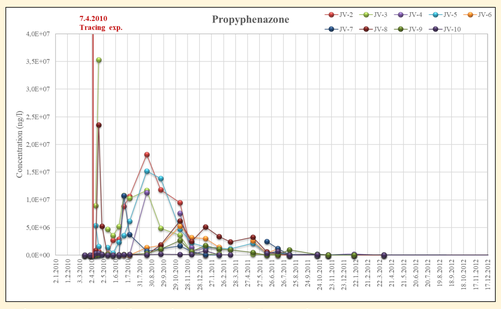

Figure 4: Breakthrough curves of Propyphenazone

Caffeine:

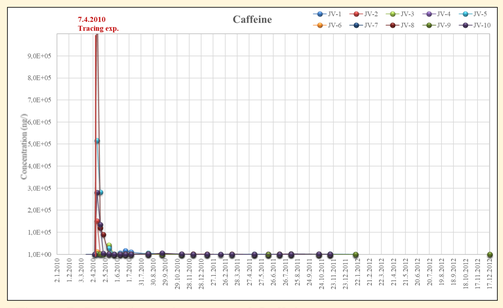

Figure 5: Breakthrough curves of Caffeine

Carbamazepine:

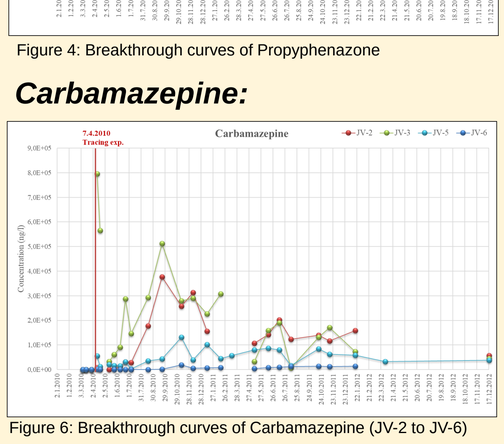

Figure 6: Breakthrough curves of Carbamazepine (JV-2 to JV-6)

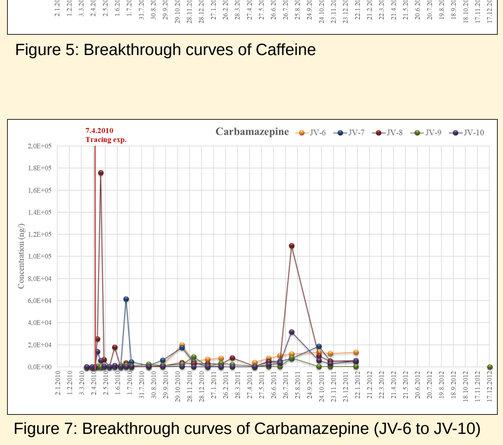

Figure 7: Breakthrough curves of Carbamazepine (JV-6 to JV-10)

	Kd (Lkg^{-1})			1st order constant degradation (μ)			$T_{1/2}$ (day)		
	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Propyphenazone	0.02	0.07	0.10	0.01	0.02	0.03	23.9	51.22	92.42
Caffeine	0	0.03	0.10	0.01	0.19	0.42	1.65	14.67	69.31
Carbamazepine*	0.13	2.44	6.30	0	0.01	0.02	46.2	231.96	819.68

*(Kodešová et al., 2015; Kodešová et al., 2016)

5. CONCLUSIONS

- Even though it is a coarse gravel aquifer, the water flow is mainly influenced by small fractions in the unsaturated zone, i.e. proportions of clay, sand and silt.

-The parameters for carbamazepine with an advection dispersion equation could not be determined, which indicating on different transport mechanisms.

- **Sorption capacity**: *Carbamazepine* (according to other studies) (mean Kd = 2.44 Lkg^{-1}) > *Propyhenazone* (mean Kd = 0.07 Lkg^{-1}) > *Caffeine* (mean Kd = 0.03 Lkg^{-1}).

- **Degradation**: *Caffeine* (mean μ = 0.19; mean $T_{1/2}$ = 14.67 days) > *Propyphenazone* (mean μ = 0.02; mean $T_{1/2}$ = 51.22 days) > *Carbamazepine* (according to other studies) (mean μ = 0.01; mean $T_{1/2}$ = 231.96 days).

References

- Kodešová R, Grabic R, Kočárek M, Klement A, Golovko O, Fér M, et al. Pharmaceuticals' sorptions relative to properties of thirteen different soils. Science of the Total Environment 2015; 511: 435-443.
- Kodešová R, Kočárek M, Klement A, Golovko O, Koba O, Fér M, et al. An analysis of the dissipation of pharmaceuticals under thirteen different soil conditions. Science of the Total Environment 2016; 544: 369-381.
- van Genuchten, M. T. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Sci. Soc. Am.J., 44, 892–898.
- Nash, J. E.,Sutcliffe, J. V. 1970. River flow forecasting through conceptual models part I — A discussion of principles. Journal of Hydrology 10, 3: 282–290.

Acknowledgements

The presented study was financially supported by the Slovenian Research Agency (ARRS) within research programme Groundwater and Geochemistry (P1-0020), the PhD work of A. Koroša and GeoERA project (European Union's Horizon 2020 research and innovation programme under grant agreement No 731166) which are carried out by the Geological Survey of Slovenia.