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Sorption of Atenolol, Sulfamethoxazole and Carbamazepine onto Soil Aggregates from the Illuvial Horizon of the Haplic Luvisol on Loess

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Abstract

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The leakage of pharmaceuticals present in soils towards groundwater is largely controlled by sorption of those compounds in soils. In some soils, soil aggregates are covered by coatings, which may have considerably different composition in comparison to that in an inner part of the aggregates. The aim of this study was to evaluate the sorption of three pharmaceuticals, which were applied in single or all compounds solutions, onto soil samples taken from the Bt horizon of a Haplic Luvisol. Analyses were performed on three types of disturbed soil samples: (1) entire aggregates, (2) aggregates from which coatings were removed, and (3) clay-organic coatings. Sorption of atenolol onto material from coatings was slightly higher than that onto material from the inner parts of the aggregates. On the other hand, sorption of sulfamethoxazole onto material from the coatings was lower than that from the aggregate interior. Both associates with a dominant fraction of clay particles (that are mostly negatively charged) in the coatings in comparison to soil composition in interiors and thus larger cation exchange capacity, which increased sorption of the positively charged atenolol and decreased sorption of the negatively charged sulfamethoxazole. Sorption of carbamazepine, which was in neutral form, did not substantially differ. The sorption of all three compounds did not decrease due to the competition between these compounds for the same sorption sites when applied simultaneously. Atenolol sorption was similar for both applications. Sorption of sulfamethoxazole increased when applied in solution with the other two compounds in comparison to its negligible sorption measured for the single compound solution likely due to sorption of the positively charged molecules of atenolol onto the negatively charged surface of soil components and reduction of repulsion between the soil components and the negatively charged molecules of sulfamethoxazole. Carbamazepine sorption also increased probably due to ionization of molecules due to dipole - induced dipole interaction between non-polar and polar molecules in solution.

Keywords: aggregates; aggregates interior; clay-organic coatings; illuvial horizon; pharmaceuticals; sorption

Human and veterinary pharmaceuticals have emerged as significant contaminants of the environment. Pharmaceuticals occur in soils due to application of animal wastes, biosolids, and from the reuse of treated

wastewaters (e.g., BOXALL *et al.* 2012; VERLICCHI & ZAMBELLO 2015). Sorption of pharmaceuticals in soils is one of crucial factors that controls pharmaceuticals mobility in the subsurface water environ-

ment (e.g., SCHAFFER & LICHA 2015) or their uptake by plants (WU *et al.* 2015). The number of studies dealing with the sorption of different compounds in various matrices related to soil and subsurface water environment has recently increased (e.g. KODEŠOVÁ *et al.* 2015; SCHAFFER & LICHA 2015; KLEMENT *et al.* 2018). The sorption of non-ionic (neutral) molecules is mainly driven by hydrophobic partitioning to the soil organic matter via van der Waals and electron donor-acceptor interactions and by hydrogen bonding with hydroxyl groups on the solid surfaces and therefore is highly dependent on the soil organic matter content. The sorption of cationic molecules is mainly governed by the attraction to negative charges of the solid surface (e.g., a clay mineral surface or organic matter) and thus is controlled by the cation exchange capacity or by the basic cation saturation (KODEŠOVÁ *et al.* 2015). The anionic molecules are eventually sorbed on the positively charged surface of soil constituents (edges of layered clay, radical fragment of humus) via cation bridging on negative charges. Sorption of such molecules is usually (when not assuming for instance tropical soils, e.g. DUŠEK *et al.* 2015) low due to repulsion between negatively charged molecule and mostly negatively charged soil surface. Sorption of pharmaceuticals onto soil components can be reduced due to competition between molecules of different compounds when applied in their mixture (CONKLE *et al.* 2010; LERMAN *et al.* 2013; JUNG *et al.* 2015; CARRILLO *et al.* 2016; KOČÁREK *et al.* 2016; WU *et al.* 2017) or increased due to synergy of compounds in soil solution (KOČÁREK *et al.* 2016; ZHANG *et al.* 2017).

It has been suggested in several studies (e.g., VAN BEINUM *et al.* 2005; VILLAVERDE *et al.* 2009) that sorption of organic compounds (in these cases pesticides) evaluated on disintegrated soils (i.e. in suspension) could be greater than that measured on soil aggregates. The main reason is that a part of the sorption capacity of the soil components is not available due to their interaction in aggregated soil. In addition, retarded diffusion into pores of soil aggregates influences kinetics of sorption. In some soils, interaction between applied solution and soil inside the aggregates could be affected by various coatings on soil aggregates. Then, for instance in the case of clay coatings in a luvisol (Bt) horizon, water inflow into aggregates and associated transport of dissolved substances may be reduced due to the low hydraulic conductivity of clay coatings (FÉR & KODEŠOVÁ 2012). In addition, sorption onto clay-

organic coatings and onto aggregate matrix can differ due to different compositions of soil components in coatings and the soil matrix. ELLERBROCK *et al.* (2016), FÉR *et al.* (2016), and LEUE *et al.* (2010, 2015, 2016) documented that the aggregate coatings in the Bt horizons of Haplic Luvisols may contain a larger amount of organic matter of different quality in comparison to aggregate interiors, which may increase the sorption of some organic compounds. Both parts (i.e. aggregate coatings and interiors) could differ also in their clay composition (FÉR *et al.* 2016). In this study, the main clay minerals in coatings were vermiculite and illite, whereas minor clay minerals were kaolinite and illite-smectite. The aggregate interior contained almost no illite, considerably lower contents of kaolinite and vermiculite in comparison to those in coatings, and a dominant content of illite-smectite. Among others, STYSZKO *et al.* (2015) showed that different clay minerals may differ in their sorption capacity. They documented that the potential of vermiculite to sorb tested pharmaceuticals (carbamazepine, diclofenac, ibuprofen, keprofen and biseptol A) was higher in comparison to kaolinite and montmorillonite (i.e., a member of the smectite group of clay minerals).

In the present study, we tested the hypothesis that coatings (due to their different clay mineral and organic matter composition) modify compound sorption affinity onto soil aggregates. The objective was to evaluate the sorption of compounds onto soil samples taken from aggregate coatings and interiors in the Bt horizons of the Haplic Luvisol. In addition, we evaluated competitive and synergic effect of simultaneous sorption of differently charged compounds (positively, negatively and neutral) on a particular compound sorption affinity.

MATERIAL AND METHODS

The study was performed on the soil samples taken from the Haplic Luvisol developed on loess substrate. Soil profile consisted of 3 horizons (A, Bt and C). The illuvial Bt horizon could be divided into two horizons, Bt1 and Bt2, with blocky, and large and long prismatic aggregates, respectively, which were covered by clay-organic coatings (KODEŠOVÁ *et al.* 2008, 2009, 2012). The basic soil properties of each horizon are shown in Table 1. The undisturbed soil aggregates were taken from both the Bt horizons. Three soil samples were prepared: (1) entire aggregates, (2) aggregates from which coatings were removed, and (3) clay-organic

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Table 1. Basic soil properties: $\text{pH}_{\text{H}_2\text{O}}$, pH_{KCl} , $\text{pH}_{\text{CaCl}_2}$, organic carbon content (C_{OX}), CaCO_3 content, cation exchange capacity (CEC) soil hydrolytic acidity (HA), basic cation saturation (BCS), sand, silt and clay contents (KOČÁREK *et al.* 2016)

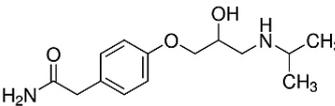
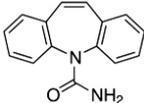
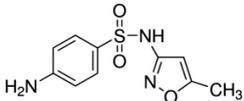
Soil horizon	Depth (cm)	$\text{pH}_{\text{H}_2\text{O}}$	pH_{KCl}	$\text{pH}_{\text{CaCl}_2}$	C_{OX}	CaCO_3	CEC	HA	BCS	Sand	Silt	Clay
		(-)										
Ap	0–32	6.5	5.5	5.8	0.79	0.05	140.9	9.9	131.0	14.2	63.2	22.8
Bt1	33–50	6.7	5.5	5.9	0.70	0.18	169.3	9.4	159.9	12.7	62.5	24.8
Bt2	51–95	7.4	5.7	6.5	0.27	0.18	187.0	5.9	181.1	0.1	66.6	28.9
C	96–170	7.9	6.4	7.1	0.15	0.15	180.0	3.2	176.8	7.1	66.2	26.7

coatings. Procedure was similar to that published by FÉR *et al.* (2016). Several large intact soil blocks of approximate $30\,000\text{ cm}^3$ were removed from both horizons using a spade, and were then wrapped in tinfoil and plastic backs. The blocks were transported within 1 day to the laboratory and stored in a refrigerator until analyzed. Individual aggregates were manually separated by carefully breaking the blocks. Coatings were cut by a scalpel from aggregates, which had some relatively plane intact sides with coated surfaces allowing coatings removal. Next all sides of some aggregates were cut to ensure removal of all coatings. Entire aggregates (1), cut aggregates (2) and coatings (3) were air-dried, ground, and sifted through a 2 mm sieve. Different compositions of each part of the aggregates from the Bt2 horizon were described before by FÉR *et al.* (2016) (see also introduction). Since the amount of soil material from coatings was limited, analyses were not done separately for each Bt horizon but on mixed samples from both the Bt horizons.

Three compounds (Table 2) were selected from a set of seven pharmaceuticals that have been applied previously by KODEŠOVÁ *et al.* (2015, 2016) or by KOČÁREK *et al.* (2016) in an evaluation of the impacts of soil properties on sorption affinities, or in an assessment of dissipation half-lives in various soils taken from 11 topsoils and 2 substrates. Pharmaceuticals (Table 2) were chosen based on their different forms depending on pH (Table 1) of the soil-water environment, their pK_a values (Table 2) and their corresponding sorption behaviour (KODEŠOVÁ *et al.* 2015): atenolol (cation), sulfamethoxazole (anion) and carbamazepine (neutral). All tested pharmaceuticals were purchased from BDL Czech Republic Ltd. (Turnov, Czech Republic), and are of 98% (atenolol, sulfamethoxazole) and 97% (carbamazepine) analytical grade purity.

The sorption isotherms were measured using a standard batch equilibrium method (OECD 2000). Three grams of dry soil was placed directly into a plastic centrifuge tube and 6 cm^3 of solution of a

Table 2. Selected pharmaceuticals

Pharmaceutical	CAS No.	Use	pK_a	log Kow	MW (g/mol)	Water solubility (mg/l)	Molecular structure
Atenolol	29122-68-7	beta blocke (hypertension)	$\text{pK}_{a1} = 9.7^a$ (basic) $\text{pK}_{a2} = 14.1^a$ (acidic)	0.16 ^a	266.34	429	
Carbamazepine	298-46-4	anticonvulsant (brain disorders), analgesic	$\text{pK}_{a1} = 1.0^c$ (basic) $\text{pK}_{a2} = 13.9^c$ (acidic)	2.45 ^a	236.27	152	
Sulfamethoxazole	723-46-6	antibiotic (also veterinary use)	$\text{pK}_{a1} = 1.7^b$ (basic) $\text{pK}_{a2} = 5.6^b$ (acidic)	0.89 ^a	253.28	459	

^a<http://www.drugbank.ca>; ^bLUCIDA *et al.* (2000); ^cOPPEL *et al.* (2005); pK_a – the dissociation constant; Kow – the octanol/water partition coefficient; MW – the molecular weight

single compound (sulfamethoxazole, carbamazepine and atenolol) or mixtures of all 3 pharmaceuticals at the same concentration for each (1, 2.5, 5, and 10 $\mu\text{g}/\text{cm}^3$ in 0.01 M CaCl_2) was added. Each soil-solution suspension was prepared in duplicate. The tube was shaken using an analog reciprocating shaker (GFL 3006, GFL Gesellschaft für Labortechnik mbH, Germany) at 20°C for 24 h. The suspension was centrifuged for 10 min at 6000 rpm and filtered through a regenerated cellulose syringe filter (0.45 mm). The actual initial ($c_{\text{ini},a}$) and final equilibrium (c_{eq}) pharmaceutical concentrations were analyzed using the normal injection LC-MS/MS method, described for instance in the paper by GOLOVKO *et al.* (2016). The concentration adsorbed onto soil particles (s) was calculated as the difference between $c_{\text{ini},a}$ and c_{eq} values multiplied by two. The Freundlich equation was used to fit the data points of the sorption isotherms [relating concentration adsorbed onto soil particles, s ($\mu\text{g}/\text{g}$), and equilibrium concentration in soil solution, c ($\mu\text{g}/\text{cm}^3$) = c_{eq}]:

$$s = K_F c^{1/n} \quad (1)$$

where:

K_F ($\text{cm}^{3/n} \mu\text{g}^{1-1/n}/\text{g}$), n – empirical coefficients

RESULTS AND DISCUSSION

The resulting Freundlich sorption isotherms and their parameters are shown in Figure 1 and Table 3. Findings partly confirmed our hypothesis. Sorption of atenolol onto material from coatings was always slightly larger than that onto material from the inner parts of the aggregates. The larger sorption in coatings can be likely attributed to a dominant fraction of clay particles (that are mostly negatively charged) and organic matter in those coatings in comparison to soil texture in interiors and thus larger cation exchange capacity, which increased sorption of the positively charged pharmaceutical (KODEŠOVÁ *et al.* 2015; SCHAFFER & LICHÁ 2015; KLEMENT *et al.* 2018). On the other hand, sorption of sulfamethoxazole onto material from the coatings was lower than that from the aggregate interior. This could be explained by a larger repulsion between negatively charged molecules and surface of soil components in coatings. The reason could be also the presence of a larger fraction of hydrophobic SOM (FÉR *et al.* 2016) in comparison to those in aggregates' interior. Organic matter in these coatings likely originated due to a precipitation of the dissolved organic matter in a percolated soil-solution. Among others LERMAN

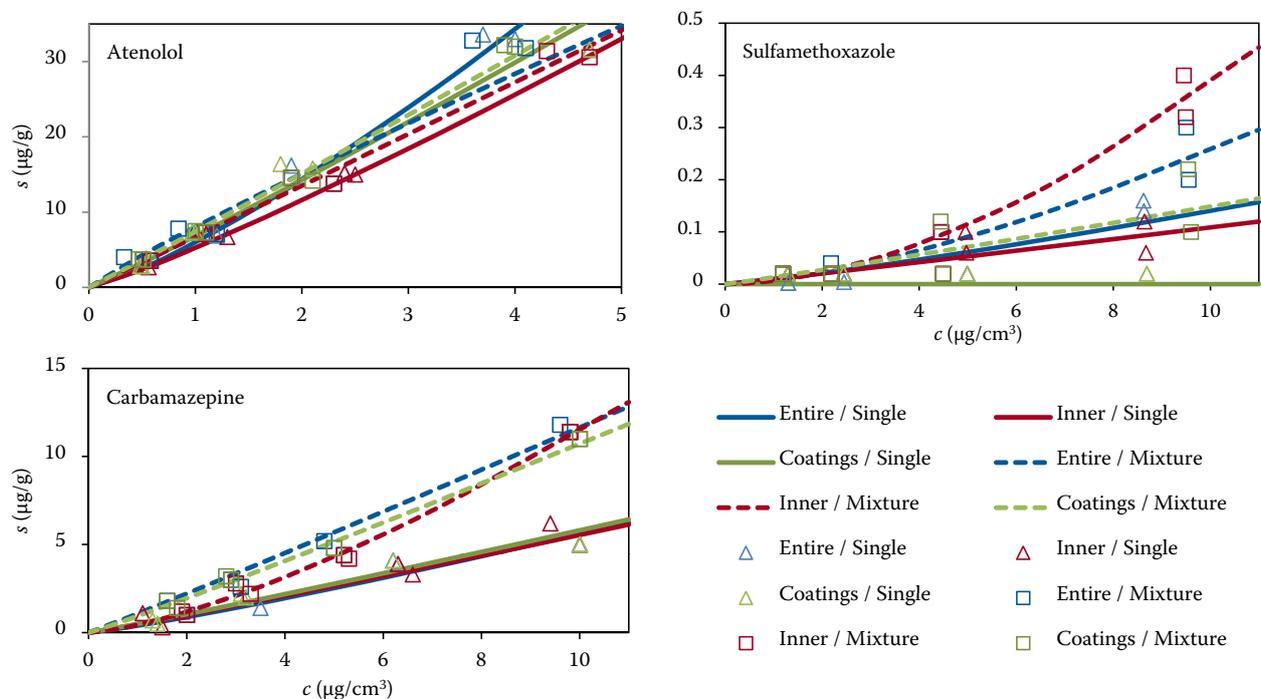


Figure 1. Sorption isotherms evaluated for soil material from the Bt horizon of the Haplic Luvisol

Entire – entire soil sample; Inner – inner part of the aggregate; Coatings – aggregate coatings; Single – single applied compound; Mixture – compound applied together with other two compounds

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Table 3. Parameters K_F ($\text{cm}^3/\text{n} \mu\text{g}^{1-1/\text{n}}/\text{g}$) and n (–) of the Freundlich adsorption isotherms evaluated on the soil samples from the Bt horizons of the Haplic Luvisol

Pharmaceutical	Part of the soil aggregates	Single applied compound		Compound applied together with other two compounds	
		K_F	n	K_F	n
Atenolol	entire	6.02	0.80	8.02	1.10
	inner	5.27	0.88	6.71	0.99
	coatings	6.82	0.94	7.42	0.97
Carbamazepine	entire	0.40	0.87	1.08	0.97
	inner	0.47	0.94	0.45	0.71
	coatings	0.50	0.94	0.94	0.95
Sulfamethoxazole	entire	0.009	0.84	0.008	0.67
	inner	0.010	0.97	0.007	0.57
	coatings	0	–	0.013	0.95

et al. (2013) showed (in this case for DOC from two composts) that the hydrophobic acid fraction is usually the dominant fraction compared to other hydrophobic fractions. Hydrophobic acid fraction (if present in the coatings) could again increase repulsion between the soil surface and negatively charged molecules of sulfamethoxazole. In the case of carbamazepine, sorption of its neutrally charged molecules (which should be mainly controlled by the organic matter content; KODEŠOVÁ *et al.* 2015; KOČÁREK *et al.* 2016) did not substantially differ.

When comparing the sorption affinities resulted from the different applications of the compounds (i.e., single and in a mixture) it is evident that the sorption of all three compounds did not decrease due to the competition between these compounds for the same sorption sites. Atenolol sorption was similar for both applications. As observed in our previous study (KOČÁREK *et al.* 2016), sorption of sulfamethoxazole increased when applied in solution with the other two compounds in comparison to its negligible sorption measured for the single compound solution. This can be again attributed to sorption of the positively charged molecules of atenolol onto the negatively charged surface of soil components and reduction of repulsion between the soil components and the negatively charged molecules of sulfamethoxazole. Other reason for enhanced sorption of sulfamethoxazole could be cation bridging. The negative electrostatic interaction between the molecules of sulfamethoxazole and the sorbent surface likely decreased with the increasing concentration of atenolol in solution, which resulted in concave shapes of the sorption isotherms (i.e., $n < 1$). Interest-

ingly, carbamazepine sorption also increased, which was not observed in our previous study (KOČÁREK *et al.* 2016), where trimethoprim was also included in solution. Increased sorption of carbamazepine can be possibly explained by ionization of molecules due to dipole - induced dipole interaction between non-polar and polar molecules in solution. It should be noted, that ZHANG *et al.* (2017) also observed slightly greater absorption of ibuprofen and greater desorption affinity of ibuprofen (IBF), naproxen (NPX), keprofen (KTF) and diclofenac (DCF) when applied in mixture to the loam-texture soil (pH of 6.1), despite that molecules of all four chemicals were negatively charged (pKa acidic: 4.91 – IBF, 4.15 – NPX, 4.45 – KTF, and 4.15 – DCF). They suggested that through multilayer cooperative adsorption, DCF was chemically adsorbed to the limited binding sites on soil surface, whereas IBF NPX and KTF saturated synergistically on the relatively weaker binding sites on the firsts layer of soil surface and formed absorbable layers to accommodate more molecules.

CONCLUSIONS

The results of this study documented that the sorption of the ionic compounds onto the clay-organic coatings covering the soil aggregates in the Bt horizon of Luvisols may differ from that in the inner part of the aggregates. Sorption of ions in clay-organic coating can be influenced either positively (cations) or negatively (anions). The results also showed that sorption of three compounds, which are differently charged (one positive – atenolol, one negative – sulfamethoxazole and one neutral – carbamazepine) does

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not have to be competitive. Rather synergic impact of the simultaneous application of all three compounds on the increased compound sorption was found in the case of sulfamethoxazole and carbamazepine.

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