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Pharmaceuticals' sorptions relative to properties of thirteen different soils

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HIGHLIGHTS

- Adsorption isotherms of 7 selected pharmaceuticals were measurement for 13 soils.
- Adsorption of ionizable compounds was highly affected by soil pH.
- Depending on compound pKa diverse properties correlated with adsorption coefficients.
- Functions for estimating adsorption coefficients from soil properties were obtained.

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ABSTRACT

Transport of human and veterinary pharmaceuticals in soils and consequent ground-water contamination are influenced by many factors, including compound sorption on soil particles. Here we evaluate the sorption isotherms for 7 pharmaceuticals on 13 soils, described by Freundlich equations, and assess the impact of soil properties on various pharmaceuticals' sorption on soils. Sorption of ionizable pharmaceuticals was, in many cases, highly affected by soil pH. The sorption coefficient of sulfamethoxazole was negatively correlated to soil pH, and thus positively related to hydrolytic acidity and exchangeable acidity. Sorption coefficients for clindamycin and clarithromycin were positively related to soil pH and thus negatively related to hydrolytic acidity and exchangeable acidity, and positively related to base cation saturation. The sorption coefficients for the remaining pharmaceuticals (trimethoprim, metoprolol, atenolol, and carbamazepine) were also positively correlated with the base cation saturation and cation exchange capacity. Positive correlations between sorption coefficients and clay content were found for clindamycin, clarithromycin, atenolol, and metoprolol. Positive correlations between sorption coefficients and organic carbon content were obtained for trimethoprim and carbamazepine. Pedotransfer rules for predicting sorption coefficients of various pharmaceuticals included hydrolytic acidity (sulfamethoxazole), organic carbon content (trimethoprimand carbamazepine), base cation saturation (atenolol and metoprolol), exchangeable acidity and clay content (clindamycin), and soil active pH and clay content (clarithromycin). Pedotransfer rules, predicting the Freundlich sorption coefficients, could be applied for prediction of pharmaceutical mobility in soils with similar soil properties. Predicted sorption coefficients together with pharmaceutical half-lives and other imputes (e.g., soil-hydraulic, geological, hydro-geological, climatic) may be used for assessing potential ground-water contamination.

1. Introduction

The presence of human and veterinary pharmaceuticals in the environment has been recognized as a potential environmental threat (Boxall et al., 2012; Fent et al., 2006; Ternes et al., 2002). There are several potential sources of surface- and ground-water (i.e., also drinking water) contamination that operate via multiple pathways. Animal waste, which has been commonly applied to agriculture crop fields as a source of organic fertilizer, is a prominent source (Bin Ho et al., 2014; Tanoue et al., 2012; Wu et al., 2014). Some pharmaceutical ingredients may be retained in soils, while the remainder can be transported to the surface- and ground-water through surface runoff and infiltration (Thiele-Bruhn, 2003). Another source of pharmaceutical pollution is urine from domestic wastewater streams originating in new sanitation systems based on decentralized treatment (Winker et al., 2009). Some

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of the organic pollutants from human and animal sources are not fully eliminated during wastewater treatment and can therefore be found in the aquatic environment (Derksen et al., 2004; Golovko et al., 2014a,b; Heberer, 2002a,b) and in soil (because of their application for irrigation) (Wu et al., 2010). Pharmaceuticals can be found in sewage sludge and sediments (Andersen et al., 2003; Ternes et al., 2002), which can cause surface- and ground-water pollution when processing (dumping, field applications, etc.). Direct contamination from sewer leaks may also be considered.

The problem of contamination by pharmaceuticals is not limited to drinking water. Several studies have shown that pharmaceuticals may accumulate in plants (Rajapaksha et al., 2014; Tanoue et al., 2012; Winker et al., 2010; Wu et al., 2010, 2012, 2013) (i.e., they may subsequently occur in animal and human food).

Several studies have addressed pharmaceutical transport through a porous soil media (Fan et al., 2011; Kay et al., 2005; Srivastava et al., 2009; Unold et al., 2009a,b; Vithanage et al., 2014; Wehrhan et al., 2007; Zhang et al., 2014). Sorption on soil particles is a principle parameter affecting pharmaceutical mobility in porous media and root uptake availability. Previous studies addressing pharmaceutical sorption on solids have mostly concentrated on pharmaceutical sorption in sewage sludge [e.g., study by (Horsing et al., 2011) who studied sorption of 75 pharmaceuticals], due to their main interest in characterizing the behavior of pharmaceuticals during wastewater treatment. Some studies have focused on the sorption of selected pharmaceuticals in sediments (Martínez-Hernández et al., 2014; Niedbala et al., 2013; Schaffer et al., 2012a,b) to characterize the mobility of these compounds in groundwater. Sorption of selected pharmaceuticals on soils have also been studied (Tolls, 2001) and the frequency of such studies has recently increased noticeably. However, the behavior of a wide range of pharmaceuticals in soils has yet to be revealed. In addition, there is limited information about how the properties of various soils influence pharmaceutical sorption. This is due to the fact that previous studies have typically used model matrices or individual soils in their analyses. For instance, Chefetz et al. (2008) studied naproxen and carbamazepine sorption in one soil sampled from 3 depths (0–5, 5–15, and 15–25 cm). Williams et al. (2006, 2014) presented carbamazepine sorption and mobility in soil columns for one soil type. Xu et al. (2009) evaluated clofibric acid, ibuprofen, naproxen, triclosan, diclofenac, and bisphenol sorption in four agricultural soils collected from the 0 to 20 cm surface layer. Zhang et al. (2011) documented the sorption of the antibiotics trimethoprim and sulfonamide in agricultural soil collected from 3 depths (0–20, 20–80, and 80–100 cm) of a single soil profile. Doretto et al. (2014) studied sulfonamides sorption on 4 Brazilian soils collected from the 10–20 cm depth. Sulfoamide's sorption was also evaluated by Srinivasan et al. (2013) on 4 pasture, and by Srinivasan et al. (2014) on 6 agricultural soils (in both cases collected from a depth of 0–5 cm). Various studies have documented that sorption of a number of pharmaceuticals is due to their ionization highly influenced by soil pH (e.g., Srinivasan et al., 2013; Zhang et al., 2014). It was also documented that mineral surface (Martínez-Hernández et al., 2014) and clay minerals (Gao and Pedersen, 2005) influence compound sorption, likely due to electrostatic interaction between the particle surface and ionized compounds. Thus, in such cases soil organic matter is not a principle effector of organic compound sorption, as might be expected for non-ionizable compounds or compounds in neutral form. However, none of the above cited studies could relate evaluated sorption coefficients to particular soil properties. Such knowledge would be valuable when evaluating compound mobility over small and larger scale (Kodešováet al., 2011). Therefore, we focused on evaluating the sorption of selected pharmaceuticals across a wide range of soils. The goals of this study were to: (1) describe the physical and chemical properties of the representative soils of the Czech Republic; (2) characterize sorption isotherms of selected pharmaceuticals on these soils; (3) evaluate the impact of soil properties on pharmaceutical sorption and propose pedotransfer rules for estimating sorption coefficients from the measured soil properties; and (4) asses pharmaceutical mobility in the soil-water environment.

2. Material and methods

2.1. Pharmaceutical and soil properties

Seven pharmaceuticals were studied (Table 1) that were selected based on their frequent occurrence in waste-water (Fedorova et al., 2014a; Golovko et al., 2014a,b) and surface-water (Fedorova et al., 2014b) in the Czech Republic.

Thirteen soils (Table 2) that had been previously selected by Kodešová et al. (2011) to evaluate the properties that affect sorption of selected pesticides were also used here. These soils cover a large variability of soil properties that may influence pharmaceutical behavior in soils. Samples were taken from surface (0–25 cm) and subsurface horizons (from the depths of 60–80 and 50–70 cm in the cases of loess and sand, respectively). Soils were air-dried, ground, and sifted through a 2 mm sieve. The basic chemical and physical properties were obtained using standard laboratory procedures under a constant laboratory temperature of 20 °C: soil pH (pH_{H_2O}, pH_{KCl}) (ISO, 10390:1994), organic carbon content (Cox) (Skjemstad and Baldock, 2008), $CaCO_3$ content (Loeppert and Suarez, 1996), cation exchange capacity (CEC) (Bower and Hatcher, 1966), hydrolytic acidity (HA) (Klute, 1996), exchangeable acidity (EA) (Hendershot et al., 1993), base cation saturation (BCS, the difference between CEC and HA), sorption complex saturation (SCS, the percentage of BCS in CEC), soil salinity (Rhoades, 1996), particle density (ρ_s) (Flint and Flint, 2002), and particle size distribution (fractions of clay, silt, and sand) (Gee and Or, 2002). Table 3 shows the relationships between these soil properties (i.e., the Pearson product moment correlation coefficient and the statistical significance of the estimated correlations assessed as P-value).

2.2. Pharmaceutical sorption isotherms

Sorption isotherms were measured using a standard batch equilibrium method. In triplicate, each soil was mixed with various concentrations of each pharmaceutical (0.5, 1, 2.5,5, and 10 μg mL^{-1} in 0.01 M $CaCl_2$), resulting in 195 analyses per pharmaceutical. Concentrations were set to cover the nonlinear shape of the sorption isotherms. The range of selected values is similar to the concentration ranges usually applied (e.g., Doretto et al., 2014; Chefetz et al., 2008; Vithanage et al., 2014; etc.). Ten grams of dry soil was placed directly into a plastic centrifuge tube and 20 mL pharmaceutical solution of a given concentration was added. The tube was shaken using an analog reciprocating shaker (GFL 3006, GFL Gesellschaft für Labortechnik mbH) 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 μm). The possible impact (due to compound sorption) of syringe filter material on the measured pharmaceuticals' concentrations was tested previously (Lindberg et al., 2014). No noticeable effect on the recovery of the studied compounds was found.

The actual initial ($c_{ini,a}$) and final equilibrium (c_{eq}) pharmaceutical concentrations were measured using liquid chromatography–tandem mass spectrometry (LC–MS/MS) and either isotope dilution or internal standard (IS) method. Briefly, about 10 mL of filtrate was transferred to the autosampler vial and IS was added. The samples were extracted and analyzed in one step using on-line SPE/LC–MS/MS. Matrix effects were corrected using matrix matching standard. The details of the methods are described in corresponding analytical papers (Fedorova et al., 2014a; Grabic et al., 2012; Lindberg et al., 2014).