



Sorption/desorption of non-hydrophobic and ionisable pharmaceutical and personal care products from reclaimed water onto/from a natural sediment



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HIGHLIGHTS

- Sorption–desorption of wide usage groups of PPCPs to sediment was quantified.
- Positively ionized PPCPs showed higher sorption than negatively and neutral ones.
- More than 70% of the total sorption was due to interaction with mineral surfaces.
- No competition of PPCPs with inorganic ions was observed in desorption processes.
- The potential of PPCPs to infiltrate decreases as follows CBZ > ACP > NPX > ATN > SXZ > CAF.

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ABSTRACT

In the present work, the sorption of pharmaceutical and personal care products (PPCPs) (acetaminophen, atenolol, carbamazepine, caffeine, naproxen and sulphamethoxazole) onto the natural organic matter (NOM) and the inorganic surfaces of a natural sandy loam sediment was quantified separately. The quantification was based on the PPCP charge, their degree of ionisation, their octanol–water partitioning coefficient (K_{OW}) and the sediment organic carbon fraction (f_{OC}). PPCP desorption from the sediment was examined under conditions of infiltrating water containing a high concentration of inorganic ions (mimicking infiltrating reclaimed water), and a low concentration (and smaller diversity) of inorganic ions (mimicking rainwater infiltration). Batch tests were performed using a sediment/water ratio of 1:4 and a PPCP initial concentration ranging from 1 to 100 $\mu\text{g L}^{-1}$. The results showed the type and degree of PPCP ionisation to strongly influence the sorption of these compounds onto the sediment. The sorption of cationic species onto the sediment was higher than that of anionic species and mostly reversible; the sorption of neutral species was negligible. The anionic species sorbed less onto the sediment, but also desorbed less easily. More than 70% of the total sorption was due to interaction with mineral surfaces. This holds especially true for cationic species (atenolol and caffeine) which sorption was enhanced by the negative surface charge of the sediment. The presence of inorganic ions had no impact on the desorption of the PPCPs from the sediment. According to the calculated percentages of removal, the mobility followed the order: carbamazepine > acetaminophen > naproxen > atenolol > sulfamethoxazole > caffeine.

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1. Introduction

The problems of an increasing population, water resource contamination and climate change have led to the scarcity of water in many countries, especially in the Middle East and Mediterranean (Lazarova et al., 2001). The use of reclaimed water may often provide a technically and economically feasible solution (Kiziloglu et al., 2008; Molinos-Senante et al., 2011), but its use in irrigation and/or aquifer recharge can introduce a range of contaminants into the

environment if these are not removed during wastewater treatment (Levine and Asano, 2004; Toze, 2006). Indeed, a number of pharmaceutical and personal care products (PPCPs) are very often found in different water compartments. Several studies have reported PPCPs present in Spanish surface water and groundwater (Estévez et al., 2012; García-Galán et al., 2010; González Alonso et al., 2010; Jurado et al., 2012; Koeck-Schulmeyer et al., 2011; Martínez Bueno et al., 2010; Teijon et al., 2010). In general, groundwater PPCP concentrations are lower than those of surface and wastewater (ng L^{-1} compared to $\mu\text{g L}^{-1}$), suggesting that these compounds are subject to retention and/or degradation during infiltration (Jurado et al., 2012).

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The mobility of PPCPs in the environment depends essentially on their sorption onto and desorption from sediments, and their degradation (physical and biological) during infiltration (Sabljic et al., 1995). These processes clearly affect their bioavailability (Katayama et al., 2010). In the last 10 years, several batch experiments investigating sorption of PPCPs onto sediments have been carried out (Chefetz et al., 2008; Durán-Álvarez et al., 2012; Fenet et al., 2012; Karnjanapiboonwong et al., 2010; Kibbey et al., 2007; Lin et al., 2010; Lorphensri et al., 2007; Ramil et al., 2009; Stein et al., 2008; Xu et al., 2009; Yamamoto et al., 2009; Yu et al., 2013). Some of them pointed out a direct correlation between the amount of sediment organic matter and the degree of sorption (Chefetz et al., 2008; Fenet et al., 2012; Kibbey et al., 2007; Yu et al., 2013). However, other studies have also shown that sediment inorganic surfaces may affect PPCPs sorption (Lin et al., 2010; Pan et al., 2009; Schaffer et al., 2012a; Tolls, 2001; Yamamoto et al., 2009) and therefore this process should be taken into account besides partitioning onto natural organic matter (NOM). Only recently, the degree of ionisation of some functional groups of PPCPs at environmental pH has been recognized as an additional factor that may control the sorption of these compounds onto natural sediments (Schaffer et al., 2012b).

Only few articles have included desorption essays in their research (Chefetz et al., 2008; Durán-Álvarez et al., 2012; Karnjanapiboonwong et al., 2010; Lin et al., 2010; Stein et al., 2008; Teijón et al., 2013) and results showed cases of hysteretic and reversible sorption of several PPCPs. This emphasizes the importance of linking/coupling sorption and desorption studies to correctly assess the mobility of PPCPs through the subsurface.

Information on the sorption/desorption behaviour of PPCPs in sediments is, however, conflicting when it is available. For example, Lin and Gan (2011) reported moderate to strong sorption onto soil for an anti-inflammatory drug and Durán-Álvarez et al. (2012) found low sorption rates for the same compound in two soils. Ramil et al. (2009) and Yamamoto et al. (2009) identified different sorption degrees onto sediments for a drug belonging to the group of β -blockers. Drillia et al. (2005) showed a higher degree of sorption for a sulphonamide antibiotic than that described by Stein et al. (2008) for the same contaminant. Furthermore, papers in this area commonly fail to separate the individual effects of PPCP ionisation and partitioning (Durán-Álvarez et al., 2012; Karnjanapiboonwong et al., 2010; Löffler et al., 2005; Lorphensri et al., 2007; Stein et al., 2008; Williams et al., 2009).

Studies on how sorption/desorption onto/from sediments affects their transport are therefore needed. Competition between inorganic ions and PPCPs also occurs during the latter's sorption onto sediments and has only recently been suspected to influence PPCP concentrations in infiltrated water (Niedbala et al., 2013; Schaffer et al., 2012a). Once sorbed onto sediments they may be desorbed again by water carrying dissolved ions, e.g., reclaimed irrigation water or by water carrying few inorganic ions, e.g., rainwater.

The present paper focuses on a number of compounds with different chemical properties representative of a range of PPCP classes: the analgesic acetaminophen (ACP), the β -blocker atenolol (ATN), the anticonvulsant carbamazepine (CBZ), the stimulant caffeine (CAF), the non-steroidal anti-inflammatory drug naproxen (NPX), and the antibiotic sulfamethoxazole (SXZ). All these compounds are non-hydrophobic chemicals. They can be either neutral or positively or negatively ionised depending on the pH of the environment. With the exception of ACP, all have been detected at concentrations of $>100 \text{ ng L}^{-1}$ in Spanish groundwater (Jurado et al., 2012). These high concentrations, together with the limited information available on their sorption/desorption onto/from sediments point to a special concern for their environmental fate.

The aims of this study are: i) to investigate the impact of PPCP ionization (neutral, positive, negative) on the extent of sorption-desorption processes; ii) to separately quantify PPCP sorption onto

the natural organic matter and the inorganic surfaces and discuss potential sorption mechanisms; iii) to evaluate the possibility of competition between PPCPs and inorganic ions through a desorption test that contemplates two scenarios: the infiltration of reclaimed irrigation water carrying dissolved inorganic ions, and the infiltration of rainwater carrying few ions.

2. Materials and methods

2.1. Sediment sampling and analysis

Sediment samples were collected from the unsaturated zone of the Manzanares-Jarama groundwater body, part of the Madrid Detrital Tertiary Aquifer. From a hydrogeological point of view, this area can be divided into 3 sectors with similar characteristics (Torres et al., 1995). The collected samples belong to the middle sector, characterized by loamy and sandy sediments, that constitutes the recharge area of the main aquifer. Moreover, to avoid misleading of experimental results, sampling was carried out in an area free of PPCP contamination sources.

Sediment samples were air-dried, gently crushed and passed through a 2 mm sieve. pH and electrical conductivity (EC) were measured in a sediment-water suspension (sediment-water ratio 1:2.5 and 1:5 respectively). Particle size distribution was determined following the method of Gee and Bauder (1986). Part of the air-dried, sieved sample was crushed for the determination of the sediment organic carbon fraction (f_{OC}) following the method of Nelson and Sommers (1982). Oxalate-extractable Fe_{tot} and Al_{tot} were obtained by a 4 h extraction of 1 g of dried sediment in 100 mL of 0.2 M acid ammonium oxalate at pH 3 (McKeague and Day, 1966). The cation exchange capacity (CEC) was determined at natural sediment pH by extracting 5 g of dried sediment with 1 M sodium acetate and 1 M ammonium acetate. The potentiometric titration method was used to determine the sediment point of zero charge (PZC). The properties of the sandy loam sediment are summarised in Table 1.

2.2. Synthesis of reclaimed water

Samples of reclaimed water ($n = 5$) were collected from wastewater treatment plant secondary effluent (which fulfilled the requirements for water reuse (BOE, 2007)) from the study area. Standard analyses were performed (see the Section 2.6) to determine the inorganic ion composition and dissolved organic carbon content (DOC) of these samples, and the means recorded. Using this information, a stock solution of synthesized reclaimed water (SRW) was then produced dissolving the following reagents (purity $> 95.0\%$) in tap water: NH_4Cl (0.07 g L^{-1}), $MgSO_4$ (0.1 g L^{-1}), $CaCl_2$ (0.01 g L^{-1}), K_2HPO_4 (0.02 g L^{-1}), $NaHCO_3$ (0.25 g L^{-1}), peptone (0.01 g L^{-1}), and meat extract (0.01 g L^{-1}) (all purchased from Scharlab, Spain). Table 2 shows the final composition of the SRW.

2.3. Target PPCPs

The target compounds – ACP, ATN, CAF, CBZ, NPX, paraxanthine (PXT) and SXZ (purity $> 98\%$) – were purchased from Sigma-Aldrich. All were dissolved in methanol (99.9%) from Sigma-Aldrich.

2.4. Sorption experimental design

The sorption isotherms of the studied PPCPs were determined in parallel batch experiments following OECD guideline 106 (OECD, 2000). SRW (200 mL) in 1 L glass vessels containing 50 g sterilized sediment was spiked with PPCPs at different concentrations (1, 5, 10, 25, 50, 75 and $100 \mu\text{g L}^{-1}$). The sediment and vessels were autoclaved for 15 min at $121 \text{ }^\circ\text{C}$. It was believed that the conventional use of 10% sodium azide to inhibit microbial activity might affect the sorption capacity of the sediment (Trevors, 1996). The final methanol

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