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Investigating natural attenuation of pharmaceuticals through unsaturated column tests

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HIGHLIGHTS

- Caffeine and acetaminophen have a low environmental concern.
- Carbamazepine is the most persistent contaminant.
- Increasing input concentrations reduce microbial degradation.
- Naproxen removal data under dynamic flow conditions are given for the first time.
- The TPs N4-Acetylsulfamethoxazole and epoxycarbamazepine are detected.

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ABSTRACT

The growing consumption of pharmaceuticals together with their incomplete removal in wastewater treatment plants (WWTPs) implies the occurrence of these compounds in natural water resources. To investigate the natural attenuation of selected pharmaceuticals (caffeine, acetaminophen, sulfamethoxazole, naproxen and carbamazepine) during vadose zone infiltration, unsaturated column (L 26.67 cm, Ø 7.62 cm) experiments, filled with a sandy-loamy soil, were performed using two input concentrations (100 and 1000 μg L^{-1}). The software Hydrus 1D was used to simulate experimental data. Caffeine and acetaminophen were never detected at the column outlet indicating a low environmental concern. On the other hand, attenuation of the detected pharmaceuticals could be reproduced by a combination of retardation and removal approaches. Carbamazepine is among the selected contaminants the most persistent. A dependence of removal rates on input concentrations was detected for sulfamethoxazole (μ_w from 2.78 d^{-1} to 1.16 d^{-1}) and naproxen (μ_w from 1.16 d^{-1} to 0.63 d^{-1}) attributed mainly to decreased metabolism of microorganisms when a higher input concentration is applied. Two transformation products (TPs) (N4-Acetylsulfamethoxazole and epoxycarbamazepine) derived from sulfamethoxazole and carbamazepine transformation, respectively, were detected during the experiment with the highest input concentration.

1. Introduction

As a consequence of incomplete removal in wastewater treatment plants (WWTPs), pharmaceuticals are found worldwide in different environmental compartments such as surface water, groundwater and soils (Loos et al., 2010; Martinez-Bueno et al., 2010; Chen et al., 2011a; Cabeza et al., 2012; Estévez et al., 2012; Pascual-Aguilar et al., 2013; Meffe and de Bustamante, 2014). The recent inclusion of some pharmaceuticals in the European priority substance watch list means that they may pose a significant risk to or via the aquatic environment (EU, 2015). When pharmaceuticals infiltrate through the soil and the unsaturated zone, sorption and biodegradation are the major attenuation processes (Yu et al., 2006). This attenuation depends on both soil and compound

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properties and determines the fate not only of these substances but also of their potential transformation products (TPs). Indeed, recent studies have indicated that transformation of the parent pharmaceuticals not only occurs in humans, animals and WWTPs but also in soils (Dodgen et al., 2014; Li et al., 2014; Martínez-Hernández et al., 2016). The importance of investigating such processes depends on the evidence that the transformation of pharmaceutical compounds normally produces more polar and soluble and, therefore, more mobile TPs (Celiz et al., 2009). However, data on the formation of TPs when pharmaceuticals are in contact with soils are still scarce.

To determine the fate and potential exposure of soil microbial community to contaminants during infiltration, the use of laboratory scale experiments is frequently considered as a consolidated methodology since they allow the measurement and control of environmental variables. Experimental data can be simulated using numerical and/or analytical modelling of coupled transport and geochemical reactions to obtain reactive transport parameters. Laboratory approaches dealing with pharmaceutical transport through soils use batch assays and column experiments (Williams et al., 2009; Xu et al., 2009; Yamamoto et al., 2009; Rauch-Williams et al., 2010; Arye et al., 2011; Greenhagen et al., 2014; Im et al., 2016). Most of the column experiments available in the recent literature have been performed under saturated conditions to simulate transport of these compounds during aquifer recharge, agriculture irrigation and soil aquifer treatment (Rauch-Williams et al., 2010; Arye et al., 2011; Chen et al., 2011b; Banzhaf et al., 2012; Onesios and Bouwer, 2012; Duran-Alvarez et al., 2014). However, there is a lack of information of its behaviour under unsaturated conditions. Indeed, biodegradation and sorption are strongly influenced by the oxygen availability and the water-soil proportion that are remarkably different between saturated and unsaturated conditions (Klemedtsson et al., 1988; Tindall et al., 1995; Scheytt et al., 2006). Laboratory experiments simulating infiltration under unsaturated conditions are therefore crucial and should be coupled to reactive transport modelling for contaminant fate prediction.

Recently, there have been researches dedicated to investigate the effect of input concentrations on the attenuation of pharmaceuticals, especially of sulphonamide antibiotics (Wehrhan et al., 2007; Unold et al., 2010; Srinivasan and Sarmah, 2014a). Indeed, the biodegradation rate constant of pharmaceuticals could be a concentration dependent parameter. Pharmaceuticals are biologically active substances which concentration may affect the microbiology responsible of biodegradation processes. Their input concentrations can provide hints about the development of resistant pathogens. However, results of studies about concentration-dependent transport give controversial results even within the same class of contaminants. Wehrhan et al. (2007) report concentration influence on the transport of sulfadiazine, whereas Srinivasan and Sarmah (2014a) discard any impact of input concentration on the transport of three different sulfonamides. On the other hand, Ma et al. (2001) describe a decline of fumigant biodegradation rate constant by increasing the input concentration two orders of magnitude.

The current study provides information about the transport of a group of pharmaceuticals in the vadose zone simulating unsaturated conditions by means of specifically designed laboratory equipment. The selected pharmaceuticals are acetaminophen (analgesic), naproxen (anti-inflammatory), sulfamethoxazole (antibiotic), carbamazepine (antiepileptic) and caffeine (stimulant). Caffeine is found naturally in foods and beverages and is a common additive to pharmaceuticals, therefore it has been considered as part of the pharmaceutical group. All substances belong to frequently prescribed therapeutic groups, possibly contributing to a higher environmental risk (Cooper et al., 2008). Under the experimental pH (7.8), acetaminophen, carbamazepine and caffeine are in their neutral form, while sulfamethoxazole and naproxen are negatively ionized. All compounds present a moderate to high hydrophilicity ($\log K_{ow} < 4$). The ionization coupled with the hydrophobicity of the compounds influences the degree and type of sorption (Martínez-Hernández et al., 2014, 2015).

The objectives of the present work are (i) to investigate which sorption approach: chemical equilibrium or kinetics better describes the attenuation of the selected pharmaceuticals under unsaturated conditions, (ii) to determine the influence of the input concentration on pharmaceutical removal and (iii) to analyse the formation of potential TPs as a consequence of biodegradation during infiltration through the unsaturated zone.

2. Material and methods

2.1. Soil and synthetic reclaimed water

Soil samples (first 35 cm depth) 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). Samples were taken from 1 m^2 plot by digging a 35 cm depth hole. The collected soil (10 kg), made up by loam and sand (82.5% sand, 10.0% silt and 7.5% clay), constitutes the recharge area of the main aquifer. To exclude any result biasing, sampling was carried out in an area free of pharmaceutical contamination sources. Before column packing, a composite sample from the collected soil was air-dried, mixed, gently crushed and passed through a 2 mm sieve. It has a limited edaphic development but an organic carbon content of 1.44% measured by applying the method of Nelson and Sommers (1982). The potentiometric titration method (Appel et al., 2003) was used to determine the soil point of zero charge which value corresponds to 6.8. Oxalate-extractable Fe_{tot} and Al_{tot} were obtained following the method proposed by McKeague and Day (1966). Fe_{tot} and Al_{tot} are 0.22 and 0.20 g kg^{-1}, respectively. Samples were maintained refrigerated (4 °C) until the experimental set-up.

Synthetic reclaimed water (SRW) was simulated in the laboratory and reproduces the water matrix where pharmaceuticals can be found based on real analyzed wastewater. A stock solution of SRW was 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). The physical and chemical properties of the SRW are fully described in Martínez-Hernández et al. (2014).

2.2. Experimental set-up

The column experiments (Fig. 1) were performed using the equipment available from Soil Measurement Systems (SMS, Tucson, AZ). The stain steel column (L 26.67 cm, Ø 7.62 cm) was previously sterilized with sodium hypochlorite. The column outlet was connected to a vacuum chamber where a constant pressure was applied by a vacuum pump. The first centimetre from the bottom of the column was packed with glass beads (Ø 0.6–1.2 mm) to prevent membrane clogging. The column was placed vertically and packed with soil increments of 100 g using a pestle for compaction. The packing was carried out avoiding the formation of stratified layers or preferential flow paths and producing a homogenous soil column with a bulk density resembling that measured in the field (1.5 g cm^{-3}).