Science of the Total Environment 559 (2016) 232–241

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The role of sorption and biodegradation in the removal of acetaminophen, carbamazepine, caffeine, naproxen and sulfamethoxazole during soil contact: A kinetics study

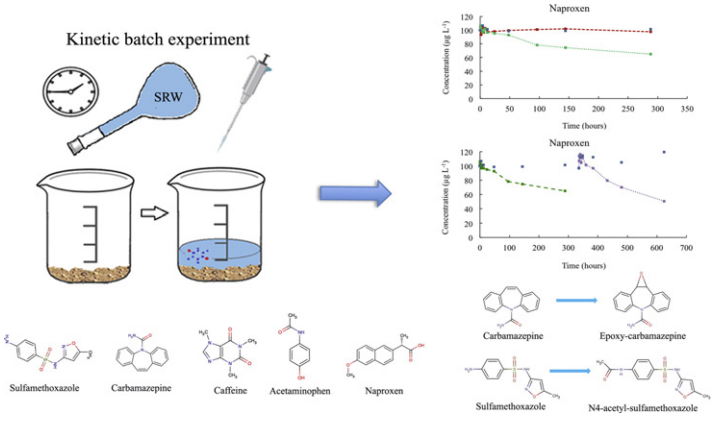
Virtudes Martínez-Hernández [a,*], Raffaella Meffe [a], Sonia Herrera López [b], Irene de Bustamante [a,c]

[a] IMDEA Water, Avda Punto Com, 2, 28805 Alcalá de Henares, Madrid, Spain
[b] University of Almería, Chemistry and Physics Department, Ctra. Sacramento s/n, La Cañada de San Urbano, 04120 Almería, Spain
[c] University of Alcalá, Geology, Geography and Environment Department, Faculty of Sciences, External Campus, Ctra. A-II km 33.6, 28871 Alcalá de Henares, Madrid, Spain

HIGHLIGHTS

- The role of sorption and biodegradation in pharmaceutical attenuation was identified.
- Serial batch-type experiments were performed to determine the kinetics behaviour.
- Sorption played a key role during the first 48 h of contact with soil.
- First-order model described the kinetic removal of the compounds.
- Two transformation products were identified indicating incomplete biodegradation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form 17 March 2016
Accepted 18 March 2016
Available online 9 April 2016

Editor: D. Barcelo

Keywords:
Pharmaceuticals
Biodegradation
Sorption
Kinetics
Soil
Transformation products

ABSTRACT

In countries like Spain, where water is a limited resource, reusing effluents from wastewater treatment plants may imply the introduction of incompletely eliminated pollutants into the environment. Therefore, this work identified the role of sorption and biodegradation in attenuating pharmaceutical compounds (acetaminophen, carbamazepine, caffeine, naproxen and sulfamethoxazole) in natural soil. It also determined which sorption and removal ("sorption + biodegradation") kinetics models describe the behaviour of these substances in the water-soil system. Presence of potential transformation products (TPs) as a result of pharmaceuticals biodegradation was also studied. To this end, serial batch-type experiments were performed with a soil:water ratio of 1:4 and an initial pharmaceutical concentration of 100 μg L^{-1}. Despite results are dependent on soil characteristics, they revealed that, for those substances with a higher affinity to the soil used (loamy sand), sorption seems to play a key role during the first 48 h of contact with soil, and gives way to biodegradation afterwards. The sorption of the pharmaceuticals studied follows a pseudo second-order kinetics. Caffeine and sulfamethoxazole displayed the fastest initial sorption velocities (h = 2055 and h = 228 μg kg^{-1} h^{-1}, respectively). The removal kinetics experiments, satisfactorily simulated by the first-order kinetics model, indicated the presence of potential microbial adaptation to degradation. Indeed, half-lives decreased from 1.6- to 11.7-fold with respect to initial values. The

* Corresponding author.
E-mail address: virtudes.martinez@imdea.org (V. Martínez-Hernández).

http://dx.doi.org/10.1016/j.scitotenv.2016.03.131

microbial capacity to degrade sulfamethoxazole could be a matter of concern if bacteria have developed resistance to this antibiotic. Caffeine, acetaminophen and sulfamethoxazole were mitigated to a greater extent, whereas the removal of naproxen and carbamazepine was more limited. The appearance of epoxy-carbamazepine and N4-acetyl-sulfamethoxazole as possible TPs of carbamazepine and sulfamethoxazole, respectively, indicated that biodegradation was incomplete and showed the capacity of soil microbes to transform these substances.

1. Introduction

The ageing population entails higher production and consumption of pharmaceutical compounds. Indeed, acquiring such substances has increased not only in terms of expenditure, but also in the quantities consumed (OECD, 2009). Nevertheless, conventional wastewater treatment plants (WWTPs) are not capable of completely eliminating pharmaceutical compounds and their metabolites from wastewater (Gómez et al., 2007; Kasprzyk-Hordern et al., 2009).

In countries like Spain, where water is a limited resource, reusing effluents from WWTPs is often considered a feasible solution both technically and economically (Molinos-Senante et al., 2011). Using reclaimed water, particularly for artificial aquifer recharge and irrigation purposes, can imply the introduction of these incompletely eliminated pollutants into the environment (Fatta-Kassinos et al., 2011). In fact, these substances have been encountered in effluents from secondary and tertiary treatments used in water reuse activities (Drewes et al., 2003; Teijón et al., 2010; Cabeza et al., 2012; Estévez et al., 2012) and in water employed for irrigation (Calderon-Preciado et al., 2011; Pascual-Aguilar et al., 2013).

The fundamental processes that determine the fate of pharmaceutical compounds while they infiltrate through soil and the unsaturated zone are mainly biodegradation and sorption (Yu et al., 2006). The greater or lesser influence of either of these processes will condition whether the pollutant is retained and accumulates in soil, is completely mineralised or is biodegraded in other transformation products (TPs). Whether a process is more influential or not is conditioned by, among other factors, biodegradability, the microbial population's capacity to degrade it, and the substance's affinity to be retained in soil. Determining the role played by both biodegradation and sorption during infiltration is fundamental to evaluate the arrival of pharmaceutical compounds to groundwater either as original compounds or TPs.

Although sorption velocity conditions the bioavailability of these substances and affects their mobility in soil, it has not been widely studied for pharmaceutical compounds. Most pharmaceuticals studies deals with sorption isotherms as our previous work (Martínez-Hernández et al., 2014) and very few articles have applied and compared sorption kinetics models to describe the sorption velocity. The only examples found in the literature are by Zhang et al. (2012) and Tanis et al. (2008), who investigated sorption kinetics of two antimicrobials in humic acids and iron oxides in soil. The capacity of removing ("sorption + biodegradation") pharmaceuticals in a porous medium has been evaluated in soils and sediments during infiltration by simulating aquifer recharge, riverbank filtration and soil treatment (Lin and Gan, 2011; Hoppe-Jones et al., 2012; Henzler et al., 2014). The transformation of pharmaceutical compounds normally produces more polar and soluble and, therefore, more mobile TPs (Celiz et al., 2009). However, very few studies have jointly addressed the removal of original compounds and the evolution of any TPs produced.

Microbial adaptation to degrade organic substances beyond the environment can be found in the literature (Meffe et al., 2010), and even for some of the pharmaceutical compounds that are the object of this study (Hoppe-Jones et al., 2012). The effect of microbial adaptation to degrade pharmaceuticals is especially important for antibiotics since bacteria could develop resistance.

The current kinetic study provides information about the availability of these compounds in water and the potential TPs produced. The concentrations at which these substances are available in water, plus studies about the ecotoxicity of these concentrations, will improve estimates of possible effects on the natural environment (Kagle et al., 2009), and will facilitate the control of pharmaceuticals, if necessary.

The studied pharmaceuticals were acetaminophen (an analgesic), naproxen (an anti-inflammatory), sulfamethoxazole (an antibiotic), carbamazepine (an anti-epileptic), and caffeine (a stimulant). Caffeine is found naturally in foods and beverages and is a common additive to foods and pharmaceuticals, therefore, it has been considered a part of the pharmaceutical group. The compounds were selected for their physico-chemical characteristics: moderate to high hydrophilicity ($\log K_{ow} < 4$) (Jurado et al., 2012), for being frequently prescribed therapeutic groups, implying a higher environmental risk (Cooper et al., 2008) and for their high production as three of the five investigated compounds (caffeine, carbamazepine and naproxen) were on the list of chemicals produced in larger quantities in 2004 (OECD, 2004).

This article aims to: a) determine which biodegradation or sorption process plays the most important role in lowering the concentration of each compound; b) obtain the sorption and removal models that best describe the kinetics of both processes; c) analyse whether the soil microbial community is capable of degrading the selected compounds; d) study the possible production of TPs in water resulting from biodegradation processes.

2. Methodology

2.1. Soil and synthetic reclaimed water

To run the experiments, synthetic reclaimed water (SRW) was employed to simulate the matrix where the selected pharmaceuticals are found. The use of SRW was necessary to overwhelm the different initial concentration among pharmaceuticals in real water. Details of SRW synthesis are reported in Martínez-Hernández et al. (2014). Physico-chemical variables and ionic species concentrations of the SRW are shown in Supplementary information (Table SI 1). Soil was collected from the first top centimetres in the unsaturated zone of the Manzanares-Jarama groundwater body, which is part of the Madrid Tertiary Detrital Aquifer. From a hydrogeological viewpoint, this zone can be divided into three sectors, each with similar characteristics, as a result of sediment deposition of fluvial fans from the Madrid Mountain Range during the Paleogene and the Neogene periods (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 (Martinez-Santos et al., 2010). The soil (loamy sand) displayed no edaphic development, but presented a large quantity of organic matter (1.44%) compared to the underlying sediment materials. Sampling is described in detail in Martínez-Hernández et al. (2014) and soil properties are shown in Supplementary information (Table SI 2).

2.2. Experimental design

2.2.1. Sorption kinetics

The sorption kinetics of pharmaceuticals in soil was determined by serial batch-type experiments, following OECD Guide 106 (OECD, 2000). Contact was established between SRW (1200 mL) and soil (300 g) in 3-litre glass beakers to which an initial 100 μg L^{-1}