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Monitoring the occurrence of pharmaceuticals in soils irrigated with reclaimed wastewater☆

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ABSTRACT

The use of reclaimed wastewater for irrigation is foreseen as a possible strategy to mitigate the pressure on water resources in dry regions. However, there is the risk of potential accumulation of contaminants of emerging concern (CECs) in the edaphic environment, their percolation and consequently contamination of aquifers. In the present study, we measured the levels of a wide range of commonly used pharmaceutically active compounds (PhACs) in sewage from a local wastewater treatment plant (WWTP) and in soils irrigated with treated wastewater. Analysis of target compounds showed total concentrations between 73 and 372 $\mu g\,L^{-1}$ in WWTP influents, and from 3 to 41 $\mu g\,L^{-1}$ in effluents. The total concentrations of PhACs detected in surface soil samples were in the range of 2 and 15 $ng\,g^{-1}$, with predominance of analgesics and anti-inflammatories (maximum concentration = 10.05 $ng\,g^{-1}$), followed by antibiotics and psychiatric drugs (maximum concentration = 5.45 $ng\,g^{-1}$ and 3.78 $ng\,g^{-1}$, respectively). Both effluent samples and irrigated soils shared similar compositional patterns, with compounds such as hydrochlorothiazide and diclofenac being predominant. Additionally, PhACs were also detected in soil samples at a depth of 150 cm, indicating that these chemical undergo leaching associated with heavy-rain episodes. Their occurrence in soils was affected by temperature too, as maximum concentrations were measured in colder months (up to 14 $ng\,g^{-1}$), indicating higher persistence at lower temperatures. Finally, the ecotoxicological risk of PhACs in soil was evaluated by calculating their risk quotients (RQs). The risk was very low as RQ values ranged between <0.01 and 0.07. However, this initial assessment could be improved by future works on toxicity using specific terrestrial organisms.

1. Introduction

Pharmaceutically active compounds (PhACs) are regarded as emerging environmental contaminants as many of them are ubiquitous, persistent and biologically active substances (Daughton and Ternes, 1999; Jelić et al., 2012; McEneff et al., 2015). Pharmaceuticals such as antibiotics or analgesics have frequently been found in surface waters at the ng L^{-1} level (Baena-Nogueras et al., 2016; Jelić et al., 2012; Loos et al., 2013; López-Serna et al., 2011). There are several direct and indirect pathways through which PhACs can be introduced into the aqueous environment. Treated and untreated wastewater discharges are identified as the major route responsible for surface water contamination with pharmaceuticals (Castiglioni et al., 2006; Gros et al., 2010; Jelić et al., 2012; Li, 2014; Loos et al., 2010; Santos et al., 2009). A considerable number of studies have reported the presence of PhACs in influent and effluent samples from wastewater treatment plants (WWTPs). For instance, and just in Spain, Gros et al. (2010) reported the occurrence of 73 pharmaceuticals in seven municipal WWTPs in the Ebro River basin, whereas Santos et al. (2009) measured concentrations of four anti-inflammatory drugs, an antiepileptic drug and a nervous stimulant up to 353 $\mu g\,L^{-1}$ in four WWTPs in Seville. In Europe, 21 different PhACs were found in 6 WWTPs in Italy (Castiglioni et al., 2006), including ciprofloxacin, ofloxacin, sulfamethoxazole, ibuprofen, atenolol, furosemide, hydrochlorothiazide, ranitidine, and bezafibrate, whereas in Czech Republic, similar results were achieved by Golovko et al. (2014). Other recent studies in the United States (Lara-Martín et al., 2014; Subedi and Kannan, 2015) have evaluated the removal efficiencies of many other WWTPs. Overall, and after treated wastewater discharge, many of

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these chemicals can not only be detected in the receiving surface waters but also in sediments and even in drinking water (Ternes, 1998; Petrović et al., 2003; Carballa et al., 2004; Gros et al., 2006). Additionally, and due to the enormous pressure on water supplies, treated wastewater from WWTPs can also be used to supplement irrigation on golf courses, crops, parks and gardens. This raises a safety concern as such supplemental irrigation can lead to the potential contamination of soils and groundwater resources. While disease-causing pathogens and heavy metals are often routinely monitored in these cases, contaminants of emerging concern (CECs), especially pharmaceuticals, are not, resulting in very limited information on their occurrence and fate.

Compared to aquatic systems, pharmaceuticals have hardly been studied in soil environmental matrices, and the very limited data on their presence in the terrestrial environment mostly consist of some investigations on the pharmaceutical removal following effluent irrigation onto land (Kinney et al., 2006; Ternes et al., 2007; Gielen et al., 2009). Previous studies have also reported the presence of pharmaceutical compounds in European aquifers (Teijon et al., 2010; Cabeza et al., 2012). The likelihood of soil and groundwater contamination by PhACs as a result of the discharge of WWTP effluents depends on several factors such as the physicochemical properties of these pollutants, the type of wastewater treatment technology implemented, and climatic conditions (e.g., dilution of wastewater effluent, rainfall, temperature, and irradiance) (Kasprzyk-Hordern et al., 2009). As many of these compounds are ionizable, soil hydraulic properties (e.g. hydraulic conductivity, soil moisture content, etc.) and environmental conditions (e.g., pH) also strongly influence their transport (Schaffer and Licha, 2015). So far, occurrence of 5 PhACs has been reported in volcanic sandy loam soils irrigated with treated wastewater in New Zealand (Gielen et al., 2009), whereas Durán-Alvarez et al. (2009) detected pharmaceuticals and potential endocrine disruptor compounds at concentrations bellow 1 ng g^{-1} in agricultural Mexican soils irrigated with untreated wastewater for approximately 90 years. Leaching and contamination of groundwater by bisphenol-A, triclocarban, triclosan, 4-nonylphenol, salicylic acid, oxytetracycline, tetracycline, trimethoprim and primidone have been also recently observed in irrigated soils in China (Chen et al., 2011). Regarding our previous work, we have reported up to 7 out of 64 target PhACs in SW Spain after analysis of 21 sludge-amended surface soil samples (Pérez-Carrera et al., 2010) and soil cores at different depths (Corada-Fernández et al., 2015), showing values for individual components up to 1.3 ng g^{-1}.

When treated wastewater is used for irrigation, contaminants in reclaimed water may transfer to soil through water leaching onto the vadose zone, potentially negatively affecting organisms inhabiting this zone (e.g., earthworms, plants, etc.). However, information on the accumulation of PhACs in soils and their environmental risks towards terrestrial species is scarce (Muñoz et al., 2009; Martín et al., 2012; Jones et al., 2014; Verlicchi and Zambello, 2015). Among the few available examples, Amorim et al. (2010) assessed the toxicity of triclosan in the terrestrial environment using several soil species including invertebrates (*Eisenia andrei*, *Enchytraeus albidus* and *Folsomia candida*) and the plants *Triticum aestivum* and *Brassica rapa*. Another study investigated the ecotoxicological risk of carbamazepine on species the macrophyte genus *Typha* (Dordio et al., 2011) by measurements of relative growth rates (RGR). For most of the PhACs, however, information is not available and the equilibrium partitioning method, relying on the use of toxicity data towards aquatic species and the partition coefficients of chemicals, has been used to predict toxicity data (ECB, 2003).

In order to gain novel information on the distribution and fate of CECs, we monitored a wide number of PhACs in wastewater ($n = 78$) and soil ($n = 45$) samples taken along a period of two years from a WWTP and its adjacent garden (irrigated with effluent water) in Jerez de la Frontera (SW Spain). The target compounds were selected taking into account the agricultural, urban and industrial activity of the area and the results from previous studies (Pérez-Carrera et al., 2010; Corada-Fernández et al., 2015; Baena-Nogueras et al., 2016) on the distribution of PhACs in receiving surface waters and sludge-amended agricultural soils. Some of the analyzed chemicals (e.g., diclofenac and several macrolide antibiotics) are also included in the first watch list and EC list of priority substances from the European Parliament and the Council of the European Union (European Commission, 2015). The main objectives of this research were: a) to monitor the concentrations of different classes of PhACs (analgesic/anti-inflammatories, antibiotics, antiepileptics, beta-blocker drugs, lipid regulating agents, etc.) in influent and effluent wastewater samples and in soils, b) to evaluate the effects on the vadose zone of utilizing this type of water by taking samples at different times of the year and analyzing the vertical distribution of PhACs in soil cores, and c) to perform a preliminary environmental risk assessment towards terrestrial species considering the measured PhAC concentrations and the current available ecotoxicity data.

2. Materials and methods

2.1. Chemicals and materials

All the pharmaceutical standards for target compounds (Table S1, Supporting information) were of high purity grade (>95%) and were obtained from Sigma–Aldrich (Madrid, Spain). Isotopically labelled compounds, used as internal standards, were atenolol-d_7, phenazone-d_3, acetaminophen-d_4, ibuprofen-d_3 from LGC Standards (Barcelona, Spain), carbamazepine-d_{10}, gemfibrozil-d_6, glyburide-d_3 from CDN Isotopes (Quebec, Canada) and sulfadimethoxine-d_6, ofloxacin-d_3, trimethoprim-d_9, naproxen methoxy-d_3, albuterol-d_3, hydrochlorothiazide $^{13}C_6$ from Sigma–Aldrich.

LC-MS grade methanol and water were purchased from Scharlau (Barcelona, Spain), formic acid (98%), ammonia (25%), ammonium formate (97.8%), ammonium acetate (97%) and acetic acid (99%) were purchased either from Sigma Aldrich (Madrid, Spain) or Panreac (Barcelona, Spain). Water was Milli-Q quality and the cartridges used for solid phase extraction were Oasis HLB (200 and 500 mg) from Waters Corporation (Barcelona, Spain).

Standard solutions of pharmaceuticals and isotopically labelled internal standard were prepared in methanol or methanol-water, depending on the compound, at concentrations of 250 mg L^{-1} and 1000 mg L^{-1}, respectively, and stored at −20 °C. Stock solutions of pharmaceuticals were prepared every six months, except for antibiotics, which were prepared monthly due to their limited stability. Before analysis, a calibration curve was prepared by appropriate dilution of the aforementioned standards in methanol–water (25:75, v/v).

2.2. Wastewater samples

The municipal WWTP serves 215 000 inhabitants from Jerez del Frontera city and is designed to treat up to 103 000 cubic meters of water per day. Water treatment consists in three main stages: a primary physicochemical treatment followed by a secondary biological treatment, comprising nitrification and denitrification zones, and finally an elimination step by disinfection through ultraviolet radiation. Most of the Jerez de la Frontera sewage (between 50 000–65 000 m^3 day^{-1}) is treated at this WWTP and, after secondary treatment, discharged into the Guadalete River and also used for irrigation of the WWTP gardens. Additionally, a fraction of