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Short communication

Comparison of the removal efficiencies of selected pharmaceuticals in wastewater treatment plants in the region of Murcia, Spain

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ABSTRACT

The presence of certain pharmaceutical compounds in ground- and surface waters may constitute a serious environmental problem, even at low concentrations. The occurrence of pharmaceuticals in the environment indicates incomplete removal of these pharmaceuticals from municipal wastewater treatment plants (WWTPs). In this study four representative pharmaceutical compounds were identified and quantified in influent and effluent of WWTPs around the Region of Murcia. In addition, the removal efficiencies of the five different treatment systems employed by these WWTPs were evaluated for the four pharmaceutical compounds. Influent and effluent wastewaters were sampled on a weekly basis during four consecutive weeks and compound concentrations were quantitatively determined by HPLC-DAD.

Pharmaceuticals were detected at μg/L levels (0.34–26.52 μg/L) in influent and effluent samples from all five different systems of the twelve WWTPs sampled in this work. The two most abundant pharmaceutical compounds were carbamazepine and naproxen. WWTPs that worked with extended aeration activated sludge processes, coagulation-flocculation, sand filtration and as tertiary treatment processes are used ultraviolet and chlorination systems (EAAS + C-F + SF + UV + Cl) removed better carbamazepine and ketoprofen than conventional activated sludge system with a double aeration tank, sand filtration, lamination, coagulation-flocculation and as tertiary treatment processes are used ultraviolet systems (CAS-DS + L + C-F + SF + UV) that removed better naproxen and diclofenac.

1. Introduction

Current consumption habits of our society are generating a wide range of contaminants for which until a few years ago, there was insufficient information available about their presence in the environment. These substances, known as "emerging contaminants" (ECs), represent an environmental problem which is not yet included in regulatory frameworks for control and prevention of environmental pollution. Emerging contaminants include biologically active compounds such as pharmaceuticals, personal care products, and consumer products from domestic, agricultural and industrial origin which have been released in the environment. An important feature of these contaminants is that they do not need to be persistent in the environment to cause adverse effects because emissions from WWTPs may be high enough to maintain concentrations at dangerous levels (Robles et al., 2011). Of all the emerging contaminants in present day use, the compounds that are probably of most concern are pharmaceuticals. Active pharmaceutical compounds (PhACs), which include prescription pharmaceuticals, non-prescription pharmaceuticals, pharmaceuticals used in hospitals and veterinary pharmaceuticals, have been widely detected in the water cycle (Boxall et al., 2012).

Several studies in Europe and the United States indicate that many of these compounds are present in the effluents of wastewater treatment plants, surface water, and groundwater (Puijker and Mons, 2004). Since the late 1990s, several studies reported that concentrations of pharmaceutical compounds in aquatic ecosystems vary in a range between ng/L–mg/L (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999). As pharmaceuticals are designed to have specific biological effects at low concentration levels, their presence in the environment could create a risk to ecosystems (Fong, 1998; Schmitt et al., 2006) and to the production of drinking water (Ternes et al., 2002; Snyder et al., 2003). These compounds can affect river ecosystems and may have an adverse effect on bio-

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diversity (Boxall et al., 2012). Although there are few studies on the direct effects of the presence of these substances in the environment, problems were observed in some fish species that may be caused by the presence of antidepressant pharmaceuticals in surface waters. The accumulation of antidepressant active components in the brain, liver and muscles of three different types of fish in rivers in which the effluents from sewage treatment plants are discharged, are said to have altered the behaviour and physiology of insects, the inhibition or stimulation of growth of aquatic plants and algae, and the development of antibiotic resistance of bacteria (Heberer, 2002a, 2002b; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Cortacans Torres et al., 2007).

Pharmaceutical compounds can enter the aqueous medium by several routes, primarily through human and animal excretion or run-off from agricultural fields. Pharmaceutical compounds are metabolized to a greater or lesser degree after ingestion. The compounds are subsequently excreted in urine and feces and will travel from the sewer system to the wastewater treatment plant (WWTP) (Lienert et al., 2007). These plants are not specifically designed to remove pharmaceuticals from wastewater (Camacho-Muñoz et al., 2009). Pharmaceuticals can leave the treatment plants also partly transformed into by-products and they will be directly emitted into the environment.

In recent years, analytical methods have been developed and optimized for the determination of pharmaceutical compounds in order to improve sensitivity and accuracy to be able to quantify low concentrations in environmental samples (Camacho-Muñoz et al., 2009). Drug monitoring in the environment is restricted by the difficulty of analysis or the absence of suitable analytical protocols. The selection criteria for monitoring these pharmaceuticals are often based on the choice of analyzed compounds in earlier studies. In a study on various pharmaceutical compounds in five WWTPs in Catalonia, the following average concentrations were detected in effluent waters: analgesics and anti-inflammatories between 108 and 2102 ng/L; statins between 10–120 ng/L; antiepileptics (carbamazepine) between 410 and 620 ng/L; antibiotics between 96 and 390 ng/L; and beta-blockers between 167 and 395 ng/L (Petrović et al., 2005).

WWTPs typically employ conventional activated sludge (CAS) systems consisting of primary sedimentation followed by secondary activated sludge treatment and final sedimentation. WWTPs studied in Region of Murcia, consist mainly of these different systems: Conventional activated sludge system (CAS), extended aeration activated sludge processes (EAAS) and membrane bioreactor system (MBR). The secondary clarifiers could be used with sand filtration (SF), lamination (L) and/or coagulation-flocculation (C-F) as post treatments. As tertiary treatment processes are used ultraviolet (UV) and Chlorination (Cl) to reduce the number of microorganisms in the water to be discharged back into the environment for the later use of drinking, bathing, irrigation, etc. The secondary and primary sludge is digested in mesophilic sludge digesters and the digested sludge is centrifuged to remove excess of water. In Fig. S1 the different deviations from the typical design and different post-treatment strategies studied are schematized.

To our knowledge hardly any studies have been conducted into measured concentrations and loads of these pharmaceuticals in the wastewater influent and effluent in WWTPs throughout the Region of Murcia. This approach can be very useful in order to have a realistic knowledge of the presence of pharmaceuticals in this region. In this study, four representative pharmaceutical compounds were identified and quantified in WWTPs using five different treatment systems throughout the Region of Murcia. The monitoring was performed in June and September 2013 during one week in sewage influents and sewage effluents. The relative efficiencies of different technologies in eliminating these four pharmaceuticals were compared and assessed.

2. Material and methods

2.1. WWTPs and pharmaceutical compounds selected

The WWTPs selected are located at the Region of Murcia, Southeast Spain. There are currently 90 WWTPs that give service to the entire Region, treating more than 97% of the wastewater. The WWTPs selected for this study were chosen to represent different treatment stages and technologies with some duplication to enhance comparisons.

The pharmaceuticals studied were carbamazepine (antiepileptic) and diclofenac, ketoprofen and naproxen (NSAID). The criteria for selecting these pharmaceuticals were compounds that are generally present in the wastewater and in the environment (Petrović et al., 2005) and compounds that have been studied in other works (Camacho-Muñoz et al., 2009)

2.2. Sample collection and analyses

Pooled influent and effluent wastewater samples were collected over a period of 24 h in automated samplers. Wastewater volumes collected each hour were proportional to influent and effluent flows. Sampling was carried out on a weekly basis and in two campaigns (3–28 June and 3–28 September 2013, respectively). All samples were stored at 4 °C.

Prior to extraction, water samples (500 mL of influent wastewater and 1000 mL of effluent wastewater) were filtered through a 1.2 μm glass fibre membrane filter (Whatman, Mainstone, UK) and acidified to pH 2 with sulphuric acid. Due to the high organic content of influent wastewater, 500 mL of influent samples were used to avoid the blockage of the cartridges. Pharmaceuticals were analyzed following a method that is described in detail in Camacho-Muñoz et al. (2009). Solid-phase extraction was done using ExtraBond® NH2 500mg–6 mL cartridges (Scharlab). Chromatographic analyses were performed using a Shimadzu SPD-M10Avp instrument, equipped with a FCU-10L binary pump, a SIL-10ADVP automatic injector, a OGU-14AL degasser, a CTO-10ACVP thermostated column compartment, a SPD-M10AVP UV diode array detector (DAD) and a RF-10AXL fluorescence scanning detector (Fl) connected on line.

Recovery studies were done in triplicate by spiking aliquots of 500 mL of influent wastewater and aliquots of 1000 mL of effluent wastewater with pharmaceuticals at a concentration level of 5 μg/L. Sample preparation procedure described above was applied. Recoveries were calculated by comparison of the peak areas obtained from spiked samples with the peak areas from the same samples without standard solution addition (blanks) and, finally, with the areas obtained by direct injection of a standard solution at the concentration level expected after sample treatment. Calibration curves were constructed in the concentration ranges expected for each compound in wastewater according to the concentration levels reported by several authors (Ternes, 2001). Calibration curves were generated by linear regression of peak areas of the standard solutions against their respective concentrations. Instrumental LODs were calculated as the lowest observable concentration giving an S/N ratio of 3:1 while instrumental LOQs were calculated as the concentration resulting in an S/N ratio of 10:1 (the ratio between peak intensity and intensity of the noise was used). LODs were in the range of 0.004–0.081 Rodríguez et al., 2003 μg/L and LOQs were between and 0.015–0.314 μg/L (Table S1).