Chemosphere 87 (2012) 453–462

Contents lists available at SciVerse ScienceDirect

Chemosphere

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

Occurrence and removal of pharmaceuticals in wastewater treatment plants at the Spanish Mediterranean area of Valencia

Emma Gracia-Lor, Juan V. Sancho, Roque Serrano, Félix Hernández *

Research Institute for Pesticides and Water, University Jaume I, Avda. Sos Baynat, E-12071 Castellón, Spain

ARTICLE INFO

Article history:
Received 21 June 2011
Received in revised form 8 December 2011
Accepted 9 December 2011
Available online 4 January 2012

Keywords:
Pharmaceuticals
Liquid chromatography–tandem mass spectrometry
Effluent and influent wastewater
Waste water treatment plant
Occurrence
Removal efficiency

ABSTRACT

A survey on the presence of pharmaceuticals in urban wastewater of a Spanish Mediterranean area (Castellon province) was carried out. The scope of the study included a wide variety of pharmaceuticals belonging to different therapeutical classes. For this purpose, 112 samples, including influent and effluent wastewater, from different conventional wastewater treatment plants were collected. Two monitoring programmes were carried out along several seasons. The first was in June 2008 and January 2009, and the second in April and October 2009. During the first monitoring, the occurrence of 20 analytes in 84 urban wastewater samples (influent and effluent) was studied. The selection of these pharmaceuticals was mainly based on consumption. From these, 17 compounds were detected in the samples, with analgesics and anti-inflammatories, cholesterol lowering statin drugs and lipid regulators being the most frequently detected groups. 4-Aminoantipyrine, bezafibrate, diclofenac, gemfibrozil, ketoprofen, naproxen and venlafaxine were the compounds most frequently found. In the highlight of these results, the number of analytes was increased up to around 50. A lot of antibiotic compounds were added to the target list as they were considered "priority pharmaceuticals" due to their more potential hazardous effects in the aquatic environment. Data obtained during the second monitoring programme (spring and autumn) corroborated the results from the first one (summer and winter). Analgesics and anti-inflammatories, lipid regulators together with quinolone and macrolide antibiotics were the most abundant pharmaceuticals. Similar median concentrations were found over the year and seasonal variation was not clearly observed. The removal efficiency of pharmaceuticals in the wastewater treatment plants was roughly evaluated. Our results indicated that elimination of most of the selected compounds occurred during the treatment process of influent wastewater, although it was incomplete.

1. Introduction

Pharmaceutical consumption is continuously increasing around the word. Only in Spain, about 729 millions of prescriptions were sold in 2004. Six years later, the consumption increased around 30% reaching 958 millions prescriptions (http://www.msps.es/profesionales/farmacia/datos/home.htm). This has lead to an increasing concern regarding possible ecological risks coming from pharmaceuticals released into the environment.

Pharmaceuticals are used extensively in human and veterinary medicine to prevent illness and also as growth promoters in livestock and fish farming as well as in agriculture. After administration, pharmaceuticals can be transformed in the human body into more polar and soluble forms as metabolites or as conjugates of glucuronic and sulphuric acid (Heberer, 2002; Nikolaou et al., 2007). Pharmaceuticals and their metabolites are readily excreted with urine and faeces and enter into urban wastewater treatment plants (WWTPs). Some of these compounds are eliminated by chemical or biological processes while others are degraded during sewage treatment processes or removed from the water phase by adsorption onto solid phase (e.g. sludge) (Jones et al., 2005). Data recently reported show that some pharmaceuticals are accumulated in sewage sludge. This indicates that even good removal rates obtained in aqueous phase (i.e. comparison of influent and effluent wastewater concentrations) do not imply degradation to the same extent. In general, the elimination of most of the substances is incomplete and improvements of the wastewater treatment and subsequent treatments of the produced sludge are required to prevent the introduction of these micro-pollutants in the environment (Jelic et al., 2011). At present, urban wastewaters are considered the most important source of pharmaceutical compounds in the aquatic environment. WWTPs were designed to remove organic pollutants, mainly estimated as dissolved organic matter, solids and nutrients but not pharmaceutical compounds. Disposal of unused pharmaceuticals directly into domestic waste and application to livestock as veterinary drugs and feed additives can also

* Corresponding author. Tel.: +34 964 387366; fax: +34 964 387368.
E-mail address: felix.hernandez@qfa.uji.es (F. Hernández).

0045-6535/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2011.12.025

contribute to their introduction in the environment (Heberer, 2002; Nikolaou et al., 2007).

Removal efficiencies in WWTPs depend on several factors such as compound physico-chemical properties, the climate conditions (e.g. temperature and sunlight intensity), the type of treatment process employed, the operational conditions of the treatment process (temperature of operation, redox conditions, solids retention time and hydraulic retention time) as well as the age of the activated sludge used in the plant (Castiglioni et al., 2006; Suárez et al., 2008; Le-Minh et al., 2010). Therefore, removal efficiencies can vary significantly from plant to plant and within a plant at different time periods (Vieno et al., 2007).

WWTPs typically employ conventional sewage treatment consisting on primary sedimentation followed by secondary treatment and final sedimentation. Organic pollutants can be transformed from the aqueous phase by hydrolysis, biotransformation or sorption to primary and secondary sludges (Le-Minh et al., 2010). However, the removal efficiency is variable as it is highly affected by the compound affinity to remain in the aqueous phase of the treated effluent (hydrophilic pharmaceuticals) or to be adsorbed to sludge (hydrophobic chemicals). In contrast, tertiary treatment or advanced treatment processes such as membrane filtration, activated carbon or oxidative processes (chlorination, ozonation and ultraviolet irradiation) seem to be more efficient when they work under optimum conditions. Nevertheless, their use is not widespread due to their high cost in terms of energy consumption.

Little is known about possible human and ecological adverse effects derived from the presence of pharmaceuticals in the aquatic environment. Although the concentration levels detected after wastewater treatment processes seem not to cause toxic effects on human health and in the aquatic environment, there is a big concern on the long-term exposure of aquatic organisms to pharmaceuticals. Antibiotics are of special interest because they can promote bacterial resistance in the environment due to continuous exposure (Kümmerer, 2009a, 2009b; Zuccato et al., 2010). It is a problematic issue for flora and fauna as well as for humans, especially in those places where treated effluents are used to supplement drinking water supplies (Le-Minh et al., 2010). Consumption on antibiotics varies from country to country. Spain is one of the most consuming countries in terms of total amount. Broad spectrum antibiotics, which have the greatest impact on the development of resistance, are widely consumed according to the European Surveillance of Antimicrobial Consumption (ESAC) homepage (http://app.esac.ua.ac.be/public/index.php/en_eu/antibiotic/antibiotic-consumption).

The aim of this paper is to investigate the occurrence and behavior of pharmaceuticals in wastewater treatment plants placed in the Castellon province (Spanish Mediterranean area) in order to have a realistic knowledge of the presence of pharmaceuticals in this region. A total of 112 samples (untreated and treated urban wastewater samples) from three WWTPs were analyzed by liquid chromatography coupled to tandem MS, along two monitoring programmes over the four seasons: summer (June), winter (January), spring (April), and autumn (October). Up to 47 pharmaceuticals were determined including a notable number of antibiotics. The occurrence and removal of these pharmaceuticals in different WWTPs and the effect of the seasonal variation on the elimination of pharmaceuticals was assessed.

2. Experimental

2.1. Reagents and chemicals

Reference standards were purchased from Sigma–Aldrich (St Louis, MO, USA), LGC Promochem (London, UK), Toronto Research Chemicals (Ontario, Canada), Across Organics (Geel, Belgium), Bayer Hispania (Barcelona, Spain), Fort Dodge Veterinaria (Gerona, Spain), Vetoquinol Industrial (Madrid Spain) and Aventis Pharma (Madrid, Spain).

Isotopically labeled compounds used were omeprazole-d_3, acetaminophen-d_4, diclofenac-d_4, salicylic acid-d_3 and ibuprofen-d_3, from CDN Isotopes (Quebec, Canada); atorvastatin-d_5, paroxetine hydrochloride-d_4 and olanzapine-d_3, from Toronto Research Chemicals (Toronto, Canada); sarafloxacin-d_8 hydrochloride trihydrate, from Sigma–Aldrich; and sulfamethoxazole-$^{13}C_6$ and trimethoprim-$^{13}C_3$, from Isotope Cambridge Laboratories (Andover, MA, USA).

HPLC-grade methanol (MeOH) and HPLC-grade acetonitrile (ACN) were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained from purification of demineralised water in a Milli-Q Gradient A10 (Millipore, Bedford, MA, USA). Formic acid (HCOOH, content >98%), ammonium acetate (NH_4Ac, reagent grade) and sodium hydroxide (NaOH, >99%) were supplied by Scharlab (Barcelona, Spain).

Standards were dissolved in MeOH, except macrolides, sulfonamides and lincosamides that were prepared in ACN. The addition of NaOH was necessary for the proper dissolution of acidic analytes like quinolones. A mix of all compounds was prepared in MeOH and subsequently diluted with water to obtain working standard solutions. A mix of isotopically labeled internal standards (ILISs) was also prepared in MeOH and used as surrogate. All standard solutions and ILIS mix were stored in amber glass bottles at −20 °C in a freezer.

Cartridges used for SPE were Oasis HLB (60 mg) from Waters (Milford, MA, USA).

2.2. Instrumentation

Ultra-high performance liquid chromatography–tandem mass spectrometry (UHPLC) analysis was carried out using an Acquity UPLC system (Waters, Milford, MS, USA), equipped with a binary solvent pumping. In the first monitoring, chromatographic separation of the 20 pharmaceuticals was achieved using an Acquity UPLC BEH column, 1.7 μm, 50 mm × 2.1 mm (i.d.) (Waters). Later, when the number of compounds increased up to 47, a longer column (Acquity UPLC HSS T3, 1.8 μm, 100 mm × 2.1 mm (i.d.)) was required for a satisfactory separation of all analytes but maintaining similar chromatographic runs. The LC system was interfaced to a TQD (triple quadrupole) mass spectrometer with an orthogonal electrospray ionization source Z-spray (Waters Corp.). MS/MS analysis was performed under selected reaction monitoring (SRM) mode, working in positive and negative ionization modes simultaneously. Chromatographic and mass spectrometry conditions can be found in detail in our previous papers (Gracia-Lor et al., 2010, 2011).

2.3. Analytical procedure

Water samples were extracted as described in Gracia-Lor et al. (2010, 2011). Briefly, the procedure was as follows: 100 mL water sample (100 mL effluent wastewater (EWW) or 20 mL influent wastewater (IWW) diluted with water to 100 mL) spiked with the ILIS mix working solution was passed through the Oasis HLB cartridge, previously conditioned. Analytes were eluted with 5 mL MeOH and the extract was evaporated and reconstructed with 1 mL MeOH–water (10:90, v/v). Finally, 20 μL of the final extract were injected in the UHPLC–MS/MS system. Quantification was made using calibration standards prepared in solvent, based on relative responses analyte/ILIS or on absolute analyte responses, depending on whether ILIS was used for correction or not. All