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Investigation of PPCPs in wastewater treatment plants in Greece: Occurrence, removal and environmental risk assessment

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HIGHLIGHTS

- Comprehensive study of 18 PPCPs in eight WWTPs in Greece
- Further confirmation was accomplished by LC–MS/LTQ Orbitrap.
- Report on the occurrence of trimethoprim transformation products in wastewaters
- Occurrence of budesonide, a glucocorticoid steroid, is extensively studied in WWTPs.
- Triclosan was the most critical compound in terms of contribution and environmental risk.

GRAPHICAL ABSTRACT

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ABSTRACT

In the present work, an extensive study on the presence of eighteen pharmaceuticals and personal care products (PPCPs) in eight wastewater treatment plants (WWTPs) of Greece has been conducted. The study covered four sampling periods over 1-year, where samples (influents; effluents) from eight WWTPs of various cities in Greece were taken. All WWTPs investigated are equipped with conventional activated sludge treatment. A common preconcentration step based on SPE was applied, followed by LC–UV/Vis–ESI–MS. Further confirmation of positive findings was accomplished by using LC coupled to a high resolution Orbitrap mass spectrometer. The results showed the occurrence of all target compounds in the wastewater samples with concentrations up to 96.65 μg/L. Paracetamol, caffeine, trimethoprim, sulfamethoxazole, carbamazepine, diclofenac and salicylic acid were the dominant compounds, while tolfenamic acid, fenofibrate and simvastatin were the less frequently detected compounds with concentrations in effluents below the LOQ. The removal efficiencies showed that many WWTPs were unable to effectively remove most of the PPCPs investigated. Finally, the study provides an assessment of the environmental risk posed by their presence in wastewaters by means of the risk quotient (RQ). RQs were more than unity for various compounds in the effluents expressing possible threat for the aquatic environment. Triclosan was found to be the most critical compound in terms of contribution and environmental risk, concluding that it should be seriously considered as a candidate for regulatory monitoring and prioritization on a European scale on the basis of realistic PNECs. The results of the extensive monitoring study contributed to a better insight on PPCPs in Greece and their presence in influent and effluent wastewaters. Furthermore, the

Abbreviations: PPCPs, Pharmaceuticals and personal care products; WWTPs, Wastewater treatment plants; WW, Wastewaters; LC–MS, Liquid chromatography–mass spectrometry; ESI, Electron spray ionization; LTQ, Linear trap quadrupole; USD, US dollar; OECD, Organization for Economic Co-operation and Development; SPE, Solid phase extraction; PI, Positive ionization; NI, Negative ionization; SIM, Selected ion monitoring; LOD, Limit of detection; LOQ, Limit of quantification; RQ, Risk quotient; EMEA, European Medicines Agency; MEC, Measured environmental concentration; PNEC, Predicted no-effect concentration; AF, Assessment factor; WFD, Water Framework Directive; LC_{50}, Lethal concentration 50; EC_{50}, Effective concentration 50; NOEC, No observed effect concentration; HRT, Hydraulic retention time; SRT, Sludge retention time.

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unequivocal identification of two transformation products of trimethoprim in real wastewaters by using the advantages of the LTQ Orbitrap capabilities provides information that should be taken into consideration in future PPCP monitoring studies in wastewaters.

1. Introduction

In recent years, presence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment has been referred as one of the most urgent environmental concerns (Al-Odaini et al., 2010). These compounds are released mostly through urban wastewater and many of them can further spread through the water cycle, even reaching drinking water, due to their hydrophilic character and low removal at wastewater treatment plants (WWTPs). This fact has initiated a huge scientific effort to better understand the occurrence and fate of most commonly administered PPCP compounds in urban and hospital wastewaters and assess their potential environmental effects. In this light, several of investigations have been conducted in various types of wastewater samples in different areas around the World (Gracia-Lor et al., 2011, 2012a; Gros et al., 2010; Kosma et al., 2010; López-Serna et al., 2011; Stamatis and Konstantinou, 2013; Verlicchi et al., 2012a).

Very little data are currently available in Greece on the occurrence and fate of PPCPs in wastewaters. Until recently, research and monitoring data on the environmental occurrence of PPCPs in wastewaters of Greece have been limited to studies focused on a small number of targeted compounds in localized areas, with no considerations on the WWTP efficiency (Botitsi et al., 2007; Samaras et al., 2010). To the author's knowledge, only two specialized reports have been published (Kosma et al., 2010; Stamatis and Konstantinou, 2013) dealing with the monitoring of a number of PPCPs during one whole year and their treatment removal in wastewaters.

Despite its small size relative to other European countries, Greece is one of the big pharmaceutical per capita spenders after the United States and Canada, with expenditure of USD 677, much higher than the OECD average of USD 487 (OECD, 2011). In 2001 Greece was the second and fifth European country in total antibiotic use of ambulatory and hospital care, respectively (Botitsi et al., 2007). In addition, according to data collected by the OECD (OECD, 2003), pharmaceutical expenditure in Greece, ranged around 14% of total health care expenditure in 2001, approximately equal to Germany's (14.3%), Sweden's (13.5%) and the UK's (15.8%) but lower than those of other Mediterranean countries (Portugal 22.8%, Italy 22.3%, Spain 22%) and the OECD countries' average of 16.9%. Nevertheless, the real amount of applied drugs is uncertain, but significantly higher for some pharmaceuticals, taking into account that the annual consumption of a certain drug is difficult and often based on estimates (Thacker, 2005).

Current information thus suggests that the high pharmaceutical consumption in Greece will reflect high PPCP inputs of local WWTPs. Therefore, it is important to study more extensively and comprehensively the occurrence and fate of the most widespread PPCPs in Greek conventional WWTPs.

In order to address this, the present study constitutes an attempt to accurately measure the concentrations of eighteen PPCPs in untreated and final effluent of eight contrasting WWTPs located in various provinces of North West (N.W.) Greece. These pharmaceuticals were the analgesic/anti-inflammatory drugs salicylic acid, ibuprofen, paracetamol, naproxen, diclofenac, tolfenamic acid and phenazone, the lipid regulators gemfibrozil, fenofibrate, bezafibrate and clofibric acid, the antibiotics trimethoprim and sulfamethoxazole, the antiepileptic carbamazepine, the psychomotor stimulant caffeine, the glucocorticoid steroid budesonide, the disinfectant triclosan and the hypolipidemic statin simvastatin. They were mainly chosen according to their high annual consumption, previous studies about their occurrence and removal in wastewaters and surface waters, their stability and poor elimination during WWTPs as well as the concern about their possible effects on human and aquatic organisms (Gracia-Lor et al., 2012a; Gros et al., 2010; Kosma et al., 2010; Verlicchi et al., 2012a). Although the present study was limited to target compounds, further investigations shall be carried out to increase the number of measured analytes and to elucidate levels of conjugated or metabolic forms of the active compounds.

The compared WWTPs are equipped with conventional activated sludge secondary treatment and nitrogen and phosphate removal. A snapshot of the ability of these systems to remove such compounds is provided by comparing their global removal efficiencies for each substance. The biodegradability of the target PPCPs in different operational systems was overviewed and the seasonal variation in the elimination of PPCPs was also assessed. To the best of our knowledge this is the first report referring to such a big monitoring plan in wastewaters in Greece at the same period of time, which would provide a more comprehensive snapshot of the studied area. In addition, there is a lack of data on the removal efficiency across the varying configurations of WWTPs and only very few works (Kosma et al., 2010) consider a relatively broad set of PPCPs in several types of wastewaters in N.W. Greece (Epirus, Macedonia, Aitoloakarnania), an area characterized by an important rural population, humid climate and the operation of small WWTPs. Finally, a risk analysis is provided in order to assess and compare the potential environmental risk of various types of wastewaters (hospital and municipal effluents) by evaluating the ratio between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC) for these wastewaters (Gros et al., 2010; Valcárcel et al., 2011; Zhao et al., 2010).

2. Experimental materials and methods

2.1. Chemicals

Pharmaceutical analytical standards were purchased from Promochem (Wesel, Germany). Simvastatin and Trimethoprim (vetranal) were supplied from Sigma-Aldrich (Steinheim, Germany). Solvents such as methanol and acetone were obtained from Pestiscan (Labscan, Ltd., Dublin, Ireland) and anhydrous sodium sulfate from Merck (Darmstadt, Germany). Acetonitrile (ACN) and water (for chromatographic analysis, LC–MS grade) were received from Fisher Scientific (Leicestershire, UK). Formic acid (purity, 98–100%), was obtained from Merck KGaA (Darmstadt, Germany). Oasis HLB (200 mg, 6 cm^3) and Oasis MCX (150 mg, 6 cm^3) cartridges were purchased from Waters Corporation (Milford, MA, U.S.A.). Stock 1000 mg/L solutions of each pharmaceutical were prepared in methanol and stored at −20 °C. A mixture of all pharmaceuticals was prepared by appropriate dilution of individual stock solutions in methanol–water (50–50 v/v). Table 1 lists the physicochemical properties of pharmaceuticals investigated.

2.2. Sampling sites and sample collection

Samples were collected from eight WWTPs located in various cities in Greece. Table 2 shows the characteristics of the WWTPs studied.

As can be seen from Table 2, all WWTPs investigated are equipped with conventional activated sludge secondary treatment and nitrogen and phosphate removal. Main differences among them refer to their water treatment capacity, the hydraulic retention times and solid retention times. Hospital WWTP is the smaller unit from all the units investigated as it receives lower loads than the other bigger municipal