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Assessment of 83 pharmaceuticals in WWTP influent and effluent samples by UHPLC-MS/MS: Hourly variation

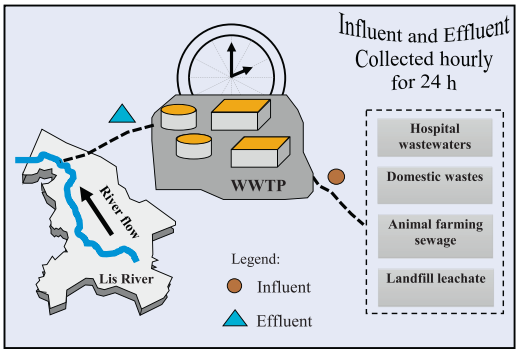
Paula Paíga [a], Manuela Correia [a,*], Maria João Fernandes [a,b], Ana Silva [a,b], Manuela Carvalho [a], Joana Vieira [c], Sandra Jorge [c], Jaime Gabriel Silva [d,e], Cristina Freire [f], Cristina Delerue-Matos [a]

[a] REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4249-015 Porto, Portugal
[b] IIT/LTA - Instituto de Investigaciones Tecnológicas, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain
[c] Águas do Centro Litoral, SA, Grupo Águas de Portugal, ETA da Boavista, Avenida Dr. Luís Albuquerque, 3030-410 Coimbra, Portugal
[d] Águas de Santo André, Cerca da Água, Rua dos Cravos, 7500-130 Vila Nova de Santo André, Portugal
[e] Departamento de Engenharia Civil, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Porto, Portugal
[f] REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

HIGHLIGHTS

- Hourly variation of 83 pharmaceuticals in WWTP influent and effluent is presented.
- Pharmaceuticals belonging to different therapeutic classes were analysed.
- Some pharmaceuticals were detected in the influents in the μg/L range.
- The importance of the determination of metabolites and transformation products is highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal efficiency of pharmaceuticals in wastewater treatment plants (WWTPs) is variable and some of these compounds pass these plants almost intact and others presenting a removal efficiency close to 100%. Their incomplete removal results in a continuous discharge of pharmaceuticals into the environment. To assess the profile of contamination of influents and effluents over a day, a set of 83 pharmaceuticals were evaluated hourly in a WWTP in Leiria, Portugal. The composite samples of the influent and effluent were also collected. Concentrations varied from <MDL for ketoprofen, clarithromycin, ofloxacin, and diltiazem to 63.97 μg/L for caffeine in the WWTP influent composite sample and <MDL for clarithromycin, bupropion, and diltiazem to 2.01 μg/L for *O*-desmethylvenlafaxine for effluent composite sample. Concentrations in the range of μg/L were found for hydroxyibuprofen, salicylic acid, D,L-norephedrine, and caffeine in the WWTP influent, and diclofenac, carbamazepine, *O*-desmethylvenlafaxine in the WWTP effluents.
For the samples collected hourly, thirty-eight and twenty-nine pharmaceuticals were detected in at least one WWTP sample. In the WWTP influent the total concentration of detected pharmaceuticals was higher between 15 and 22 h and lower in the period from 23 to 10 h in the morning. In the WWTP effluent, a slight variation was noticed throughout the sampling hours.

* Corresponding author.
E-mail address: mmb@isep.ipp.pt (M. Correia).

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Carbamazepine, fluoxetine, sertraline, atorvastatin, caffeine, simvastatin, and trazodone were the pharmaceuticals with risk quotient (RQ) >1 in WWTP influents, and carbamazepine, fluoxetine, sertraline the pharmaceuticals with an RQ > 1 in WWTP effluents.

1. Introduction

Modern societies have benefited from the introduction of thousands of synthetic chemicals in the last century. However, the importance of their environmental fate has only been recognized in the last few decades, particularly in the case of micropollutants, such as pharmaceutical compounds (Rivera-Utrilla et al., 2013).

Little is known about the possible ecological risks of most of these pollutants. This lack of knowledge results in a substantial amount of ongoing efforts to develop data and approaches that may be useful in assessing the impact of pharmaceuticals on the environment (Ankley et al., 2007). The assessment of their presence in the aquatic environment, at very low levels (ng/L), has been possible due to the developments in analytical determination, such as the use of ultra-high performance liquid chromatography coupled to tandem mass spectrometry detection (UHPLC-MS/MS) (Paíga et al., 2015; Paíga et al., 2016; Petrovic et al., 2010). This method proved to be a robust and reliable instrument for monitoring pharmaceuticals in environmental samples (Paíga et al., 2016).

The massive use of pharmaceuticals for both human and veterinary purposes leads to the introduction of tons of these compounds in wastewaters, which is mainly attributed to the effluents of manufacturing processes, human and animal excretion, disposal of unused or expired pharmaceutical products, and unintentional shed through the manufacturing or distribution process (Diaz-Cruz et al., 2003).

After treatment in wastewater treatment plants (WWTPs), considerable amounts can be transferred to surface waters either due to insufficient removal efficiencies or, if high removals are attained, concentrations up to ng/L and μg/L can still be found, depending on the compounds' mass loadings (Paíga et al., 2015; Rivera-Utrilla et al., 2013). Although it is not legally required in Europe, the control of this type of substances in surface waters is crucial, because it may affect water quality and potentially impact drinking water supplies, ecosystems, and human health (EU_L78/40, 2015).

Outcomes of different studies showed that the concentrations of some pharmaceutical substances in wastewater and their treated effluents might fluctuate along the year (Fernández et al., 2014; Gago-Ferrero et al., 2017; Golovko et al., 2014; Vatovec et al., 2016). In Portugal, this fluctuation is coherent with the existent statistical data that refers a monthly sales variation of pharmacotherapeutic subgroups (INFARMED, 2018). The main reasons found for the seasonal variation of the presence of pharmaceuticals in wastewater were the changes in some substances/products consumption rate in response to each season characteristic diseases (respiratory infections, depression and allergies treatment drugs, etc.) (Gago-Ferrero et al., 2017; Golovko et al., 2014; Moreno-González et al., 2014; Sun et al., 2014; Vatovec et al., 2016), demographic characteristics (population age) associated or not with demographic mobility (areas strongly influenced by educational institutions, holyday period, tourism areas) (Moreno-González et al., 2014; Pereira et al., 2015; Vatovec et al., 2016) and weather variation (abundance/lack of precipitation, temperature changes, per capita domestic water consumption), all influencing the dilution rate (Diaz-Cruz et al., 2003; Fernández et al., 2014; Sun et al., 2014).

Some seasonal conditions, such as long periods of sunlight exposure of the effluent during the treatment were also referred as a cause to the reduction of some substances susceptible to photodegradation (Gago-Ferrero et al., 2017; Moreno-González et al., 2014). In addition to seasonal oscillation, weekly fluctuations in the concentrations of pharmaceutical substances in water courses were observed in several sampling points, associated with the same behavior in WWTP effluents, that occurred mainly between the weekend and the rest of the week (Moreno-González et al., 2014). Furthermore, daily variations were also noticed for some pharmaceutical products in wastewater, associated with daily drug administration patterns (Coutu et al., 2013; Plósz et al., 2010).

In a previous study, the occurrence of 33 pharmaceuticals and metabolites was evaluated along the Lis river (Leiria, Portugal) and in influents and effluents of two WWTPs located along the river (Paíga et al., 2016). In samples collected from August 2013 to June 2014, pharmaceuticals, such as ibuprofen, ketoprofen, carbamazepine and fluoxetine, and the metabolite salicylic acid showed 100% of detection frequency, at levels up to 1.3 μg/L for ibuprofen (Paíga et al., 2016).

The purpose of this study was to extend the number of pharmaceutical compounds analysed, using a new sampling campaign that took place in June 2017. Samples of one WWTP (Leiria, Portugal) influent and effluent were collected hourly, for 24 h. Effluent samples were collected considering the WWTP hydraulic retention time. Flow proportional 24-h composite samples of the influent and the effluent were also collected. A set of 83 pharmaceuticals belonging to different therapeutic classes, including non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, antibiotics, anorectics, anxiolytics, beta-blockers, laxatives, antidiabetic drug, antipsychotic, calcium channel blocker, fibrate lipid lowering agent, stimulants, lipid regulator and cholesterol lowering statin drugs, proton pump inhibitor, and psychiatric drugs were assessed. The variation throughout the day of pharmaceutical concentrations, and the removal efficiency of the WWTP were characterized.

2. Materials and methods

2.1. Sampling site and sample collection

Leiria is a city and a municipality in the Centre Region of Portugal. Lis river is one of Leiria's most important resources. Almost 40 km long, the river drains in Vieira beach, after crossing the Lis fields, a wide farming area watered by its abundant flow (Vieira et al., 2012). Nowadays, after an extensive requalification project as part of the POLIS Programme, the riverbanks are the chosen place to exercise and play sports. Lis River also constitutes an important inland water resource for domestic, industrial and irrigation purposes (LeiriaMunicipality, 2018), thus it is imperative to prevent and control water pollution.

Hog farming located along the basin of the Lis river is known for being one of the sources of pollution in the river (Vieira et al., 2012). According to the news, Lis river basin has been subjected in the past 30 years to constant ecological disasters, mainly due to piggery untreated wastewater discharges (Vieira et al., 2012). Freshwater pollution problems are gaining attention regionally due to their social, economic, and health impacts. Moreover, the sources of contamination may be influenced by different geographical patterns of pharmaceuticals consumption (Vieira et al., 2012), and important fluctuations due to seasonal variations might also occur (Paíga et al., 2016).

The influents and effluents of a WWTP located along the Lis river are target of the present study. The wastewaters treated by the Coimbrão WWTP are domestic and hospital wastewaters, and landfill leachate. The WWTP also treats animal farming sewage (pigs manure), through the sludge treatment process, since the manure is discharged by trucks on the WWTP, going directly to anaerobic digesters, where that slurry joins the sludge removed from the liquid phase in the treatment