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Review

Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment—A review

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ABSTRACT

This review focuses on 118 pharmaceuticals, belonging to seventeen different therapeutic classes, detected in raw urban wastewater and effluent from an activated sludge system, a usual treatment adopted for urban wastewaters worldwide prior to final discharge into surface water bodies. Data pertaining to 244 conventional activated sludge systems and 20 membrane biological reactors are analysed and the observed ranges of variability of each selected compound in their influent and effluent reported, with particular reference to the substances detected most frequently and in higher concentrations. A snapshot of the ability of these systems to remove such compounds is provided by comparing their global removal efficiencies for each substance. Where possible, the study then evaluates the average daily mass load of the majority of detected pharmaceuticals exiting the secondary treatment step. The final part of the review provides an assessment of the environmental risk posed by their presence in the secondary effluent by means of the risk quotient that is the ratio between the average pharmaceutical concentration measured in the secondary effluent and the predicted no-effect concentration.

Finally, mass load rankings of the compounds under review are compared with those based on their risk level. This analysis shows that the highest amounts discharged through secondary effluent pertain to one antihypertensive, and several beta-blockers and analgesics/anti-inflammatories, while the highest risk is posed by antibiotics and several psychiatric drugs and analgesics/anti-inflammatories. These results are reported with a view to aiding scientists and administrators in planning measures aiming to reduce the impact of treated urban wastewater discharge into surface water bodies.

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1. Introduction

In recent years, pharmaceutical compounds (PhCs) have provoked increasing concern, particularly as no legal requirements have been set for discharge into surface water bodies of these ubiquitous, persistent and biologically active substances (Furhacker, 2008; Salgot et al., 2006; Ternes et al., 2007). Recent investigations document that PhC production and administration may vary both between countries and over time (Goossens et al., 2007, Kümmerer, 2009a), fluctuating not only on an annual basis, but also from one year to the next (Alexy et al., 2006). In addition, the continually ageing population and improving quality of life worldwide mean that their consumption is set to increase in future years (Van der Aa et al., 2011).

Once administered, PhCs are metabolised to varying degrees, and their excreted metabolites and unaltered parent compounds can also undergo further modification due to biological, chemical and physical processes in both sewage treatment facilities and receiving water bodies (Deblonde et al., 2011; Fatta-Kassinos et al., 2011; Miège et al., 2009; Monteiro and Boxall, 2010; Onesios et al., 2009). Municipal wastewater treatment plants (WWTPs) are generally not equipped to deal with complex pharmaceuticals, as they were built and upgraded with the principal aim of removing easily or moderately biodegradable carbon, nitrogen and phosphorus compounds and microbiological organisms, which regularly arrive at the WWTP in concentrations to the order of mg L^{-1} and at least 10^6 MPN/100 mL, respectively. PhCs in raw wastewaters are generally in the range of 10^{-3}–10^{-6} mg L^{-1}, in addition, their chemical and physical properties, namely solubility, volatility, adsorbability, absorbability, biodegradability, polarity and stability, vary greatly (Le Minh et al., 2010; Ziylan and Ince, 2011), with obvious repercussions on their behaviour during the treatments and consequently their removal efficiencies.

Indeed, several PhCs have been found in river biota, some at high levels (Rimkus, 1999), thereby evidencing the risk that environmental concentrations of PhCs can be higher than their predicted no-effect concentrations (PNECs) (Santos et al., 2007; Stuer-Lauridsen et al., 2000), especially in effluent-dominant rivers whose dilution capacity and self-purifying processes are insufficient to temper the risk to aquatic life (Kasprzyk-Hordern et al., 2009).

Although much research has been conducted on this topic, studies have generally been limited to single treatment plants. Hence, in order to provide an overview of the findings, we set out to collate the data pertaining to 264 WWTPs from various global locations, mostly in Europe.

Reflecting the abundance of conventional activated sludge systems (CAS) among existing municipal WWTPs, 244 of them were considered in this review, the remaining 20 plants examined were membrane biological reactors (MBR), included for comparative purposes.

Data pertaining to a wide spectrum of PhCs, 118 compounds belonging to 17 different classes distinguished by their function or biological activity, were considered: 23 analgesics/anti-inflammatories, 36 antibiotics, 1 antidiabetic, 1 antifungal, 3 antihypertensives, 1 barbiturate, 12 beta-blockers, 2 diuretics, 9 lipid regulators, 10 psychiatric drugs, 6 receptor antagonists, 4 hormones, 4 beta-agonists, 3 antineoplastics, 1 topical product, 1 antiseptic and 1 contrast agent.

First we reported raw influent and secondary effluent concentrations for the 118 PhCs, and their removal efficiencies observed in CAS and MBRs, the objective being to provide a snapshot of their occurrence and of the efficacy of suspended growth mass biological processes in their removal. Based on the collected data, we then evaluated the average daily mass load (mg/1000 inh/d) in the secondary effluent for the majority of the compounds under study, ranking them accordingly. The PhCs were then also ranked according to their environmental risk, using a quotient derived from the ratio between their measured concentrations in secondary effluents and their corresponding PNEC. This strategy provides an overview of the situation, clearly identifying a group of compounds in need of more intensive monitoring further to safeguarding the environment.

1.1. Review framework

The survey drew data from 78 peer-reviewed papers published in books or international journals, collating data on the occurrence of PhCs in raw urban wastewaters and secondary biological effluents from suspended growth biomass systems (CAS and MBRs) and/or the corresponding removal efficiencies achieved by these WWTPs. Compounds are grouped according to their therapeutic class and presented in terms of their chemical formula and molecular weight; literature references are also provided for each (Table 1). In addition, in the Supplementary data, their main physical and chemical properties (protonation constant as pK_a, octanol–water partition coefficient as Log K_{ow}, solubility S_w, sludge–water distribution coefficient as Log K_d, reaction rate constant k_{biol}, molecular charge at pH 7) as well as their molecular structure are provided (see Table SD1). The main features of the WWTPs are investigated in each study and details of the corresponding experimental campaigns are compiled in Table 2. Through the last column of Table 1, it is possible to know the previous works investigating the substance under study and then, once known the cited work, through Table 2 to know the details of the experimental campaign and the characteristics of the WWTPs under consideration.

Based on the collected literature data, we defined variability ranges for the concentration of each examined compound in both raw urban influent (Figs. 1–6 and Table SD2) and secondary effluent (Figs. 7–12 and Table SD3), as well as for their corresponding removal efficiencies (Figs. 14–19 and Table SD4). To complete the analysis of literature data, the percentage partitions, for some of the compounds under study, among biodegradation, sorption onto sludge and occurrence in the secondary effluent are provided (Table 3) as well as removal efficiencies for the different selected PhCs with respect to the sludge retention time of the corresponding biological reactor (referring to CAS in Table 4 and MBR in Table 5).

Subsequently, the average daily mass discharged from the secondary biological system was evaluated, where possible, for the examined compounds, and their corresponding risk quotients (average concentration/PNEC) in the secondary effluent (Figs. 20 and 21). As a whole, the results of these two analyses revealed the most critical compounds in terms of mass load and/or environmental risk.

2. Materials and methods

2.1. Investigated pharmaceutical compounds

Table 1 reports the list of the investigated contaminants, grouped according to their therapeutic class, in addition to their molecular weight (MW) and chemical formula, together with the number and details of the references reviewed.