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Suspended solids moderate the degradation and sorption of waste water-derived pharmaceuticals in estuarine waters

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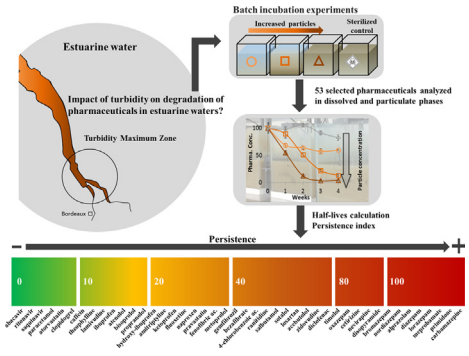
HIGHLIGHTS

- Wastewater derived pharmaceuticals were incubated in estuarine waters.
- Dissolved and particulate concentrations were monitored over 4 weeks.
- Only 7/43 pharmaceuticals were persistent.
- Degradation rates were enhanced by increasing particle concentrations.
- Limited degradation in sterilized conditions

GRAPHICAL ABSTRACT



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ABSTRACT

This study focuses on the fate of pharmaceuticals discharged into an estuarine environment, particularly into the Turbidity Maximum Zone (TMZ). Batch experiments were set up to investigate the factors regulating the degradation of 53 selected pharmaceuticals. Treated effluents from Bordeaux city (France) were mixed with water from the estuarine Garonne River during 4 weeks under 6 characterized conditions in order to assess the influence of suspended particulates, sterilization, untreated wastewater input and dilution on the degradation kinetics. Of the 53 pharmaceuticals monitored, 43 were quantified at the initial time. Only 7 exhibited a persistent behavior (e.g. carbamazepine, meprobamate) while biotic degradation was shown to be the main attenuation process for 38 molecules (e.g. abacavir, ibuprofen highly degradable). Degradation was significantly enhanced by increasing concentrations of suspended solids. A persistence index based on the half-lives of the compounds has been calculated for each of the 43 pharmaceuticals to provide a practical estimate of their relative stability. The stability of pharmaceuticals in estuarine environments is likely to be highly variable and attenuated primarily by changes in suspended solid concentration.

1. Introduction

Since pharmaceuticals were identified as contaminants of emerging concern (Daughton and Ternes, 1999), their occurrence in urban and natural aquatic systems has been increasingly studied. Multi-residue screenings have confirmed their presence in wastewater (López-Serna et al., 2010; Rosal et al., 2010), surface water (Baker and Kasprzyk-Hordern, 2013; Silva et al., 2011), seawater (Benotti and Brownawell, 2007; Vidal-Dorsch et al., 2012) and groundwater (Hass et al., 2012; Vulliet and Cren-Olivé, 2011).

After discharge into a water body, concentrations of pharmaceuticals in the dissolved phase are governed by physical processes such as dilution, diffusion and transport as well as by chemical (abiotic) or

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biochemical (biotic) processes. While the physical processes are likely to be similar between all contaminants, physico-chemical and biochemical processes will differ according to molecular structures (Fatta-Kassinos et al., 2011). In environmental waters, physico-chemical processes relate mainly to photodegradation and sorption. Photodegradation is well documented, with many studies for each carbamazepine, diclofenac, sulfamethoxazole and propranolol (Challis et al., 2014; Trawinski and Skibinski, 2017). Concerning sorption to suspended solids (SS) and sediments, pharmaceuticals have received less attention owing to their perceived hydrophilic nature. However, historical records of pharmaceutical contamination have been recently detected in an urban impacted estuary (Lara-Martín et al., 2015) and some authors have reported significant partitioning to sediment of compounds such as psychotropics and β-blockers (Aminot et al., 2015; Baker and Kasprzyk-Hordern, 2011; Burke et al., 2013).

To date, most of the studies on pharmaceutical biodegradation focus on their fate through wastewater treatment and during biological secondary treatment (Lahti and Oikari, 2011; Pomiès et al., 2013). However, despite their continuous input to surface waters through treated urban effluents and/or combined sewers overflows (Verlicchi et al., 2012), little is known of the parameters governing the fate of pharmaceuticals after discharge. Biodegradation can be investigated through in-stream studies (Aymerich et al., 2016; Kunkel and Radke, 2011; Writer et al., 2013) and laboratory experiments (Baena-Nogueras et al., 2017; Benotti and Brownawell, 2009; Bradley et al., 2007; Grenni et al., 2013; Yamamoto et al., 2009). Even if laboratory experiments do not strictly represent natural aquatic systems (Kunkel and Radke, 2011) they can provide important information concerning the factors governing in-stream attenuation. Previous studies (Bradley et al., 2007; Radke and Maier, 2014) have evaluated the ability of river sediments to biodegrade pharmaceuticals. Other incubation experiments (Benotti and Brownawell, 2009) have revealed important differences in the biodegradation rates of studied compounds e.g. a paracetamol half-life of <1 day compared to a half-life of carbamazepine which is >100 days. The authors also observed that in coastal waters kinetics of degradation were faster under eutrophic conditions.

In this context, and as numerous cities like Bordeaux in France, are located along estuaries subject to tidal cycles, there is a real need to investigate the fate of pharmaceuticals in such environments (Zhao et al., 2015). Previous research evidenced a removal of some compounds within the Garonne estuary, with an increase of the attenuation rates in low flow summer periods (Aminot et al., 2016). Water dynamics in tidal estuaries are complex and a zone of high turbidity, known as the Turbidity Maximum Zone (TMZ), is generally observed at the freshwater/seawater interface. In this area, the number of freely suspended bacteria and their growth rate are small compared to those living on the particles (Plummer et al., 1987; Servais and Garnier, 2006), so the particles of the TMZ are expected to play a key role on the biochemical processes governing the water quality, in particular the organic contaminant concentration (Abril et al., 1999; Lanoux et al., 2013).

Up to now, the transport and reactivity of emerging contaminants in estuarine environments are poorly understood, yet it closely relates to their effects in such coastal ecosystems. In particular, it remains unclear if the estuarine TMZ acts as a passive vector of contaminants from land to sea or as an active incubator, and, if so, whether sorption or biodegradation is the dominant transformation process. This study, therefore, aims to fill in an important gap in our knowledge by identifying in which way selected pharmaceuticals and estuarine particles characteristic of the TMZ interact. Laboratory batch experiments simulating mixing conditions of the discharge of wastewater into a turbid estuary were performed to assess the influence of suspended solid concentration, type of effluent and dilution on a selection of 53 pharmaceuticals present in waste water from the city of Bordeaux.

2. Experimental methods

2.1. Estuarine river water and waste water characteristics

River water (approx. 100 L) was collected in 20 L HDPE (High Density PolyEthylene) flasks from the estuarine Garonne River adjacent to the city of Bègles (coordinates 44°47′58.31″N; 0°31′37.99″W). This hydrosystem is a macrotidal estuary characterized by a tidal cycle dependent TMZ (Lanoux et al., 2013). Water was sampled at mid-ebb to ensure the highest SS concentration. Three 20 L flasks were subject to magnetic stirring to prevent particle settlement while two others were left unagitated for three days at room temperature in the dark. This treatment provided samples from the same water body under three different suspended solid conditions: unagitated flask supernatants, stirred waters and unagitated flask concentrates from the settled particles at respectively low (0.1 g L^{-1}), intermediate (1 g L^{-1}) and high (10 g L^{-1}) SS concentration. Water salinity was representative of TMZ particularity (0.5‰) (Lanoux et al., 2013).

A few hours before the start of the experiment, large volume wastewater grab samples (approx. 80 L effluent and 20 L influent) were collected in 20 L HDPE flasks from one of the two major waste water treatment plants (WWTP) of the Bordeaux urban area in October 2012 (*Clos de Hilde* WWTP). This WWTP served 264,600 inhabitants (estimate of *Lyonnaise des Eaux*, manager). The WWTP is equipped with biofilters as a secondary treatment.

2.2. Chemicals and selection of 53 pharmaceuticals

Fifty-three commonly used pharmaceuticals were chosen using multistep selection based upon sales statistics, occurrence and fate in aquatic environment. Selected pharmaceuticals belong to various therapeutic classes and physicochemical properties and were quantified in the studied wastewater effluent in preliminary studies. Details on pharmaceuticals and chemicals used are given elsewhere and in Table 1 (Aminot et al., 2015). Mercury (II) chloride (99%) was purchased from Sigma-Aldrich (Saint Quentin Fallavier, France).

2.3. Incubation experiment set-up

Incubation experiments were adapted from previous works on the characterization of organic matter degradation in TMZ (Lanoux, 2013).

Cubic 30 L glass aquariums were filled with river water and wastewater under the 6 following conditions (Fig. 1): *low SS (LSS)* 12.5 L effluent, 12.5 L river water supernatant; *intermediate SS (MSS)* 12.5 L effluent, 12.5 L stirred river water; *high SS (HSS)* 12.5 L effluent, 12.5 L river water concentrate; *untreated wastewater (Unt)* 12.5 L influent, 12.5 L stirred river water; *sterilized condition (HgCl2)* 12.5 L effluent, 12.5 L stirred river water, mercury (II) chloride at 100 mg L^{-1}; *higher dilution (10xD)* 2.5 L effluent, 22.5 L stirred river water.

Continuous mixing was performed by homemade glass rotors mounted on overhead stirrers while air was bubbled in through immersed frits at an approximate 1 L min^{-1} rate. The 6 experimental devices remained in an air-conditioned room (room temperature varied between 18 and 22.5 °C) in the dark.

The ambient pharmaceutical concentrations in wastewater effluent samples mixed with estuarine water were sufficient that additional spiking was not required (no introduction of carrying solvent). The dilution rates were chosen as a compromise of environmental relevant levels and to ensure the detection of the analytes on their whole degradation kinetics. Tenfold wastewater dilution (10xD) is comparable to an effluent discharge into a small river. To compensate for this higher dilution, 7 selected compounds (abacavir, carbamazepine, fenofibric acid, ibuprofen, naproxen, paracetamol, sotalol) were spiked into this aquarium to achieve a target concentration of 500 ng L^{-1} (Fig. 1).

Poisoning with mercury (II) chloride has already been used efficiently for soil sterilization prior to PAH analysis (Wang et al., 2011),