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Inputs and seasonal removal of pharmaceuticals in the estuarine Garonne River

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ABSTRACT

Pharmaceuticals were screened in the estuarine Garonne River to investigate the role of estuaries as passive or active transfer compartments in the removal of these compounds. Monthly monitoring of 53 pharmaceuticals from various therapeutic classes at 6 sampling points over 18 months showed that most compounds were frequently detected with median concentrations in the low ng L^{-1} range. Saline intrusion was responsible of an overall dilution but an enrichment from the treated urban effluents of Bordeaux city was also observed with increases resulting from this input being compound dependent. An average cumulated load of 10 kg of the monitored pharmaceuticals was found to enter the estuary daily from the catchment area. After normalization to the persistent marker carbamazepine, a large majority of the compounds were found to exhibit in-stream attenuation during summer while this removal was enhanced farther down the estuary, indicating a likely effect of residence time, temperature and suspended solid concentration on the stability of the pharmaceuticals.

1. Introduction

Thousands of pharmaceuticals are used in human (2800 authorized in France) and veterinary medicines (ANSM 2013). After ingestion, they are excreted by the human body unchanged or as metabolites and enter sewage networks prior to waste water treatment plants (WWTP) where they undergo partial degradation. This route has been identified as the major pathway for inputs of pharmaceuticals into the aquatic environment. Agricultural leachates or direct inputs in the context of aquaculture are examples of secondary sources that concern more specific veterinary compounds (Ashton et al. 2004; Boxall et al. 2012; Daughton and Ternes 1999). Recently, combined sewer overflows (CSO) of waste waters and rainfall runoff have also received attention as they discharge raw wastewater when the capacities of the network are exceeded (Del Río et al. 2013; Ryu et al. 2014). An annual monitoring of a WWTP in the USA (Phillips et al. 2012) revealed that CSO discharges contribute 40–90% of the annual load for compounds with high wastewater treatment removal efficiency but <10% in the case of compounds with low removal efficiencies. Although the sources of pharmaceuticals to the environment are well identified, the understanding of their fate after discharge remains incomplete. Indeed, few studies consider large water bodies impacted by urban effluents and most focus on small streams impacted by individual WWTPs (Kunkel and Radke 2012; Writer et al. 2013).

Estuaries are areas of particular biological and economical relevance: they are sheltered habitats, nurseries and migratory passages for biota as well as ocean/land interfaces for sea trade and associated industrial activities. Not only do they drain inland inputs, it has also been estimated that 23% of the world's population lives within 100 km distance of the coast, including estuaries, where population densities are about three times higher than the global world average (IPCC, 2007). Consequently, studying pharmaceuticals as indicators of urban inputs is of high relevance in an estuarine context. For example, pharmaceuticals have been significantly detected in 5 UK estuaries (Thomas and Hilton 2004), in San Francisco Bay, USA (Klosterhaus et al. 2013), in the Seine estuary, France (Togola and Budzinski 2007) and in the Yangtze estuary, China (Yan et al. 2015). In addition, conservative behavior was further observed for most of the studied pharmaceuticals under dry-weather conditions in Jamaica Bay, USA (Benotti and Brownawell 2007). However, a recent study in the Yangtze estuary (Zhao et al. 2015) showed that most of the analyzed compounds were non-conservative with either estuarine inputs (e.g. sulfadiazine, sulfapyridine) or removal (e.g. omeprazole, fenofibrate). In another recent study, pharmaceuticals screened in dated estuarine sediment cores from Jamaica Bay, New York, revealed a good correlation between their distributions and their historical use (Lara-Martín et al. 2015). Organic contamination (and pharmaceuticals in particular) appears to be complex in estuaries which seem to act as vectors of upstream contamination together with sources of local input and act as reactors for degradation and sinks of contaminants.

In this context, pharmaceuticals have been scarcely studied in the Gironde estuary, France, despite it being one of the largest European

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estuaries (tidal influence 150 km upstream its mouth). It is formed mainly by the Garonne River (60–70% of its fresh water flow) which has a catchment area with an estimated 4 million inhabitants population. Focusing on the example of the estuarine Garonne River with regards to pharmaceuticals, this study aims at improving the understanding of estuaries as transfer compartments between land and ocean involving complex biochemical reactions. A total of 53 pharmaceuticals were screened over 18 months in 2011–2012. This covered a wide range of hydrological conditions.

2. Material and methods

2.1. Study area

The Garonne River in the South-West of France forms Western Europe's widest estuary, the Gironde, after meeting with the Dordogne River 20 km downstream Bordeaux (Fig. 1). It drains a 56,000 km^2 catchment area with an estimated 4 million population including the two major urban centres Toulouse and Bordeaux (about 1 million inhabitants in each). The Garonne River had an average flow of 340 $m^3 \cdot s^{-1}$ in 2011–2012 and ranged from 82 $m^3 \cdot s^{-1}$ to 2000 $m^3 \cdot s^{-1}$ (www.hydro.eaufrance.fr). Currents and hydro-sedimentary processes (water body mixing, turbidity maximum zone – TMZ) are mainly controlled by the tide in its estuarine part from the Bay of Biscay to 150 km inland of the mouth. Tidal intrusion is responsible for a complex estuarine circulation with water flushing times ranging from a few days to about 86 d in low flow periods (Jouanneau and Latouche 1981). The TMZ is situated mainly between Bordeaux and Pauillac as a function of the river discharge and the tidal cycle with Suspended Solid (SS) concentrations reaching 10 $g \cdot L^{-1}$. High frequency measurements of tide level, salinity, turbidity and temperature are available in Bordeaux and Pauillac through the MAGEST monitoring program (Etcheber et al. 2011). The estuary has previously been studied with regards to hydro-sedimentary processes, dissolved oxygen and organic matter, trace metals and biological populations. Thorough analysis of these parameters in the Garonne-Dordogne system is available in the following references (Abril et al. 1999; Chaalali et al. 2013; Lanoux et al. 2013; Schäfer et al. 2002, 2009; Sottolichio and Castaing 1999).

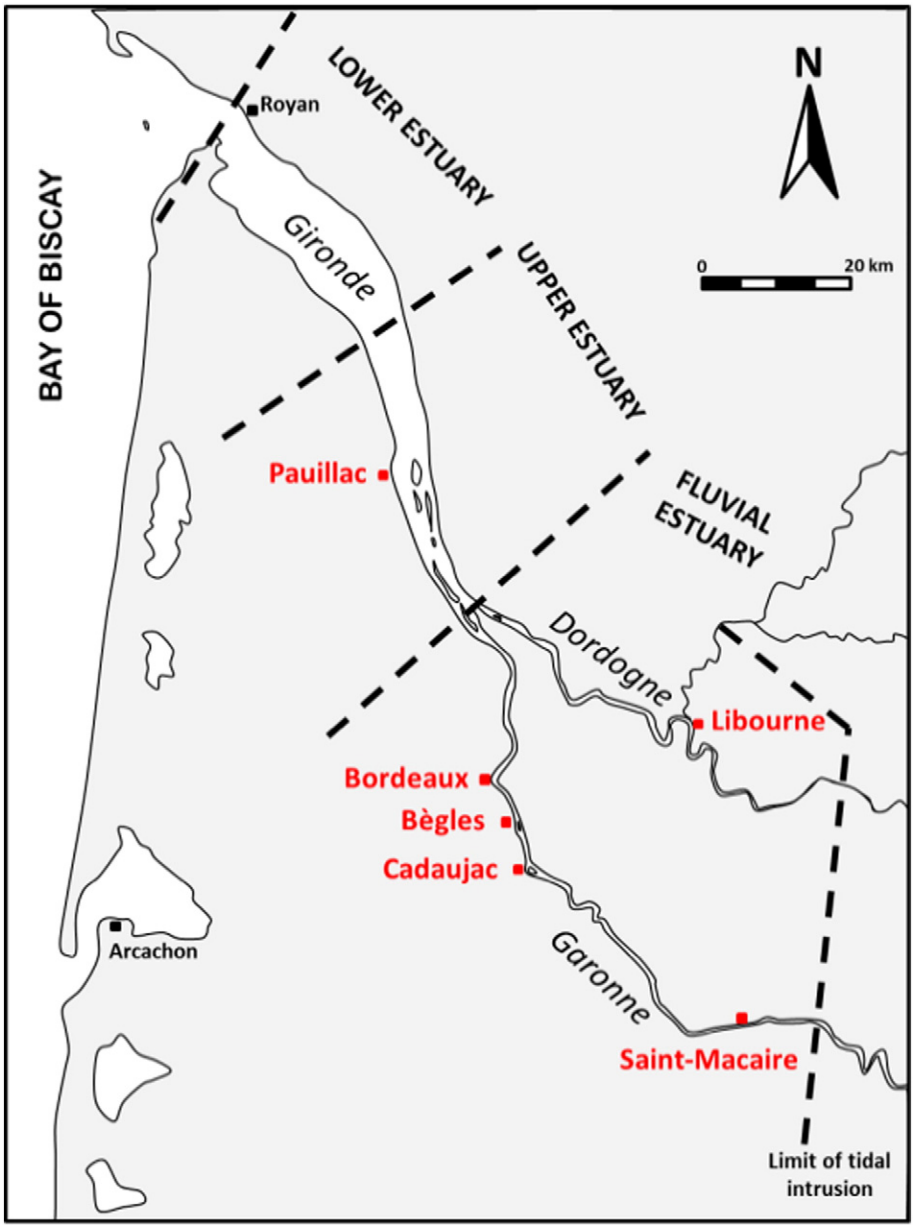

Fig. 1. Map of the Garonne and Dordogne Rivers and the Gironde estuary in the South-West of France.