



Occurrence and modeling of pharmaceuticals on a sewage-impacted Mediterranean river and their dynamics under different hydrological conditions

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HIGHLIGHTS

- ▶ The occurrence of pharmacological compounds in a Mediterranean river at variable hydrological conditions was studied.
- ▶ The impact of the flow changes on the concentrations was assessed using relative sensitivity coefficients.
- ▶ A plug-flow model was developed to explain the observed variations in the load of the most relevant compounds analyzed.
- ▶ The model takes into consideration the circulating flow, the average upstream emissions and an overall decay constant.

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ABSTRACT

The occurrence of 73 representative pharmacologically active compounds (PhACs) was assessed in a sewage-impacted section of the Llobregat River (NE Catalonia, Spain). This Mediterranean river is characterized by flow rate fluctuations strongly influenced by seasonal rainfall. River flow variations increase the potential environmental risk posed by organic micro-pollutants as their concentrations may increase substantially under low flow conditions. Little is known about the transport behavior of emerging contaminants in surface waters once they are discharged from waste water treatment plants (WWTP) into rivers. This research aimed to study the presence and fate of emerging contaminants under different hydrological conditions by sampling two different sites along the river in different seasons. The highest levels of pharmaceuticals were determined during cold and dry periods. The impact of the flow changes on the concentration of the pharmaceuticals in the river was assessed with the relative sensitive coefficients. Due to expected dilution effects, the response of pharmaceuticals to river flow was negative. Only in a few cases, positive relationships between drug concentrations and flow were detected, suggesting an important role of other hydrological phenomena like sediment re-suspension as well as the source of pollutants. To evaluate the role of other factors influencing PhAC concentrations, a plug-flow model was applied to obtain disappearance constants “k” for a set of selected compounds. Erythromycin presented k values of -0.15 h^{-1} in both sites being the compound more efficiently removed from the water column. The k values for ibuprofen, furosemide, enrofloxacin, enalapril, acetaminophen, diclofenac and Ketoprofen were between -0.04 and -0.10 h^{-1} showing less disappearance than erythromycin in the water column. However, other compounds presented k values < 0.06 , which suggested conservative behavior of these compounds in the water column. This study supports the reliability of the calculated k values for the disappearance of compounds in river waters.

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1. Introduction

Pharmacologically active compounds (PhACs) constitute an environmentally relevant group of compounds due to their increasing consumption and their intrinsic biological activity. Around 3000 different compounds belonging to different therapeutic classes are used in human medicine in the European Union (EU), covering a

broad range of chemical structures and physico-chemical properties (Richardson and Ternes, 2005). The main route of entry of PhACs into the aquatic environment is through waste water treatment plant (WWTP) effluents because their generally polar nature makes their removal from WWTPs challenging (Conley et al., 2008). Despite physico-chemical and biological treatment, many PhACs are able to reach surface and ground waters. As a consequence, PhACs are now recognized to be widespread pollutants in the aquatic environment (Petrovic et al., 2010). More than 150 PhACs have been identified in surface, ground and even drinking waters (Benotti et al., 2009). Levels of PhACs detected in WWTP effluents are in the range of

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$\mu\text{g/L}$, whereas they are much lower in river and groundwater, generally in the ng/L range (Gros et al., 2010). Nevertheless, little attention has been paid to the transport behavior of these emerging contaminants in surface waters once they are discharged from WWTP into a river. They are transported by water and may be removed from the dissolved phase through adsorption to suspended particles and may accumulate in sediments. Chemical bounded to sediments can be remobilized by re-suspension (Petrovic et al., 2011). Levels of PhACs can also be reduced by biotic and abiotic (e.g. photodegradation) natural degradation processes. However, the efficiency of these processes is highly dependent on seasonally fluctuating environmental factors such as sunlight intensity, water temperature, and stream flow.

The Llobregat River (Catalonia, NE Spain) constitutes a typical example of a Mediterranean behavior (Marcé et al., in press), suffering from low flows during normal conditions ($5 \text{ m}^3/\text{s}$) and extraordinary peak events (maximum recorded of $2500 \text{ m}^3/\text{s}$). In addition, the river receives the effluent discharges of more than 55 WWTPs, and at some places the effluents may represent almost 100% of the total flow, especially during drought periods. This fact can explain the high levels of emerging organic contaminants detected on the river including PhACs, increasing together with the volume of effluent discharged by WWTPs when moving downstream along the river (Ginebreda et al., 2010). Furthermore, according to the predictions of the Intergovernmental Panel on Climate Change (IPCC) (Christensen et al., 2007), such tendency is expected to increase in the medium/long term in the Mediterranean area (Acuña and Tockner, 2010).

As far as contamination is concerned, and as a result of the hydrological situation above described, different physical phenomena may occur at the same time: first, the lack of dilution during water scarcity periods may increase the concentration of pollutants; second, and working in the opposite direction, low flows increase the hydraulic residence time, thus facilitating natural degradation processes (Lam et al., 2004); finally, floods may contribute to remobilization of pollutants from sediments (Petrovic et al., 2011).

In this context, the present study aimed (a) to trace the presence of PhACs in sewage impacted surface waters in the lower course of the Llobregat River as a representative example of a stressed Mediterranean River, and (b) to determine some quantitative relationships between levels of PhACs and flow under different hydrological conditions. To this end, we applied a rough modeling approach based on the plug-flow model as proposed by Pistocchi et al. (2010), in order to have a preliminary quantitative assessment on (a) the load of each pollutant generated by the sewage systems upstream from the point under control, and (b) the overall observed decay of the different compounds in the river channel.

2. Materials and methods

2.1. Basin and site description

The Llobregat River is the second longest river in Catalonia (NE Spain), with a total length of 156 km and a catchment area of 4957 km^2 . Its hydrology is characterized by a high variable flow, which is strongly influenced by seasonal rainfall. The mean annual bulk precipitation is 3330 hm^3 and it has an annual average bulk discharge of $693 \cdot 10^6 \text{ m}^3$. The year-round hydraulic conditions are characterized by several peak flow events that are highly variable, from $50 \text{ m}^3/\text{s}$ on May 2004, to $1 \text{ m}^3/\text{s}$ on March 2008 (Figure S-1). The maximum flow recorded in April 2000 ($90 \text{ m}^3/\text{s}$), followed by a drastic drop down to $10 \text{ m}^3/\text{s}$ is a clear example of the strength of seasonal rainfall effects on the Llobregat River. Its watershed is densely populated, with more than 3 million inhabitants living therein. Together with its two main tributaries, the River Cardener and the River Anoia, the Llobregat is subjected to a heavy anthropogenic pressure. The Llobregat River is one of

the main drinking water sources for Barcelona, with nearly 30% of its discharge being used for drinking water. Furthermore, the middle part of the basin receives natural salt slurries from salt formations and mining activities, which have caused an increase in water salinity downstream. The river receives extensive urban and industrial wastewater discharges ($137 \cdot 10^6 \text{ m}^3/\text{year}$; 92% coming from WWTPs) as well as surface runoff from agricultural areas that cannot be diluted by its natural flow ($0.68\text{--}6.5 \text{ m}^3/\text{s}$ basal flow). Forty-eight percent of these point sources are located in the studied area (Fig. 1 and Table S-1). Therefore, this typical Mediterranean River turns into an illustrative example of overexploited river, with high flow variability being caused by a mixture of natural and human-driven components (Marcé et al., in press).

2.2. Sampling

Two sampling sites were selected at the lower reach of the Llobregat River, Abrera (ABR) and Sant Joan Despí (SJD) which were 17 km apart. One sampling point (ABR in Fig. 1) is located in a sparsely populated area in which the Llobregat River receives some urban and industrial wastewater inputs. Another sampling site (SJD) is located in the greater metropolitan area of the city of Barcelona and therefore expected to be more impacted than ABR. In fact, according to the previously existing monitoring data from the Catalan Water Agency (ACA), SJD is the most polluted section of the River. Since previous studies suggested that the levels of PhACs could vary over time depending on the meteorological conditions (Choi et al., 2008; Kolpin et al., 2004), the Llobregat River was sampled during four periods in order to investigate variations in PhAC concentrations under different river flow conditions. With this aim, sampling was performed from October 2009 to July 2010, covering four seasonal periods: Campaign A from 13/10/2009 to 11/11/2009 (Fall), Campaign B from 23/11/2009 to 18/12/2009 (Fall/Winter), Campaign C from 10/03/2010 to 12/04/2010 (Winter/Spring), and Campaign D from 09/06/2010 to 12/07/2010 (Spring/Summer). Campaign A was a sampling period characterized by low flow conditions (mean flows of $6.48 \text{ m}^3 \text{ s}^{-1}$ in ABR and $5.82 \text{ m}^3 \text{ s}^{-1}$ in SJD) but with a typical short-lasting flood event (peak flows of $10.06 \text{ m}^3 \text{ s}^{-1}$ in ABR and $19.98 \text{ m}^3 \text{ s}^{-1}$ in SJD) in response to the first rainfall event after summer. Campaign B was characterized by steady low flow conditions (mean flows of $5.38 \text{ m}^3 \text{ s}^{-1}$ in ABR and $4.16 \text{ m}^3 \text{ s}^{-1}$ in SJD), while campaign C was performed under high steady flow conditions (mean flows of $25.01 \text{ m}^3 \text{ s}^{-1}$ in ABR and $25.98 \text{ m}^3 \text{ s}^{-1}$ in SJD). Finally, campaign D started with a severe flood event (peak flows of $215.09 \text{ m}^3 \text{ s}^{-1}$ in ABR and $111.72 \text{ m}^3 \text{ s}^{-1}$ in SJD) followed by high flow conditions (mean flow of $49.95 \text{ m}^3 \text{ s}^{-1}$ in ABR and $34.03 \text{ m}^3 \text{ s}^{-1}$ in SJD). River water samples were collected twice a week over the four periods (9–13 samples per campaign and monitoring site,) from the thalweg of the river. Composite water samples were collected in 500 mL amber PET bottles that had been pre-rinsed several times with deionized water in the laboratory, and were rinsed with sample water onsite. Bottles were placed in a cooler (at 4°C) and delivered to the laboratory within 2 h. Samples were immediately pre-treated (filtration) and stored in a refrigerator (-20°C) until analysis within two days.

2.3. Pharmaceutical standards

We selected 73 PhACs from the major therapeutic groups based on high frequency of usage, physico-chemical properties, and behavior in WWTPs (Gros et al., 2010; Petrovic et al., 2006), (see Table S-2 in Supporting Information). The standards were purchased from Sigma-Aldrich (Steinheim, Germany), Jescuder (Rubí, Spain); LGC Promochem (London, UK) and Cerilliant (Texas, USA). Isotopically labeled compounds were used for internal standard calibration. All standards were of purity grade ($>98\%$). Stock standard solutions were prepared on a weight basis in methanol, with the exception of

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