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Impact of urban chemical pollution on water quality in small, rural and effluent-dominated Mediterranean streams and rivers

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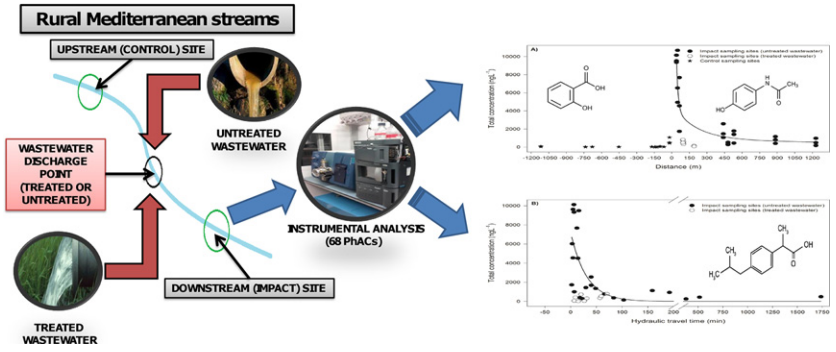
HIGHLIGHTS

- Effluent-dominated streams showed higher concentration levels of pharmaceuticals.
- Non-steroidal anti-inflammatory drugs were the most ubiquitous compounds detected.
- Travel time is an important factor affecting the in-stream attenuation of pharmaceuticals.
- After 100 min of travel time concentrations equalized with the background concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The impact and occurrence of wastewater (treated and untreated) derived pharmaceutically active compounds (PhACs) have been investigated in small, rural and effluent-dominated tributaries of the lower Ebro River located in the North-Eastern Spain (Catalonia). We have observed the predominant effect of stream flow and consequently dilution factor on the concentration levels of detected PhACs that combined with the absence of wastewater treatment plants (WWTP) resulted in 12 times higher concentrations in streams with direct discharge of untreated wastewater. Non-steroidal anti-inflammatory drugs (NSAIDs) were the most ubiquitous compounds, in terms of both individual concentration and frequency of detection. In the sites impacted by raw wastewater, acetaminophen and ibuprofen showed the highest concentrations among all analyzed PhACs, reaching concentrations up to 7.78 μg L^{-1} and 2.66 μg L^{-1}, respectively. However, PhACs detected in the sites impacted by treated wastewater showed generally lower concentration levels and frequencies of detection. Also, effluent-dominated streams showed higher concentration levels of PhACs due to a generally lower stream flows and small dilution factors. However, concentration levels of detected PhACs were dependent on the hydraulic travel time and distance from the discharge point and related with the in-stream attenuation. As a result, this study highlights the combined impact of hydrological and chemical stressors on the water quality of the rural Mediterranean aquatic ecosystems.

Abbreviations: D.F., detection frequency; ESI, electrospray ionization; HRT, hydraulic retention time; LOD, limit of detection; LOQ, limit of quantification; MANOVA, multivariate analysis of variance; Ni, negative electrospray ionization; NSAIDs, non-steroidal anti-inflammatory drugs; OTC, over-the-counter; PhACs, pharmaceutically active compounds; PI, positive electrospray ionization; QqLIT-MS/MS, quadrupole linear ion trap tandem mass spectrometry; r, Pearson moment correlation factor; SM, supplementary material; SPE, solid phase extraction; SRM, selected reaction monitoring; UHPLC, ultra-high-performance liquid chromatography; WWTP, wastewater treatment plant.

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1. Introduction

Pharmaceutically active compounds (PhACs) include all prescription and non-prescription over-the-counter (OTC) drugs and represent an important group of emerging environmental contaminants (Richardson and Ternes, 2005). Even though PhACs can enter aquatic ecosystem through many pathways such as human excretion, disposal of unused and expired drugs, agricultural and livestock practices (Jorgensen and Halling-Sorensen, 2000; Vera-Candioti et al., 2008; Boxall et al., 2012; Tijani et al., 2016), treated and untreated (raw) wastewater discharges represent the main route of entrance (Heberer, 2002; Vieno et al., 2005). As a result of their continuous release into the aquatic environment, PhACs are considered as pseudo-persistent compounds and as such may cause unwanted and unexpected effects on the living organisms and environment (Daughton and Ternes, 1999; Hirsch et al., 1999; Dietrich et al., 2002; Ellis, 2006). Many PhACs in surface waters do not exhibit acute toxicity due to their usually very low environmental concentrations but instead have a rather significant cumulative effect on the metabolism of aquatic organisms and on the ecosystem as a whole (Halling-Sorensen et al., 1998; Daughton and Ternes, 1999). However, due to lack of chronic toxicity data regarding the effects of long-term and low-level PhACs exposures (Ávila and García, 2015), further investigation of PhACs toxicity in the aquatic environment is required.

The capacity of rivers to naturally attenuate PhACs relates to water turbidity, temperature, water flow, biofilm biomass, pH, dissolved oxygen and even mixing between surface and subsurface compartments (Lin et al., 2006; Acuña et al., 2014). However, impact of contaminants downstream from wastewater discharge is mostly determined by distance and in-stream attenuation processes such as biotransformation, photolysis, sorption and volatilization (Vieno et al., 2005; Brooks et al., 2006; Gurr and Reinhard, 2006; Barber et al., 2013; Chiffre et al., 2016), while dilution, together with the hydraulic travel time (time it takes for a body of water to travel between wastewater discharge point and downstream sampling site) represents the critical components in estimating concentration levels of PhACs in rivers (Rueda et al., 2006; Keller et al., 2014).

So far, the presence of PhACs in treated effluents from wastewater treatment plants (WWTPs) and their receiving waters has been ranged in ng L^{-1} up to μg L^{-1} (Da Silva et al., 2012; Verlicchi et al., 2012; Luo et al., 2014). However, the research literature on the impact of PhACs from untreated wastewaters remains notoriously limited. Further, most research regarding the occurrence of PhACs in waste and surface waters has been limited to larger river systems supporting high population densities (Fernández et al., 2010; Jelic et al., 2011; Fernández-López et al., 2016; Osorio et al., 2016), while knowledge regarding the impact of PhACs occurrence in surface waters of small perennial and non-perennial Mediterranean rural streams remains limited and scarce (Skoulikidis et al., 2017).

In this work, the main objective is to study combined effect of hydrological (flow, hydraulic travel time) and chemical stressors (urban pollution, wastewater treatment) in small, Mediterranean streams and rivers of the lower Ebro River, spanning in their dilution capacity. These systems experience strong seasonal river flow variability, and are prone to eutrophication, hypoxia and increased levels of agricultural and industrial pollutants due to the intense human pressure they receive (Cooper et al., 2013; López-Doval et al., 2013; Acuña et al., 2014; Petrovic et al., 2011). In some cases, these systems receive municipal and industrial wastewaters that dominate the stream flow (Hassan and Egozi, 2001; Poff and Zimmerman, 2010). Consequently, effluent-dominated streams represent the worst-case scenarios for PhACs exposure to aquatic ecosystem and human population (Brooks et al., 2006), since they have higher PhACs concentrations than those having dilution, being irrespective of the type of received wastewater (treated or untreated).

2. Materials and methods

2.1. Basin and sampling sites description

This study was performed in a series of small to medium-sized tributaries of the lower Ebro River basin (Sabater et al., 2009) (See Fig. 1). These systems show typical Mediterranean interannual hydrological variations and seasonal flow reductions in summer and floods in spring and autumn (Gasith and Resh, 1999). All are characterized by a small resident population (Table 1.), with forest and non-irrigational agriculture as the main land uses upstream of the studied sites. Three sampling campaigns were performed at eleven different sites (See Table 1 and Fig. 1), all previously defined with a control (upstream) and impact (downstream) reaches of the wastewater discharge. Three sites received treated wastewaters (effluents from nearby WWTPs), while eight others were impacted by a discharge of raw (untreated) wastewater (Fig. 1). Five sites presented effluent-dominated stream flows (See Fig. 1S in Supplementary material, SM), particularly during October 2015 that was the driest period studied. Effluents were in all cases of urban origin. The daily outflows from WWTPs were obtained from the Agència Catalana de l'Aigua (http://aca-web.gencat.cat/aca/appmanager/aca), and the main characteristics of the treatment process, population served and average monthly WWTP outflows are provided in Table **1**S (SM). The resident population in each municipality concerning the effluents was obtained from the IDESCAT (Catalan Government, 2017) and INE (Spanish Government, 2017).

2.2. Sampling campaign

Extensive sampling campaigns were conducted on April 2015 (wet period), on October 2015 (dry period) and April 2016 (relatively wet

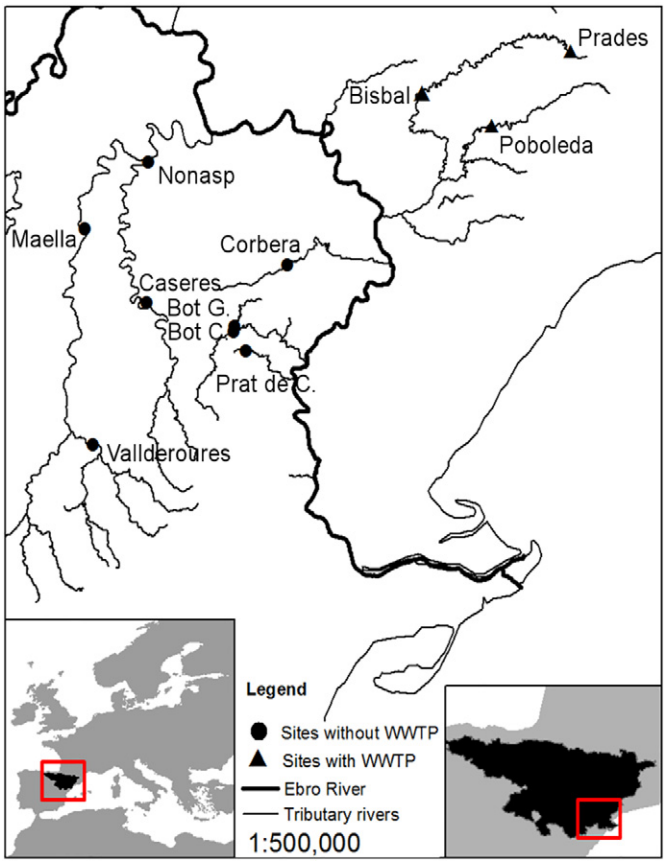

Fig. 1. Sampling sites (black dots and triangles) in the lower Ebro River basin. The bottom left inset shows the location of the Ebro River basin within the Europe and the Iberian Peninsula, while the bottom right inset shows the location of the lower Ebro River basin.