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Concentration and risk of pharmaceuticals in freshwater systems are related to the population density and the livestock units in Iberian Rivers

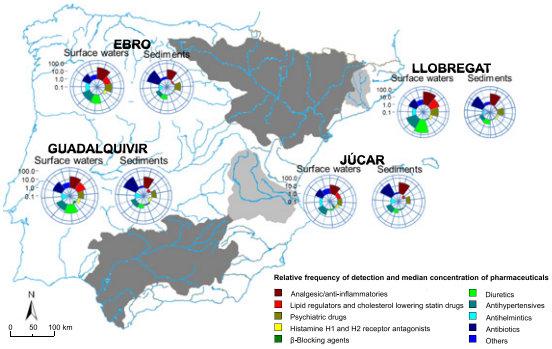
Victoria Osorio [a,1], Aitor Larrañaga [b,1], Jaume Aceña [a], Sandra Pérez [a,*], Damià Barceló [a,c]

[a] Water and Soil Quality Research Group, IDAEA-CSIC, c/ JordiGirona, 18–26, 08034 Barcelona, Spain
[b] Laboratory of Stream Ecology, Dept. of Plant Biology and Ecology, University of the Basque Country, UPV/EHU, PO Box 644, 48080 Bilbao, Spain
[c] Catalan Institute for Water Research (ICRA), Scientific and Technological Park of the University of Girona, Emili Grahit 101, 17003 Girona, Spain

HIGHLIGHTS

- Spatial distribution of pharmaceuticals was assessed across 4 Iberian River basins.
- Ecotoxicological effects of pharmaceuticals to aquatic biota were estimated in SW.
- Hotspots of pharmaceuticals concentration and ecotoxicological risk were identified.
- Concentration and ecotoxicological risk was related to human/animal pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

Considerable amounts of pharmaceuticals are used in human and veterinary medicine, which are not efficiently removed during wastewater and slurries treatment and subsequently entering continuously into freshwater systems. The intrinsic biological activity of these non-regulated pollutants turns their presence in the aquatic environment into an ecological matter of concern. We present the first quantitative study relating the presence of pharmaceuticals and their predicted ecotoxicological effects with human population and livestock units. Four representative Iberian River basins (Spain) were studied: Llobregat, Ebro, Júcar and Guadalquivir. The levels of pharmaceuticals were determined in surface water and sediment samples collected from 77 locations along their stream networks. Predicted total toxic units to algae, *Daphnia* and fish were estimated for pharmaceuticals detected in surface waters. The use of chemometrics enabled the study of pharmaceuticals for: their spatial distribution along the rivers in two consecutive years; their potential ecotoxicological risk to aquatic organisms; and the relationships among their occurrence and predicted ecotoxicity with human population and animal farming pressure. The Llobregat and the Ebro River basins were characterized as the most polluted and at highest ecotoxicological risk, followed by Júcar and Guadalquivir. No significant acute risks of pharmaceuticals to aquatic organisms were observed. However potential chronic ecotoxicological effects on algae could be expected at two hot spots of pharmaceuticals pollution identified in the Llobregat and Ebro basins. Analgesics/antiinflammatories, antibiotics and diuretics were the most relevant therapeutic groups across the four river basins. Among them, hydrochlorothiazide and gemfibrozil, as well as azithromycin and ibuprofen were widely spread and concentrated pharmaceuticals in surface waters and sediments, respectively. Regarding their predicted ecotoxicity, sertraline,

* Corresponding author.
E-mail address: spsqam@idaea.csic.es (S. Pérez).
[1] These authors contributed equally to this work.

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gemfibrozil and loratidine were identified as the more concerning compounds. Significantly positive relationships were found among levels of pharmaceuticals and toxic units and population density and livestock units in both surface water and sediment matrices.

1. Introduction

Freshwaters receive considerable inputs of non-regulated pollutants like pharmaceutically active compounds (PhACs), which are consumed by human population and used in livestock farming (Kemper, 2008; Awad et al., 2014). Reliable information about PhACs consumption patterns in livestock farming and treatment of humans is scarce but a straightforward approach to indirectly assess them is their determination in PhAC-impacted surface waters. Up to now, the occurrence of more than 200 different PhACs has been reported in lakes, rivers and streams, for instance at concentrations of up to a maximum of 6.5 mg L^{-1} for the antibiotic ciprofloxacin (Petrie et al., 2015; Hughes et al., 2013). Of particular concern are antibiotics, which are used in great quantities in animal farming not only for therapeutic purposes (see Kools et al., 2008), but they are also administered to healthy livestock to promote growth (Van Boeckel et al., 2015). The second important source of PhACs in surface waters is expectedly the human population. The combined effects of improved health standards in developing countries with their rapidly growing populations and of aging populations in industrialized nations are anticipated to lead to an increase in the consumption of PhACs and ultimately their environmental burden. To date most publications on the environmental occurrence of PhACs study their presence in different matrices in conjunction with their spatial and temporal distribution. In many studies the sites with the highest levels of PhACs were located in the vicinity of big cities with high population densities (Fernández et al., 2010).

The intrinsic biological activity of PhACs turns their presence in the aquatic environment into an ecological matter of concern, since, despite intense research over the past 15 years, there are still substantial knowledge gaps in terms of chronic effects on non-target aquatic organisms and the effects on ecosystem functioning and biodiversity loss (Bartelt-Hunt et al., 2011; Hughes et al., 2013). Recently, several studies conducted at laboratory scale showed that some PhACs can act as endocrine disruptors suspected of causing intersex, while the widespread presence of antibiotics has been shown to lead to the selection of antibiotic resistant bacteria in the environment.

The application of chemometrics in environmental studies has facilitated the assessment of a huge volume of data and thus allowing statistically reliable conclusions (Mas et al., 2010). The more recent research on the environmental occurrence of PhACs has been carried out relying on chemometrics (Dai et al., 2015; Jia et al., 2011). The role of livestock and agricultural activities was proposed as a source of antibiotic contamination in the Huangpu River (Jiang et al., 2011). In other studies, however, the use of chemometrics allowed to statistically identify human discharge as the main source of antibiotic sulfonamides and other PhACs to Liaodong Bay and Beiyun River (China) (Jia et al., 2011; Dai et al., 2015). However to the best of our knowledge there are no quantitative studies in the literature relating their presence and their predicted ecotoxicity with human population and livestock. In this context, this study aimed (I) to determine the presence of the contaminants in four main river basins of the Iberian Peninsula, (II) to evaluate their spatial and temporal distribution between water and sediment compartments of the river along the four river basins, (III) to assess the ecotoxicological risk to aquatic organisms related to the PhAC presence in these freshwater systems and to correlate the predicted risk with sources of emission.

2. Materials and methods

2.1. River basins

Four representative Spanish River basins and 77 sampling sites located along their stream networks were studied: Llobregat (15 sites), Ebro (23), Júcar (15) and Guadalquivir (24) river basins (see Fig. S-1 in supporting material). These sampling sites were subjected to very different kind and degree of stresses, with some sites in clean headwater reaches and the others at various positions along the stream network. The Llobregat River (NE, Spain) is 156 km long and drains a 4957 km^2 catchment. This typically Mediterranean river is characterized by a highly variable hydrology, which is strongly influenced by seasonal rainfall. The Ebro River (NC-NE, Spain) is 910 km long and drains an area of 85,534 km^2. Due to its larger size, the river covers contrasting climates thus being characterized by a complex hydrological regime. The Júcar River (E, Spain) is 498 km long and drains a 21,632 km^2 catchment. Its hydrology is typically Mediterranean, with considerable hydrologic variability and rapid alternation of droughts and floods. The Guadalquivir River (S, Spain) is 657 km long and drains a 57,527 km^2 catchment. The entire basin is under a Mediterranean climate, receiving some influence from the Atlantic Ocean in the lowest part. Summer droughts are especially severe as a result of high temperature and lack of rain. These basins are characterized by a high population, agricultural and industrial pressure. As a consequence, water pollution is common all along these Iberian River basins. To test the relationship between the sources of PhACs, i.e. humans and livestock, and the occurrence of PhACs in the water and the sediments, we processed geographic data. Raster layers provided by the Food and Agriculture Organization of the United Nations (FAO, http://www.fao.org) were used to calculate the human population density and the livestock units (LSU) at each of the catchments. For the human population the 2015 estimate of global population map was used with a pixel size of 2.5 arc-minutes. The livestock densities were obtained for 2014 as separate layers for cattle, pigs, sheep, goats and chicken with a pixel size of 0.5 arc-minutes. The density values of those layers were multiplied by the coefficients specified in Eurostat (http://ec.europa.eu/eurostat) for each kind of animal: cattle = 1, pigs = 0.5, sheep and goat = 0.1 and chicken = 0.014. Those multiplied values were summed to obtain a new layer representing the livestock units (LSU), i.e. the cattle-equivalent density of domesticated animals at each pixel. This aggregation is based on the nutritional requirements of the animals, but we used it as an approach to represent the stockbreeding intensity as a source of PhACs in our sites. Both for the population density and for the LSU the average value of the pixels located in the upstream catchment for each of the sampling site was used as descriptor. The subcatchments in the four basins studied (Llobregat, Ebro, Júcar and Guadalquivir) spanned two orders of magnitude in terms of population density (from 1.8 to 208.7 human km^{-2}) and an order of magnitude for LSU (from 10.9 to 147.4 LSU km^{-2}) (Fig. 1). The population density was significantly higher in the catchments of Guadalquivir and Llobregat and lowest in Júcar, with Ebro showing values in between (ANOVA: $F_{3,73}$: 70.37, $p < 0.0001$) (Table S-1). On the other hand, the highest values for LSU were estimated for Llobregat, followed by Ebro and then by Guadalquivir and Júcar. Both variables were uncorrelated to each other (Pearson $r = 0.094$, $p = 0.42$).

2.2. Sampling campaign and sample analysis

Two extensive field campaigns were carried out in autumn 2010 (C1) and 2011 (C2) under different hydrological conditions. The