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Risk assessment based prioritization of 200 organic micropollutants in 4 Iberian rivers

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HIGHLIGHTS

- Ranking index has been developed based on toxic units and detection frequency.
- Two hundred micropollutants have been prioritized for Iberian rivers.
- Pesticides and alkylphenols were identified as priority according to ranking index.
- Emerging contaminants do not pose risk of acute effects in studied rivers.
- Chronic toxicity research of emerging contaminants is proposed.

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ABSTRACT

The use of chemicals is continuously growing both in total amount as well as in a number of different substances, among which organic chemicals play a major role. Owing to the growing public awareness on the need of protecting both ecosystems and human health from the risks related to chemical pollution, an increasing attention has been drowned to risk assessment and prioritization of organic pollutants. In this context, the aims of this study were (a) to perform an environmental risk assessment for 200 organic micropollutants including both regulated and emerging contaminants (pesticides, alkylphenols, pharmaceuticals, hormones, personal care products, perflourinated compounds and various industrial organic chemicals) monitored in four rivers located in the Mediterranean side of the Iberian Peninsula, namely, the Ebro, Llobregat, Júcar and Guadalquivir rivers; and (b) to prioritize them for each of the four river basins studied, taking into account their observed concentration levels together with their ecotoxicological potential. For this purpose, a prioritization approach has been developed and a resulting ranking index (RI) associated with each compound. Ranking index is based on the measured concentrations of the chemical in each river and its ecotoxicological potential (EC50 values for algae, *Daphnia* sp. and fish). Ten compounds were identified as most important for the studied rivers: pesticides chlorpyriphos, chlorfenvinphos, diazinon, dichlofenthion, prochloraz, ethion carbofuran and diuron and the industrial organic chemicals nonylphenol and octylphenol that result from the biodegration of polyethoxylated alkyphenol surfactants. Also, further research into chronic toxicity of emerging contaminants is advocated.

1. Introduction

The use of chemicals by our technological society is continuously growing both in total amount as well as in a number of different substances among which organic chemicals play a major role. According to the European Inventory of Commercial Chemical Substances (EINECS), the number of substances commercially available in Europe is ca. 100,000 compounds and similar figures hold for the USA (Arnot et al., 2006; Muir and Howard, 2007). Depending on their intrinsic physical–chemical properties, volume and mode of use (Guillén et al., 2012) many of these compounds may find their way into the aquatic environment either from the point or diffuse sources (Schwarzenbach et al., 2006) where they can affect freshwater ecosystems. In fact, chemical pollution is recognized as one of the major causes of their impairment (Vörösmarty et al., 2010). As regards chemical pollution, there are two aspects that seem of special concern. First, many of these pollutants are continuously and steadily released into the environment in low but measurable concentrations (Barceló and Petrovic, 2007). Second, the long-term environmental and health effects of many of the compounds that are found in the environment are still

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unknown, especially because they occur in the in the form of complex chemical mixtures rather than alone.

Owing to the growing public awareness on the need of protecting both ecosystems and human health from the risks associated with chemical pollution, an increasingly important body of regulations has raised in the last years, especially in developed countries. In this context, the elaboration of lists of chemical substances based on a risk assessment procedure plays a major role. For instance, the Water Framework Directive (WFD), which aims the achievement of good ecological and chemical status of European water bodies by the year of 2015. To achieve good chemical status water bodies must meet the Environmental Quality Standards (EQS) for 45 so-called priority substances (PS) and priority hazardous substances (PHS) from previous legislation (European Commission, 2011). Furthermore, under the WFD, EU member states are obliged to set quality standards for river basin-specific pollutants discharged in each water body and to take action to meet those quality standards by 2015 as part of ecological status.

Advances in environmental analytical chemistry (Barceló and Petrovic, 2007) have shown that regulated and monitored chemicals are only a small fraction of all the chemicals present in the environment (Petrovic et al., 2011). Recently, attention has been directed to several families of contaminants (i.e., pharmaceuticals, personal care products, endocrine disrupting compounds, perfluorinated compounds, pesticides, etc.) that are biologically active but still unregulated (Pal et al., 2010), collectively referred to as Emerging Organic Contaminants (EOCs) (Kuster et al., 2008) and which have been detected in aquatic systems worldwide (Focazio et al., 2008; Fromme et al., 2002; Kolpin et al., 2002; Leong et al., 2007; Loos et al., 2009; Ternes, 1998; B.F.D. Silva et al., 2011).

Due to the great number of chemical compounds potentially occurring in the environment, there is a need to prioritize them for management optimization purposes (Daginnus et al., 2011; von der Ohe et al., 2011). Therefore, identifying the chemicals of concern for a given river basin requires performing a suitable combination of monitoring and reliable assessment of risk. Risk assessment procedures consider both the potential hazard effect of a given substance and its exposure level (Daginnus et al., 2011; Guillén et al., 2012). While exposure can be obtained either from measurement (monitoring) or modeling, hazard is derived from its intrinsic properties. Typically, these encompass persistence, bioaccumulation and toxicity (referred to as PBT approach). However, in practice, due to the aforementioned continuous introduction into the environment of many compounds persistence becomes less relevant (i.e., many pollutants are ubiquitous in the environment due to their continuous input). On the other hand, bioaccumulation and toxicity are often correlated. For that reason, many risk-assessment procedures are focused on ecotoxicity as a hazard measure, while persistence and bioaccumulation are disregarded.

Since risk assessment depends both on the occurrence and effects of the compounds concerned, a reliable ecotoxicity based prioritization exercise should ideally fulfill the following requirements: (i) it should include ecotoxicity data corresponding to test organisms associated with different trophic levels, so that the effects on the real ecosystem are likely reflected, and (ii) it should be based on comprehensive and on-site monitoring, so that exposure levels are representative of the catchment under study. We like to emphasize the latter point since the pollution pattern (and hence the associated priority pollutants) is strongly dependent on local conditions such as climate, hydrology, land-use and economical activities; (von der Ohe et al., 2011; Vörösmarty et al., 2010; Acuña et al., 2014).

Whereas there are a number of prioritization exercises based on western and northern European and US rivers (Daginnus et al., 2011; Kumar and Xagoraraki, 2010; Slobodnik et al., 2012; Smital et al., 2013), they are much less abundant for Mediterranean rivers and limited to regulated compounds (López-Doval et al., 2012) or are focused on certain families (Ginebreda et al., 2010; Vazquez-Roig et al., 2012). In this context, the aims of this study were (a) to perform an environmental risk assessment for ca. 200 organic micropollutants including both emerging and WFD priority contaminants monitored in four rivers located in the Mediterranean side of the Iberian Peninsula, namely, the Ebro, Llobregat, Júcar and Guadalquivir rivers; (b) to prioritize them for each of the four river basins studied, taking into account their observed concentration levels together with their ecotoxicological potential. To this end, standard test data corresponding to three organisms (algae, invertebrates and fish) representative of different trophic levels were used, as recommended by the WFD. The results of this work might contribute to the knowledge of river basin-specific pollutants (RBSP) for Iberian rivers concerned as that is one of the requirements of the WFD, also the importance of emerging pollutants is compared to priority pollutants in terms ecological risk.

2. Materials and methods

2.1. Study area

Four Iberian river basins (Fig. 1) were studied as representatives of Mediterranean streams. The main features of the studied rivers (Ebro, Llobregat, Jucar and Guadalquivir) such as catchment area, river length annual precipitation, population density, etc., vary greatly between this four river basins (Table 1). Mediterranean rivers are characterized by low summer flow and large floods in autumn and winter seasons as a consequence of Mediterranean climate (Gasith and Resh, 1999). In comparison to other regions of the world, the Mediterranean basin is one of the most vulnerable to climate changes (Barceló and Sabater, 2010). In particular, Mediterranean rivers and streams are subjected to severe alterations in the flow regime because of a decreasing number of precipitation days and increase of heavy rain events. Resulting imbalance of available water during low flow periods (Acuña et al., 2014) and increasing anthropogenic pressures and demands for water lead to severe ecological and socioeconomic problems. As a consequence, water scarcity and its quality preservation are becoming important issues of Mediterranean countries.

The Llobregat River is situated in North East of Spain. Because of its proximity to the Barcelona town and its metropolitan area, the lowest course of the river receives strong anthropogenic pressures. Urban and industrial wastewater are discharged in Llobregat, in addition to the surface run-off coming from salt mining (both natural and caused by human activities) occurring in its middle basin. Diffuse pollution from agriculture is also present. In spite of the severe pressures received, this river constitutes the major supply source of drinking water for Barcelona and surrounding cities (ca. 3 million inhabitants). Furthermore, as a typical Mediterranean river, it is regularly subjected to periodic floods and drought periods. Overall, this results in reduced dilution capacity during the periods of water scarcity and increasing the potential risk to the aquatic ecosystem.

The Ebro river basin is located in the North East of Spain, and it is the largest river of the Iberian Peninsula in terms of flow discharge. It generates the Ebro Delta, a relevant wetland area (320 km^2) in the western Mediterranean region with a high ecologic value. The most important economic activity in the basin is agriculture (i.e., vineyards, cereals, fruit, corn and horticulture along the river and rice production in the delta). In the last century, the river flow has decreased ca. 40% due to land use change (reforestation and increase of irrigated agriculture) as well as precipitation decrease. Although it is not densely inhabited (ca. 2.8 million inhabitants), almost half of the population is concentrated in the big cities. Industrialized regions are mainly situated in the North and central part around big cities of Zaragoza, Pamplona and Lleida. The Ebro River receives urban contamination coming from the effluent discharges of many wastewater treatment plants (WWTPs).

The Júcar river basin is located in the East of Spain its population accounts approximately for 2.5 million inhabitants. Most of agricultural and industrialized areas are located in the medium and lower parts of the river basin. Because of the semiarid climate of this region, the

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