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Do pharmaceuticals bioaccumulate in marine molluscs and fish from a coastal lagoon?

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ABSTRACT

The bioaccumulation of 20 pharmaceuticals in cockle *(Cerastodema glaucum)*, noble pen shell (*Pinna nobilis*), sea snail (*Murex trunculus*), golden grey mullet (*Liza aurata*) and black goby (*Gobius niger*) was evaluated, considering their distribution throughout the Mar Menor lagoon and their variations in spring and autumn 2010. The analytical procedure was adapted for the different matrices as being sensitive and reproducible. Eighteen out of the 20 compounds analysed were found at low ng g^{-1} in these species throughout the lagoon. Hydrochlorothiazide and carbamazepine were detected in all species considered. The bioaccumulation of pharmaceuticals was heterogeneous in the lagoon, with a higher number of pharmaceuticals being detected in fish (18) than in wild molluscs (8), particularly in golden grey mullet muscle (16). B-blockers and psychiatric drugs were preferentially bioccumulated in fish and hydrochlorothiazide was also confirmed in caged clams. The higher detection frequency and concentrations found in golden grey mullet suggested that mugilids could be used as an indicator of contamination by pharmaceuticals in coastal areas. To the best of our knowledge, this is the first study that shows data about hydrochlorothiazide, levamisole and codeine in wild marine biota.

1. Introduction

In recent years, the number of studies reporting the occurrence of emerging contaminants in the marine environment has increased as a consequence of anthropogenic activities worldwide, the greater sensitivity of new analytical techniques and the rising scientific interest in this subject. The pressure and impact of organic pollutants are greater in coastal areas than in the rest of the marine environment, since these are where many human activities are concentrated and direct and indirect discharges occur (Sánchez-Bayo et al., 2011). Pharmaceuticals have frequently been detected in the aquatic environment in the range of low ng L^{-1} to low μg L^{-1} (Gros et al., 2012; Baker and Kasprzyk-Hordern, 2013; Bayen et al., 2013, 2014) and are considered as pseudo-persistent contaminants due to their degradation rate being lower than their access rate (Daughton, 2002). In the marine environment, the site conformation and hydrodynamic conditions largely determine the spatial distribution of marine pharmaceutical concentrations (Arpin-Pont et al., 2014) and they have predominantly been found in seawater (Weigel et al., 2004; Pait et al., 2006; Su et al., 2007; Xu et al., 2007; Wille et al., 2010; Yang et al., 2011; Zhao et al., 2011; Zou et al., 2011; Zhang et al., 2012, 2013; Zheng et al., 2012; Bayen et al., 2013; Rodríguez-Navas et al., 2013; Bayen et al., 2014; Xu et al., 2014; Moreno-González et al., 2015), but less so in sediment (Morales-Muñoz et al., 2005; Cueva-Mestanza et al., 2008; Landford and Thomas, 2011; Pintado-Herrera et al., 2013, 2014; Stewart, 2013; Na et al., 2013; Moreno-González et al., 2015).

Due to the general hydrophility of pharmaceuticals, their bioaccumulation potential can be considered irrelevant according to the criteria for accumulation proposed by the OECD, namely log K_{ow} (octanol-water partition coefficient) > 3 (OECD Guideline 315, 2008, Zenker et al., 2014). However, several authors reported that compounds with log K_{ow} < 2 can show high bioaccumulation (Le Bris and Pouliquen, 2004; Na et al., 2013), as has also been observed for pharmaceuticals in freshwater fish (Connors et al., 2013). In fact, the bioaccumulation of pharmaceuticals is not only determined by chemical lipophilicity but recent studies have also clearly pointed out other processes that participate in uptake and bioaccumulation, such as effects on animal homoeostasis (Van der Oost et al., 2003; Tierney et al., 2014; Daughton and Brooks, 2011; Meredith-Williams et al., 2012; Franzelliti and Fabbri, 2014), inhalational exposure as primary uptake (Du et al., 2014) and metabolization by gills (Gómez et al., 2010, 2011). Environmental pH can play an important role on their bioaccumulation since these

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compounds tend to bioaccumulate in a non-ionized state (Ratola et al., 2012). Nevertheless, sulphonamides showing anionic forms at environmental pH presented high values of BAFs (Kudwadkar et al., 2007). In addition to the physicochemical properties of the environment and of the compound, other factors also affect accumulation, such as biological processes (respiration, feeding, etc). Several studies have assessed the effects of pharmaceuticals and their bioaccumulation in fish (Triebskorn et al., 2007), molluscs (Almeida et al., 2014), crustaceans (Fong and Ford, 2014) or in edible animals (Azzouz et al., 2011; Federova et al., 2014) under controlled laboratory conditions. The majority of studies on wild fish focus on riverine and lacustrine fish (Brooks et al., 2005; Chu and Metcalfe, 2007; Ramirez et al., 2007, 2009; Schultz et al., 2010; Li et al., 2012a; Du et al., 2012; Wang and Gardinali, 2012; Huerta et al., 2013a; Valdés et al., 2014) or after exposing them to known sources of pollutants (Fick et al., 2010; Lajeunesse et al., 2011; Togunde et al., 2012). However, field data of the bioaccumulation of pharmaceuticals in marine organisms exposed to environmental conditions is rather sparse (Bringolf et al., 2010; Wille et al., 2011; Boxall et al., 2012; Li et al., 2012b; McEneff et al., 2013; Klosterhaus et al., 2013; Gaw et al., 2014; Dodder et al., 2014; Álvarez-Muñoz et al., 2015) and concentrations of pharmaceuticals in marine fish have only been determined in a small number of areas (Gelsleichter and Szabo, 2013; Maruya et al., 2012; Wang and Gardinali, 2012). Studies on wild marine molluscs have gained in frequency and interest in recent years (Cueva-Mestanza et al., 2008; Martínez-Bueno et al., 2013, 2014; Ronan and McHugh, 2013; McEneff et al., 2013; Na et al., 2013; Dodder et al., 2014; Álvarez-Muñoz et al., 2015). The fact that pharmaceutical bioaccumulation is now a hot research topic brings with it the need to address potential exposure scenarios in order to understand the risks of pharmaceuticals in the environment. To date the most widely studied and detected pharmaceuticals in biota have been psychiatric drugs (carbamazepine, citalopram, and fluoxetine), antibiotics (macrolides, quinolones and sulphonamides), non-steroidal drugs and anti-inflammatories (salicylic acid and diclofenac) and β-blockers (carazolol, propanolol, and sotalol), all of which are usually detected at low ng g^{-1} levels. For these reasons it is necessary to identify not only pharmaceuticals which can bioaccumulate but also the best sentinel species for these compounds. Coastal organisms such as mussels are indeed of high importance in environmental toxicology as sentinel species, and they are extensively used in well established monitoring programmes (CEMP and MED POL) for persistent pollutants due to their sessile nature, wide geographical distribution and high bioaccumulation capacity. However, there is no useful mussel population (very small specimens) for monitoring in certain areas, such as the Mar Menor lagoon. Consequently, there is a need to identify alternative indicator organisms for pharmaceuticals, as has been recommended for other pollutants (María-Cervantes et al., 2009; León et al., 2013) in studies that suggest the use of sea snail for trace metals and oyster for PAHs and pesticides, respectively.

The Mar Menor lagoon is the largest hypersaline (42–47 psu) coastal lagoon (135 km^2) in the Mediterranean Sea (SE Spain), and it is connected with the sea through only 3 channels. It is close to the Campo de Cartagena area, which is subject to intensive agriculture, seasonal tourism, recreational activities and a sporadic torrential rainfall regime (farming soils and mine residues). The input of pharmaceuticals in this lagoon through a watercourse (El Albujón Watercourse) has been previously confirmed (Moreno-González et al., 2014) and their occurrence and distribution in seawater and sediment from the lagoon have also been seasonally characterized (Moreno-González et al., 2015): 20 and 14 pharmaceuticals were found in seawater and sediments respectively, with cardiovascular system drugs, antibiotics and non-steroidal anti-inflammatory drugs being the most predominant. However, no information about the bioaccumulation of pharmaceuticals in wild aquatic organisms is available in this area.

The study of the transfer and bioaccumulation of pharmaceuticals in the marine food web is particularly interesting since only few studies have so far addressed this topic (Oaks et al., 2004; Du et al., 2014; Ding et al., 2015).

The aims of this study were therefore: a) to adapt a proposed analytical method for fish (Huerta et al., 2013a) in molluscs; b) to determine the concentration of pharmaceuticals in several wild aquatic organisms from the Mar Menor lagoon: cockle (*Cerastoderma glaucum*), noble pen shell (*Pinna nobilis*), sea snail (*Murex trunculus*), golden grey mullet (*Liza aurata*) and black goby (*Gobius niger*); c) to evaluate the variation of pharmaceutical concentrations in biota in spring and autumn, as a way of estimating the impact of seasonal human activities; d) to evaluate the bioaccumulation of pharmaceuticals in caged clams (*Ruditapes decussatus*) for a defined exposure time both in spring and autumn; and e) to estimate pharmaceutical bioaccumulation factors in these species from water and prey (biomagnification), in this case bioaccumulation in sea snail from cockle.

2. Materials and methods

2.1. Sampling campaigns and procedure: wild and caged organisms

Two sampling strategies were applied in the Mar Menor lagoon, the first consisting of wild mollusc and fish sampling and the second using caged clams transplanted from an area less exposed to pollution.

Wild biota was sampled in nine sampling areas from the Mar Menor lagoon (Fig. 1) and one nearby area in the Mediterranean Sea (MMREF), used as an external reference (Fig. 1). The sampling points MM1, MM10, MM15 and MM25 are close to urban nuclei or/and relevant ports in the lagoon, whereas MM11 is close to the El Albujón watercourse mouth (the main continuous flow of fresh water into the lagoon), which extends its influence to the south (MM18, MM21 and MM25) as a consequence of predominant circulatory currents (Pérez-Ruzafa et al., 2005). This watercourse is the main water collector in the drainage basin (Campo de Cartagena), and maintains a regular water flux due to the contribution of excess irrigation water, brackish waters from desalinization plants and treated wastewater effluents. Other areas are somewhat further away from the main identified pollution sources (MM23 and MM31). Whenever it was possible, two fish species (golden grey mullet and black goby), two bivalves (cockle and noble pen shell) and one gastropod (sea snail) were collected at each sampling area together with samples of surface sediment and seawater (Fig. 1). Moreover, noble pen shell was sampled where enough population density was present under the terms of the licence issued by the Protection and Nature Conservation Service of the Autonomous Community of the Region of Murcia (Spain), as it is a protected species (European Council Directive 92/43/ECC). In contrast, sea snails were widespread in the lagoon and were sampled at the majority of sampling points. Sampling campaigns were performed in June (spring) and November (autumn) 2010, in order to evaluate possible seasonal variations in pharmaceuticals bioaccumulation.

Golden grey mullet was entirely sampled by net, but the rest of species were hand-sampled by snorkelling. Biota samples were maintained at 4 °C and transported to the laboratory (less than 5 h), and stored at −20 °C until analysis.

In the case of cockle and golden grey mullet (muscle and liver) two size ranges were considered whenever possible (see Table 1). Specimens larger than 2 cm and 20 cm respectively were