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Assessment of non-steroidal anti-inflammatory and analgesic pharmaceuticals in seawaters of North of Portugal: Occurrence and environmental risk

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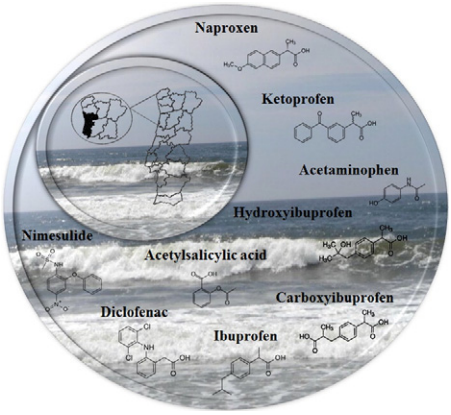
HIGHLIGHTS

- Occurrence of NSAIDs and analgesics in seawaters was followed during bathing season.
- NSAIDs and analgesics were detected in Portuguese seawaters.
- Pharmaceuticals were found in seawaters classified as excellent bathing water.
- Highest concentrations were detected in months of August and September.
- Diclofenac was detected at levels able to pose a risk for aquatic organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of seven pharmaceuticals and two metabolites belonging to non-steroidal anti-inflammatory drugs and analgesics therapeutic classes was studied in seawaters. A total of 101 samples covering fourteen beaches and five cities were evaluated in order to assess the spatial distribution of pharmaceuticals among north Portuguese coast. Seawaters were selected in order to embrace different bathing water quality (excellent, good and sufficient). Acetaminophen, ketoprofen and the metabolite hydroxyibuprofen were detected in all the seawater samples at maximum concentrations of 584, 89.7 and 287 ng L^{-1}, respectively. Carboxyibuprofen had the highest seawater concentration (1227 ng L^{-1}). The temporal distribution of the selected pharmaceuticals during the bathing season showed that, in general, higher concentrations were detected in August and September. The environmental risk posed by the pharmaceuticals detected in seawaters towards different trophic levels (fish, daphnids and algae) was also assessed. Only diclofenac showed hazard quotients above one for fish, representing a potential risk for aquatic organisms. These results were observed in seawaters classified as

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UHPLC–MS/MS
Environmental risk assessment

excellent bathing water. Additional data is needed in order to support the identification and prioritization of risks posed by pharmaceuticals in marine environment.

1. Introduction

In the last few years, a special attention has been given to the assessment of the presence of emerging pollutants in natural waters and their effects on ecosystems. As the analytical capacity has improved in order to allow the quantification of very low concentrations (e.g. in the ng L^{-1} range) with the high degree of certainty given by the use of tandem mass spectrometry, scientists have been able to quantify these xenobiotics in the aquatic systems (surface waters, ground waters, treated and untreated wastewaters and even tap waters) (Loos et al., 2010, 2013a).

Pharmaceuticals play an important role in assuring populations' health. However their use is not exempt from negative effects whose importance just more recently has been recognized. Indeed, every day tons of these compounds are loaded in the sewage systems and reach wastewater treatment plants (WWTPs). These have been mainly designed to remove suspended solids and organic loadings and their effect on the removal of micropollutants may be, in some cases, negligible. In fact, the removal efficiency of pharmaceuticals in WWTPs have been studied and a very wide range of values is observed, from compounds which pass these plants almost intact and others presenting a removal efficiency close to 100% (Kunkel and Radke, 2012). Their incomplete removal makes that there is a continuous discharge of pharmaceuticals into the environment, which may result in a chronic exposure of aquatic organisms to these compounds and/or their bioactive metabolites and transformation products. These products have shown, in some cases, quite similar toxicological consequences in aquatic environment.

Although the present knowledge in the occurrence and behaviour of pharmaceuticals in surface waters is well documented (e.g. Gros et al., 2006, 2012; Paíga et al., 2013; Rabiet et al., 2006), such knowledge in seawaters is still very limited and recent.

The presence of pharmaceuticals in seawaters has been evaluated in different geographical areas, namely in the North Sea (Weigel et al., 2002), Mediterranean Sea (Gros et al., 2012; Rodriguez-Navas et al., 2013; Togola and Budzinski, 2008), Adriatic Sea (Loos et al., 2013b) and in the Pacific (Vidal-Dorsch et al., 2012) and Indian Oceans (Fang et al., 2012; Wu et al., 2010). Several therapeutic groups were studied, including, for example, non-steroidal anti-inflammatory drugs (NSAIDs) (Gros et al., 2012; Wille et al., 2010), analgesics (Gros et al., 2012; Nödler et al., 2010), antibiotics (Nebot et al., 2007; Wille et al., 2010), β-blockers (Gros et al., 2012; Wille et al., 2010), lipid regulators (Fang et al., 2012; Gros et al., 2012) and psychiatric drugs (Gros et al., 2012; Wille et al., 2010). Diclofenac (Rodriguez-Navas et al., 2013), ibuprofen (Loos et al., 2013b), naproxen (Vidal-Dorsch et al., 2012), ketoprofen (Gros et al., 2012), salicylic acid (Wille et al., 2010), acetaminophen (Gros et al., 2012) and codeine (Gros et al., 2012) are among the most detected NSAIDs/analgesics in seawaters of the North, Mediterranean and Adriatic Seas and even in the Pacific and Indian Oceans at levels up to few hundred ng L^{-1}. Some examples of levels of NSAIDs/analgesics detected in seawaters are present in Table 1.

Recently, European Union established regulatory guidance to assess the presence of pharmaceuticals in the aquatic environment (Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC) (European Comission, 2013) as regards priority substances in the field of water policy. A watch list of pharmaceuticals including the sex hormones 17alpha-ethinylestradiol and 17beta-estradiol, and the NSAID diclofenac was created and is being updated with data gathered among the European Union countries. Regarding marine waters,

Table 1
Examples of concentrations of NSAIDS/analgesics found in seawaters.

Pharmaceutical	Seawater	Country	Concentration (ng/L^{-1})	Reference
Acetaminophen	Mediterranean Sea	Spain	23	Gros et al. (2012)
		France	~200,000	Togola and Budzinski (2008)
Diclofenac	North Sea	UK	<0.12	Nebot et al. (2007)
	Mediterranean Sea	Spain	4	Gros et al. (2012)
		Spain	n.d.–<LOQ	Rodriguez-Navas et al. (2013)
		France	~1500	Togola and Budzinski (2008)
	Indian Ocean	Singapore	4–38	Wu et al. (2010)
		Taiwan	<2.5–53.6	Fang et al. (2012)
Ibuprofen	North Sea	UK	<0.52	Nebot et al. (2007)
	Mediterranean Sea	Spain	16	Gros et al. (2012)
		France	~1500	Togola and Budzinski (2008)
	Adriatic sea	Italy	<0.049–1.146	Loos et al. (2013b)
	Indian Ocean	Singapore	41–121	Wu et al. (2010)
		Taiwan	<2.5–57.1	Fang et al. (2012)
Ketoprofen	Mediterranean Sea	Spain	<8.0	Gros et al. (2012)
		France	~6000	Togola and Budzinski (2008)
	Indian Ocean	Taiwan	<1.7–6.59	Fang et al. (2012)
Naproxen	Mediterranean Sea	Spain	6	Gros et al. (2012)
		France	~2000	Togola and Budzinski (2008)
	Pacific Ocean	USA	n.d.–26	Vidal-Dorsch et al. (2012)
	Indian Ocean	Singapore	13–30	Wu et al. (2010)
Acetylsalicylic acid	Mediterranean Sea	France	~8000	Togola and Budzinski (2008)
Salicylic acid	North Sea	Belgium	n.d.–855	Wille et al. (2010)
	Mediterranean Sea	Spain	2	Gros et al. (2012)
Mefenamic acid	North Sea	UK	<0.04	Nebot et al. (2007)
Indomethacine	Mediterranean Sea	Spain	3	Gros et al. (2012)
Phenazone	Mediterranean Sea	Spain	2	Gros et al. (2012)
Propyphenazone	Mediterranean Sea	Spain	<0.6	Gros et al. (2012)
Codeine	Mediterranean Sea	Spain	2	Gros et al. (2012)