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Baseline

Occurrence of alkylphenols and bisphenol A in wild mussel samples from the Spanish Atlantic coast and Bay of Biscay

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ABSTRACT

Wild mussels (*Mytilus galloprovincialis*) were selected as bioindicators of chemical pollution to evaluate the occurrence and spatial distribution of five endocrine disrupting compounds in the Spanish Atlantic coast and Bay of Biscay. A total of 24 samples were collected in May, 2011 and analysed by selective pressurized liquid extraction followed by liquid chromatography tandem mass spectrometry determination. Branched alkylphenols (4-*tert*-octylphenol and nonylphenol) were determined in more than 90% of the analysed samples whereas the presence of linear alkylphenols (4-*n*-octylphenol and 4-*n*-nonylphenol) was scarcely detected (<12% of the samples). Wastewater treatment plants discharges and nautical, fishing and shipping activities were considered the primary sources of contamination by alkylphenols. Bisphenol A was found in 16% of the analysed samples associated to punctual industrial discharges. A total endocrine disrupting compound (alkylphenols and bisphenol A) average concentration of 604 ng g^{-1} dw was calculated and nonylphenol was the main contributor in almost all sampling points.

Urban, industrial, agricultural and wastewater treatment plants (WWTP) discharges can contain many pollutants that pose risk to organisms and human health, especially in the case of endocrine disrupting compounds (EDCs) which affect the development, growth, reproduction and behaviour of human beings and wildlife at low concentrations (Zhang et al., 2011).

Alkylphenols (APs) and bisphenol A (BPA) are well-known EDCs used in industrial and household applications, particularly in plastic manufacture (plasticizers), and also in the production of textiles, paper and agricultural chemical products (Salgueiro-González et al., 2012). Because of their physical and chemical properties, these pollutants have moderate potential for their bioaccumulation in aquatic organisms (David et al., 2009).

To preserve the environment, maintain biodiversity and protect public safety, APs (4-octylphenols and 4-nonylphenols) were included in the list of 45 priority substances set in the new water Directive 2013/39/EU (Directive-, 2013/39). Although BPA was not included in water legislations, the use of this compound in plastic infant feeding bottles manufacturing was restricted by Directive 2011/8/EU (Commission Directive, 2011/2), showing its toxicity. Whereas the fate of the target EDCs in freshwater environment were extensively reported (Bennie et al., 1997; Brix et al., 2010; Pojana et al., 2007), their presence in marine complex is still limited (David et al., 2010). Nevertheless, these compounds should be controlled also in marine environment as it was established in Marine Strategy Framework Directive (MSFD) 2008/56/EC (Directive-, 2008/56). Consequently, researches based on the fate and behaviour of APs and BPA in marine ecosystem are required.

Marine monitoring programmes can be carried out by measuring pollutant concentrations both in seawater and in alternative matrices like sediments or aquatic organisms (European-Commission, 2011). Some biota species (such as bivalve molluscs) can bioaccumulate transient pollution present in the water column that is not recorded in sediments, being in these cases better pollution indicators. For this reason, and taking into account their ability to accumulate contaminants, their limited capacity for metabolizing them and their resistance to a wide range of pollutant levels, bivalve molluscs are commonly used as sentinel organisms (bioindicators) (Bouzas et al., 2011). In the case of the target compounds, no Environmental Quality Standards (EQS) for biota were set by Directive 2013/39/EU; however, a limit value of 10 mg kg^{-1} ww for NP and 4-tOP in edible organisms (biota tissue) was proposed in different technical documents (European-Commission, 2005a, 2005b).

Coastal and estuarine areas located in Spanish Atlantic coastline and Bay of Biscay are affected by touristic, industrial, fishing, shipping and aquaculture activities. These actions could be possible sources of contamination by the target compounds and therefore, the analysis of

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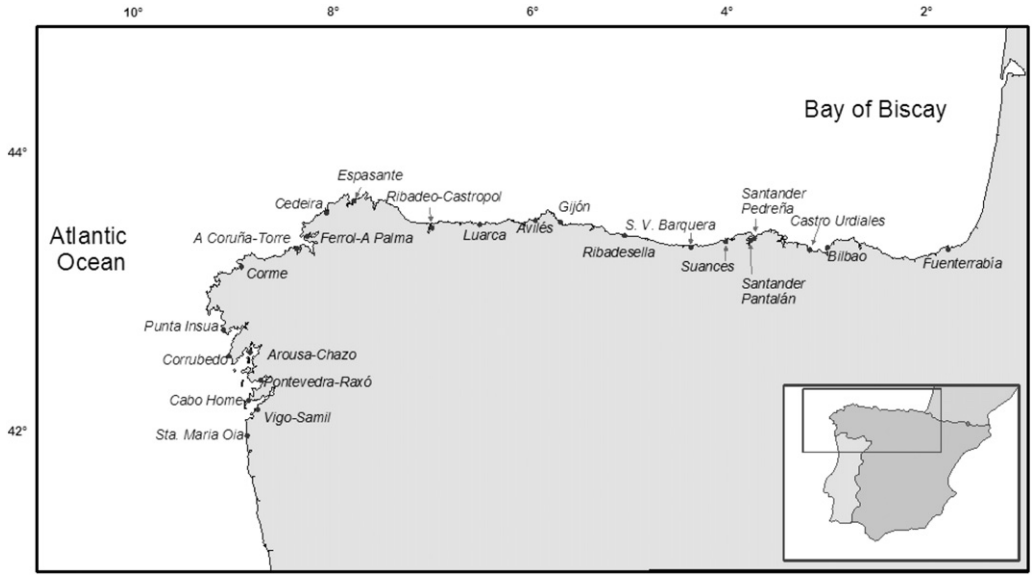

Fig. 1. Location of the 24 sampling points along the Spanish Atlantic coast and Bay of Biscay.

these EDCs seems to be interesting in these regions, according to Marine Strategy Framework Directive (MSFD) 2008/56/EC (Directive-2008/56). Although different pollutants such as metals, polycyclic aromatic hydrocarbons and organochlorine compounds (Bellas et al., 2014; Besada et al., 2014) were investigated in mussels from the Spanish Atlantic coast and Bay of Biscay, as far as we know no previous studies focused on APs and BPA in these areas were found in the literature.

In this work, wild mussel species (*Mytilus galloprovincialis*, *Lamarck 1819*) was selected to investigate APs (linear and branched isomers) and BPA contamination in Spanish Atlantic coastline and Bay of Biscay. To the best of our knowledge, the information about the presence of the target EDCs in these regions is still limited and consequently, more research about this topic is needed in order to understand their distribution and behaviour in these areas as well as background levels or locations of pristine areas. Moreover, the possible sources of contamination can be examined and recognized to control and minimize chemical pollution by APs and BPA if it was necessary, in order to ensure the good quality of marine environment. Furthermore, the obtained results could contribute to the feasible establishment of the EQS for these analytes in biota (Directive, 2013/39/EU) which are non-available at this moment because of the absence of data about APs and BPA in marine tissues samples.

Samples were collected in 24 sampling points located in the Spanish Atlantic coast and Bay of Biscay during May 2011, including different sub regions: Galicia (13 samples), Asturias (4 samples), Cantabria (5 samples) and Basque Country (2 samples), which are shown in Fig. 1. These areas are subject to the environmental impacts generated by touristic, industrial, fishing and aquaculture activities. Moreover, harbour and business labours such as maritime traffic and ship discharge also occur. Sampling points were chosen near possible sources of contamination as well as locations where no sources were known and "background levels" were expected.

Wild mussel analyses were made in pools of soft tissue (50 individuals), representing the available size (35–60 mm). After removing the shell, mussels were lyophilized and stored at −20 °C. Samples were extracted by selective pressurized liquid extraction (SPLE) followed by liquid chromatography tandem mass spectrometry determination, as it was previously described by Salgueiro-González et al. (Salgueiro-González et al., 2012). Briefly, 0.5 g of freeze-dried mussel samples was blended with a dispersing agent (C_{18}, 1.5 g) until homogenization and extracted with methanol at 40 °C using an ASE 200 instrument (Dionex, Sunnyvale, CA, U.S.A.). Neutral alumina (5% water deactivated, 3 g) was placed at the bottom of the extraction cell for the simultaneous clean-up of the co-extracts. The PLE extracts were reduced almost to dryness in a Syncore® Analyst evaporator from Büchi Labortechnik AG (Flawil, Switzerland) and redissolved in 1 mL of methanol before LC injection. Standard addition curves were used to ensure a reliable quantitation of the target compounds.

LC determination was performed using an Agilent HP-1200 Series LC system coupled to a mass spectrometer with a triple quadrupole detector and an APCI/ESI source (API 3200, Applied Biosystems, Carlsbad, CA,

Table 1
Analytical quality parameters of the selective pressurized liquid extraction-liquid chromatography tandem mass spectrometry methodology (Salgueiro-González et al., 2012).

Analyte	t_R	MS transitions	Accuracy	Precision (%)		Method limits	
			Recovery%	Repeatability (n = 7)	Intermediate precision(n = 10)	MDL (ng g^{-1} dw)	MQL (ng g^{-1} dw)
4-*tert*-octylphenol (4-tOP)	10.62	205 > 113 205 > 116	80	5	7	1.1	2.6
Nonylphenol (NP)	10.89	219 > 106 219 > 119	87	5	1	1.4	4.7
4-*n*-octylphenol (4-*n*-OP)	10.99	205 > 106	88	4	5	0.5	1.7
4-*n*-nonylphenol (4-*n*-NP)	11.23	219 > 113 219 > 116	93	4	6	0.8	2.3
Bisphenol A (BPA)	9.40	227 > 212 227 > 133	93	3	4	0.9	3.3

Accuracy and precision were evaluated at a concentration level of 50 ng g^{-1} dw.