Chemosphere 131 (2015) 241–247

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence of endocrine disrupting compounds in five estuaries of the northwest coast of Spain: Ecological and human health impact

N. Salgueiro-González [a], I. Turnes-Carou [a], L. Viñas-Diéguez [b], S. Muniategui-Lorenzo [a,*], P. López-Mahía [a], D. Prada-Rodríguez [a]

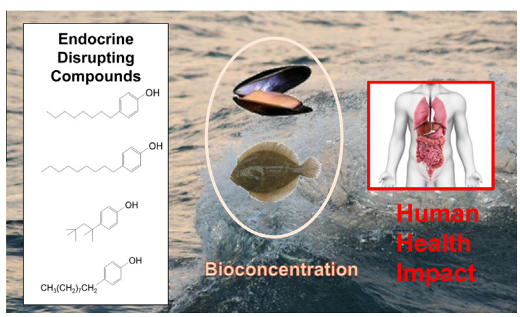
[a] Grupo Química Analítica Aplicada (QANAP), Instituto Universitario de Medio Ambiente (IUMA), Departamento de Química Analítica, Facultade de Ciencias, Universidade da Coruña, Campus de A Coruña, E-15071 A Coruña, Spain

[b] Centro Oceanográfico de Vigo, Instituto Español de Oceanografía, IEO, Subida a Radio Faro, 50, 36390 Vigo, Spain

HIGHLIGHTS

- First study about occurrence of APs and BPA in 5 estuaries of NW Spain.
- Harbours, WWTPs and industrial discharges main sources of contamination.
- 4-*tert*-Octylphenol water levels higher than EQS of Directive 2013/39/EU.
- Calculation of risk quotient. Low and medium ecological impact.
- Estimation of the possible risk to biota and human health. No risk was evidenced.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 17 December 2014
Accepted 19 December 2014
Available online 30 January 2015

Handling Editor: Caroline Gaus

Keywords:
Alkylphenols
Bisphenol A
Directive 2013/39/EU
Risk quotient
Human health impact

ABSTRACT

The occurrence and spatial distribution of alkylphenols (4-*tert*-octylphenol, 4-*n*-octylphenol, 4-*n*-nonylphenol, nonylphenol) and bisphenol A were examined in five estuaries along the Northwest coastal area of Spain. As far as we know, no previous works about this topic could be found in the literature. A total of 98 seawater samples were collected during May 2011–July 2012 and analyzed by a highly sensitive DLLME–LC–MS/MS methodology recently developed. Results indicated nonylphenol was the most ubiquitous compound with maximal concentration of 0.337 $\mu g\ L^{-1}$ (Ría de Vigo). The environmental quality standards (EQS) established in Directive 2013/39/EU for 4-*tert*-octylphenol were slightly exceeded in some sampling points. Fishing harbours, water treatment plant and industrial discharges were supposed as the main sources of contamination. Low and medium ecological risk was determined in all estuaries. Possible endocrine effects on biota and population were estimated in terms of estrogenic activity and daily intake respectively, and no risk was found in any case.

1. Introduction

Endocrine disrupting compounds (EDCs) have attracted public attention in the recent years due to their capability to affect the development, growth, reproduction and behaviour of human beings and wildlife (Diamanti-Kandarakis et al., 2009). Since 1999, European Commission has worked on the problem of endocrine disruption through the adopted strategy *"Community Strategy for Endocrine Disrupters – a range of substances suspected of interfering with the hormone systems of humans and wild life"* (EU, 1999) which try to identify its causes, consequences and a policy action to respond quickly and effectively to this problem. More recently, the United Nations Environment Programme (UNEP) and the World Health Organization (WHO) also published a full report in

* Corresponding author. Tel.: +34 981 167000; fax: +34 981167065.
E-mail address: smuniat@udc.es (S. Muniategui-Lorenzo).

http://dx.doi.org/10.1016/j.chemosphere.2014.12.062
0045-6535/

which exposure to endocrine disrupting compounds, sources and effects were considered (WHO, 2012).

A wide range of EDCs, such as alkylphenols (APs) and bisphenol A (BPA), have been identified in coastal and marine environments due to an incomplete elimination in sewage treatment plants, producing sexual dysfunction or cancer in organisms and changing the ecosystem balance at low concentrations (Sánchez-Avila et al., 2011).

These estrogenic EDCs are widely used in industrial and household applications. APs are used as plasticizers in high density polyethylene (HDPE), polyethyleneterephthalate (PET) and polyvinylchloride (PVC) and also in the manufacture of textiles, paper and agricultural chemical products (Salgueiro-González et al., 2012a). Meanwhile, BPA is used as a monomer for the production of epoxy resins, phenol resins, polycarbonates, polyesters and lacquer coatings for food cans (Ahn et al., 2007). Because of its toxicity, the use of this pollutant in plastic infant feeding bottles manufacturing was restricted by Directive 2011/8/EU of 28 January 2011 amending Directive 2002/72/EC (Directive, 2011).

In order to preserve and maintain the biodiversity of marine ecosystems, and protect public health, Marine Strategy Framework Directive (MSFD) 2008/56/EC (Directive, 2008a) requires from the Member States to establish and implement programs for monitoring of hazardous compounds in marine environment. Hence, both non-synthetic and synthetic compounds, such as priority substances under Water Framework Directive (WFD) 2000/60/EC (Directive, 2000) should be considered.

Taking into account the discharges, emissions, impacts and losses of hazardous substances (including APs), Environmental Quality Standards (EQS) were set in Directive 2008/105/EC (Directive, 2008b) and the recent Directive 2013/39/EU (Directive, 2013) with the aim of achieving a good surface water chemical status, according to the WFD.

However, the inclusion of BPA has been controversial. The Directive 2008/105/EC (Directive, 2008b) considered this compound as "possible future priority substance" while it was not prioritized by Directive 2013/39/EU (Directive, 2013). Toxicological effects of BPA have been demonstrated in human and animals (Venisse et al., 2014) and, furthermore, risk assessment models demonstrated that aquatic systems may not be protected from adverse effects at the current predicted no-effect concentration (PNEC) established value ($100\ \mu g\ L^{-1}$) (Wright-Walters et al., 2011). Consequently, and in our opinion, more studies are needed to take an adequate decision.

The ubiquity of the target compounds in freshwater ecosystem is well-known; however, data about the presence of these pollutants in marine environment is still limited. Coastal and estuarine areas are the most seriously affected by pollution impacts (urban, industrial and agricultural discharges) posing a risk to organisms and human health and therefore, the assessment of seawater quality is required.

APs and BPA were determined in different estuaries around the world (Ferguson et al., 2001; Pojana et al., 2004; Sánchez-Avila et al., 2011; Arditsoglou and Voutsa, 2012). Nevertheless, and as far as we know, no previous works related to the presence of these EDCs in the studied area (NW Spain) can be found in the literature.

The most important estuaries in terms of tourism and industrial, fishing, shipping and aquaculture activities, such as mussel and oyster farming (located in Galician and Cantabrian coast) are considered in this research. In fact, Galicia is the first European producer of cultured mussels, with an annual production of 250000 tons (135×10^6 Euros); moreover, shellfish production in this region ranks first in Spain, with more than 10% of the total production (Quelle et al., 2011).

The main objectives of this paper are: (1) to comprehensively investigate the occurrence and spatial distribution of APs (including linear isomers) and BPA in five estuaries in the NW of Spain, located in Galician Atlantic coast (*Ría de Arousa*, *Ría de Vigo*, *Ría de Pontevedra and Ría de A Coruña*) and Bay of Biscay (*Santander*) which are affected by urban, agricultural, industrial and marine activities. For the first time, data on the level of these compounds in these regions are provided; (2) to evaluate the possible anthropogenic sources of pollution in these estuaries in order to control and minimize them; (3) to assess the environmental impact that these pollutants pose to aquatic system, determining the ecological risk quotient; (4) to estimate the possible endocrine effects of these EDCs on biota and population of these areas.

2. Materials and methods

Information about chemicals and suppliers is provided in Supplementary Material.

2.1. Study area and sample collection

As it can be seen in Fig. S1, different coastal areas located in the Northwest of Spain were selected according to their industrial and urban development. Four of the largest "rías" (coastal inlets formed after some river valleys sunk) in Galicia were investigated: Ría de Arousa (37 samples), Ría de Vigo (38 samples), Ría de Pontevedra (11 samples) and Ría de A Coruña (8 samples). One sampling area situated in Santander/Bay of Biscay (4 samples) was also considered. The location of the sampling points in each area can be seen in Fig. S2. It is known that these areas are subject to the socioeconomic impacts generated by touristic, industrial, fishing and aquaculture activities. Furthermore, harbour and business activities such as maritime traffic and ship discharge also occur.

The studied area consists of coastal and transitional waters; in the transition zone between land and ocean, morphology parameters reflect historical and present-day changes in sea level, human activities within the coastal area, river loads and sediment (Besada et al., 2008). Sampling points were chosen near possible sources of contamination as well as locations where no sources were known and "background levels" were expected.

Water samples were collected during May 2011–July 2012. Glass containers (2L) previously precleaned were used for the sampling and stored refrigerated at 4 °C before the analysis. Due to the low stability of APs and BPA (Salgueiro-González et al., 2012a), samples had to be analyzed within five days of their sampling.

2.2. Sample preparation and analytical determination. QA/QC

Samples were analyzed according to an analytical methodology previously published (Salgueiro-González et al., 2012b), based on a dispersive liquid–liquid extraction (30 mL of non-filtered seawater samples) followed by a high performance liquid chromatography-tandem mass spectrometry determination (DLLME–HPLC–MS/MS). More details about analytical methodology can be found in Supplementary Material.

QA/QC was performed to ensure reliable results in the analysis. As these compounds were used as plasticizers and/or surfactants, plastic material and detergents were discarded to avoid contamination and blank problems. Furthermore, glassware was carefully washed with acetone, Milli-Q water and methanol prior to use (Salgueiro-González et al., 2012a). All procedural blanks were far below that previously established method quantitation limits (MQL) showed in Table S1.