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Endocrine Disruptors in Estuarine Environments: We Still Need a Simple and Cost-Effective Framework for Environmental Monitoring

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Introduction

Due to runoffs, urban and industrial effluent discharges into the aquatic environment (both inland and costal), emergent pollutants like pharmaceuticals, pesticides and corresponding by-products, natural and artificial hormones and several industrial chemicals (e.g. alkylphenols, phthalates, bisphenol A, polychlorinated biphenyls) are starting to be detected at environmental concerning concentrations in several ecosystems [1,2]. River estuaries, in particular, are known for their high productivity, ecological value and for the functions they perform (e.g. food production) [3]. Thereby, the estuarine pollution is one of the most worrying [4], being highly affected by direct discharges and activities as well as by upstream contamination.

Some of the emergent compounds are endocrine disruptor chemicals (EDCs), as they interfere with the normal functioning of the endocrine system of invertebrates and vertebrates (fish, birds and reptiles), causing abnormalities in the reproductive system of animals, intersex gonads, changes in the expression patterns of genes involved in the synthesis of sexual hormones and of vitellogenin, reduction in the quantity of sperm, decrease in outbreaks of eggs delayed metamorphosis as well as changes in growth and behavior [5-11]. In humans, these effects include a reduction in sperm count, increased incidence of breast, testicular, prostate cancer and endometriosis [12]. Unfortunately, these pollutants resist to conventional treatments in water treatment plants [13] and several studies arise reporting meaningful concentrations of several EDCs in estuaries around the world, both in water and sediment compartments. For instance estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2) have been found in different estuary waters and animals in Portugal [14-16], Spain [17], Australia [18], China [19] and Argentina [20], always in concentrations in the range of ngL^{-1}. Nonylphenol (NP) is another endocrine disruptor, resulting from the environmental breakdown of nonyphenol-oxylates (NPEO) which are important industrial surfactants, was also largely detected in Chinese rivers [13,21] as well as in Portugal [22] in the range of ngL^{-1} too. Despite the low range of concentrations and although mixture effects cannot be discarded, EDCs have proved to be able to cause meaningful effects on biota. Further, the few PNEC (Predicted No Effect Concentrations) values available for some EDCs, derived based on species sensitivity distribution curves [e.g. EE2 – 0.1 ngL^{-1} [23]; E2 – 2 ngL^{-1} [23]; E1 – 6 ngL^{-1} [23]; BPA – 1.5 gL^{-1} [24]; NP – 0.48 and 0.28 gL^{-1} for freshwater and marine organisms, respectively [25], provide an additional evidence of the high hazardous potential of each EDCs individually.

Table 1 summarizes some of the endocrine disruptors found around the world, accordingly some recent published studies and, with a brief calculation of hazardous quotients (HQ) using available PNECs it is possible to perceive that, considering each EDC individually high risks are expected for aquatic biota in almost all the systems monitored, since HQ highly greater than 1 were recorded.

Another important point to be noted is the importance of developing analytical techniques to detect and identify these pollutants in low concentrations [19] in estuarine sediments and water. Available studies already provide a very relevant amount of ecotoxicological data that could be compiled to support the development of a simple and cost-effective framework for monitoring EDCs in the environment. Such framework should include sensitive bio indicator species and sensitive, reliable and highly specific biomarkers to monitor the exposure and the effects of concerning concentrations of ECDs mixtures in the environment. The Organization for the Economic Cooperation and Development (OECD) has already developed a conceptual framework for screening and testing chemicals for endocrine disruption [26], which will be crucial for registration and authorization purposes, as well as for the derivation of threshold values (PNECs) for a high number of EDCs. However, it is necessary to provide a tool-box and guidance to those involved in the management of water bodies, to track for concerning situations in a routine basis and to create an early warning system based on the analysis of the main discharges of a particular water body.

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EDCs	Estuary	Concentrations ng L^{-1} or ng g^{-1}	Environmental matrix	HQs	References
17β-estradiol (E2)	Douro River (Portugal)	≅ 5.5	Water	≅ 2.75	[22]
	Río de la Plata (Argentina)	369.0	Water	184.5	[20]
	Yangtze River (China)	<0.30	Sediment	-	[27]
	Mondego River (Portugal)	2.8	Water	1.4	[28]
17α-ethynylestradiol (EE2)	Ave River (Portugal)	>10.0	Water	-	[14]
	Little River (Australia)	<0.2	Water	-	[18]
	Río de la Plata (Argentina)	43.0	Water	430	[20]
	Yangtze River (China)	<0.1	Water	-	[27]
	Yangtze River (China)	<0.7	Sediment	-	[27]
	Mondego River (Portugal)	4.4	Water	44	[28]
Nonylphenol	Ave River (Portugal)	>250.0	Water	-	[14]
	Sado River (Portugal)	>230.0	Water	-	[15]
	Douro River (Portugal)	>550.0	Water	-	[22]
	Daliao River (China)	83.6-777.0	Water	0.17-1.6	[23]
	Daliao River (China)	1.5-456.0	Sediment	-	[23]
	Taiwan	<3.3-1178.7	Water	0.007-2.46	[29]
	Mondego River (Portugal)	18.1	Water	0.04	[28]
	Nakdong River (Korea)	137.1-10931.5	Water	0.29-22.8	[30]
	Suyoung River (Korea)	144.0- 2469.6	Water	0.3-5.1	[30]
	Bay of Biscay, Gernika (Spain)	91.9-193.7	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	197.8-257.2	Sediment	-	[31]
nonylphenol diethoxylate	Sado River (Portugal)	>900.0	Water	-	[15]
	Douro River (Portugal)	>2000.0	Water	-	[22]
	Leça River (Portugal)	>2 mgL^{-1}	Water	-	[16]
	Mondego River (Portugal)	6.6	Water	-	[28]
	Taiwan	<1.2-238.4	Water	-	[29]
sitosterol	Ave River (Portugal)	>6.0	Water	-	[14]
	Mondego River (Portugal)	3.1	Water	-	[28]
Estrone (E1)	Sado River (Portugal)	>10.0	Water	-	[15]
	Leça River (Portugal)	>10.0	Water	-	[16]
	Little River (Australia)	2.5-23.2	Water	0.42-3.86	[18]
	Yangtze River (China)	<1.5	Water	-	[27]
	Yangtze River (China)	<1.9	Sediment	-	[27]
	Mondego River (Portugal)	3.2	Water	0.53	[28]
Tributyltin	Bay of Biscay, Gernika (Spain)	8.0-28.0	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	1599.0-9377.0	Sediment	-	[31]
Bisphenol A	Daliao River (China)	29.2-124.0	Water	<<1	[23]
	Daliao River (China)	3.7-25.3	Sediment	-	[23]
	Yangtze River (China)	0.98-43.8	Water	<<1	[27]
	Yangtze River (China)	1.2-6.5	Sediment	-	[27]
	Mondego River (Portugal)	2.4	Water	<<1	[28]
	Bay of Biscay, Gernika (Spain)	0.01	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	0.04	Sediment	-	[31]
4-*t*-butylphenol	Daliao River (China)	3.4-10.6	Water	<<1	[23]
	Daliao River (China)	1.9-2.1	Sediment	-	[23]
4-*t*-Octylphenol	Daliao River (China)	0.5-25.6	Water	-	[23]
	Daliao River (China)	0.7-12.1	Sediment	-	[23]
	Mondego River (Portugal)	4.8	Water	-	[28]
	Dahan River Taiwan	<1.0-1458.7	Water	-	[29]
	Bay of Biscay, Gernika (Spain)	<0.01	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	0.02	Sediment	-	[31]
4-n-octylphenol	Mondego River (Portugal)	2.0	Water	-	[28]
2,4-dichlorophenol	Daliao River (China)	4.6-63.4	Water	-	[23]
	Daliao River (China)	1.2-2.6	Sediment	-	[23]
Formononetin	Mondego River (Portugal)	8.6	Water	-	[28]
Biochanin A	Mondego River (Portugal)	4.6	Water	-	[28]
Daidzein	Mondego River (Portugal)	4.1	Water	-	[28]
Genistein	Mondego River (Portugal)	3.8	Water	-	[28]

Dibutyltin	Bay of Biscay, Gernika (Spain)	3.0-4.0	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	463.0-2380.0	Sediment	-	[31]
Monobutyltin	Bay of Biscay, Gernika (Spain)	4.0-7.0	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	116.0-503.0	Sediment	-	[31]
Diethyl phthalate	Bay of Biscay, Gernika (Spain)	2551.3-6218.1	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	484.1-1665.0	Sediment	-	[31]
Dibuthyl phthalate	Bay of Biscay, Gernika (Spain)	998.23-1010.1	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	175.6-736.6	Sediment	-	[31]
Di-2-ethylhexyl phthalate	Bay of Biscay, Gernika (Spain)	688.0-8871.2	Sediment	-	[31]
	Bay of Biscay, Arrilluze (Spain)	1484.2-2529.7	Sediment	-	[31]

Table 1: Environmental concentrations of some endocrine disrupting chemicals (EDCs) in water and sediments of different world river estuaries and corresponding hazard quotients (HQ) calculated based on available PNEC values (HQ=Environmental concentration/PNEC).

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