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Endocrine disruptors: strategies for determination and occurrence in marine environments *

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ABSTRACT

Research examining the occurrence of endocrine disruptors (ED) in the marine environment has substantially increased. These contaminants have been observed in several environmental compartments and matrices, and they may cause severe adverse effects in humans and ecosystems. In this study more than 240 papers investigating the analytical developments regarding the analysis on ED in environmental matrices and the occurrence of these compounds were critically evaluated. Modern sample preparation procedures aiming the use of minimal sample manipulation, minimal amount of solvents and energy according to the Green Chemistry principles are widely used. The ED in marine environments occurs in trace concentrations and their quantification still represents a challenge. The effects of these contaminants in marine ecosystems are poorly understood. However, due to their large use, it is predicted that new analytical developments to deal with ED contamination will promote a large increase in the number of scientific publications in the near future. Regulations and mitigation measures for the presence of these contaminants in the environment are still scarce and need to be quickly implemented to reduce potential future adverse effects on ecosystem services of coastal environments.

Keywords: Emerging contaminants; Endocrine disrupters; Contamination; Sample preparation; Environmental analysis

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RESUMO

Pesquisas que examinam a ocorrência de interferentes endócrinos (IE) no ambiente marinho têm aumentado substancialmente. Estes contaminantes podem causar efeitos adversos em seres humanos e nos ecossistemas e têm sido observados em vários compartimentos e matrizes ambientais. Neste estudo, mais de 240 trabalhos que relataram o desenvolvimento analítico de IE em diversas matrizes e a ocorrência destes compostos no ambiente marinho foram criticamente avaliados. Procedimentos de preparo de amostra, visando a mínima manipulação, a mínima quantidade de solventes e energia de acordo com os princípios de Química Verde estão sendo amplamente utilizados. Os IE em ambientes marinhos ocorrem em concentrações traço e sua quantificação ainda representa um grande desafio. Como resultado, os efeitos desses contaminantes em ecossistemas marinhos ainda são mal compreendidos. No entanto, devido ao amplo uso destes compostos é previsto que novos desenvolvimentos analíticos para a determinação de IE irão promover um grande aumento no número de publicações científicas no futuro. Regulações e medidas mitigadoras para a ocorrência destes contaminantes ainda são bastante reduzida e precisam ser rapidamente implementadas para reduzir os futuros potenciais efeitos adversos nos serviços ecossistêmicos dos ecossistemas costeiros.

1. Introduction

The lifestyle adopted by humans in the modern society has favored the occurrence of continuous physical, chemical and biological changes in the environment. The contamination of water bodies due to the presence of domestic and industrial wastewater, water runoff and agricultural activities stand out among the major human impacts on the coastal zones. Thousands of substances (e.g., pharmaceuticals, personal care products, surfactants, nanomaterials, metals, phthalates, and hydrocarbons, among others), which have allegedly subsidized the improvement of the quality of human life and ensured the growth of activities such as aquaculture and agriculture, are produced and released in the environment.

The development of new analytical techniques of separation, identification and quantification of substances (e.g., high performance liquid chromatography (HPLC) coupled to mass spectroscopy, among others) has allowed the identification of a large number of compounds in samples of water, air, sediments and biological tissues so far unknown (Locatelli *et al*., 2016; Casatta *et al*., 2015; Emnet *et al*., 2015; Benjamin *et al*., 2015; Cai *et al*., 2012a, 2012b; Bartolomé *et al*. 2010; Richardson & Ternes, 2011; Rubio & Pérez-Bendito, 2009). The sensitivity of many analytical techniques has improved, reducing the limits of detection from parts per million to parts per trillion and, in some cases, to parts per quadrillion (Huerta *et al*., 2015; Bhandari *et al*., 2009). As a result, the potential for studying traces of contaminants in the environment, especially in complex matrices, such as seawater, has also increased. The substantial improvement in analytical sensitivity enabled the detection of a series of compounds known, generically, as emerging contaminants (EC). Emerging contaminants can be defined as a class of natural or synthetic chemicals, or any group of microorganisms that are not naturally found in the environment (Richardson & Ternes, 2011; EPA, 1997). In general, the ECs are present unknown toxicity, large industrial production and they are ubiquitous in the environment (Birch *et al*., 2015; De la Cruz *et al*., 2012; Deblonde *et al*., 2011; Bhandari *et al*., 2009). ECs are not necessarily new compounds, they are input in environment for several years. However, the identification and quantification of these compounds was only possible after the development of new analytical techniques that allows detection of trace and ultratrace concentrations.

Among the emerging contaminants, a number of compounds have been receiving special attention from the scientific community, due to their potential capacity of interfering with the functioning of the endocrine system of organisms. The literature uses several names for these compounds: xenobiotics, pseudo-estrogens, pseudo-androgens, endocrine disruptors (ED), and interfering endocrines (Lisboa *et al*., 2013; Menzies *et al*., 2013; Grassi *et al*., 2013; Ghiselli & Jardim, 2007; Lathers, 2002; Kardinaal *et al*., 1997). Many of them are not degraded or broken down by any biochemical and/or natural photochemical pathways and may also undergo bioaccumulation and/or biomagnification (Colin *et al*., 2016). In this paper, this group of compounds will be referred to as endocrine disruptors.

Several contaminants, both organics and inorganics, have their ecotoxicological profiles and modes of action well determined. As a result decision makers can plan accordingly in order to regulate their use, minimize adverse effects for the provision of ecosystems services or even ban some compounds. The literature has already showed examples of the positive effect of such regulations in contamination levels in the environment. For instance, Sutton *et al*. (2014) observed declines in Polybrominated compounds in sediment and biota of San Francisco Bay. However, for most of the EDs dealt in this manuscript it still is necessary a better knowledge and understanding of the environmental cycles and toxicity in order to subsidize the development of regulations and management practices.