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Review

Sensors and biosensors for monitoring marine contaminants

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ABSTRACT

The marine environment plays an important role in the global climate regulation, mainly as a major source of biodiversity. However, the climate change and the human activity impacts have increasingly disrupted the natural balance in marine environment. The European Union, through the commitment undertaken in 2008 by the Marine Strategy Framework Directive (MSFD) determined to take until 2020 every necessary step to achieve a healthy marine environment. Thus, the continuous monitoring of contaminants at low concentrations is of great importance for the environmental protection. In this field, the marine sensors and biosensors have been identified as potentially important analytical devices using technological developments such as miniaturized electronics, small scale networks, and wireless communication in order to produce advanced analytical tools for the continuous monitoring of the 'good environmental status' of the marine environment. This overview provides a state of the art of sensors and biosensors for monitoring contaminants in marine waters.

Contents

1. Introduction

The marine environment plays an important role in the global climate regulation, being a major source of biodiversity. The marine resources can be used to obtain new products and develop new services, presenting potential solutions regarding the challenges that affect our planet, including a sustainable supply of food and energy, new industrial materials and processes, new bioactive compounds, and new health treatments [1]. However, the marine environment is also increasingly vulnerable to climate change, and human activities impacts attendant on industrial, tourist, and urban development [2]. The Integrated Maritime

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Policy was proposed in 2007 in order to enhance the sustainable development of the European maritime economy to the "Europe 2020", with the following priorities: (a) a smart growth, developing an economy based on knowledge and innovation; (b) a sustainable growth, promoting a more resource efficient, greener, and more competitive economy; and (c) an inclusive growth, fostering a high-employment economy delivering social and territorial cohesion [3,4]. Furthermore, the most important initiative of the European Union was the Marine Strategy Framework Directive (MSFD), undertaken in 2008, where every necessary step to achieve a healthy, protected, and preserved marine environment was agreed to be taken until 2020 [5].

This review paper has the objective of reviewing the state of the art of current sensors and biosensors (2008–2015) over other analytical methodologies used for monitoring the contaminants in the marine waters which are covered by the MSFD, as well as other contaminants with a potential for screening the marine water quality.

2. The Marine Strategy Framework Directive (MSFD)

The objective of the MSFD is to achieve or maintain a good environmental status in the marine environment by the year 2020 at the latest (Art. 1 of MSFD) [5], being the GES defined in the MSFD as the environmental status of marine waters where these provides ecologically diverse and dynamic oceans and seas which are clean, healthy, and productive, allowing the use of the marine environment to a sustainable level, therefore protecting its potential for current and future generations. The definition of GES is based upon 29 criteria and 56 indicators specified for 11 high-level qualitative descriptors by the Commission Decision of 1 September 2010 [6] on criteria and methodological standards on good environmental status of marine waters. For that purpose, the MSFD suggests the development and implementation of marine strategies to the protection and preservation of the marine environment, preventing its deterioration and reducing inputs to phasing out pollution, also ensuring that there are no significant impacts on or risks to marine biodiversity, marine ecosystems, human health or legitimate uses of the sea" (Art. 1(2) of MSFD) [5].

The marine strategies consist in two major tasks, that is, the preparation and the programme of measures. The preparation includes: (a) the analysis of essential features and characteristics (*e.g.*, physical, biological, and chemical features, as well as habitat types and hydro-morphology), analysis of predominant pressures and impacts on the environmental status of marine waters, as well as economic and social analysis of the use of the waters and of the cost of degradation of the marine environment, by each Member State; (b) determination of good environmental status; (c) establishment of environmental targets and associated indicators; and (d) establishment and implementation of monitoring programs. The program of measures consists in the development of measures to achieve or maintain GES. Under the MSFD and in order to assess the achievement of a GES, the concentrations of contaminants must be at levels not giving rise to pollution effects, being the concentration of contaminants in the marine environment (listed as priority substances in Annex X of the Directive 2000/60/EC [7] and further regulated in Directive 2008/105/EC – Annex II [8]) and their effects need to be assessed considering the impacts and threats to the ecosystem [6]. The task group 8 report from the European Commission [9] referred that the combination of new and conventional effect-based methodologies with the assessment of environmental concentrations of contaminants provides a powerful and comprehensive approach and recommended three core elements for data assessment: (a) concentrations of contaminants in water, sediment and/or biota are below environmental target levels identified on the basis of ecotoxicological data; (b) levels of pollution effects are below environmental target levels representing harm to the organism, population, community and ecosystem levels; and (c) concentration of contaminants in water, sediment and/or biota, and the occurrence and severity of pollution effects, should not be increasing. In addition, "The Ocean of Tomorrow 2013" [10] referred that the development of competitive and innovative marine technologies is necessary to assess and monitor the good environmental status of the seas, contributing to their sustainable operation. In particular, sensing technologies are necessary to improve reliable measurements of key parameters in the sea, being the biosensors for real time monitoring of biohazard and man-made chemical contaminants in the marine environment and the innovative multifunctional sensors for *in situ* monitoring of marine environment and related maritime activities, two of the joining research forces to meet challenges in ocean management [10]. Thus, the development of early warning systems such as small-scale sensor technologies is urgently required in order to provide selective and sensitive detection of marine contaminants.

3. Contaminants of concern for obtaining good environmental status of marine waters

According to Law et al. [9], contaminants are defined as substances (*i.e.*, chemical elements or compounds) or groups of substances that are toxic, persistent, and liable to bioaccumulate, and other substances or groups of substances, which give rise to an equivalent level of concern. Furthermore, chemical contaminants are commonly classified as: (a) stable trace elements, such as cadmium, lead, mercury, and tin; (b) organic substances, such as persistent organic pollutants, hormones, veterinary medicines, and pharmaceuticals; (c) hydrocarbon pollution as fuel, crude oil, and oil products; and (d) radionuclides [9]. On the other hand, several factors should be considered in order to monitor the marine environment, such as contaminant nature, sources, distribution, concentration, persistence, uptake into biota, and effect on ecosystem [11]. Thus, the monitoring of contaminants for the protection of the marine environment is the purpose of the Descriptor 8 under the MSFD, also being an urgent concern in marine research.

Concerning the contaminants which are hazardous substances, the MSFD (Annex III, Table 2) [6] considered as contamination, the introduction of: (a) synthetic compounds (*e.g.*, priority substances under the Directive 2000/60/EC [7], which are relevant for the marine environment such as pesticides, pharmaceuticals, anti-foulants); (b) non-synthetic substances and compounds (*e.g.*, heavy metals and hydrocarbons); and (c) radionuclides. Thus, the Directive 2000/60/EC [7] has included a list of 33 priority substances/groups of priority substances and among them 20 considered as priority hazardous substances (H), which are listed in Table 1. Recently, such list was revised in Report COM(2011) 875 [12] and 15 additional priority substances (among them 6 hazardous priority substances) was included, as also shown in Table 1.

It should be referred that in the MSFD, there are no specifications for monitoring frequency, since the cycle of assessment, determination of GES, target setting, monitoring and establishment of measures should be reviewed and updated every six years [13]. However, some indicators should be assessed and monitored with high data acquisition frequency, such as in the case of priority substances with a frequency of one month [13].

4. Current marine strategies for monitoring contaminants in marine waters

There are several strategies and tools employed for the assessment of marine environment, *i.e.*, in sampling, observation