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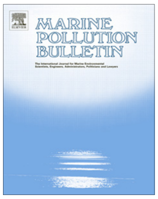

Application of a new integrated sediment quality assessment method to Huelva estuary and its littoral of influence (Southwestern Spain)

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ABSTRACT

A new integrated sediment quality assessment method composed of several assays (particle size profile, total metal content, protease K extraction, total organic carbon, toxicity bioassay with *Photobacterium phosphoreum* and macrobenthic community alteration) that provides a single result, the environmental degradation index (EDI), has been developed. The new method was tested on the Huelva estuary (southwest of Spain), a highly polluted area where metals dissolved in the water of the Tinto and Odiel rivers precipitate after flowing through the Iberian Pyrite Belt, one of the largest metallogenic areas of massive sulphide deposits in the world.

The proposed method satisfactorily was able to reflect different degrees of pollution on the environmental degradation index. Thus, EDI categorized littoral samples as slightly degraded and all the Tinto and some of the Odiel as very highly degraded, emphasizing the lower zone of the Tinto estuary as the most deeply degraded of the entire study area.

1. Introduction

Aquatic ecosystems have suffered the discharge of large amount of waste for decades (Salomons et al., 1987), and pollution is reaching worrying levels in some areas (Soto-Jiménez and Páez-Osuna, 2001). Pollutants are present in aquatic ecosystems in both water and sediments, where they accumulate over time and can reach concentrations that are much higher than those in the water.

However, changes in pH, redox potential, or other environmental conditions can release a portion of the contaminants retained in the sediments and re-solubilize them in water (Ashokkumar et al., 2009). Thus, sediments may act as a sink or a source of contamination and, in the latter case, may affect aquatic life that live, feed and reproduce there, or even humans, through the food chain. Because of this mechanism, contaminants in the sediments of aquatic ecosystems have become one of the most important environmental problem at present (Sainz and Ruiz, 2006; Chapman and Wang, 2001; Ruiz et al., 2008).

In aquatic ecosystems, sediments are the main sink for trace elements, such as heavy metals, and can reach levels many times higher than water column concentrations (Ridgway and Shimmield, 2002). Trace elements are bioavailable and persistent in the environment causing bioaccumulation and toxicity effects in the biota. Typically, benthic invertebrates start bioaccumulation because of their close association with sediments and transfer them to higher trophic levels (Burgos and Rainbow, 2001). The uptake of trace metals by benthic organisms depends largely on their chemical forms (Morillo et al., 2008).

People's awareness of environmental issues, particularly the pollution of aquatic sediments, has led to the development of new methods for assessing their environmental quality, such as chemical analysis, bioavailability, toxicity and alteration of the macrobenthic communities. Nevertheless, each of these alternatives individually only provides partial information on the environmental quality of the studied ecosystem and is insufficient to give a clear idea of its general status. The latter requires to fully answer the three basic questions that arise in environmental assessment studies (Chapman, 1992): (i) What kinds of contaminants are present in the ecosystem? (ii) What are the levels of these pollutants? (iii) What biological effects do they have on the ecosystem?

Integrated sediment quality assessment methods are used to answer these questions (Ghirardini et al., 1999; Chapman, 2002; Cherry, 2001; DelValls et al., 1998; Anderson et al., 2003). These methods consist of a group of the above simple methods, ensuring that each provides as much information as possible and that they are used in such a way that they complement each other (Chapman, 1995). Thus, the correlation between the results

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obtained by different methods provides higher quality information than when they are employed separately (Chapman, 1995).

This research has two main objectives. First, to develop a new integrated sediment quality assessment method that can be implemented over a wide area: applicable to all kinds of sediments, simple, low-cost and with an easily understandable and comparable result. Second, to implement the proposed integrated sediment quality assessment method for the Huelva estuary and its littoral of influence, where natural and anthropogenic sources of pollutants and areas of high ecological and economic value coexist in a relatively small zone.

2. Huelva estuary

The Huelva estuary is located in the southwest of Spain, along the municipalities of Huelva, Punta Umbria and Palos de la Frontera. It is formed by the confluence of the rivers Tinto and Odiel and consists of estuaries of both rivers and the Padre Santo Canal (Fig. 1). The estuary of the Odiel has a secondary outlet to the sea known as Punta Umbria estuary. Its waters are influenced by flows from the Tinto and Odiel rivers and by seawater from the Atlantic Ocean.

The Huelva estuary empties into the Atlantic Ocean in the area known as the Huelva littoral. This 145 km-long coast is bounded by the mouths of two major rivers, the Guadiana and the Guadalquivir. The prevailing currents in this area are from west to east and causes littoral drift, a process by which water and sediments are transported along the shoreline. Littoral drift has a high carrying capacity of materials whose deposition tends to fill any irregularities, leaving a smooth and straight coastline, interrupted only by river mouths.

The Tinto and Odiel rivers flow through the Iberian Pyrite Belt, one of the largest metallogenic areas of massive sulphide deposits in the world (Galán et al., 2003; Leistel et al., 1997). Thus, both waterways are characterized by low pH values (2–4) and contain large amounts of sulphates and sulphide-related metals due to pyrite oxidation (Morillo and Usero, 2008). Furthermore, the basins of the Tinto and Odiel rivers have hosted mining activity since Phoenician and Roman times because of the excellent conditions of the Iberian Pyrite Belt (Sánchez-Moyano and García-Asencio, 2010). Therefore, a great number of abandoned mine sites still contribute to high metal concentrations due to waters emanating from both surface and underground mining (Galán et al., 2003; Morillo and Usero, 2008).

Since the 1960s, Huelva estuary has been surrounded by heavily industrialised areas (phosphate fertilizer plant, power plants, chlor-alkali industry, petroleum refinery and other factories) and additional inputs of potentially toxic elements started to be discharged into the estuary. This waste contains high levels of sulphide-associated heavy metals. A third source of metals for the estuarine environment is the urban sewage from the city of Huelva (Ruiz, 2001).

In spite of this, many protected areas are located close to the Huelva estuary, such as the Odiel Marshes Nature Reserve and Doñana National Park, both wetlands where birds stop for their migrations and, thus, declared biosphere reserves by Unesco, Ramsar sites and European Union Special Bird Protection Zones (Sánchez-Moyano and García-Asencio, 2010).

3. Materials and methods

3.1. Sampling and sample pre-treatment

16 sampling points were chosen to cover the Huelva estuary and its area of influence (the Huelva littoral), one of them located in a pollution free zone (Usero et al., 2008) to serve as a reference. According to these guidelines, 12 points were located in the Huelva estuary (see Table 1 and Fig. 1): 5 in the Odiel River estuary (O1–O5), 4 in the Tinto River estuary (T1–T4) and 3 in the Padre Santo Canal (C1–C3). Four points correspond to the littoral (L1–L4). The reference point (L1) was placed west of the estuary to avoid its influence by prevailing west to east water currents.

Sediment samples were taken in October 2013 with a Van Veen grab and in duplicate at each point. Only grabs that achieved adequate penetration (2/3 of total volume) to collect the first 5 cm of the sediment and that showed no evidence of leakage or surface disturbance were retained, transferred and stored in a dark cooler at 4 °C.

In the laboratory, a representative sample from each station was prepared by mixing and homogenizing the two samples taken at each sampling point. Then they were divided into two fractions as shown in Table 2: fraction 1, without any further treatment, to determine particle size profiles, and fraction 2, dried (60 °C) and sieved (<63 μm), to perform metal analysis (totals and protease K), total organic carbon and the toxicity bioassay. All conventional

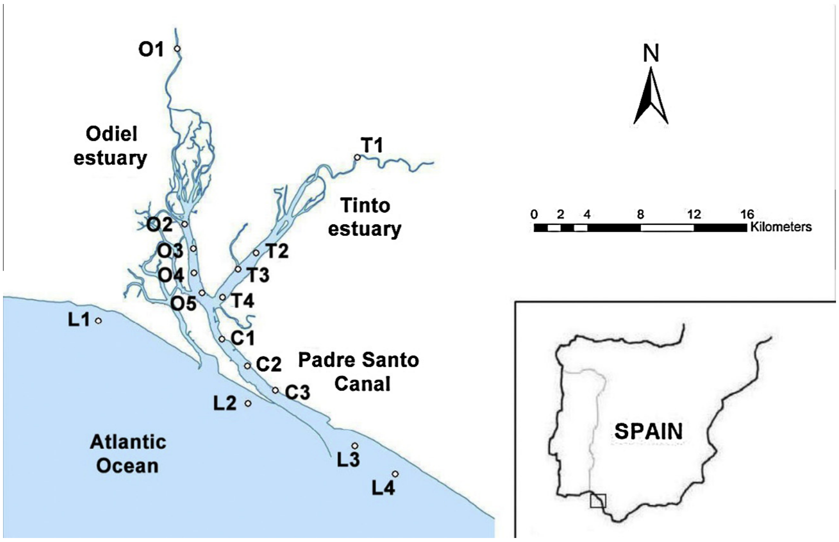

Fig. 1. Location of the sampling points in the Huelva estuary.