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A new index to sort estuarine sediments according to their contaminant content

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ABSTRACT

When dealing with potentially contaminated regions, simple tools are needed to identify in a fast and first approach the areas of the highest concern. In this work we propose a new, intuitive, easy-to-use and versatile tool to accomplish this task. This tool comprises the calculation of a new cumulative index, the Normalised-and-Weighted Average Concentration (NWAC) and its visualisation on a map of the area investigated using a colour based code. The NWAC is a cumulative index that is calculated for each sample using the concentration of freely selected contaminants present in that sample. The NWACs can be used to sort samples in a scale from 0 to 10 according to their contaminant content. A colour-based visualisation of the NWACs on a map facilitates an easy identification of the areas of higher concern within the studied region. The methodology has been exemplified in a case study, for example, the estuary of the Nerbioi-Ibaizabal River (Bilbao, Basque Country) using a representative set of sediments and their metals and metalloids content. The NWAC values obtained have been compared to the corresponding values of mERMq, another cumulative index of general acceptance and frequently used to estimate the toxicity of sediments, with comparable results.

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1. Introduction

Estuaries are considered the most productive marine ecosystems. These transition areas present high capacity to feed and bring up many organisms, but unfortunately they also store different kinds of contaminants, especially in their sediments (Holder, 2002). The presence of chemicals in sediments significantly increases due to human activities. Moreover, under certain physico-chemical conditions sediments may act as a secondary source of contamination to the estuary (Kennish, 1998). Among these pollutants trace elements are of special interest due to their potential toxicity and long persistence in the environment. Sediments have been largely used as indicators of metal pollution in estuaries (Larrose et al., 2010).

Different methodologies have been proposed to estimate the quality of estuarine sediments. The simplest ones use the ratio between the actual concentration of a given contaminant in sediment and the background value estimated for the area. The geoaccumulation index (I_{geo})(Müller, 1979), enrichment factor (EF) (Salomons and Förstner, 1984) and degree of contamination (DC)

http://dx.doi.org/10.1016/j.ecolind.2014.04.038 1470-160X/© 2014 Elsevier Ltd. All rights reserved. (Hakanson, 1980) belong to this category. Some authors claimed that, as these methodologies only use chemical data, they are not able to give us information about the toxicity of the sediments (Wolska et al., 2007). Other methodologies, the so-called sediment quality guidelines (SQGs), combine chemical information with biological effects, providing us with an idea of the toxicity of sediments. Specifically, the SQGs express the individual relation between each chemical available in sediment and the adverse effects it causes on benthic communities. The most popular SQGs include the effects-range median (ERM) (Long et al., 1995), the probable effects level (PEL) (MacDonald et al., 2000). Important limitations of these methodologies, however, have also been described (Burton, 2002; McCauley et al., 2000).

All the methodologies mentioned before are contaminantspecific. That is, each contaminant susceptible to be present in the sediment is considered individually. Cumulative indexes have been also proposed, however, in order to consider simultaneously the combined effect of several contaminants present in the sediment. All of them are purely additives, so that they do not take into account possible synergic or antagonist effects due to the combined action of several chemicals. Probably, the most used one is the socalled mean Effects Range-Median quotient (mERMq) (Long, 2006), that sums up the toxic effect of selected pollutants on a wide variety of benthic organisms.







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Fig. 1. Location of the study area and sampling points in the Nerbioi-Ibaizabal estuary.

During a surveillance monitoring of pollution in a given region of interest susceptible to be at an unacceptable level of risk, the identification of the area of the highest concern is an important task when, for example, remediation actions are to be taken but only a reduced budget is available to afford them. In such cases very simple tools are required to estimate, in a first approach, the magnitude of the problem and to establish priorities for a possible future actuation. To tackle this task, we propose in this work the use of a new cumulative index, the Normalised-and-Weighted Average Concentration (NWAC), to sort sediments collected in a selected region according to their contaminant content. Each sediment is characterised by a single score in a scale from 0 to 10, the NWAC, which is calculated taking into account exclusively the concentration of contaminants freely selected by the user and present in the sample. The calculation of the NWACs and their representation on a map according to a colour based code allow us identifying, in a very simple and intuitive way, the sampling sites of higher concern in an area susceptible to be contaminated. The methodology has been exemplified in a case study, for example, the estuary of the Nerbioi-Ibaizabal River (Bilbao, Basque Country), and the values of NWAC obtained have been compared with the corresponding mERMqs.

2. Calculation of the Normalised-and-Weighted Average Concentrations (NWACs)

A set of samples representative of the study area and the concentration of selected contaminants in the samples are required for the calculation of the NWACs. First, for each contaminant the concentrations (c) found within sampling sites are normalised (c_{norm}) by linear scaling transformation $(c_{\text{norm}} = (c - c_{\min})/(c_{\max} - c_{\min}))$. Then, a weight is calculated for each contaminant according to the dispersion of the concentrations of that contaminant within the sampling sites. When the concentrations are spread out over a large range of values - which means a high capacity to discern among sampling sites (a high discrimination power) - a high value of weight is adopted, and vice versa. To do that, the relative standard deviations (RSD) calculated for each contaminant within sampling sites are normalised (RSD_{norm}) by linear scaling transformation $(RSD_{norm} = (RSD - RSD_{min})/(RSD_{max} - RSD_{min}))$ and the resulting numbers from 0 to 1 are used to weight the normalised concentrations (c_{norm}) of the contaminants. Then, the obtained normalised weighted concentrations (c_{norm}^w) are averaged for each sampling site $(\overline{C_{norm}^w})$. Finally, these averaged values are again normalised from 0 to 1, and finally multiplied by 10 to obtain a score (the Normalised-and-Weighted Average Concentration, NWAC) for each sediment ranging from 0 to 10. This new index allows us sorting the sampling sites in a very simple and intuitive way according to the average contaminant content of the sediments, taking into account their spread within the sampling sites. A colour-based map can be further produced to facilitate an easy identification of the areas of higher concern within the studied region.

3. Case study: metallic pollution in the sediments of the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country)

Our case study describes the application of the NWAC methodology to classify sediment samples collected in a representative area of the estuary of the Nerbioi-Ibaizabal River (Bilbao, Basque Country) according to their metallic content.

3.1. Study area

The estuary of the *Nerbioi-Ibaizabal* River (Bilbao, Basque Country) is located in the continental shelf of the Cantabrian Sea, in the north coast of the Iberian Peninsula (Fig. 1). Its principal freshwater input comes from the Nerbioi and Ibaizabal Rivers (68%), but also from the Kadagua (27%), Galindo (4%), Asua (0.7%) and Gobela (0.3%). Bilbao is nowadays one of the most important urban areas in the Cantabrian coast with about one million inhabitants. Its climate is oceanic, with wet weather all the year around (average rainfall about 1200 mm) and moderate temperatures (an average temperature of 14.5 °C in 2012, with a minimum of -4 °C and a maximum of 39 °C).

Exploitation of local iron started at the end of XIXth century and marked the beginning of an important industrial activity, which resulted in a dramatic increase in population. Until the middle seventies all the urban and industrial wastewater was directly dumped into the estuary, thus causing the environmental collapse of the system (Barreiro and Aguirre, 2005). The closure of most of the polluting industries at the end of the XXth century and the implementation of the so-called "strategy for the integral recovery of the estuary of Bilbao (SIREB)" led to a gradual recovery of the estuary. The actuations in the framework of the SIREB started in 1979 and have recently finished with spectacular results (Fdez-Ortiz de Vallejuelo et al., 2010, 2011; Fernández et al., 2008; García-Barcina et al., 2006). Nowadays, however, the sediments of the estuary faithfully reflect historical pollution episodes, and their concentration of pollutants, specifically trace metals and metalloids, has been reported to be relevant (Amigo et al., 2012; Belzunce et al., 2001; Cearreta et al., 2000; Fdez-Ortiz de Vallejuelo et al., 2010; Gredilla et al., 2013; Landajo et al., 2004; Moros et al., 2009, 2010). Background values (mg kg⁻¹) for As (16), Cd (0.24), Cr (85), Cu (20), Fe (25,000), Mn (300), Ni (23), Pb (21) and Zn (63) have been estimated for the area (Cearreta et al., 2000; Rodríguez et al., 2006). In such situations, the European Water Framework Directive recommends the implementation of a surveillance monitoring programme to follow the evolution of contamination and pollution in time and space (WFD, 2000).

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