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Combining contamination indexes, sediment quality guidelines and multivariate data analysis for metal pollution assessment in marine sediments of Cienfuegos Bay, Cuba

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HIGHLIGHTS

- Contamination indexes, TELs and PELs for assessing metal pollution in sediments.
- Arsenic, Cu, Ni, Zn and V concentrations decreased respect to previous studies.
- Cd and Cu were the most contaminated elements in most sediments.
- Cu and Ni were linked with occasional adverse biological effects in most sediments.
- Cu could be considered as the most dangerous in the whole bay.

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ABSTRACT

The purpose of the present work was to combine several tools for assessing metal pollution in marine sediments from Cienfuegos Bay. Fourteen surface sediments collected in 2013 were evaluated. Concentrations of As, Cu, Ni, Zn and V decreased respect to those previous reported. The metal contamination was spatially distributed in the north and south parts of the bay. According to the contamination factor (CF) enrichment factor (EF) and index of geoaccumulation (I_{geo}), Cd and Cu were classified in that order as the most contaminated elements in most sediment. Comparison of the total metal concentrations with the threshold (TELs) and probable (PELs) effect levels in sediment quality guidelines suggested a more worrisome situation for Cu, of which concentrations were occasional associated with adverse biological effects in thirteen sediments, followed by Ni in nine sediments; while adverse effects were rarely associated with Cd. Probably, Cu could be considered as the most dangerous in the whole bay because it was classified in the high contamination levels by all indexes and, simultaneously, associated to occasional adverse effects in most samples. Despite the bioavailability was partially evaluated with the HCl method, the low extraction of Ni (<3% in all samples) and Cu (<55%, except sample 3) and the relative high extraction of Cd (50% or more, except sample 14) could be considered as an attenuating (Ni and Cu) or increasing (Cd) factor in the risk assessment of those element.

1. Introduction

Despite the common use of sediments in metal pollution assessment, their classification into different levels of contamination and the prediction of the associated adverse biological effects still represent a significant challenge from a practical point of view

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due to several factors. A diversity of approaches has been proposed to tackle these significant challenges (Burton Jr., 2002; Caeiro et al., 2005; Peña-Icart, 2012; Thu Dung et al., 2013; Quevedo Alvarez et al, 2014). In this context, the use of indexes of contamination is one of the most commonly used approaches, with approximately sixteen indexes proposed to date (Caeiro et al., 2005).

The contamination factor (CF) and degree of contamination (DC) (Hakanson, 1980; Huang et al., 2013; Samhan et al., 2014), index of geoaccumulation (I_{geo}) (Muller, 1969, 1981; Ruiz, 2001; Veerasingam et al., 2015) and enrichment factor (EF) (Sinex and Helz, 1981; Santos et al., 2005; Young Choi et al., 2012; Zhao et al., 2014) are among the most frequently used, and they are selected in the present study. The quantification and classification of the metal pollution status of sediments using CF, DC, EF and I_{geo} indexes is based on the comparison of the total concentration of metal in sediments under study with the background concentrations.

The total concentrations of metals used in the calculation of the contamination indexes considered in the present study has been carried out following different procedures. For instance, EF was calculated with the total concentration of metals extracted using: aqua regia and HF (Santos et al., 2005); HNO_3, $HClO_4$ and HF (Young Choi et al., 2012) and HNO_3, HF and HCl (Morelli and Gasparon, 2014). In other reports, I_{geo} was calculated using the total concentration of metals determined previous digestion of sediments with HF and HNO_3 (Veerasingam et al., 2015) or determined directly on the sediment by X-Ray Fluorescence without previous digestion of sample (Ruiz, 2001). Interestingly, partial digestion of sediment was carried out in some occasions, but, the total extraction of metals was ensured by comparing extracted concentrations with total concentrations in certified reference materials. See, for example, the reports by Samhan et al. (2014) and Davutluoglu et al. (2011), where total content of metals was determined previous extraction using HCl and HNO_3 for subsequent calculation of CF, and EF and Igeo, respectively.

In spite of the usefulness of contamination indexes to detect and classify metal pollution, they do not provide information on the possible occurrence of adverse biological effects associated to contaminated sediments. In fact, those indexes were not designed to that purpose.

In this context, comparison of the concentrations of metals to reference concentrations in the sediment quality guidelines (SQGs) is frequently employed to estimate biological effect. A variety of approaches to derive SQGs have been developed, which can be classified in two groups (McCauley et al., 2000; Burton Jr., 2002; Hübner et al., 2009): a) empirical, frequency-based approaches to establish the relationship between concentration of contaminant in sediment and toxic response, and b) theoretically based approaches that attempt to account for differences in bioavailability through equilibrium partitioning (EqP), i.e., using organic carbon or acid volatile sulfides.

SQGs for Cuban bays have not been yet developed. For that reason, one of the most widely-used SQGs the threshold (TELs) and probable (PELs) effect levels (Buchman, 2008) are employed in the present study due to their ease of use, their scientifically defensible basis and the broad coverage worldwide (Hübner et al., 2009).

TELs and PELs define three ranges of chemical concentrations (C_c) of pollutant in the bulk sediment with regard to biological effects (MacDonald et al., 1996, 2000): C_c < TEL (adverse effect rare), TEL < C_c < PEL (adverse effects occasional), C_c > PEL (adverse effect frequent). This way, the total concentration of contaminant in sediment under study is compared to TELs and PELs, and the frequency of occurrence of adverse biological effect is predicted. The use of total concentrations of contaminants, including metals and As, in the development of TELs and PELs guidelines has been mentioned in many reports, for instance, in the report by Batley and Simpson (2008) and the critical reviews by Burton (2002), Hübner et al. (2009) and Thu Dung et al. (2013).

Generally, total concentrations of metals in sediments under study were determined previous digestion of sample using different mixtures of strength acids, including HF (Carr et al., 1996; Barakat et al., 2012; Morelli and Gasparon, 2014; Vallius, 2015) or aqua regia without HF (Muñoz-Barbosa et al., 2012; Rosado et al., 2015). But in all cases, the total content of metal was ensured, comparing determined concentration with total concentrations of metals in certified reference materials. Precisely, one of the disadvantages of this type of SQGs is that metal bioavailability is not well addressed because these guidelines were derived from total concentrations of contaminants. Several attempts have been made to compensate for this weakness. However, they are, generally, site-specific and therefore not, or only to a very limited degree, applicable for direct implementation into general SQGs (Hübner et al., 2009).

Following a conceptually different approach, the pollution assessment of metals has focused on estimating the fraction of metal that can reach the aquatic environment surrounding the sediment. In this approach, two methods have been proposed: estimation of the metal fraction desorbed into the water column or into the gastrointestinal tract of fishes. For the first case, the extraction methods proposed can be divided in two broad categories: one-step and sequential extraction procedures. In one-step procedures, metals are extracted into solution using different solvents, among which Acetic and Hydrochloric acids are ones of the most used (UNEP/IOC/IAEA, 1995; Sutherland, 2002; Sahuquillo et al., 2003; Snape et al., 2004; Larner et al., 2008). Sequential extraction procedures (Tessier et al., 1979; Quevauviller et al., 1997; Craba et al., 2004) experienced a boom approximately 20 years ago that involved the production of certified reference materials (CRMs) to guarantee the quality of metal quantification in different fractions of sediment using the 3-step BCR (Community Bureau of References) sequential extraction procedure. One-step and sequential extraction procedures were designed to quantitatively determine the metal part bound to a specific fraction of sediment and to then evaluate the metal bioavailability, i.e., the metal fraction that reached the water column with relative ease. This way, a higher mobility of metal is associated to a greater potential damage to the environment. But, the fraction of metal that actually reaches the trophic chain is not considered. In this context, several methods were proposed to estimate the metal fraction of sediments that truly reaches the trophic chain, selecting fishes as the target samples. This way, a better estimation of the metal fraction present in sediment that can reach the trophic chain via metal desorption in the gastrointestinal tract of fishes can be made. Among the digestion methods proposed, metal extraction with hydrochloric acid is one of the most attractive methods because, in addition to the inherent simplicity of the procedure, the extraction time can be adjusted to the specific characteristics (kinetics of reaction) of the sediment and the temperature of the extraction can be selected according to the temperature of the marine environment under study (Peña-Icart, 2012; Peña-Icart et al., 2014). Therefore, the determination of metal fraction extracted from sediments using the HCl extraction method was also considered in the present study as a complementary information to take into account in the metal pollution assessment.

In Cienfuegos Bay, few studies on metal assessment contamination in sediments have been reported (González, 1991; Alonso-Hernández et al., 2006b; Pérez Santana et al., 2007; Peña-Icart et al., 2014). The first study (González, 1991) was addressed, principally, to the comparison of metal concentrations among sediments sampled in the five more important Cuban bays (González,