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Research article

A chemical status predictor. A methodology based on World-Wide sediment samples

A. Gredilla [a,*], S. Fdez-Ortiz de Vallejuelo [a], A. de Diego [a], G. Arana [a], T. Stoichev [b], J.M. Amigo [c], J.C. Wasserman [d], A.V. Botello [e], S.K. Sarkar [f], J. Schäfer [g], C. Moreno [h], M. de la Guardia [i], J.M. Madariaga [a]

[a] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Spain
[b] CIMAR/CIIMAR, Centro Interdisciplinar de Investigação Marinha e Ambiental, Universidade do Porto, Rua dos Bragas, 289, 4050-123 Porto, Portugal
[c] Department of Food Science, Spectroscopy and Chemometrics, Faculty of Sciences, University of Copenhagen, DK-1958 Frederiksberg C, Denmark
[d] Universidade Federal Fluminense, Rede UFF de Meio Ambiente e Desenvolvimento, Av. Litorânea s/n, Boa Viagem, Niterói 24020 149, Brazil
[e] Laboratorio de Contaminación Marina, Instituto de Ciencias del Mar y Limnología, National Autonomous University of Mexico, 70-305, México, 04510 D.F., Mexico
[f] Department of Marine Science, University of Calcutta, 35 Ballygunge Circular Road, Calcutta 700 019, West Bengal, India
[g] University of Bordeaux, EPOC, UMR 5805, F-33400 Talence, France
[h] Faculty of Marine and Environmental Sciences, Department of Analytical Chemistry, University of Cádiz, 11510 Puerto Real, Cádiz, Spain
[i] Department of Analytical Chemistry, University of Valencia, 50 Dr. Moliner Street, E-46100 Burjassot, Valencia, Spain

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ABSTRACT

As a consequence of the limited resources of underdeveloped countries and the limited interest of the developed ones, the assessment of the chemical quality of entire water bodies around the world is a utopia in the near future.

The methodology described here may serve as a first approach for the fast identification of water bodies that do not meet the good chemical status demanded by the European Water Framework Directive (WFD). It also allows estimating the natural background (or reference values of concentration) of the areas under study using a simple criterion. The starting point is the calculation the World-Wide Natural Background Levels (WWNBLs) and World-Wide Threshold Values (WWTVs), two indexes that depend on the concentration of seven elements present in sediments. These elements, As, Cd, Cr, Cu, Ni, Pb and Zn, have been selected taking into account the recommendations of the UNEP (United Nations Environment Programme) and USEPA (United States Environmental Protection Agency), that describe them as elements of concern with respect to environmental toxicity.

The methodology has been exemplified in a case study that includes 134 sediment samples collected in 11 transitional water bodies from 7 different countries and 4 different continents.

Six of the water bodies considered met the good chemical status demanded by the WFD. The rest of them exceeded the reference WWTVs, at least for one of the elements. The estuaries of the *Nerbioi-Ibaizabal* (Basque Country) and *Cavado* (Portugal), the sea inlet of *Río San Pedro* (Spain), the *Sepetiba* Bay (Brazil) and the *Yucateco* lagoon (Mexico) belong to that group.

1. Introduction

Many terms have been used to refer to a contaminant concentration found in undisturbed soils and sediments: typical, baseline, natural, pre-industrial, etc. Nevertheless, “background” is undoubtedly the most used one, with a large number of citations in different areas of environmental science (de Paula Filho et al., 2015; Fiore et al., 2014; Molinari et al., 2012; Preziosi et al., 2010).

The first definitions of background levels were originally linked to the differentiation between “normal” element concentration and “anomalies”. Later, these definitions were mainly used to identify environmental contamination in soils and rivers (Reimann and Garrett, 2005).

* Corresponding author.
E-mail address: ainara.gredi@gmail.com (A. Gredilla).

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Regarding surface water bodies, the European Water Framework Directive (WFD) and the European Marine Strategy Framework Directive (MSFD) define the background values as boundary values to be considered in the ecological status of a water body (Solaun et al., 2013). For the WFD the main goal is to ensure the "good" status of all the water bodies of the member states. This fact implies obtaining both, the good ecological and the good chemical status of the area under study. While choosing the adequate Environmental Quality Standards (EQS) for the determination of the chemical status is essential (Tueros et al., 2009), the abovementioned background values are absolutely necessary to assess the ecological status.

Numerous methodologies have been proposed for the determination of background and threshold values of different water bodies concerning a given contaminant, but they have always been based on three procedures: i) the selection of an unaltered area close to the area under study or with similar characteristics; ii) analysing a sediment core dated before a contamination episode or iii) estimations obtained using statistical tools. In many cases the first two procedures are unviable since unimpacted areas are extremely difficult to find. Regarding statistical tools, several methods have been traditionally applied to estimate background values (Buckley et al., 1995; Matschullat et al., 2000). Nevertheless, they are not easily accessible for non-experts in statistics.

Although some other strategies have been designed for the calculation of background and threshold values, most of them are focused on groundwater. This is the case of the work carried out within the Background cRiteria for the IDentification of Groundwater thrEsholds (BRIDGE) project (Wendland et al., 2008). The overall aim of BRIDGE was to develop and test a method for the derivation of pollutant threshold values for groundwater bodies in support of the Status provisions of the WFD and the Groundwater Daughter Directive (GWDD). Despite the success of the project, sediment is the preferred compartment used for the quality status assessment of water bodies due to the spatial and seasonal variations commonly found in waters (Collins and Anthony, 2008; Magni et al., 2008; Wetzel et al., 2012). For the USEPA contaminated sediments are of major concern too and it specifically recommends the development and improvement of methods to identify them (EPA, 1995).

Reviewing previous works using sediments as quality status indicators, it can be found that a great part of them directly compare the contaminant concentration with the background value defined for that contaminant in a specific area. This is the case of the geoaccumulation indexes ($_{\mathrm{Igeo}}$) (Müller, 1979) and the degree of contamination (DC) (Hakanson, 1980) quotients, among others. Some authors focus on the effect that the simultaneous presence of contaminants may cause in sediments. The Normalised-and-Weighted Average Concentrations (NWAC) (Gredilla et al., 2014) or the mean Effects Range-Median quotients (mERMq) (Long et al., 2006) represent good examples in this category. Data normalization is another way to study sediment contamination levels. Depending on the nature of sediments the normalization techniques vary: for sediments with high organic matter content, for instance, the ratio between contaminant concentration and organic carbon content can be considered a good indicator of the contamination level (Cato, 1989). Contaminant concentrations in sediments are frequently normalized with conservative elements such as aluminium or titanium and, afterwards, compared to background values (Covelli and Fontolan, 1997). Recently, multicriteria approaches, which combine chemical, social, political, ecological and economic variables, have also been considered to predict contamination (Chon et al., 2012).

The methodology presented in this work is an alternative to evaluate the quality of surface water bodies according to the chemical status of their sediments. It relies on the calculation of the World-Wide Natural Background Values (WWNBLs) and World-Wide Threshold Values (WWTVs) for a given contaminant, according to the recommendations emerging from the BRIDGE project (Hart et al., 2006). These two variables can be calculated using exclusively chemical information, e.g., contaminant concentration.

The proposed methodology has been exemplified with a case study including several transitional water bodies. The lack of homogeneity of this type of waters, with continuous gradients in temperature, conductivity, pH, redox potential, salinity, total dissolved solids and dissolved oxygen, has seriously limited the evaluation of their chemical and ecological quality status (Gredilla et al., 2013). In fact, the amount of works aiming the implementation of the WFD in transitional bodies is scarce (Bald et al., 2005). In our case study sediment samples collected at 11 transitional water bodies from 4 different continents were used and the concentration of seven toxic elements (As, Cd, Cr, Cu, Ni, Pb and Zn) (EPA, 1995) was measured in all of them.

The WWNBLs obtained in this work have been compared to those obtained by other classic methods used in the determination of background values, such as the 4δ Outlier test (Matschullat et al., 2000), the Relative Cumulative Frequency Curves (RCFC) (Díez et al., 2009), and comparison with concentration values found in the Earth's crust (Turekian and Wedepohl, 1961).

2. Description of the proposed methodology

A five-step methodology is proposed to evaluate the chemical status of a water body (see Fig. 1):

2.1. Sample collection and analysis

In a first step, sediment samples representative of the water body under study must be sampled and analysed. The result is a data table with *m* rows (sediment sample) and *n* columns (contaminant concentration) ready for statistical analysis.

2.2. Outlier detection

Although most of environmental samples are affected by different anthropogenic impacts to a greater or lesser extent, we propose to remove from the data table those contaminant concentrations which are extremely impacted, since they may strongly distort the results. Accordingly, those contaminant concentrations

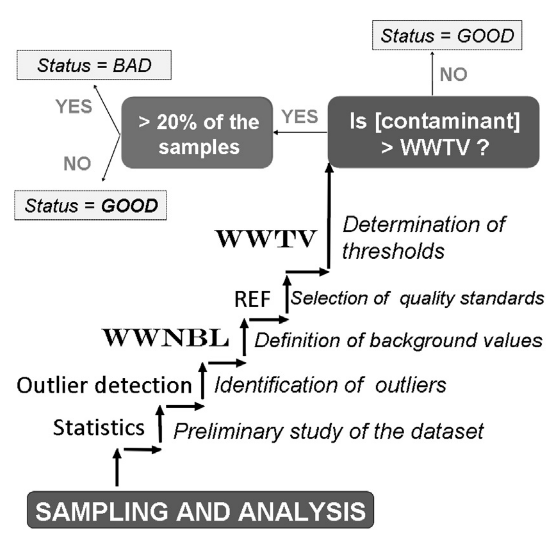

Fig. 1. Schematic configuration of the methodology presented in this work.