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Chemometric approach to visualize and easily interpret data from sequential extraction procedures applied to sediment samples

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HIGHLIGHTS

- Two sequential schemes discriminating different oxide phases were used.
- Tucker4 model made possible to visualize and explain the data set information.
- Although different, the 2 sequential procedures used give similar information.
- Metal mobility/availability was assessed for estuarine sediment samples.

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ABSTRACT

The aim of this study was to assess metal mobility/availability in coastal surface (oxic) sediment samples from the Bahía Blanca estuary. Particularly, two sequential extraction procedures able to discriminate metals associated to amorphous Fe and Mn oxides and those associated with crystalline oxides of Fe were applied. Sequential procedures differ in the number of steps, type of reagents used, and in the order in which metals associated to organic matter are extracted. The studied metals were Cd, Cr, Cu, Pb, Ni and Zn because of their hazardous potential and relative abundance in the estuary. Tucker4 model with three factors describes appropriately the data sets (explained variance of 64.05%). This model made it possible to visualize and explain the information underlying in the data set. From the multivariate analysis, it was possible to evaluate the metal behaviour and their availability. In this way, Cd and Zn are associated to the more available fractions whereas Ni, Cr, Cu and Pb are mainly associated to the unavailable fractions. On the other hand, Zn and Cu are associated to organic matter fraction. Despite the fact that the two-fractionation schemes are quite different, the results obtained with both schemes are comparable.

1. Introduction

Sediments are constituted by fragments derived from soils and rocks, biological materials and other contributions of anthropogenic origin. Conditions of the aquatic environment, critically affect the chemical characteristics of the sediments. Sediments can act as sinks or sources of heavy metals depending on their geochemical composition and changes in the physicochemical conditions, i.e. pH, presence of organic chelates, redox potential, dissolved oxygen, etc. [1,2].

Heavy metals may be associated to several solid phases in the sediments, i.e. clays, organic matter, oxides, carbonates, sulphides and residual silicates, which are mutually interrelated [1–3]. Heavy metals are adsorbed on the surface of clay particles and are also occluded in amorphous materials such as Fe and Mn oxyhydroxides, sulphides and organic matter that can act as coatings of other sediment particles. They also take part of the crystalline lattice of primary minerals such as residual silicates [4].

Currently it is normally accepted that total metal concentration gives less information about the metal behaviour than fractionation analyses [1]. The fractionation methods consist of extraction/lixiviation procedures carried out under operationally defined conditions. The term ‘operational’ is established to indicate that metal concentrations obtained in each fraction depend on the used experimental procedure [5–7]. Most widely used chemical

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extractants are classified as inert electrolytes, weak acids, reducing and oxidizing agents, complexing reagents and strong acids. The aim of a particular fractionation study determines the appropriate sequence of reagents to obtain the required partitioning degree (number of steps). These procedures are based on selecting different reagents with increasing dissolving power respect to the geochemical phases. The relative solubility of metal species associated to a particular geochemical phase depends on the degree of reagent's dissolving power [8]. In this sense, there are traditional sequential extraction schemes described in the literature [6,9–12] and others recently reported [13–16].

In the last decades, Fe and Mn oxyhydroxide phases have received major attention because of their significant role in the heavy metal fixation. This is reflected in the application of sequential schemes tending to discriminate the metals associated to the Fe/Mn amorphous oxides and the Fe crystalline oxides [4,17–19]. These schemes are based on the different behaviours of Mn and Fe oxyhydroxides under various redox potential and pH conditions [20,21]. The most effective mixture of reagents to assess the metals associated to these phases contains both a reducing and a chelating agent able to keep the released metals in a soluble form.

These kinds of studies are particularly important in well-mixed estuaries. In such closed environments, sediments take a long time until they are deposited near the shore; therefore, physicochemical processes have enough time to occur [3]. The Bahía Blanca estuary (Buenos Aires, Argentina) is a case study of this type of closed environment, which is particularly interesting because it possesses a deep-water port (45 feet) requiring periodic dredging. This practice leads to a large movement of sediments that could derive in a potential risk of pollution. The high turbidity is an important characteristic of the system, caused mainly by an intense tidal regime and prevailing strong N and NW wind which generate water mixing and re-suspension phenomena [22,23]. Furthermore, the estuary receives water from fresh water streams and passes through important agricultural and ranching areas.

Environmental data originated in fractionation studies give rise to large multivariate arrays. They require variable reduction techniques to provide an easy visualization and interpretation of the information hidden in the data set. The obtained data show a multidimensional structure (samples, metals, fractions, extraction procedures) and could be analyzed using a four-way multivariate chemometric tools such as PARAFAC and Tucker models [24–27]. This kind of data could be rearranged in partial data sets with lower dimensions and analyzed by a simpler method such as PCA [28]. However, this approach does not have the ability of dealing with the whole data set in a unique analysis [29,30].

The goal of this study was to assess the availability and behaviour of heavy metals associated to different solid phases of sediment samples of the Bahía Estuary. To this aim, two sequential extraction schemes [10,11] were applied to oxic sediment samples from the Bahía Blanca estuary. The fractionation procedures vary in the number of steps. They also differ in the order in which organic matter and oxide phases are extracted. Cd, Cr, Cu, Pb, Ni and Zn were studied, either because of their hazardous potential or relative abundance in the estuary (probably associated with industrial activities) [26,27]. A better visualization of the results was obtained using a Tucker4 model. The choice of Tucker instead of PARAFAC (a particular case of Tucker) was based on the ability of Tucker of handle different number of factors in each mode, which make it possible to extract more information. In addition, one collateral scope of this study is to qualitatively corroborate that the results obtained by the two different sequential extraction schemes (using different reagents, temperature, and extraction times) are equivalent.

2. Experimental

2.1. Reagents and solutions

All chemicals and reagents were of analytical reagent grade. Doubly distilled demineralized water was used throughout. Before use all containers were soaked in 15% HNO_3 for 24 h, and rinse with doubly distilled water. Carlo Erba (Erbatron RSE, Milan, Italy) HF, HCl and HNO_3 were used. Stock solutions of the analytes ($1000\,mg\,L^{-1}$) were obtained from Carlo Erba Normex Standards (Milan, Italy). Multielement standard solutions were prepared by diluting suitable volumes of the stock solutions with $0.5\,mol\,L^{-1}$ HNO_3. A solution for Cr was prepared to avoid the instability of the signals observed when this element was included in the multielemental solution [31].

In order to assess the total metal concentrations, Antarctic bottom sediment (MURST-ISS-A1, provided by Italian Research Program in Antarctica) certified for total metal concentrations was used. The total metal concentration was assessed following the procedure stated in [27]. X-ray diffraction analysis showed that the mineral constitution of the Antarctic sediment resembles, in a global way, the composition of the coastal sediments studied (quartz, feldspars such as anorthite and albite, carbonates, iron oxides and hydroxides) [31].

2.2. Study area

The Bahía Blanca estuary is located in the south of the Buenos Aires Province, Argentina, (38°46′S, 62°30′W) and has a northwest-southeast direction (Fig. 1). Several fresh water streams flow into the north of the main channel, which is primarily sailed by fishing boats and cargo vessels (generally carrying fuel and cereals). Three urban nucleuses are located in the northern coast of the estuary. The largest of them is Bahía Blanca city, with a population exceeding 300,000 inhabitants. The southern coast is not well defined and varies with the tides.

This area constitutes a big industrial emplacement, composed by refineries, petrochemical industries and fertilizer manufacturers. Moreover, there are textile and tannery industries that coexist with cereal and meat factories. Pollutants reach the estuary through the different sources of fresh water carrying direct industrial discharges and municipal wastewater.

2.3. Sampling and sample treatment

The sampling zone is characterized by the presence of fine sand, silt and clay surface sediments. Eight samples (S1 to S8) were collected in the Galván port area (about 5 ha in surface) because of the proximity to important industries, i.e. the main sources of pollution (see Fig. 1). Several portions were collected along a zig-zag track [32], in the same sampling point, in order to obtain representative composite samples. Surface oxic sediment samples (light brown colour, flaky appearance, no sulphide smell) were taken from the superficial layer (1–5 cm) using a plastic spatula. The samples were kept at 4 °C before analysis.

Samples were air-dried for at least 72 h and sieved (250 mesh). The lower particle size fraction (<63 μm) was retained.

2.4. Procedure

The classical extraction schemes [6,9] consider metals linked to oxides as a unique phase (named "oxides of Fe and Mn"). By contrast, the selected sequential extraction procedures for our study are able to discriminate between metals associated to the phase comprised by Mn oxides and amorphous Fe oxyhydroxides and those adsorbed on crystalline Fe oxides [10,11]. Amorphous iron