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Redox status and heavy metal risk in intertidal sediments in NW Spain as inferred from the degrees of pyritization of iron and trace elements

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ABSTRACT

Mariculture is an important economic activity in shallow marine areas of the Rías Baixas (Galicia, NW Spain). The maintenance of high product quality requires surveillance of environmental quality, including the risk of metal toxicity. In this study the redox status of intertidal sediments in the Bay of San Simón, and the risk of toxicity posed by their As, Cd, Cr, Cu, Mn, Ni, Pb and Zn contents, were evaluated by determination of operationally defined reactive, silicate-bound, organic and pyrite-related fractions of these elements and of Fe. The large silicate-bound fractions of most of these metals indicate their lithogenic origin; the main exception is Pb, which in all respects exhibits singular behaviour associated with its predominantly anthropogenic origin in a ceramics factory. In sediments with larger fine-grained particle contents, which are oxic only in the top few centimetres, greater proportions of the trace elements are present as sulphides or associated with sulphide minerals: the degree of pyritization of Fe (DOP) is 46% overall, and the pyrite fraction of some elements doubtless increases at the expense of the reactive fraction, most overall degrees of trace metal pyritization (DTMPs) lying in the range 10–50%. A decline in pyrite genesis at depths below about 18 cm in these sediments is attributed to the exhaustion of organic matter susceptible to metabolization by sulphide-generating bacteria. In coarse-grained, oxic sediments the oxidation of sulphides makes pyrite-related fractions very small, and reactive and silicate-bound fractions are negatively correlated; reactive fractions associated with Fe–Mn oxyhydroxides are large, and DOP and DTMPs are low (generally much lower than in mud-rich sediments), except for Pb. Most of the elements studied are mainly present in forms that are neither bioavailable nor potentially bioavailable, and so do not constitute a significant environmental threat. However, the high DTMPs of Cu and Pb indicate significant potential bioavailability, which should be taken into account in evaluations of environmental quality and the risk to bivalve cultures.

1. Introduction

Seasonal upwelling in the *rías* of Galicia (NW Spain) supports a rich marine biota (Álvarez-Salgado et al., 2000; Figueiras et al., 2002), including economically important bivalve cultures in both subtidal and intertidal areas. Since these filtering organisms can accumulate heavy metals (Beiras et al., 2003), it is important to assess the risk of such accumulation, especially in view of the accelerating increase in trace metal concentrations that has occurred in the rías over the past century or so. In the Bay of San Simón, which concentrates most of the bivalve cultures of the Ría de Vigo, the sediment record shows significant pollution by Cu and Zn in recent decades, and intense pollution by Pb that began in the final decades of the 19th century and has increased since the 1950s (Álvarez-Iglesias et al., 2003, 2007). High Pb concentrations have been measured in several plant and animal species in this bay (Álvarez-Iglesias et al., 2000).

Potentially toxic metals can only realize their toxicity if they are bioavailable. Subtidal and intertidal estuarine sediments generally act as trace metal sinks, their fine grain size, anoxic conditions and high organic matter contents providing a suitable environment for intense diagenetic processes that favour the formation of pyrites and the incorporation of trace metals in these minerals (Berner, 1970, 1984; Williams et al., 1994). Several trace metals, notably Cd, Cu, Ni, Pb and Zn, also form their own sulphides (Luther et al., 1980; Huerta-Díaz and Morse, 1992). However, if conditions become more oxidizing, oxidized forms of trace metals can become available for uptake by living organisms (Otero et al., 2005).

The intertidal bivalve cultures of the Bay of San Simón (mostly clam and cockle beds) are in principle at greater risk of exposure to heavy metals than subtidal cultures, firstly because of their closer proximity to heavy-metal-bearing sediment (subtidal cultures are mainly mussels grown on cables suspended from rafts), and secondly because the redox conditions of intertidal sediments are

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more variable than those of subtidal sediments due to the actions of the tide, intertidal biota, and bivalve extractors. Evaluation of the risk of metal accumulation is therefore especially necessary for these intertidal cultures, and requires determination of the pool of heavy metals in oxidizable forms such as pyrites in intertidal sediments (Morse, 1994).

Few studies of trace metals in the Galician rías have considered the forms adopted by the metals studied, and most of those that have have focused on subtidal sediments (Belzunce-Segarra et al., 1997; León et al., 2004; Otero et al., 2005). In a previous paper (Álvarez-Iglesias et al., 2003) we reported that a significant proportion of the Pb, and Zn in the intertidal sediments of the Bay of San Simón is present in the oxidizable fraction. Here we distinguish operationally defined reactive, organic, pyrite and silicate-bound fractions of the trace elements As, Cd, Cr, Cu, Mn, Ni, Pb and Zn in these sediments; we relate the genesis of pyrite and other sulphides to grain size, hydrodynamic conditions, and the quantity and reactivity of organic matter content; and we use the degrees of pyritization of iron and the trace elements as indicators of redox status and heavy metal risk, respectively.

2. Material and methods

The Bay of San Simón, which constitutes the inland end of the Ría de Vigo, is a sheltered mesotidal waterbody with and average depth of less than 7 m (Fig. 1). At its northern end it receives fresh water from the Rivers Xunqueira, Ulló and Oitavén-Verdugo, the latter of which is the main supplier of fresh water to the Ría. The slow currents and generally low-energy hydrodynamics of the Bay are a consequence of its sheltered location and the morphology of the Rande Strait, its outlet to the outer Ría. These conditions have led to the development of large intertidal sandflats, mixed flats, mud flats and incipient marshes drained by a complex network of tidal and estuarine channels; the most recent deposits are mainly tidal-flat and spill-over, mud now occupying previously sandy areas due to vertical aggradation (Pérez-Arlucea et al., 2007). C/N ratios indicate that both the subtidal and intertidal sediments of this bay have organic matter contents of both marine and terrestrial origin, the terrestrial contribution increasing landward (Álvarez-Iglesias, 2006).

In July 1999, three 20–24 cm cores (C1, C2 and C3) were collected with a hand-driven PVC pipe of 12 mm inner diameter in the intertidal zone close to the mouth of the River Oitavén-Verdugo (Fig. 1), in an area where the surface sediments are unlaminated spill-over or tidal deposits of near-neutral pH with large siliciclastic coarse fractions (Table 1). The cores were immediately taken to the laboratory, cooled to 4 °C, and divided in 2 cm segments; plastic and glass material being used in these and all subsequent operations to avoid contamination with metal. The general characteristics of these sediments include high total organic carbon (TOC) contents, low calcium carbonate contents, and a predominance of siliciclastic material of granitic origin (Table 1); more details have been published elsewhere (Álvarez-Iglesias et al., 2003).

Subsamples of the 2 cm segments were taken for determination of the degree of pyritization of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the mud fraction (<63 µm), which is usually the fraction of greatest relevance to trace metal pollution (Förstner, 1989; Soares et al., 1999). This fraction was separated by wet sieving with distilled water, and relevant average properties are listed in Table 1. Four operationally defined metal/metalloid fractions were separated from duplicate 2 g subsamples of the mud fraction by sequential acid digestion with – in this order – HCl (to extract M_{react}, *i.e.* reactive metal and metalloid associated with carbonates, Fe and Mn oxyhydroxides and Fe monosulphides; in the cases of Pb, Zn and Cd this fraction also contains their sulphides, which

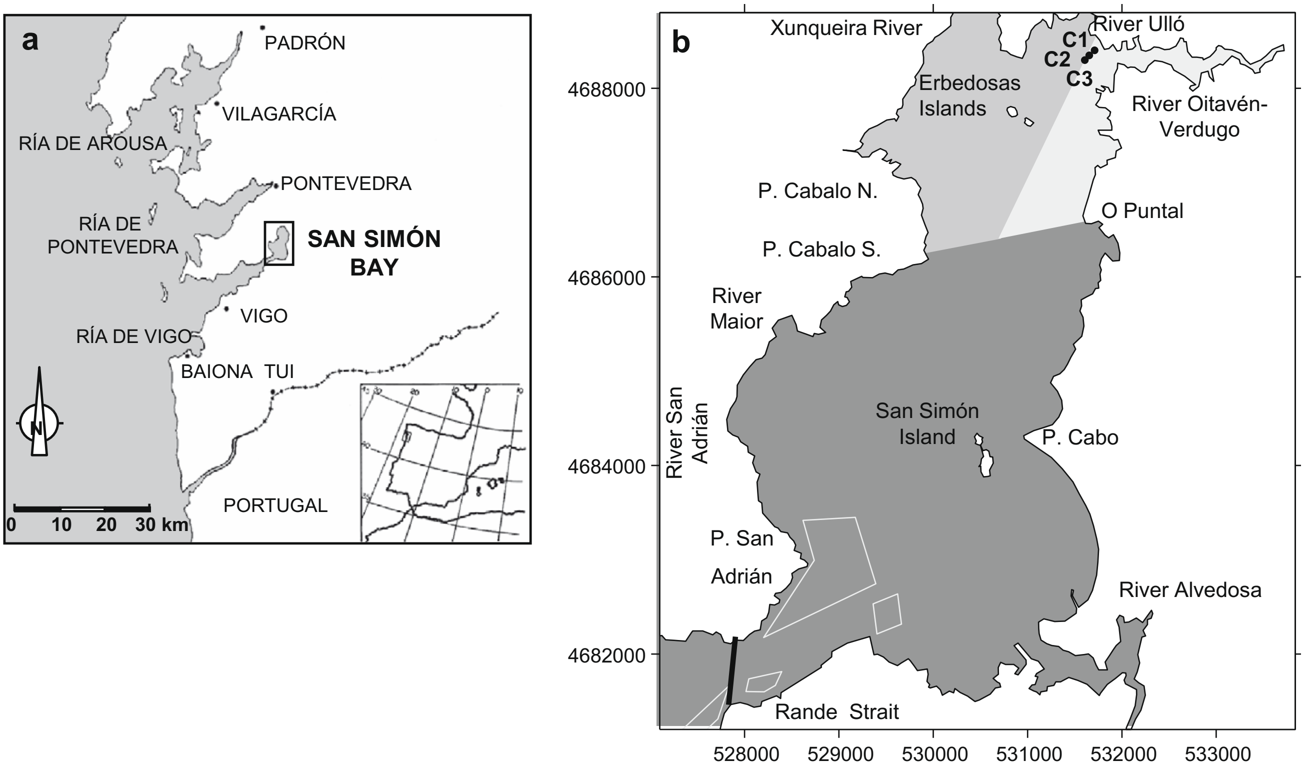

Fig. 1. (a) Location of the Bay of San Simón on the coast of Galicia (NW Spain). (b) The Bay of San Simón, showing subtidal (dark grey) and intertidal (medium and light grey) areas, and the location of the sediment cores (C1, C2 and C3). The light grey intertidal area indicates estuarine sediments and the medium grey area tidal-flat, although in this figure the gradual, irregular transition from one to the other has been simplified. Polygonal figures in and near the Rande Strait represent mussel raft areas.