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# Trace elements in biodeposits and sediments from mussel culture in the Ría de Arousa (Galicia, NW Spain)

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*Geochemical behaviour of trace metals in mussel biodeposits and sediments were studied.*

**Abstract**

The trace elements present at highest concentrations were Cr and Zn, which probably originated from the dumping of effluent from a tanning factory. High proportions of these two elements were associated with the residual fraction. Biodeposits and sediments showed high concentrations of Cd and Pb in the reactive fraction, with a high proportion of the concentration in the reactive fraction being associated with carbonates. Nickel showed a higher degree of pyritization than the previous elements, although most of the Ni was associated with the residual and reactive fractions. Arsenic, Hg and Cu showed high degrees of pyritization, particularly below a depth of 5 cm. The results demonstrate that those elements with a high degree of pyritization may be released into the water through oxidation of the metal sulphides that they form when in suspension in oxic sea water, with the subsequent risk of increased bioavailability to benthic fauna.


*Keywords:* Aquaculture; Mussel; Biodeposits; Sediments; Trace elements; Pyritization; Ría; Galicia

## 1. Introduction

Aquaculture has undergone great development in the last 20 years, currently accounting for around 10% of the world's total fish production, and it is expected that the industry will become more important because of the gradual depletion of natural fish stocks (Barg, 1995). In Galicia, despite increasing development of the cultivation of different fish species (turbot, salmon, bass, etc.), cultivation of the mussel (*Mytilus galloprovincialis*) is the most important activity, with an annual production of 190 000 t, which represents 40% of mussel production in Europe and 95% of aquaculture production in Galicia (Xunta de Galicia, 2001). Mussels are cultivated using floating platforms (mussel rafts, known locally as *bateas*) of approximately 500 $m^2$, from which some 500 ropes are hung and to which the mussels attach, in numbers ranging from 600 to 1000 individuals per m of rope (Macías and Mora, 2001). The total number of rafts installed in Galicia is 3242 (Xunta de Galicia, 2001).

Despite the huge economic benefits that this activity generates in Galicia (78 million euros and some 11 500 job positions), concentration of a large number of rafts in

*Abbreviations:* AVS, Acid Volatile Sulfide; DOP, degree of pyritization of Fe; DTMP, degree of trace metal pyritization.

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a relatively small space and the associated handling lead to a significant impact on the prevailing marine environmental conditions. Amongst the effects described in previous studies are an increase in sedimentation due to the sweeping effect of the ropes and to the metabolic activity of the mussels themselves, which can produce between 129–190 kg of faecal material (dry weight) $day^{-1}$ $raft^{-1}$ (Cabanas et al., 1979; Collazo et al., 1993), which represents an annual input of some 69.3 t of sediment per raft (Cabanas et al., 1979). This produces changes in benthic metabolism, transforming the sea floor into an anoxic environment where mineralization of organic matter occurs by sulphate reduction and methanogenesis (Macías and Mora, 2001).

In addition, it must be taken into account that mussels are powerful filter feeders and each individual filters around 15 $m^3$ of water every year. This means that they can accumulate toxic substances dissolved in sea water or that is associated with material in suspension, and because of this they are used as bioindicators to monitor marine contamination (see e.g. Besada et al., 2002). Some studies have shown significant amounts of heavy metals in the soft tissues of mussels (Otero and Fernández-Sanjurjo, 2000; Besada et al., 2002) and in their shells (Puente et al., 1996). These metals become incorporated into the sediment after release from the mussels themselves or through the faecal matter that they produce. In the specific case of the Ría de Arousa, a study has been carried out of the heavy metal content of mussel faeces in relation to mussel size, (Collazo and Pascual, 1997). From the results obtained by these authors, taking into consideration the heavy metal contents of medium-sized mussels, we estimate average inputs per raft of: 1342 g Cu $year^{-1}$, 2495 g Pb $year^{-1}$, 6449 g Cr $year^{-1}$ and 979 kg of Fe $year^{-1}$.

Despite the importance of the previous results, few studies of the heavy metal contents of biodeposits and sediments underneath mussels rafts have been carried out to date. Moreover, recent studies have highlighted a serious lack of information about the content and geochemical behaviour of trace metals in sediments in Galician Rías, particularly of Ag, Se, As and Hg (Prego and Cobelo-García, 2003). The aims of the present study were to determine the quality of the sediments in the Ría de Arousa, a natural ecosystem of great ecological and productive interest, and to investigate the geochemical behaviour of eight trace elements (Hg, As, Pb Cu, Zn, Pb, Cd and Ni).

## 2. Materials and methods

### 2.1. Study area

Galicia is one of the Spanish Autonomous communities with the longest coastline (~1700 km), which from a geomorphological point of view, is one of the most complex littoral environments of the Iberian Peninsula, where the Rías are the most unusual features (Fig. 1). The origin of the different Rías is complex and has been the subject of many studies since they were first described in by von Richthofen (1886) (for more detail see VidalRomani, 1984). It is generally accepted that the Galician Rías are very special geological formations that exist in few parts of the world (Ireland, China, Great Britain). The Rías were formed in the Tertiary era as a consequence of the reactivation of ancient hercinic faults, giving rise to tectonic sunken valleys that were later invaded by the sea (Torre, 1958). From an economic point of view the Rías constitute a highly productive ecosystem due to coastal upwelling of deep, nutrient rich water, which generally occurs between May and September.

The Ría de Arousa is the largest of the Galician Rías, comprising an area of 230 $km^2$; it is also the Ría with the highest concentration of mussel rafts (2332), which represents more than 70% of the total number of rafts in Galicia. Geologically it is fundamentally comprised of plutonic (granites and granodiorites) and metamorphic rocks (mainly gneisses) (Fig. 1). The drainage system basically consists of the rivers Ulla and Umia. The river Ulla flows into the bottom of the Ría; the corresponding drainage area is 2804 $km^2$ and the absolute flow, 79.3 $m^3$ $s^{-1}$. The river Umia flows into the Ría near the town of Cambados on the southern coast, with a drainage area of 440 $km^2$ and an absolute flow of 16.3 $m^3$ $s^{-1}$ (Río Barja and Rodríguez, 1992).

### 2.2. Sample collection

A total of 44 samples collected from different zones of the Ría de Arousa were analysed in the present study. The sampling locations and types of corer used are shown in Table 1. Sampling was carried out in September 1999 and February 2000. For this, the Ría was divided into three zones in terms of bathymetric characteristics and oceanographic processes. The inner zone corresponds to the narrowest part of the Ría, characterized by an average depth of 10–15 m and a predominantly estuarine environment due to the mixing of fresh and salt water. The middle and outer areas are zones of water exchange between the Ría and the Atlantic Ocean. Circulation takes place in two layers with a surface outgoing current and a deeper, inflowing current (Fraga and Margalef, 1979). The age of the rafts also differs in each sector. The oldest are those situated in the inner and mid zones, which were installed more than 20 ago, whereas the rafts in the outer zone were installed between 5 and 15 years ago (Macías and Mora, 2001).