

The nature and contamination of sediments in the Plentzia estuary (Biscay province, Spain)

La naturaleza y contaminación de los sedimentos en el estuario de Plentzia (Bizkaia, España)

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ABSTRACT

Plentzia estuary bed sediments were analysed in order to determine their nature and heavy metal concentrations. It was established that this is a siliclastic sandy estuary with a high concentration of organic and shell materials (mainly in the outer zone). Moreover, significant levels of Cr and Ni were found, related possibly to Mungia metallurgical industries. Despite this, heavy metal contamination in bed sediments is low. Comparing the results of this study with those of other nearby estuaries, this was sandier. However, the levels of heavy metals in the sediments are lower, especially compared with industrialised estuaries, such as the Nervión.

Key-words: : The Plentzia estuary, sediment, grain size, mineralogy and heavy metals.

RESUMEN

Los sedimentos del estuario de Plentzia fueron analizados para conocer su naturaleza y las concentraciones de metales pesados que albergaban. Se determinó que este era un estuario arenoso y siliclastico con una gran concentración de material orgánico y bioclastico (sobre todo en la zona exterior). Por otro lado se encontraron niveles significativos de Cr y Ni relacionables con las industrias metalúrgicas de Mungia. Pese a ello la contaminación por metales pesados era baja. Comparando los resultados de este estudio con los de otros estuarios de la zona, este tiene una naturaleza más arenosa y un nivel de metales pesados en sedimento más bajo, especialmente comparado con estuarios industrializados como el Nervión.

Palabras clave: Estuario de Plentzia, sedimentos, granulometría, mineralogía y metales pesados

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Introduction

Estuaries are the natural connection between the continent and the sea. This makes them one of the most complex natural systems in geological, biological and chemical terms; they are affected, simultaneously, by physical, biogeochemical and human activities. By virtue of their nature and location, estuaries have been the focal point for a wide variety of human activities. Thus, they are locations where many contaminants (such as heavy metals) can accumulate (Ridgway and Shimmiel, 2002).

Metals are naturally-occurring compounds, which can be detected in all parts of the environment. Even uncontaminated sediments contain a certain level of trace metals. However, human activities have increased the rates at which heavy metals are introduced into the marine environment, causing elevated levels in water, sediments and biota.

The objectives of this study are the grain size distribution analysis and the detection of heavy metal concentrations in bed sediments along the Plentzia Estuary (northern Spain), in order to compare them with previous studies and other estuaries of the Basque coast.

Area under investigation

The Plentzia Estuary contains the lower 8 km of the Butron River, Biscay (43°26' and 43°23' N and 2°58'W), which rises some 18 km inland (Fig. 1). This river has a 168.3 km² catchment area and 4.7 m³.s⁻¹ average annual water discharge. Water depths in the estuary lie between 0-8 m (Gyssels and Muxika). Tidal amplitudes vary between approximately 1m on neap tides and >4.5m on spring tides. As such, the Plentzia Estuary can be considered generally as a mesotidal system, although it presents some features characteristic of macrotidal estuaries. During

most of the year, tidal currents are the most important source of energy (Villate *et al.*, 1990).

Plentzia Estuary is located in the syncline of Biscay, inside the Basque-Cantabrian Basin, which was created by Pyrenean Orogeny (Mesozoic-Tertiary). This area is filled mainly with turbiditic materials and volcanic rocks of the Late Cretaceous, with Tertiary flyschoid pre-tectonic sediments that extend into the middle Eocene (Pascual *et al.*, 2004). Within the Butron River catchment area, there are geological units composed by limestone, marls, clays and quartz-arenites. However, there is basaltic formation in the eastern part. As such, the river sediments precedence is, mainly, sedimentary rocks. In the last 20 years, Plentzia port and river mouth have been dredged periodically, to ensure the navigability of the entrance, main channel and docks (Uriarte *et al.*, 2004). However, activities such as the Astondo Beach natural shape-recovery programme

and natural salt marsh restorations (Cearreta *et al.*, 2011) will help to recuperate the natural appearance of the estuary, incoming years.

Human impact includes industrial and farming activities. Industrial activity is undertaken by small companies located within the inner zone of the Butron River catchment area; their sewage is treated at Mungia (Fig. 1), which was renewed and enhanced in 2010.

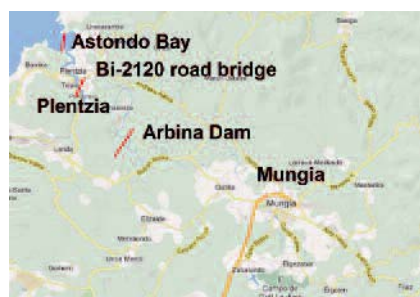


Fig. 1- Butron river water catchment area (Google Earth).

Fig. 1- La cuenca hidrográfica del río de Butrón (Google Earth).

Material and methods

The bed sampling was undertaken in the Plentzia Estuary from the Astondo Bay to the Bi-2120 road bridge (Fig. 1), on the 5th July 2012, at high tide. 24 samples were collected from estuary bed; 5 in the embayment and 19 in the estuary (Fig. 2). The samples were collected using a small Van Veen grab. The samples were analysed in two steps: a) the grain size distribution was established; and, b) the heavy metal concentrations in the sediments were determined.

Grain size analysis was undertaken using sieves according to phi (Φ) values of the Wentworth grade scale (Wentworth, 1922). Firstly, the sediments were sieved through a 32 μ m sieve, using water in order to avoid mud agglutination. Subsequently, the samples were dried and sieved, using a sieve shaker; afterwards, the sediments from each sieve were weighed.

Heavy metal analysis was carried out using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Perkin-Elmer SCIEX (Thornhill, Ontario, Canada) ELAN 9000 model. Before using the ICP-MS, the samples underwent several processes: they were sieved in order to obtain the < 63 μ m grain size fraction, then were frozen and lyophilized; subsequently, they were digested in a HNO₃-HCl mixture and heated up to 150°C using

an Anton Paar Multiwave 3000 (Graz, Austria) microwave oven.

Results and discussion

Nature of the sediments

The Plentzia Estuary can be defined as a medium sandy siliciclastic estuary (Gravel 2%; Sand 91%; Mud 7%), with high concentrations of bioclastic calcareous grains and organic material (composed of wood fragments and fuel); this pattern is especially representative of the embayment.

The muddiest sediments are found in the *inner zone* of the estuary. In the intertidal areas, the sediments are composed of muddy-sand (Sand 60%; Mud 40%); however in the bed of the small channels, the sediments are fine sand (Wentworth, 1922). As such, it can be considered as a sedimentary depositional zone.

In the *middle zone* the grain size is 250 μ m diameter (fine-medium sand). In addition, the sediments in this part of the estuary are moderately well sorted, which means that they have been more exposed to currents and over a long period of time, i.e. they have been reworked. Subsequently, sorting and morphological aspects of these samples mean that this is a "sediment reworking" zone, where the current energy is higher than in the *inner zone*.

In the *outer zone* of the estuary the grain size median is the coarsest of the estuary, especially at stations near the bay, with 295 μ m and 337 μ m grain size (medium sand, Wentworth, 1922). Such observations characterise this zone as being one of "sediment reworking", within a marginal erosional setting. This pattern is related to the high energy levels generated by the tidal currents. However, the morphology of this zone has been modified by dredging activities (Uriarte *et al.*, 2004).

Astondo Bay is composed of fine sands (65-75%), which are moderately well sorted. On the basis of the information available, Astondo Bay is defined as a "sediment reworking" zone. Such grain reworking could be related to wave action, because here the tidal currents influence is low (Gyssels and Muxika, 2005).

The mineralogy of the sediments from this estuary can be classified as siliciclastic, with a high content of calcareous bioclastic grains and organic matter. The quartz percentages are higher in the fine grain size (50-



Fig. 2- Sampling stations and general locations. Key: SR- Station Ria; S-Station.

Fig. 2- Puntos de muestreo. Leyenda: SR- Estación Ría; S- Estación.

70%). However, calcareous bioclastic grains and organic matter concentrations increase in the estuary mouth and embayment, where bioclastic grains are the principal component of the sand, reaching percentages of 60% in >500 μ m grain (the bioclastic grains are composed mainly of marine bivalves). In Astondo Bay, organic matter (hardened fuel, oil material and wood fragments) percentages are markedly higher than in the estuary, reaching 20-30%.

Grains are poorly-rounded, especially the coarsest ones. However, the bioclastic grains become more rounded in the *outer estuarine zone* and in the *bay*, due to sediment reworking. These observations mean that the grains lie generally close to their provenance.

If these results are compared with those obtained previously by other authors, the

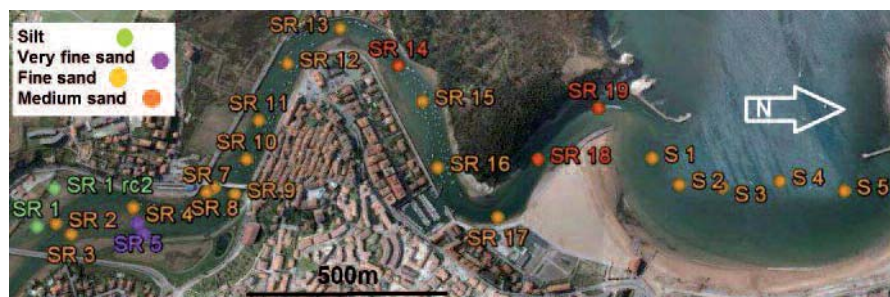


Fig. 3- Sampling stations coloured depending upon their mean grain size description.

Fig. 3- Puntos de muestreo coloreados dependiendo del tamaño medio del sedimento.

granulometry has just suffered punctual variations in the estuary mouth since 1990 (Villate *et al.*, 1990); probably dredging activities. In addition, skewness values from the embayment have become coarser over the last 7 years (Gyssels and Muxika, 2005). However, these changes could be related to the fact that the sampling of 2005 (Gyssels and Muxika, 2005) and that of this study were carried out in different seasons (winter and summer respectively).

Compared with other Basque estuaries, the Plentzia Estuary has less concentration of fine-grained sediments and higher levels of sandy sediments. It has to take into account that metals are concentrated within the <63 μm fraction and that sand acts as a diluent of heavy metals in the sediments (Horowitz, 1985). This relates to the surface area of the sediments.

Metal concentrations in the estuarine sediments

In order to examine the concentration of each metal in the different samples, they were scaled and plotted on a Principal Component Analysis diagram (Fig. 4A).

The derived PCA model (Fig. 4A) has revealed that SR 12, 14, 16 and 18 distorted the model, due to their high concentrations of some metals. If these samples were removed from the data set (Fig. 4B), the first two Principal Components (PCs) explained up to 75% of the total variance. The scores and loadings of these two PCs are shown in figures 4B and 4C: on both diagrams, a clustering of stations and metals can be observed. On the one hand, the plot of the scores shows that the bay and the estuary samples can be clearly distinguished; this could be related to salinity, pH and mineralogical differences between them, that could change the metals precipitation, or to different water sources (sea-estuary). On the other hand, the plot of loadings showed five important groupings.

The first group includes the variation in Cr and Ni; the second includes the variation of Fe, Mn and As; the third includes Pb and Zn; whilst the fourth and fifth are related to Cd and Cu, respectively.

According to the published literature, Fe and Mn are variables linked usually to the geochemical matrix of sediments. The other groups of metals indicate an overall pattern

of sediment contamination. In the case of Ni and Cr, the correlation can be attributed to certain industrial activities, where those two metals are linked, such as in metal electroplating and finishing or smelting.

Fifty-one small metal industries are located around the town of Mungia (Mungia City Council web page), in the upper part of the river. Nowadays, all water discharges from Mungia are treated in the Mungia sewage treatment plant. Nevertheless, a study undertaken by Karvelas *et al.* (2003) has revealed that almost 50% of the Cr, Pb, Ni, Cd and Ni inputs end up in the sludge, with the other 50 % in the effluent; in this instance, the Butron River. In the case of Mn, up to 77% is released by the sludge stream.

In order to compare heavy metal values in our estuarine samples, with the background values established for the Basque Coast (Solaun *et al.*, 2001) and also to know the con-

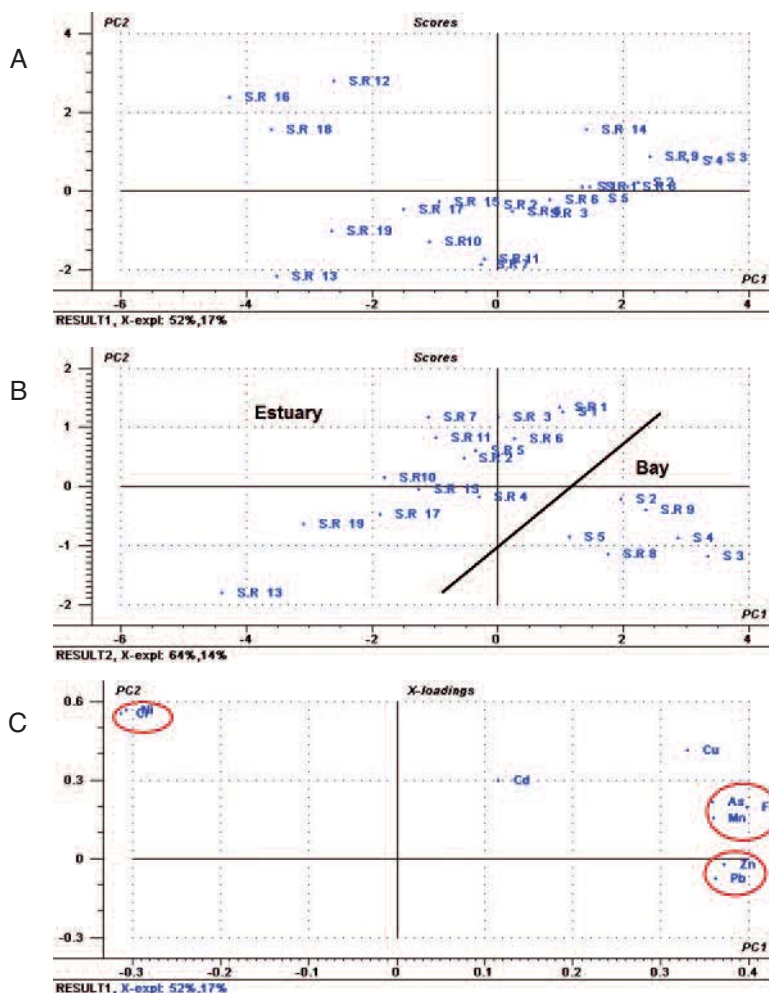


Fig. 4.- A) All Stations analysed in this study plotted on a PCA using metal concentrations as variables. B) PCA in the absence of SR 12, 14, 16 y 18. C) Loading plots from the PCA analysis of the whole data set.

Fig. 4.- A) Todos los puntos de muestreo proyectados en un PCA, usando las concentraciones de metales pesados como variables. B) PCA con la ausencia de las estaciones: SR 12, 14, 16 y 18. C) El Loading del PCA, que analiza todos los datos.

tamination level, the Enrichment Factor (EF) was determined ($EF = M_c / M_b$ (sample metal concentration) / M_b (metal background concentration)) (Table I).

	Cr	Fe	Mn	Ni	Cu	Zn	As	Cd	Hg	Pb
SR 1	LC	LC	LC	LC	LC	NC	C	NC	NC	NC
SR 2	C	NC	LC	C	LC	NC	C	NC	NC	NC
SR 3	LC	NC	LC	LC	NC	NC	C	NC	NC	NC
SR 4	LC	NC	LC	LC	NC	NC	C	NC	NC	NC
SR 5	LC	LC	LC	LC	LC	NC	C	NC	NC	NC
SR 6	LC	LC	LC	LC	LC	NC	C	NC	NC	NC
SR 7	C	NC	LC	LC	NC	NC	NC	NC	NC	LC
SR 8	LC	LC	C	LC	NC	NC	C	NC	NC	NC
SR 9	C	LC	C	LC	LC	NC	C	NC	NC	NC
SR 10	LC	NC	LC	LC	NC	NC	NC	NC	NC	NC
SR 11	LC	NC	LC	LC	NC	NC	NC	NC	NC	NC
SR 12	HC	NC	LC	HC	LC	NC	NC	NC	NC	NC
SR 13	NC	LC	NC	NC	NC	NC	NC	NC	NC	NC
SR 14	C	NC	LC	LC	LC	NC	C	LC	NC	NC
SR 15	C	NC	LC	C	NC	NC	C	NC	NC	NC
SR 16	HC	NC	NC	HC	NC	NC	NC	NC	NC	NC
SR 17	C	NC	NC	C	NC	NC	C	NC	NC	NC
SR 18	HC	NC	NC	HC	NC	NC	C	NC	NC	NC
SR 19	C	NC	LC	C	NC	NC	NC	NC	NC	NC
S 1	C	NC	LC	C	LC	NC	C	NC	NC	NC
S 2	LC	NC	LC	LC	LC	NC	C	NC	NC	NC
S 3	LC	C	C	LC	LC	NC	C	NC	NC	NC
S 4	LC	LC	C	LC	LC	NC	C	NC	NC	NC
S 5	LC	LC	C	LC	NC	NC	C	NC	NC	NC

Table I.- EF values for each sample station and metal. Key: HC, high contamination; C, medium contamination; LC, low contamination; NC, no contamination.

Tabla I.- Valores de EF para cada punto de muestreo y metal. Leyenda: HC, alta contaminación; C, media contaminación; LC, baja contaminación; NC, no hay contaminación.

If these results are compared with those of previous studies (Solaun *et al.*, 2001; Villate *et al.*, 1990), it appears that heavy metal concentrations were higher in 1990 (Villate *et al.*, 1990), when the Mungia sewage treatment plant did not exist. However, compared with the results from 2001 (Solaun *et al.*, 2001), most of heavy metals analysed in this study show higher concentrations (especially Cr and Ni). Although, it has to be taken into account that these two studies were carried out in different seasons, with different materials and methods that could affect the concentrations detected.

In order to identify the cause of this difference, a more exhaustive study should be carried out, analysing many physical and chemical factors (salinity, pH...) that could affect the precipitation of heavy metals. Also, an upstream study should be undertaken, to identify the source of the contaminants.

In spite of the higher metal concentrations, the Plentzia Estuary is still one of the most uncontaminated estuaries of the Basque Country; also, in Ni and Cr metal concentrations.

Conclusions

The Plentzia Estuary can be defined as a sandy siliclastic estuary, with high percentages of shell material throughout the estuary, particularly in the outer part (the bay). In addition, a considerable amount of organic material is present, particularly in the coarser grain sizes of the embayment samples.

The grain morphology is not well-rounded, indicating that the individual grains have not been transported any considerable distances.

Depositional areas are indicated within the inner part of the system. Zones of reworking include the channel, the outer part of the estuary and the bay. Finally, erosional areas are located within the western part of the lower estuary system, adjacent to the cliffs.

In terms of heavy metal concentrations, ignoring "outliers" in the data presented, 2 zones can be distinguished: the embayment and the estuary. A number of reasons can be proposed to explain these differences: for example, salinity, pH, mineralogical composition or different water sources. Some of these were not studied as part of the present investigation.

There are 3 main heavy metal correlations for the sediments: As, Fe and Mn-a natural association, not related to pollution; Pb and Zn-these do not reach the contamination level, so are similar to those found naturally; and Cr and Ni, very strongly related and induced by anthropogenic influences, as shown for other estuaries of the Basque Country. This latter association is related to metal industrial activities, in the Mungia area. Further sampling and analysis are required, to confirm this association.

The metal concentrations of the present study are higher in most metals, compared with those previously found by other authors in 2001, especially those of Cr and Ni in the outer part of the estuary. However, it has to be taken into account that the compared studies were undertaken in different seasons, with different materials. There are also many factors, such as pH or salinity, that have not

been studied in this work. Nevertheless, the metal concentrations from the Plentzia Estuary are still low, compared with other estuaries in the Basque Country.

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