# Physico-chemical structure of the benthic environment of a Galician ría (Ría de Ares-Betanzos, north-west Spain)

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In a preliminary study of the marine benthos of Ría de Ares-Betanzos, 50 stations covering the quadrant delineated by the coordinates 43°26′42″N–43°20′42″N and 08°18′54″W–08°10′12″W were sampled and sediment samples analysed for particle-size composition, sand, silt and clay content, degree of sorting, median diameter and grain-size diversity of sediments. Organic and inorganic content, total carbon and nitrogen, carbonates, organic carbon/total nitrogen ratio and bathymetric data were also collected. On a smaller scale a few stations were sampled for sediment redox potential and pH measurement. The salinity, temperature and oxygen content of the overlying water was also assessed.

Cluster analysis and Principal Component Analysis methods were used to describe seabed heterogeneity and the pattern of sediment distribution within the ría, and to relate the environmental variables to each sediment type. Sediments were predominantly fine to very fine sands, and exhibited a direct depth-related gradient, i.e. with the finer grades, higher organic carbon and silt and clay occurring at the shallower areas of Pontedeume, Ares and Redes inlets and Ría de Betanzos sector where terrigenous input was important. Carbonate, organic carbon and organic matter maxima occurred in the central sector of the ría where most mollusc recruitment takes place: revealing the chiefly bioclastic origin of sediments. Taking into account the geological and hydrographic processes, explanations for the formation of the sedimentary bottoms in Ría de Ares-Betanzos are provided.

# INTRODUCTION

Recent activities like seabed dredging, salmon farming, raft culture of mussels and industrial and urban inputs in the northern Galician rías have highlighted the need for more detailed information of those environments, and the possible effects of man's activities on their benthos. With the aim of assessing the effects of the discharge of effluent and other natural and anthropogenic perturbations into the benthic regions of Ría de Ares-Betanzos, a survey of the hydrographical, sedimentological and biological conditions of the ría was established; Ría de Ares-Betanzos is a double estuarine system consisting of an inlet of the sea reaching into two river valleys as far as the upper limit of the tidal rise.

The survey began in 1987 as a spatial study at 50 sampling sites covering the ría seabed (Figure 1) and was further developed at five sites on a monthly sampling basis (from August 1988 to July 1989). In December 1992, the oil tanker 'Aegean Sea' was wrecked off the Galician coast, close to Ría de Ares-Betanzos. As a result, 80,000 tons of crude oil were spilt into the sea reaching the northern coasts of Galicia (north-west of Spain). Three days after the 'Aegean Sea' oil spill, marine scientists at the University of Santiago de Compostela initiated a follow-up monitoring survey at the same five sites as before (on a monthly basis from December 1992 to December 1993), and on a longer term basis from January 1994 to October 1996. Another broad spatial study on the 50 stations initially surveyed in 1987 was carried out in

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July 1994 in order to assess the effect of the oil spill on the benthic environment.

This paper, which reports the findings of the 1987 study, is the first of a series of papers to be published on the benthic system of Ría de Ares-Betanzos before and after the oil spill. The aim of the present contribution is to provide the necessary initial description of the general benthic conditions focusing on the sedimentary environment, the nature of which has remained hitherto a matter of conjecture. Further communications will present in detail various aspects of the benthic ecology of this ría system in relation to the environmental variables delineated here and relate the observed faunal distributions to the wider boreal context of benthic communities in the Atlantic Ocean. It is hoped that this study will provide an insight into both the general ecological principles underlying the benthic ecology of ría systems and the general effects of organic and mechanical perturbations in semienclosed marine situations.

## Topography and hydrography of the study area

Ría de Ares-Betanzos is a double estuarine system (Nonn, 1966; Asensio-Amor & Grajal-Blanco, 1981) located between Ría de La Coruña and Ría de Ferrol on the northwestern coast of the Iberian Peninsula (Figure 1), covering  $\sim 272.6 \text{ km}^2$ . Depths corrected to Chart Datum (CD) range from 2 to 43 m. Four geographical sectors have been delineated in the study area. Ría de Ares sector, at the eastern part of the estuary, is 5 km long and 2 km wide with depths ranging from 2 to 6 m. Drainage from the River Eume, with a long-term mean discharge of  $9 \text{ m}^3 \text{ s}^{-1}$  is a major determinant of hydrographic conditions in the area. River outflow is mainly directed along the northern flank of the ría towards Ares and Redes inlets. South of this area, in the Ría de Betanzos sector, sheltered from the southwestern winds by the Bergantiños Plateau and from the northern and north-western winds by the Faladoira mountain range, is 7 km long and up to 5 km wide with depths that range from 2 to 12 m. The rivers Mandeo, Mendo and Lambre flow out together into the ría through the saltmarsh of Betanzos by tidal channels, with a mean annual discharge of 15 m<sup>3</sup> s<sup>-1</sup>.

In the confluence zone between the rías, bottoms in the depth range 10–20 m, are rather smooth and flat as a result of riverine deposition. The ría mouth sector, which opens onto the continental shelf is flanked by bedrock margins reducing the area of sedimentary bottom (2 km wide and 43 m deep).

The structure of the water body within the ría is highly variable in response to the varying influences of river discharge, wind and tide. Prevailing winds in the area are northerly to north-easterly in spring and summer and southerly to south-westerly in autumn and winter. Direct observations established that gales with a northerly component can disturb the bottom sediments in all but the innermost parts of the ría. The residual estuarine circulation of the water masses in the Galician rías has been investigated by Prego & Fraga (1992). In general, an important subsurface water inflow from the open ocean, known as the North Atlantic central water, flows into the ría at the bottom; moving initially east then southwards up to the Betanzos saltmarsh, then north-east towards Redes and Ares inlets and finally westwards into the Atlantic ocean. Several vortices are formed in this circulation pattern, one at the mouth of the ría generating the high sediment heterogeneity of this area.

Hydrographically, Ría de Ares-Betanzos is a normal (i.e. positive) estuary with a mixture of waters (Prego & Fraga, 1992), partially stratified in an upper level and a more salty lower level with a vertical mixture of waters (Bowden, 1980). It would fall within Beer's estuary type B category (1983); that is, one characterized by a gradual transition from continental to marine waters (Pethick, 1984; Carter, 1988). According to McLusky (1989) the study area is an euhaline estuary: annual salinities of the bottom waters range between 31 and 37 psu (Mora et al., 1994, 1996).

Tidal currents are more important than wind-induced or wave-induced currents within the ría; they flow westwards on the flood tide and eastwards on the ebb reaching near-surface velocities of  $0.89 \,\mathrm{m \, s^{-1}}$ . Predicted spring and neap mean tidal ranges at the ría are 4.14 and 0.02 m, respectively.



Figure 1. Map of Ría de Ares y Betanzos showing location of the sampling sites, geographic zones and water depth contours.

# MATERIALS AND METHODS

## Sampling design

The present investigation was carried out during a series of eight cruises, which took place during March-December 1987. The resources available dictated the methods adopted although the disadvantages of such fragmented sampling are obvious. In a preliminary survey 50 stations were sampled using a Rallier du Baty dredge (45 cm mouth diameter). Sampling locations are shown in Figure 1 and were arranged in a grid 0.5 km apart established by satellite navigation and used in conjunction with transit bearings as listed in Appendix 1. The size of the grid and the position of the stations were decided arbitrarily as there was no previous information concerning the sediments of this area. Depths at times of sampling at stations were recorded using the ship's echo-sounder and subsequently corrected to CD (Appendix 1). At each station, one sample of sediment was collected by dredging in a circle for 2 min around the point calculated from the chart. This was subsampled for total organic carbon, total nitrogen, total carbonate content, total organic matter and particle-size analysis (Buchanan, 1984). The pH and redox potential (Eh) of sediments at five stations (stations 19, 21, 30, 43 and 45; Figure 1) were determined during a single survey from undisturbed samples collected by means of a box-corer. The Eh and pH electrodes (standardized with Zobell's and buffer solutions respectively), were connected to a WTW pH 90 analyser and inserted into the sediment box at 4 cm depth (Pearson & Stanley, 1979). Temperature, pH and apparatus corrections were applied to Eh values. Water samples, from which measurements of salinity (psu), temperature ( $^{\circ}C$ ) and oxygen (ppm) contents of the bottom waters were assessed, collected by means of a Van Dorn bottle, during a single survey in August 1988 at stations 19, 21, 30, located at the central confluence zone, station 43 at Ría de Ares and station 45 at Ría de Betanzos sectors. Measurements were taken by means of WTW analysers and electrodes WTW LF 91 (for salinity) and temperature and WTW 191 (for oxygen content).

Sediment subsamples for particle-size determination were taken from the dredge and analysed in the laboratory using a combination of wet sieving of the sand fraction and pipette analysis of the silt and clay fraction as described in Buchanan (1984).

Sediment samples for organic, inorganic and total carbon and nitrogen estimations were taken from the dredge by means of a core tube and measurement of total carbon (TC) and total inorganic carbon (TIC) obtained from a Carlo Erba 1500 gas chromatography analyser following Hirota & Szyper (1975), measuring TC in a CHN analyser and determining TIC by gas chromatography analysis of a sample combusted at or below 500 °C for 4 h to remove organic matter. Total organic carbon (TOC) was then calculated as TC-TIC. The method followed was: after drying at 60 °C, the sediment was homogenized by grinding in an electric ball mill. One fraction of this sediment was introduced into the analyser in small tin containers and the carbon and nitrogen peaks obtained were compared to an acetanilide standard (C=71.09%, N=10.36%). After ignition at 480 °C for 4 h in a muffle furnace to eliminate organic

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matter (TOM) (Byers et al., 1978; Majeed, 1987), the second fraction was treated in exactly the same way and the difference between the two measures gave the organic carbon and nitrogen values.

The CHN analysis for the determination of TOC and TON was combined with the determination of TOM by loss of weight in ignition of sediments after organic matter ignition by precombustion below 500 °C. Three replicates per station (of 2 g each) were dried at 95 °C for 24 h and burned at 450 °C for 4 h. The same treatment was applied to three pure CaCO<sub>3</sub> replicates to determine methodological errors in TIC determination (Hirota & Szyper, 1975).

Sediment C:N ratios were also calculated for these sediments. This relationship is particularly useful, in combination with determinations of TOM, because some assessment of the age of organic matter or its provenance (pelagic vs terrestrial) is possible. When organic matter remains in sediments its C:N ratio usually rises, probably because of decomposition during burial.

Carbonates were estimated by gasometric determination of the  $CO_2$  delivered from hydrochloric acid digestion of the sediment sample. Analyses were done using a Bernard's gasometer using three precision replicates for each sample as described in Guitián & Carballas (1976). To assess accuracy three pure CaCO<sub>3</sub> replicates were used to standardize each analysis.

Percentages of the coarse, sand, silt and clay fractions were calculated and each station classified following the Wentworth scale within a sedimentary type. The grainsize diversity at each station was calculated from the Shannon index and the sorting coefficient used was that of Trask (1932).

# Data analyses

Prior to any numerical analysis, the statistical distribution of each variable was examined graphically and transformations (standardization by the maximum value for each variable) were applied which gave the best approximation to normality (Table 1).

An 'environmental variable × sampling site' matrix  $(23 \times 49)$  expressed as standardized values was analysed using both cluster analysis and principal component ordination. Cluster analysis was carried out first using the Bray-Curtis dissimilarity index (Bray & Curtis, 1957) coupled with unweighted pair group average linkage (UPGMA). Bray-Curtis index was chosen because of its ability to deal with matrices with a high proportion of zero data entries, i.e. it is not influenced by joint absences (Field et al., 1982). Principal Component Analysis (PCA) was used for ordination of samples and environmental factors on the basis that stations that ordinate together are more similar, based on the physico-chemical data, than stations that ordinate far apart; also, the length, direction and sense of the arrows explain the stronger or weaker degree of relationship between the axes and the variables; where appropriate, the following key variables were omitted to minimize redundancy: coarse sand, fine sand, coarse and fine silt and total carbon. Multivariate analyses were accomplished using NTSYS (Rohlf, 1990), SOLO (BMDP, Statistical Software, Inc., v. 2.0, 1988), and DECORANA (Hill, 1979) packages.

| Variable                     | Code          | Transformation                 | UPGMA<br>group |
|------------------------------|---------------|--------------------------------|----------------|
| Gravel                       | GRA           | Standardization by max. value  | IIIb           |
| Very coarse sand             | VCS           | Standardization by max. value  | IIIb           |
| Coarse sand                  | CSA           | Standardization by max. value  | IIIb           |
| Medium sand                  | MS            | Standardization by max. value  | IIb            |
| Fine sand                    | FSA           | Standardization by max. value  | IIb            |
| Very fine sand               | VFS           | Standardization by max. value  | IIa            |
| Silt and clay                | $\mathbf{SC}$ | Standardization by max. value  | IIa            |
| Coarse silt                  | CSI           | Standardization by max. value  | IIa            |
| Fine silt                    | FSI           | Standardization by max. value  | IIIa           |
| Silt                         | SIL           | Standardization by max. value  | IIa            |
| Clay                         | CLA           | Standardization by max. value  | IIIa           |
| Sediment median diameter     | MED           | Standardization by max. value  | Ι              |
| Sediment sorting coefficient | SO            | Standardization by max. value  | III            |
| Sediment diversity (Shannon) | $\mathrm{H}'$ | Standardization by max. value, | IIIa           |
| Carbon nitrogen ratio        | C:N           | Standardization by max. value  | IIb            |
| Carbonates                   | $CO_3^2$      | Standardization by max. value  | $_{\rm IIb}$   |
| Depth                        | BAT           | Standardization by max. value  | IIb            |
| Total nitrogen               | TN            | Standardization by max. value  | Ι              |
| Total organic nitrogen       | TON           | Standardization by max. value  | Ι              |
| Total carbon                 | TC            | Standardization by max. value  | IIIa           |
| Total inorganic carbon       | TIC           | Standardization by max. value  | IIIa           |
| Total organic carbon         | TOC           | Standardization by max. value  | IIIa           |
| Total organic matter         | TOM           | Standardization by max. value  | IIIa           |
| Bottom water oxygen          | $O_2$         | None                           |                |
| Bottom water temperature     | TEMP          | None                           |                |
| Bottom water salinity        | S psu         | None                           |                |
| Sediment alkalinity          | $_{\rm pH}$   | None                           |                |
| Sediment redox potential     | Eh            | None                           |                |

**Table 1.** Transformations applied, abbreviations for each variable name and classification of the environmental variables within a variable-group from the UPGMA analysis (Bray–Curtis index).

Stepwise regression was applied to the 'site-environmental factors' matrix to detect which physico-chemical parameters best matched the gradients from the sample ordination. Sample scores from axes I and II were considered as the response variable, environmental factors as dependent variables. This regression allows the determination of the most useful variables in the analysis by selecting a choice from all the variables being used in the regression equation. Analyses were performed with SPSS for Windows v. 5.0 statistical package.

# RESULTS

# Hydrography of the bottom

Summer temperatures and salinities were relatively uniform between sites, ranging from 34.7 to 35.2 psu and 14.2 to 14.8  $^{\circ}$ C (Table 2). Similarly, high oxygen content was observed in bottom water at the study area (Table 2).

# Redox potential and pH

The Eh values of the sediment, measured at 4 cm depth, at stations 19, 21, 30, 43 and 45 (Table 2), divided the Ría into two different areas. Stations 19, 21 and 30, located at the central confluence zone have corrected Eh values that range from +153 to +182 mV, i.e. showing a sufficient oxygen availability in these sediments. Lower and negative, values were recorded at the southern (station 43) and eastern (station 45) estuarine stations where the presence of dark layers was noted and H<sub>2</sub>S was detected by smell at station 45 where the redox potential discontinuity layer was found at the surface in oxygen-depleted, reduced sediments.

**Table 2.** Salinity (psu), temperature (°C), oxygen content (mg  $l^{-1}$ ) of bottom water and redox potential (Eh expressed as mV) and pH values of the top 4 cm of sediment at the selected stations (19, 21, 30, 43 and 45).

| Sites | Salinity (psu) | Temperature ( $^{\circ}C$ ) | $Oxygen \; (mg  l^{-l})$ | Redox potential (mV) | pН  |  |
|-------|----------------|-----------------------------|--------------------------|----------------------|-----|--|
| St 19 | 35.1           | 14.3                        | 7.9                      | 160.0                | 7.9 |  |
| St 21 | 34.8           | 14.2                        | 8.5                      | 153.0                | 7.9 |  |
| St 30 | 35.1           | 14.3                        | 8.8                      | 182.0                | 8.3 |  |
| St 43 | 34.7           | 14.7                        | 9.4                      | 46.2                 | 8.2 |  |
| St 45 | 35.2           | 14.8                        | 7.9                      | -51.3                | 8.1 |  |



**Figure 2.** (A) Grain-size cumulative curve-areas of the sediment types in Ría de Ares y Betanzos. HCS & GR, heterogeneous coarse sand and gravel; MS, medium sand; FSA & MFS, fine sand and very fine sand; SM & HM, sandy mud and heterogeneous mud. (B) Shepard diagram showing gravel and coarse sand, fine sand and silt and clay percentages in each sampling site.

Measurements of pH were made at a limited number of stations because of the relationship of this factor to microbial decomposition of accumulated organic matter, despite the fact that such measurements have, on the whole, not been considered to have much value as an important ecological factor in offshore sediments. These values, measured at 4 cm depth in sediments showed deviations from the normally expected range of 7.9–9.4.

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#### Sediment composition and distribution

The median grain size  $(\mu m)$  of the sediments was calculated from the cumulative curves produced from the 11 size-classes used in the Wentworth scale (Buchanan, 1984). In Figure 2, the cumulative curves grouped in four curve areas that fitted with the granulometric ranges found in the ría and a Shepard diagram with the



Figure 3. Sediment grain-size classes distribution based on the median grain-size of sediment at the sampling sites and the sediment types in Ría de Ares y Betanzos.

distribution of sites are shown graphically. Appendix 2 summarizes the percentages of sand, silt and clay ( $<63 \,\mu$ m) sized fractions. Median grain-size, grain-size diversity, the sorting coefficient (Trask, 1932), classification descriptor and sedimentary type are listed in Appendix 3.

A general decrease in the particle size of sediments was observed from the inner ría toward the Atlantic (Figure 3) with the greater part of the ría being covered by poorly to moderately sorted fine and very fine sand with variable amounts of silt, clay and coarse sediments. Extremely poorly sorted coarse sediments were found at the mouth and towards the central part of the ría where conditions are more energetic. Thus, the shallow estuarine banks of Ría de Ares and Ría de Betanzos sectors have poorly to moderately well sorted, fine to very fine sands with variable amounts of silt and clay. In the central sector of the ría, poorly to moderately sorted medium to fine sands were found. The coarser sediments occurred in the outermost area where coarse sand and gravel were indicative of prevalent high current velocities. Distributions of each particle size (gravel, coarse sand,



Figure 4. Percentage distribution of gravel, coarse sand, medium sand, fine sand, silt and clay in Ría de Ares y Betanzos seabed.

medium sand, fine sand and silt-clay) are illustrated separately in Figure 4. The sedimentary types of the ría (after Le Bris, 1988) are graphically represented in Figure 3. Five sedimentary types were found in the ría: gravel and coarse sand, medium sand, fine sand, muddy fine sand and sandy mud.

#### Total organic carbon

Total organic carbon (TOC) content in the ría sediments was distributed along a gradient that was closely related to particle-size (Figure 5); low values were found both in the outermost sector where the coarse sediments were predominant and in the clean sandy central area where the silt-clay content was <10% (Appendix 4). The outer-central sector was characterized by oceanic-type organic carbon values (Stein, 1991), i.e. <1% TOC (ranging between 0.1 and 0.5%). The confluence sector between the double estuarine system of Ares and Betanzos yielded transitional values (0.5–1.5% TOC). The inner

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estuarine sectors of Ría de Betanzos sector and Puentedeume, Redes and Cirro Inlets had particularly high carbon values 2% TOC, suggesting an association with estuarine organic inputs from the rivers Mandeo and Eume (and with detritus derived from the mussel rafts located at Cirro Inlet). The maximum values recorded were found at this area (2–3.5% TOC).

## Total organic matter

As with organic carbon, the distribution of total organic matter (TOM) in the sediments followed a gradient of enrichment towards the inner zones of the ría (Figure 5). The lowest values were found at the ocean-influenced mouth and channel (0.56% at station 7 and 1.88% at station 29), and the highest values were recorded from the sheltered areas and inner zones under continental influence where sediments were predominantly sandy muds (5.82% in station 48, 7.3% in station 15 and 8.59% in station 45).



A close correlation (r=0.67, P<0.01; df=47) was noted between total organic matter and silt and clay (SC) distributions. The equation linking these variables was:

$$\% \text{TOM} = 0.78 (\% \text{SC}) + 0.07$$
 (1)

Likewise, organic matter calculated by loss of weight in ignition was correlated (r=0.47, P<0.01; df=47) with total organic carbon calculated by chromatography analysis in the following equation:

$$\text{\%}\text{TOM} = 1.31(\text{\%}\text{TOC}) + 0.05$$
 (2)

Taking into account the high carbonate content of sediments in the ría and the variations in the determination of the organic compounds when carbonates have not been eliminated from the sample, a further correlation was established between TOM and TOC not including samples whose carbonate content was >20%. The correlation found was much higher (r=0.74, P<0.01; df=16), than would be expected; the regression equation linking these variables was:

$$\% \text{TOM} = 0.3(\% \text{TOC}) + 0.11$$
 (3)

Taking the organic carbon data obtained from chromatography (see eqn 2), a new value was calculated for the expected total organic matter (TOM'). The correlation between these two variables (r=0.86, P<0.01; df=47) was higher than the previous ones. The equation linking these variables was:

$$\text{\%}\text{TOM}' = 0.59(\text{\%}\text{TOC}) + 0.07$$
 (4)

Finally, a further correlation was established between TOM' and TOC not including samples whose carbonate content was >20%. This correlation was the highest found (r=0.89, P<0.01; df=17), the regression equation linking these variables was:

$$\text{\%}\text{TOM}' = 0.29(\text{\%}\text{TOC}) + 0.06$$
 (5)

# Total nitrogen

The distribution of TN in the sediments was closely related to TOC and TOM distributions and all were in good agreement with the distribution of fine particles (silt-clay) in the ría (Figure 5). Total nitrogen values were found within the range established for organically enriched estuarine sediments (Stein, 1991). The highest nitrogen values were found in the inner estuarine zones of Ares and Cirro inlets (0.07-0.25%) and the lowest at the mouth and adjacent areas of the central part of the ría (0.02-0.04%). Intermediate values (0.04-0.07%)

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**Table 3.** Cumulative percentage variance explained and factor weighting of components I, II and III in PCA ordination of samples and environmental parameters.

| Factor | Variance (%) | Variable              | Factor weighting |
|--------|--------------|-----------------------|------------------|
| I      | 53.93        | SIL                   | 0.9755           |
|        |              | CSI                   | 0.9747           |
|        |              | CLA                   | 0.9538           |
|        |              | FSI                   | 0.9101           |
|        |              | $\mathbf{SC}$         | 0.9030           |
|        |              | VFS                   | 0.6464           |
|        |              | TOM                   | 0.6079           |
|        |              | TN                    | 0.5725           |
|        |              | TON                   | 0.5725           |
|        |              | CSA                   | -0.7214          |
|        |              | MS                    | -0.7211          |
|        |              | MED                   | -0.6194          |
|        |              | TC                    | -0.5196          |
|        |              | TIC                   | -0.4997          |
|        |              | BAT                   | -0.4801          |
| II     | 12.9         | GRA                   | 0.8430           |
|        |              | VCS                   | 0.7386           |
|        |              | SO                    | 0.6203           |
|        |              | FSA                   | -0.4997          |
| III    | 4.5          | $\mathrm{H}^{\prime}$ | -0.4924          |

occurred in the eastern area of the estuarine system (Ría de Ares and Ría de Betanzos sectors; Appendix 4).

#### Carbon-nitrogen ratio

This ratio was advocated in the early sediment studies by Trask (1932) to explain the uniform planktonic origin of the organic matter in marine deposits. According to

**Table 4.** Cumulative percentage variance explained and factor weighting of components I, II and III in PCA ordination of samples and 18 environmental parameters.

| Component | Variance (%) | Variable                      | Factor weighting |
|-----------|--------------|-------------------------------|------------------|
| Ι         | 66.09        | SIL                           | -0.9458          |
|           |              | CLA                           | -0.9308          |
|           |              | $\mathbf{SC}$                 | -0.9272          |
|           |              | VFS                           | -0.7162          |
|           |              | TOM                           | -0.6306          |
|           |              | TN                            | -0.5537          |
|           |              | TIC                           | -0.5424          |
|           |              | MS                            | 0.7060           |
|           |              | MED                           | 0.6948           |
|           |              | VCS                           | 0.6776           |
|           |              | BAT                           | 0.5153           |
|           |              | $\mathrm{CO}_3^{2-}$          | 0.3335           |
| II        | 20.13        | GRA                           | 0.8426           |
|           |              | SO                            | 0.5939           |
|           |              | $\mathrm{H}'$                 | 0.3837           |
| III       | 8 47         | $\mathbf{C} \cdot \mathbf{N}$ | 0.8553           |
|           | 0.17         | TOC                           | 0.8500           |
|           |              | TON                           | 0.8469           |

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Redfield et al. (1963), sediments with a C:N around 6.6 have a planktonic origin. In our study area, 13 sites were found to be around this value. Bordovsky (1965), Glémarec (1964) and Majeed (1987) reported that a C:N ratio of 15 would indicate a terrestrial origin of the deposits. According to Emery (1969) higher values (>15), are due to high carbon cellulose debris from terrestrial vegetation. Fenchel & Blackburn (1979) gave C:N 16-68 for brown algae, 17-70 for sea grass and 100 for fresh leaves. In this study, C:N ratios for 25 stations were found to be near the first value (10-70), most of them being from the eastern and southern zones of the ría (Figure 5, Appendix 4). Carbon-nitrogen values higher than 15 were found in sediments all along the littoral zones of the ría, from the estuarine areas to its oceanic-influenced mouth. Due to changes during sedimentation (Bordovsky, 1965), and N and C mineralization (Blackburn, 1986), the C:N ratio gives an approximate indication about the origin of the organic matter. Nevertheless, in this study, the estuarine littoral stations were distinguished by their high C:N ratio from those from the oceanic-influenced zone.

#### Carbonates

The spatial distribution and percentage composition of carbonates in the sediments of Ría de Ares-Betanzos is shown in Figure 5 and Appendix 4. Carbonate content in the sediments of the ría followed a gradient related to the proximity to the open ocean. Minimum values were found at the oceanic-influenced area, i.e. always <15%. Values between 15 and 25% were found at the confluence zone, reaching higher values (25-35%) at the eastern and western littoral areas of Ría de Betanzos sector. It is in this area where the greatest amount of bioclastic deposits was found (probably dragged by the anticlockwise currents in the sediment transport from the central part of the ría where molluscan recruitment takes place). The highest concentrations (i.e. >35%) were found at the adjacent zones of Cirro Inlet (stations 13 and 20) as an effect of the mussel culture that is widespread in this area. Marine and estuarine bivalve, gastropod and echinoderm fragments were the commonest sources of carbonate in the sediments of the ría.

Carbonates were highest in sediments containing low amounts of silt-clay and organic matter, and lowest in sediments rich in fine sediments. An inverse particle-size related gradient existed between carbonate content and fine sediment content.

#### Comparison of sampling sites

# Classification

The cluster analysis of the sampling sites (Figure 6A) produced two distinct clusters at the 57% dissimilarity level (groups I and II), and five additional major subgroups at 54% (subgroups IIa and IIb), 43% (Ia and Ib–Ic) and 35% (groups Ib and Ic). At 46% dissimilarity level subgroups IIal and IIa2 were separated. Group I comprised the majority of the estuarine stations, while group II was composed of predominantly oceanic-influenced stations. Subgroup Ia, three sites located in the Betanzos sector, was distinguished by very fine sands,



**Figure 6.** Dendrograms showing classification of (A) 49 stations and (B) 23 environmental variables in Ría de Ares y Betanzos. The Bray–Curtis dissimilarity index with UPGMA linkage was used for comparison of stations.

with a silt-clay content >10% and by the highest TOM values (3%). Subgroup Ib united sites that were not strictly estuarine, i.e. sites not directly influenced by river drainage and characterized by very fine sands, 2-3% TOM and 20-30% carbonate content. Subgroup Ic was composed of sites with the highest silt, clay and TOM concentrations and a carbonate content <20%; they

were located at the sheltered and shallow inlets of Cirro and Redes and the Ría de Betanzos sector.

Subgroup IIa distinguished the channel and outer stations characterized by coarse, medium and fine sand bottoms while subgroup IIb comprised of the gravel and coarser sediment sites located at the ría mouth. Subgroup IIa separated the medium sand littoral sites rich in TOM

| Environmental<br>factor | Group Ia                   | Group Ib               | Group Ic           | Group IIa                                 | Group IIa2             | Group IIb                                  |
|-------------------------|----------------------------|------------------------|--------------------|---|------------------------|--|
| TOM<br>$CO^{2-}_{-}$    | 3-3.2%<br>16-26%           | 1.7 - 3.0%<br>17 - 29% | 2.2-8.6%<br>15-27% | 1.9-2.6%<br>32-51%                        | 1.2-3%<br>20-36%       | 0.5–2.1%<br>10–19%                         |
| Sediment type           | Fine to muddy<br>fine sand | Muddy fine sand        | Sandy mud          | Heterogeneous<br>coarse to<br>medium sand | Medium to fine<br>sand | Heterogeneous<br>coarse sand and<br>gravel |
| Depth                   | 2.5 - 3.5                  | 7–16 m                 | 4–12 m             | 11–19 m                                   | 8–29 m                 | 25.5–43.5 m                                |

**Table 5.** Main differences found among assemblages of stations established from the UPGMA classification as a function of their physico-chemical characteristics.

and TOC (subgroup IIal) from the northern and south-western margin sites of the central zone of the ría where medium and fine sands poor in silt-clay fraction (<10%) were clumped.

The cluster analysis of 23 environmental factors (Figure 6B) revealed the existence of three groups based on physico-chemical parameters: group I (median diameter, MED, total organic nitrogen, TON and total nitrogen, TN); group II, in which the fine particles (total silt, SIL, coarse silt, CSI and silt and clay, SC) were related to very fine sand (VFS), fine sand (FSA), medium sand (MS), carbonates ( $CO_3^{2-}$ ), carbon–nitrogen ratio (C:N) and depth (BAT); group III, that separated the fine particle-size fraction together with the variables

correlated to them (clay, CLA, fine silt, FSI, total organic carbon, TOC, total carbon TC, total organic matter, TOM, sediment diversity, H' and sediment sorting coefficient, SO) forming the subgroup IIIa and the coarse elements (coarse sand, CSA, very coarse sand, VCS and gravel, GR) of subgroup IIIb.

# Ordination

Correlation between variables was identified using PCA. An initial PCA ordination with all the physicochemical factors and sampling sites (Figure 7) revealed seven distinct outlying stations; Stations 3 and 7 at the outermost part of the ría and located on the channel were composed of coarse heterogeneous sediments; Stations 14



Figure 7. Principal Component Analysis ordination of 49 stations plotted on the plans defined by axes I and II.



**Figure 8.** (A) Principal Component Analysis ordination of 23 environmental factors plotted on the plans defined by axes I and II. (B) Principal Component Analysis ordination of stations and 18 environmental factors plotted on the plans defined by axes I and II. The sampling stations are grouped according to Figure 6 UPGMA clusters.

and 15 had special physico-chemical characteristics as they were both located on bottoms over which mussel-rafts were cultivated; Station 35 was beside Sada fishing harbour and received urban sewage from this area; Stations 45 and 48, located at the northern part of Puentedeume Inlet were the shallowest sampling sites and were subject to urban and industrial wastes from an electric power plant (sulphur and coal ashes). In this first PCA ordination, shown in Figure 8 for the environmental factors, the primary and secondary components together explained 67% of the variance in the data set, where 54% of total variance was explained by the first component (Table 3). Axis I was strongly positively correlated with the fine sediment group of variables (CSI, FSI, SC, SIL, CLA, VFS, TOM, TON, TN). By contrast, a strong negative correlation was observed for axis I with the coarse sediment group of factors: CSA, MS, MED, BAT, TIC and TC. This first axis marks a spatial gradient of shallow estuarine bottoms with high organic matter content grading to the deep and coarse oceanic-influenced sediments.

The second component, which explained 13% of the variance was positively correlated with GRA, VCS and SO and negatively with FSA, in agreement with the separation effectuated by the first component.

Five environmental factors were found to be redundant in the previous analysis: CSA, FSA, CSI, FSI and TC. Removal of the redundant variables from the data set and reanalysis produced a more distinct ordination of sites and variables. The cumulative percentage variance explained by the first three axes and weighting factors for each variable in this third analysis are shown in Table 4. Figure 8B represents sites and variables grouped by Figure 6 UPGMA cluster analysis. The ordination of the environmental variables with respect to axes I and II shows a positive weighting for VCS, MS,  $CO_3^{2-}$ , BAT and MED with axis I in opposition with SC, CLA, SIL, VFS, TOM, TIC and TN. The second factor (axis II) was only positively associated with GRA, SO and H'. Axis III was strongly correlated positively with TOC, TON and C:N ratio.

In Figure 8B, the spatial bathymetric gradient of sediment types along the ría is represented by five groups of stations: from the heterogeneous muds and sandy muds (group UPGMA Ic) of the shallow inner estuary, at the uppermost position of the diagram right quadrant, the muddy fine sand (group UPGMA Ib) belonging to the non river influenced estuary, the fine to muddy fine sand (group UPGMA Ia: stations 35, 44 and 51, not represented as a group in Figure 8B), the channel fine sand and medium sand bottoms (group UPGMA IIa2), to heterogeneous coarse sand (group UPGMA IIa1), and gravelly (group UPGMA IIb), bottoms of the ría mouth, on the negative side of axis I.

As can be seen from Figure 8B, groups of stations Ia, Ib and Ic are closely associated with the fine particle-size (the silt and clay fractions with group Ic and VFS with group Ib) and to TOC, TOM, TN and H'. Groups IIal and IIa2 are correlated with fine to medium particle size and the inorganic fraction of sediments (TIC,  $CO_3^{2-}$  and C:N) and group IIb is related to gravelly to coarse sediment fractions as well as with other sediment physical properties, such as SO, MED and BAT.

## DISCUSSION

#### Sediment grain-size characterization

The composition and distribution of sediments in the study area was highly influenced by the anthropogenic impacts detected in Ría de Ares-Betanzos: (a) from the industrial and domestic wastes concentrated in the estuarine zones; (b) from local eutrophication of water from extensive mussel and oyster raft cultures located at Cirro Inlet; and (c) from periodic dredging activities for extraction of sediment at the central confluence zone of the ría.

The distribution of sediments at the ría bottom is mainly due to three factors: the tidal current systems, the bedrock outcrops in the mouth of the ría and the influence of oceanic vs continental water interactions. The access of oceanic waters from the continental shelf takes place via the southern margin of the ría corresponding to a decreasing amount of coarse sediments

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towards the inner zones; this mass of water divides into two currents: one going up to Cirro Inlet, past Sada fishing harbour, reaching Betanzos saltmarsh, where mixing takes place between marine and continental waters from the rivers Mandeo, Mendo, Lambre and Bijoy. This current then continues upwards towards Ares Inlet, emerging by the northern margin and dragging with it fine sediments towards the ría mouth; this tidal current is subsequently divided into several vortices which generate sedimentation in tidal bays. The second branch of the oceanic flow goes directly north, due to the ascending topography of the seabed towards the north-eastern zone, forming a cyclonic vortex at the ría mouth which is continuously dragging fine sediments towards the sedimentation zone located between stations 6 and 11.

Sediment distribution throughout the ría bottom is illustrated in Figure 3. The isobaths (Figure 1) show a flat bottom with a regular slope that increases sharply towards the ría mouth. This change in steepness takes place between the 20 and 35 m isobaths (Figure 1). The area between 15 and 20 m is the confluence zone where marine and continental sediments mix, as revealed from the carbonate contribution to the medium sand in the northern part of the ría.

By contrast, in the inner estuarine zones, i.e. in water <5 m deep, high silt and clay contents are found and in the eastern (Eume) and southern (Mandeo, Mendo, Lambre and Bijoy) estuaries, sediments are composed of sandy muds. Along the margins of the ría (stations 5, 13, 16 and 21), the presence of coarse sediments at equal depths with low content in organic matter indicates a winnowing due to tidal currents (which are faster near the shore promontories) and/or a greater turbulence in the vicinity of rocky bottoms due to seabed rugosity (J.P. Pinot, personal communication).

The seabed sediments throughout Ría de Ares and Betanzos showed distinct differences in structure in different environments. In the inner estuarine zones with depths <10 m, muddy sediments with high silt and clay contents, organic matter maximum values and negative redox potentials were found; the central zone, where marine and continental waters mix, had a flat bottom composed of medium to fine sands at depths of 20-30 m; the ría mouth or oceanic-influenced area, it was the most exposed area where the oceanic water intake takes place and where coarse sediments (gravel, coarse and medium sands) were deposited at the northern and southern margins (up to stations 9 and 13) with a notable shelly input (maximum carbonate values in this area). In the channel zone muddy areas existed due to deposition (stations 6 and 11) where highest silt and clay contents and sediment negative redox values were found (Mora et al., 1996).

The sediment of the Ría de Ares-Betanzos was composed of fine and very fine sandy bottoms with high silt and clay contents over most of the bottom following a spatial and bathymetric gradient from the inner zones (composed of fine sediment fractions) towards the medium fine sand central platform, and eventually reaching the external oceanic area where the dominant sediment types were gravels and coarse sediments.

## Sediment chemical characterization

# Total organic carbon (TOC)

In the open ocean, sediments generally have very low organic carbon content (<1%). Special environmental conditions usually account for sediments rich in organic carbon (Stein, 1991). The main factors responsible for organic enrichment in marine sediments are variations in the production and preservation of marine organic carbon, and in allochthonous inputs.

In general, the preservation and depositional potential of organic carbon is higher inshore than in the open ocean. The organic carbon preservation rate is controlled by several factors, e.g. bottom water oxygen content, sedimentation rate, degree of bioturbation and the composition of the organic matter (Canfield, 1989; Reimers, 1989). Moreover, an oxygen-reduced environment is always characterized by sediments with high organic matter content (Demaison & Moore, 1980). Such an environment occurs when the oxygen demand of the water column is exceeded by organic input to the system. That is what happens in the areas with high organic carbon contents in Ría de Ares-Betanzos, as at stations 13, 15, 26, 28, 45, 48, 50 and 51, which all have organic carbon values >2% in bottoms with a varied grain-size composition.

In areas with high productivity due to upwelling, as in the Galician rías, some oxygen depletion may take place, due to the high oxygen demand induced by the decomposition of large amounts of organic matter produced in the euphotic zone leading to the formation of an oxygen minimum layer in the water. In the anoxic zones there is no correlation between sedimentation rate and sediment organic carbon content as occurs in an oxidizing environment (Stein, 1986, 1990). Changes in the organic carbon concentration of sediments with oxygen depletion are probably caused by changes in the mineral material contribution, i.e. dilution, more than to changes in the degree of organic matter preservation due to variations in sedimentation rate or productivity. Moreover, variations in the organic carbon contribution from land also influence the organic carbon content in estuarine environments in an important way. About 35% of the continental downstream flow of organic matter belongs to the labile fraction that can be directly oxidized within the estuary and adjacent littoral zones, while the remaining 65% seems to be highly resistant to decay and can be transported beyond the coast before being mineralized (Ittekott, 1988). In the St Lawrence Estuary, for example, sediments have <3% of terrigenous organic carbon; however the main carbon fraction, as deduced from the C:N ratio values, has a marine origin (Pocklington, 1976). Total organic carbon in surface sediments of the St Lawrence Estuary and Gulf is similar to that found in Ría de Ares-Betanzos, apart from differences in the riverine input and current systems (Tan & Strain, 1979). Likewise, similar values to those found in our study area have been found in the eastern Atlantic Ocean, at the River Vilaine Estuary, southern Brittany (Le Bris, 1988) and Rade de Brest (Hily, 1984). The intertidal sediments of Bay of Cádiz (south-western Spain) had mean organic carbon values of 1.48% (Establier et al., 1984). In the Galician rías, Cadée (1968) found 6% maximum TOC

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values in Ría de Arosa; Rodríguez-Castelo & Mora (1984) found 4.52–8.6% TOC at the inner estuarine zones of Ría de Pontevedra; Junoy (1988) found 4.7% TOC in Ría de Foz and Currás (1990) found 7.4% TOC in Ría del Eo. However, the most similar TOC values to those of Ría de Ares-Betanzos were found in Santander Bay (Lastra, 1991), although the maximum value (2.5%) was lower than the 3.6% reached in this study (station 13), the mean values were almost identical: 0.82% at Santander Bay and 0.84% at our study area.

## Total organic matter (TOM)

The organic matter content in the sediments is commonly found to be positively correlated with the amount of silt-clay present. This has been attributed to the similar settling velocities of the respective constituent particles (e.g. Hartnoll, 1983). In addition, colloidal and dissolved organic matter can be adsorbed onto both inorganic and organic particles, with the smaller fractions (having the larger relative surface areas) being most important (Lenz, 1972; Sharp, 1973). Suspension-feeding invertebrates also help increase the organic content of sediments through the biodeposition of undigested refractile substances. The overall distribution of organic matter within the sediment is further modified by bioturbation due to the activities of deposit-feeders and actively burrowing animals, by bacterial remineralization, and by resuspension processes (see Pearson & Rosenberg, 1978; Wassmann, 1984).

An examination of the relationship between silt-clay and organic carbon in the study area produced some interesting findings: the distribution of organic matter content followed an organic enrichment gradient towards the inner estuarine zones of the ría. This gradient can be explained by the terrigenous input of organic matter and particulate material from the rivers. A very highly significant positive correlation was found (Figure 8E) in common with the high TOM and silt-clay correlations reported from other areas (Glémarec, 1964; Mora, 1980; Shin et al., 1982; Richter, 1985; Planas, 1986), even though the correlation coefficient was lower than expected (r=0.67). Why were the correlation coefficients for TOC and TOM not as high as might be anticipated? Examination of the data revealed this to be due to several analytical factors: (1) the high carbonate content of most of the ría sediments which 'undervalues' the organic component of the samples unequally as a function of their weight; (2) the methodological differences in the analytical procedure of TOC and TOM (CHN chromatography for TOC and ignition for TOM); and (3) the dimensional differences of the samples analysed ( $\sim 50 \,\mathrm{mg}$ for CHN analyses and  $\sim 2 \,\mathrm{g}$  for ignition analyses). In spite of these considerations, strong silt-clay/TOM/TOC inter-relationships remained.

# Total organic and inorganic nitrogen (TON and TIN) and C: N ratio

The contribution of total nitrogen to sediments was mostly in the form of organic nitrogen as the inorganic fraction was almost lacking (see Appendix 4). The values found show good agreement with those recorded by Stein (1991) for organically enriched estuarine sediments where the nitrogen present is predominantly organic, and with the findings of Mackie et al. (1995) in the southern Irish Sea. Total nitrogen followed a similar trend to organic matter and silt-clay parameters with which it was highly positively correlated.

The C:N ratio indicated the origin and composition of organic matter in the area, as it approximates the ratio of animal to vegetal material that carbon analysis alone does not (Hily, 1976). According to Stein (1991), values of this ratio <10 reveal an organic component that is strictly marine in origin, values around ten represent a mixture of marine and terrestrial organic components in the sediments, while values between 10 and 30 indicate that organic matter comes from a predominantly terrigenous source. In the study area, the highest values recorded for stations 4, 13, 26, 28, 47, 50 and 51 are all due to the high terrestrial organic carbon input (i.e. combined with low total nitrogen values), affecting the C:N ratios. For the rest of the study area C:N values indicate a marine origin of the organic content at the central part of the ría and channel (C:N values  $<\!10)$  and a combination of origins is proposed for organic matter from the inner estuarine areas (values between 10 and 15).

# Carbonate content $(CO_3^{2-})$

The biological variety of carbonate-rich bioclastic debris in ría sediments allows insight into the influence of the marine versus estuarine inputs (Asensio-Amor, 1984; Currás, 1990; Hily, 1984). Although dead mollusc shells (mainly *Venus striatula, Hinia reticulata* and *Dentalium novencostatum*) were the most visible source of carbonate in the ría due to their high numbers particularly in the central platform (Sánchez-Mata et al., 1993a,b), other organisms, such as echinoderms, also contributed to a significant degree.

We conclude that the distribution of carbonates in the marine sediments of the ría has a complex origin: the topography of the seabed may explain the minimum carbonate values found in the area directly influenced by the ocean at the ría mouth, i.e. the bathymetric 'step' at  $\sim$  12–15 m deep that separates the ría from the continental shelf acts as a barrier for all the carbonate-rich fragments from mollusc recruits settling in the central area. The existence of this transition together with the type of sediment found at the mouth (gravels and coarse heterogeneous sediments with no bioclastic debris) and the known tidal current regime (tidal currents entering the ría by the southern side and exiting by the northern side) indicates an accumulation of carbonate-rich material in the zones adjacent to the central plateau; maximum carbonate levels (<50%) recorded around station 9, on the northern side of the ría, support this hypothesis. Sediment composition: Lowest carbonate levels (5% at station 48; 15% at station 49) recorded for the eastern muddy (up to 73% silt-clay at station 48) inlets of Redes and Puentedeume are a classical example of the inverse relationship between carbonate content and grain-size.

In the adjacent zones of Cirro inlet (stations 13 and 20) where mussels are cultivated, the highest carbonate content (37-40%) was recorded from mussel shell fragments deposited in the area.

Generally carbonate values in the ría reflect the presence of shelly fragments substantiating diagnosis as marine depositional material. They show the extent of the

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influence of water movement (waves and tidal currents): when these forces decrease carbonates are reduced (Asensio-Amor, 1984). High carbonate values recorded for the eastern (stations 24, 25, 26, 32, 33, 34 and 35) and western margins (stations 37, 38, 39, 41 and 51) of the southern estuary (Sada inlet) show calcareous deposition at both margins as an effect of the tidal currents that go into the ría along the southern margin, then northwards by the eastern side to Ares inlet.

As a general rule, carbonate levels in Ría de Ares-Betanzos are high; 61% of the sampling sites had  $CO_3^{2-}$  values higher than 20%. Similar levels were recorded by Currás (1990) in Ría del Eo, and by Lastra (1991) in Santander Bay.

#### Classification and ordination of samples and environmental variables

The classification of samples into five major assemblages followed a grain-size gradient from muddy fine sands (UPGMA group Ib) to heterogeneous coarse sands and gravel (UPGMA group IIb), (Table 5). This granulometric gradient is in good agreement with the disposition of samples within the ría and with the PCA ordination, since: (1) fine grain-size variables have the strongest weighting factors (Table 4); (2) the sites characterized by coarse silt (groups Ia and Ic) are at the inner estuarine areas while those belonging to very fine sands (group Ib) with a (more or less) important component of silt-clay occupy the nearby region common to both estuaries; (3) fine sands (group IIa) have a transitional situation between finer bottoms and medium sands which are located at the external northern area and finally; (4) the coarsest sediments (group IIb) are encountered at the ría mouth.

The same areas defined from the cluster analysis can be recognized by the proportional component of TOM and  $CO_3^{2-}$  as well as by the depth gradient from the estuarine shallowest to the oceanic deepest zones (Table 5). The environmental analysis gathers the samples into three main groups: those related to the organic component of sediments as TOC, TON and TOM (all three of which are associated with the finest sediments) and to sedimentary diversity (H'), and those related to the inorganic component of the substratum, e.g.  $CO_3^{2-}$ , C:N ratio and TIC. The third group is defined by the edaphic and physical factors, such as MED, SO and BAT, which are closely intercorrelated one with another and with the coarser fractions.

# CONCLUSIONS

## To conclude, some points should be highlighted:

(i) The substrate that makes up the sedimentary bottoms of Ría de Ares-Betanzos is distributed on the basis of three main factors: the water current system within the ría, the bathymetry and the oceanic vs continental influence to which the estuarine system is submitted.

(ii) The general system of water circulation within the ría has its entrance by the south shore, where the mass of water diverges into two currents, one of them parallel to the southern littoral of the ría, towards river Mandeo saltmarsh, where marine and continental waters mix together; then it goes north and eventually flows out, dragging fine sedimentary particles from Puentedeume Inlet; the second mass of water remains in the mouth of the ría, due to remarkable bathymetric differences in this area, generating a cyclonic vortex that drags the fine sediments towards a nearby sedimentary area and leaves the coarse heterogeneous sediments in the outer oceanic influence zone.

(iii) The sedimentary structure of the ría shows high contents of fine and very fine sands with significant silt and clay contents in most of it; it follows a spatial and bathymetric gradient from the two inner estuaries, mostly characterized by silt and clay bottoms, depths of less than 10 m, high organic matter contents and negative redox potentials; the central area abounds in fine and medium sands, in bottoms of 20–30 m and the external part (mouth) consists mainly of gravels and coarse sands in bottoms deeper than 30 m.

(iv) Finally, the macrobenthic faunal structure, which will be addressed elsewhere, is relatively complex since we are dealing with a double estuarine system with a central confluence area and an outer part with a direct oceanic influence; the complexity of the benthic environments in the ría lies in the differences concerning the type and properties of the bottom and indirectly, in the groups of inhabiting species. Thus, in the inner estuarine zones of both rías, with bottoms less than 10 m deep, muddy sediments with high contents of coarse silt (more than 30%) and organic matter (between 3 and 8%) can be found. These bottoms are inhabited by an impoverished community of Abra alba, facies of Diplocirrus glaucus and Spiochaetopterus costarum that shows high diversity and species richness indices, although lower than in the other areas; this is the area most exposed to urban and industrial sewage. The central zone of the ría is characterized by a medium, fine and very fine sandy plain in 10-25 m depth, with moderate organic matter contents and carbonate rates higher than 20%. It is the transition between the Abra alba and Venus gallina community. Its populations show an intermediate successional state, whose characteristic feature is the dominance of a reduced number of species. The diversity index is lower than that of the inner adjacent areas. As a general rule, molluscs are dominant in this area in terms of density as well as in biomass. In the central part of this area, dredging activities take place periodically and an extensive raft culture of mussels and oysters is located off the stations 15 and 14.

The oceanic influenced area, at the mouth of the ría, is characterized by homogeneous grain-size sediments with high contents of coarse elements, bad to moderate sorting, silt and clay rate under 5%, organic matter contents under 2% and a *Venus fasciata* community mainly represented by polychaetes which are dominant in terms of density and molluscs which are dominant in terms of biomass.

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| Site | Coordin              | nates               | Depth (m)  | Bottom type             |
|------|----------------------|---------------------|------------|-------------------------|
| 3    | 43°25′44″N           | 8°19′32″W           | 43.5       | Shelly coarse sand      |
| 4    | 43°25′21″N           | $8^{\circ}19'33''W$ | 41.0       | Gravels and coarse sand |
| 5    | $43^{\circ}26'14''N$ | $8^{\circ}18'30''W$ | 30.0       | Fine sand               |
| 6    | 43°25′45″N           | $8^{\circ}18'32''W$ | 35.0       | Gravels                 |
| 7    | 43°25′24″N           | $8^{\circ}18'34''W$ | 36.0       | Muddy fine sand         |
| 8    | $43^{\circ}24'45''N$ | $8^{\circ}18'31''W$ | 35.5       | Shelly median sand      |
| 9    | 43°26′06″N           | $8^{\circ}17'31''W$ | 11.0       | Shelly median sand      |
| 10   | 43°25′43″N           | $8^{\circ}17'30''W$ | 29.0       | Shelly fine sand        |
| 11   | 43°25′25″N           | 8°17′33″W           | 29.0       | Muddy fine sand         |
| 12   | 43°24′47″N           | $8^{\circ}17'34''W$ | 25.5       | Gravels                 |
| 13   | 43°24′14″N           | $8^{\circ}17'32''W$ | 19.0       | Coarse sand             |
| 14   | 43°23′46″N           | $8^{\circ}17'31''W$ | 16.0       | Muddy fine sand         |
| 15   | 43°23′17″N           | 8°17′33″W           | 12.0       | Sandy mud               |
| 16   | 43°25′22″N           | $8^{\circ}16'32''W$ | 26.0       | Medium sand             |
| 17   | $43^{\circ}24'44''N$ | $8^{\circ}16'34''W$ | 23.0       | Medium sand             |
| 18   | 43°24′14″N           | 8°16′31″W           | 19.0       | Muddy fine sand         |
| 19   | 43°23′46″N           | 8°16′33″W           | 16.0       | Muddy fine sand         |
| 20   | 43°23′17″N           | 8°16′32″W           | 13.0       | Muddy fine sand         |
| 21   | 43°24′48″N           | 8°15′30″W           | 16.0       | Muddy medium sand       |
| 22   | 43°24′16″N           | 8°15′35″W           | 15.0       | Muddy fine sand         |
| 23   | 43°23′47″N           | 8°15′33″W           | 14.0       | Muddy fine sand         |
| 24   | 43°23′19″N           | 8°15′31″W           | 13.0       | Shelly fine sand        |
| 25   | 43°22′46″N           | 8°15′19″W           | 10.0       | Muddy fine sand         |
| 26   | 43°22′17″N           | 8°15′17″W           | 8.0        | Muddy fine sand         |
| 27   | 43°25′09″N           | 8°14′16″W           | 7.5        | Fine sand               |
| 28   | 43°24′46″N           | 8°14′54″W           | 13.0       | Shelly medium sand      |
| 29   | 43°24′17″N           | 8°14′55″W           | 13.0       | Muddy fine sand         |
| 29   | 43°23′44″N           | 8°14′52″W           | 13.0       | Muddy fine sand         |
| 31   | 43°23′18″N           | 8°14′51″W           | 13.0       | Muddy fine sand         |
| 32   | 43°22′47″N           | 8°14′53″W           | 11.0       | Shelly fine sand        |
| 33   | 43°22′15″N           | 8°14′51″W           | 8.5        | Muddy fine sand         |
| 34   | 43°21′45″N           | 8°14′54″W           | 5.5        | Muddy fine sand         |
| 35   | 43°21′13″N           | 8°14′14″W           | 2.5        | Fine sand               |
| 36   | 43°25′24″N           | 8°13′29″W           | 7.0        | Muddy fine sand         |
| 37   | 43°24′45″N           | 8°13′28″W           | 10.5       | Muddy fine sand         |
| 38   | 43°24′15″N           | 8°13′31″W           | 11.5       | Muddy fine sand         |
| 39   | 43°23′48″N           | 8°13′27″W           | 11.0       | Muddy fine sand         |
| 40   | 43°23′15″N           | 8°13′30″W           | 12.0       | Muddy fine sand         |
| 41   | 43°22′48″N           | 8°13′26″W           | 11.0       | Muddy fine sand         |
| 49   | 43°22′16″N           | 8°13′28″W           | 9.0        | Sandy mud               |
| 43   | 43°21′45″N           | 8°13′32″W           | 5.0        | Sandy mud               |
| 44   | 43°21′13″N           | 8°13′29″W           | 3.0        | Fine sand               |
| 45   | 43°25′19″N           | 8°12′32″W           | 8.5        | Sandy mud               |
| 46   | 43°24′43″N           | 8°12′34″W           | 6.5        | Sandy mud               |
| 47   | 43°24′13″N           | 8°12′49″W           | 7.0        | Sandy mud               |
| 48   | 43°25′23″N           | 8°11′34″W           | 4.0        | Sandy mud               |
| 49   | 43°94′55″N           | 8°11/37″W           | 1.0<br>4 0 | Sandy mud               |
| 50   | 43°92′52″N           | 8°12′55″W           | т.0<br>6 О | Fine sand               |
| 51   | 43°91′45″N           | 8°19′57″W           | 2.5        | Muddy fine sand         |
| 51   | 75 41 75 IN          | 0 14 J/ W           | 5.5        | windy fille sand        |

**Appendix 1.** Coordinates, depth (m) corrected to Chart Datum and bottom type of sampling stations.

**Appendix 2.** Particle-size percentages and textural-classes (TEC) according to sediment median diameter for each sampling site. See Table 1 for codes.

| Sites | GRA   | VCS   | CSA   | MS    | FSA   | VFS   | $\mathbf{SC}$ | CSI   | FSI   | CLA   | TEC  |
|-------|-------|-------|-------|-------|-------|-------|---------------|-------|-------|-------|------|
| 3     | 5.00  | 26.80 | 32.80 | 4.80  | 3.20  | 12.80 | 14.60         | 9.47  | 4.66  | 0.47  | CSA  |
| 4     | 34.30 | 16.80 | 17.80 | 6.20  | 19.50 | 4.70  | 0.70          |       |       |       | VCS  |
| 5     | 8.80  | 16.20 | 20.20 | 14.30 | 37.80 | 2.20  | 0.50          |       |       |       | MS   |
| 6     | 0.00  | 0.40  | 3.20  | 17.80 | 19.60 | 26.80 | 32.20         | 27.78 | 0.91  | 3.51  | VFS  |
| 7     | 65.70 | 17.80 | 8.60  | 4.30  | 3.00  | 0.40  | 0.20          |       |       |       | GRA  |
| 8     | 0.20  | 0.80  | 3.00  | 12.40 | 65.80 | 15.40 | 2.40          |       |       |       | FSA  |
| 9     | 3.40  | 6.80  | 34.40 | 39.00 | 14.60 | 1.00  | 0.80          |       |       |       | MS   |
| 10    | 0.20  | 1.60  | 10.00 | 33.00 | 53.00 | 1.20  | 1.00          |       |       |       | FSA  |
| 11    | 0.00  | 0.00  | 0.00  | 0.60  | 11.80 | 38.60 | 49.00         | 42.26 | 0.72  | 6.02  | VFS  |
| 12    | 66.50 | 9.30  | 15.60 | 4.70  | 2.00  | 1.00  | 0.90          |       |       |       | GRA  |
| 13    | 2.00  | 8.20  | 53.20 | 27.60 | 7.40  | 1.20  | 0.40          |       |       |       | CSA  |
| 14    | 0.00  | 0.00  | 0.60  | 9.00  | 56.00 | 26.00 | 8.40          |       |       |       | FSA  |
| 15    | 8.00  | 3.00  | 2.80  | 2.00  | 3.20  | 10.80 | 70.20         | 36.74 | 14.85 | 18.61 | CSI  |
| 16    | 0.20  | 2.40  | 24.00 | 56.40 | 13.00 | 2.60  | 1.40          |       |       |       | MS   |
| 17    | 0.00  | 0.40  | 9.40  | 42.60 | 34.00 | 12.00 | 1.60          |       |       |       | MS   |
| 18    | 0.20  | 1.80  | 14.00 | 23.20 | 18.00 | 34.30 | 8.50          |       |       |       | FSA  |
| 19    | 0.00  | 0.00  | 0.40  | 1.80  | 19.20 | 47.00 | 31.60         | 24.16 | 0.09  | 7.36  | VFS  |
| 20    | 0.80  | 4.00  | 12.20 | 11.60 | 35.80 | 31.40 | 4.20          |       |       |       | FSA  |
| 21    | 0.00  | 0.40  | 7.60  | 57.40 | 26.00 | 4.90  | 3.70          |       |       |       | MS   |
| 22    | 0.00  | 0.80  | 3.00  | 11.00 | 32.00 | 38.20 | 15.00         | 10.98 | 0.39  | 3.63  | VFS  |
| 23    | 0.00  | 0.00  | 1.20  | 8.20  | 22.80 | 41.40 | 26.40         | 21.19 | 0.07  | 5.14  | VFS  |
| 24    | 1.20  | 0.80  | 3.80  | 15.40 | 62.00 | 15.00 | 1.80          |       |       |       | FSA  |
| 25    | 2.80  | 1.60  | 3.20  | 11.20 | 51.40 | 13.80 | 16.00         | 4.61  | 2.68  | 8.72  | FSA  |
| 26    | 1.60  | 1.40  | 1.80  | 10.80 | 71.00 | 10.40 | 3.00          |       |       |       | FSA  |
| 27    | 1.20  | 0.60  | 2.60  | 19.80 | 67.00 | 7.80  | 1.00          |       |       |       | FSA  |
| 28    | 4.60  | 5.60  | 16.20 | 53.80 | 6.40  | 10.60 | 2.80          |       |       |       | MS   |
| 29    | 0.20  | 0.80  | 3.80  | 15.40 | 26.80 | 27.20 | 25.80         | 19.63 | 0.87  | 5.3   | VFS  |
| 30    | 0.00  | 0.00  | 2.00  | 11.20 | 28.00 | 34.40 | 24.40         | 15.62 | 2.38  | 6.4   | VFS  |
| 31    | 0.00  | 0.00  | 0.80  | 4.60  | 22.60 | 38.40 | 33.60         | 24.2  | 1.77  | 7.63  | VFS  |
| 32    | 5.00  | 4.40  | 5.20  | 9.40  | 43.20 | 25.20 | 7.60          |       |       |       | FSA  |
| 33    | 2.20  | 0.40  | 3.20  | 10.00 | 30.40 | 38.60 | 15.20         | 10.79 | 0.57  | 3.84  | VFS  |
| 34    | 0.40  | 0.00  | 0.40  | 2.00  | 9.60  | 45.40 | 42.20         | 32.48 | 2.38  | 7.33  | TVFS |
| 35    | 0.00  | 0.00  | 0.00  | 0.80  | 25.00 | 69.80 | 4.40          |       |       |       | VFS  |
| 36    | 0.00  | 0.00  | 1.60  | 13.00 | 43.60 | 19.80 | 22.00         | 15.22 | 1.43  | 5.35  | FSA  |
| 37    | 0.40  | 0.40  | 3.00  | 20.00 | 16.40 | 37.00 | 22.80         | 17.39 | 1.84  | 3.57  | VFS  |
| 38    | 0.40  | 0.40  | 3.40  | 15.40 | 15.40 | 38.00 | 27.00         | 16.65 | 3.55  | 6.8   | VFS  |
| 39    | 0.40  | 0.60  | 2.80  | 9.40  | 26.40 | 29.20 | 31.20         | 16.15 | 5.02  | 10.02 | VFS  |
| 40    | 0.00  | 0.00  | 0.60  | 7.40  | 16.20 | 29.80 | 46.00         | 36.33 | 4.47  | 5.2   | VFS  |
| 41    | 0.80  | 0.60  | 1.00  | 2.80  | 14.60 | 44.40 | 35.80         | 27.42 | 2.33  | 6.06  | VFS  |
| 42    | 0.00  | 0.00  | 0.00  | 0.60  | 4.00  | 43.40 | 52.00         | 39.37 | 5.58  | 7.05  | CSI  |
| 43    | 0.00  | 0.00  | 0.00  | 0.00  | 1.80  | 35.00 | 63.20         | 47.1  | 8.76  | 7.34  | CSI  |
| 44    | 0.20  | 0.20  | 0.40  | 0.60  | 5.20  | 76.20 | 17.20         | 14.45 | 0.84  | 1.92  | VFS  |
| 45    | 2.80  | 1.40  | 1.60  | 1.40  | 2.60  | 27.20 | 63.00         | 24.98 | 16.34 | 21.68 | CSI  |
| 46    | 0.00  | 0.00  | 0.20  | 1.60  | 4.60  | 47.20 | 46.40         | 38.97 | 4.18  | 3.25  | VFS  |
| 47    | 0.00  | 0.20  | 0.80  | 2.00  | 12.80 | 33.20 | 51.00         | 40.08 | 4.43  | 6.49  | CSI  |
| 48    | 1.60  | 1.00  | 0.80  | 0.60  | 2.60  | 20.80 | 72.60         | 39.25 | 23.37 | 9.98  | CSI  |
| 49    | 0.20  | 0.00  | 0.00  | 0.40  | 4.60  | 55.00 | 39.80         | 33.74 | 1.55  | 4.51  | VFS  |
| 50    | 0.00  | 0.40  | 4.20  | 22.40 | 46.00 | 17.20 | 9.80          |       |       |       | FSA  |
| 51    | 0.00  | 0.00  | 0.00  | 0.00  | 8.00  | 72.40 | 19.60         | 13.55 | 1.88  | 4.16  | VFS  |

| Appendix 3.      | Sediment median diameter | (MED), diversity | (H'), Trask' | sorting coefficient | (SO), classification | and sediment type |
|------------------|--------------------------|------------------|--------------|---------------------|----------------------|-------------------|
| according to Fig | ure 5.                   |                  |              |                     |                      |                   |

| Sites    | MED   | $\mathrm{H}'$ | SO             | Classification          | Sediment type             |
|----------|-------|---------------|----------------|-------------------------|---------------------------|
| 3        | 1.153 | 2.478         | 7.690          | Very poorly sorted      | Heterogeneous coarse sand |
| 4        | 2.492 | 2.312         | 4.549          | Very poorly sorted      | Heterogeneous coarse sand |
| 5        | 0.578 | 2.258         | 4.178          | Very poorly sorted      | Heterogeneous coarse sand |
| 6        | 0.071 | 2.348         | 3.464          | Very poorly sorted      | Muddy fine sand           |
| 7        | 5.436 | 1.540         | 13.53          | Very poorly sorted      | Gravels                   |
| 8        | 0.169 | 1.420         | 1.116          | Very well sorted        | Fine sand                 |
| 9        | 0.659 | 1.959         | 1.925          | Poorly sorted           | Heterogeneous coarse sand |
| 10       | 0.242 | 1.533         | 1.786          | Moderately sorted       | Medium sand               |
| 11       | 0.040 | 1.758         | 2.203          | Poorly sorted           | Sandy mud                 |
| 12       | 5.830 | 1.523         | 1.707          | Moderately sorted       | Gravels                   |
| 13       | 1.033 | 1.749         | 1.759          | Moderately sorted       | Heterogeneous coarse sand |
| 14       | 0.142 | 1.327         | 1.716          | Moderately sorted       | Fine sand                 |
| 15       | 0.019 | 2.597         | 2.509          | Poorly sorted           | Heterogeneous mud         |
| 16       | 0.493 | 1.626         | 1.750          | Moderately sorted       | Medium sand               |
| 17       | 0.317 | 1.789         | 2.075          | Poorly sorted           | Medium sand               |
| 18       | 0.154 | 2.025         | 2.886          | Very poorly sorted      | Fine sand                 |
| 19       | 0.042 | 1.885         | 1.868          | Moderately sorted       | Muddy fine sand           |
| 20       | 0.154 | 2.061         | 2.327          | Poorly sorted           | Fine sand                 |
| 21       | 0.380 | 1.507         | 1.750          | Moderately sorted       | Medium sand               |
| 22       | 0.082 | 2.168         | 1.993          | Poorly sorted           | Muddy fine sand           |
| 23       | 0.066 | 2.087         | 1.896          | Poorly sorted           | Muddy fine sand           |
| 24       | 0.181 | 1.567         | 1.476          | Moderately sorted       | Fine sand                 |
| 25       | 0.154 | 2.291         | 1.868          | Moderately sorted       | Muddy fine sand           |
| 26       | 0.181 | 1.372         | 1.433          | Moderately sorted       | Fine sand                 |
| 27       | 0.185 | 1.385         | 1.419          | Moderately sorted       | Fine sand                 |
| 28       | 0 493 | 1 968         | 1 599          | Moderately sorted       | Medium sand               |
| 29       | 0.084 | 2 433         | 2 718          | Poorly sorted           | Muddy fine sand           |
| 30       | 0.078 | 2.100         | 2.710          | Poorly sorted           | Muddy fine sand           |
| 31       | 0.070 | 2.510         | 2.105          | Poorly sorted           | Muddy fine sand           |
| 32       | 0.159 | 2.150         | 1 786          | Moderately sorted       | Fine sand                 |
| 32       | 0.097 | 2.002         | 1.896          | Poorly sorted           | Muddy fine sand           |
| 33       | 0.047 | 1.950         | 2 181          | Poorly sorted           | Sandy mud                 |
| 35       | 0.074 | 0.910         | 1 419          | Moderately sorted       | Fine sand                 |
| 36       | 0.124 | 2 189         | 2 270          | Poorly sorted           | Muddy fine sand           |
| 30       | 0.079 | 2.105         | 2.270          | Poorly sorted           | Muddy fine sand           |
| 38       | 0.075 | 2.551         | 2.305          | Poorly sorted           | Muddy fine sand           |
| 30       | 0.074 | 2.130         | 2.510          | Poorly sorted           | Muddy fine sand           |
| 19<br>40 | 0.074 | 2.341         | 2.011          | Poorly sorted           | Sandy mud                 |
| 40       | 0.042 | 2.221         | 2.303          | Poorly sorted           | Muddy fine sand           |
| 49       | 0.001 | 2.113         | 9.117          | Poorly sorted           | Sandy mud                 |
| 42       | 0.033 | 1.704         | 2.117          | Poorly sorted           |                           |
| 43       | 0.025 | 1.730         | 2.127          | Modenately well control | Muddy fine cond           |
| 45       | 0.000 | 9.465         | 1.290          | Poorly sorted           | Hotorogonoous mud         |
| тJ<br>46 | 0.024 | 2.403         | 2.339<br>9.120 | Poorly sorted           | Sondy mud                 |
| 40<br>47 | 0.044 | 1.710         | 2.100          | Poorly sorted           | Sandy mud                 |
| 40       | 0.029 | 2.078         | 2.331          | rooriy soried           |                           |
| 40       | 0.015 | 2.221         | 2.033          | Poorly sorted           | neterogeneous mud         |
| 49       | 0.047 | 1.552         | 2.159          | Poorly sorted           | Sandy mud                 |
| 50       | 0.167 | 1.742         | 1.786          | Moderately sorted       | Fine sand                 |
| 51       | 0.056 | 1.318         | 1.363          | Moderately sorted       | Muddy fine sand           |

**Appendix 4.** Abundance scores of environmental data measured in each site: organic (TOC), inorganic (TIC) and total (TC) carbon, organic (TON) and total (TN) nitrogen, organic matter (TOM), carbon-nitrogen ratio (C:N) and carbonate  $(CO_3^{2-})$  percentage content in sediments and classification of sites within a site-group by UPGMA analysis (Bray-Curtis index).

| Site     | ТОС  | тіс  | ТС           | TON  | TN   | том          | $\mathbf{C}\cdot\mathbf{N}$ | $CO^{2-}$      | UPGMA        |
|----------|------|------|--------------|------|------|--------------|-----------------------------|----------------|--------------|
| 5.110    | 100  | ne   | TC.          | TON  | 110  | ТОМ          | 0.1                         | $UO_3$         | group        |
| 3        | 0.49 | 2.79 | 3.29         | 0.03 | 0.03 | 1.35         | 15.88                       | 14.18          | IIb          |
| 4        | 0.78 | 2.08 | 2.86         | 0.02 | 0.02 | 0.72         | 39.28                       | 14.79          | IIb          |
| 5        | 0.07 | 1.90 | 2.11         | 0.02 | 0.02 | 1.33         | 2.66                        | 19.18          | $_{\rm IIb}$ |
| 6        | 0.12 | 0.84 | 1.25         | 0.02 | 0.02 | 2.13         | 3.05                        | 18.08          | $_{\rm IIb}$ |
| 7        | 0.41 | 3.38 | 3.50         | 0.04 | 0.04 | 0.56         | 22.74                       | 10.27          | $_{\rm IIb}$ |
| 8        | 0.21 | 4.80 | 4.87         | 0.03 | 0.03 | 0.94         | 11.57                       | 14.59          | IIa2         |
| 9        | 0.98 | 6.32 | 7.30         | 0.05 | 0.05 | 2.61         | 19.65                       | 50.76          | IIal         |
| 10       | 0.22 | 3.36 | 3.57         | 0.02 | 0.02 | 1.21         | 12.51                       | 21.85          | IIa2         |
| 11       | 0.44 | 3.48 | 3.92         | 0.06 | 0.06 | 3.22         | 7.49                        | 22.94          | Ic           |
| 12       | 0.20 | 3.86 | 4.06         | 0.03 | 0.03 | 1.14         | 7.53                        | 18.77          | $_{\rm IIb}$ |
| 13       | 3.57 | 4.90 | 8.47         | 0.04 | 0.04 | 1.87         | 92.77                       | 40.41          | IIal         |
| 14       | 0.13 | 5.61 | 5.75         | 0.06 | 0.08 | 2.49         | 2.10                        | 25.75          | IIa2         |
| 15       | 2.24 | 2.50 | 4.73         | 0.25 | 0.26 | 7.30         | 9.03                        | 16.85          | Ic           |
| 16       | 0.30 | 3.87 | 4.18         | 0.02 | 0.02 | 1.26         | 16.46                       | 19.86          | IIa2         |
| 17       | 0.06 | 4.55 | 4.60         | 0.02 | 0.02 | 1.42         | 2.55                        | 22.12          | IIa2         |
| 18       | 0.29 | 3.83 | 4.12         | 0.03 | 0.03 | 2.02         | 9.46                        | 21.78          | IIa          |
| 19       | 0.29 | 3.99 | 4.28         | 0.05 | 0.05 | 2.89         | 6.10                        | 21.16          | Ib           |
| 20       | 1.02 | 6.06 | 7.08         | 0.05 | 0.05 | 2.84         | 21.26                       | 36.75          | IIa2         |
| 21       | 0.12 | 3.66 | 3.79         | 0.02 | 0.02 | 1.20         | 5.67                        | 19.74          | IIa2         |
| 22       | 0.14 | 3.35 | 3.49         | 0.03 | 0.03 | 1.73         | 5.10                        | 17.14          | Ib           |
| 23       | 0.16 | 3.86 | 4.02         | 0.03 | 0.03 | 2.17         | 4.62                        | 18.25          | Ib           |
| 24       | 0.14 | 5.29 | 5.42         | 0.03 | 0.03 | 1.75         | 4.39                        | 29.74          | Ha2          |
| 25       | 1.05 | 4.18 | 5.23         | 0.06 | 0.06 | 2.34         | 16.34                       | 29.74          | Ib           |
| 26       | 2.76 | 3.11 | 5.87         | 0.04 | 0.04 | 2.07         | 60.38                       | 31.00          | IIa2         |
| 27       | 0.62 | 5.10 | 5.72         | 0.04 | 0.04 | 2.02         | 13.82                       | 29.87          | IIa2         |
| 28       | 2.16 | 4.80 | 6.96         | 0.03 | 0.03 | 2.12         | 61.8                        | 32.00          | IIal         |
| 29       | 0.21 | 3.30 | 3.51         | 0.03 | 0.03 | 1.88         | 6.44                        | 22.00          | Ib           |
| 30       | 0.18 | 3.33 | 3.52         | 0.05 | 0.05 | 2.33         | 4.01                        | 21.87          | Ib           |
| 31       | 0.38 | 3.37 | 3.75         | 0.04 | 0.04 | 3.00         | 8.39                        | 22.96          | Ib           |
| 32       | 0.39 | 5.59 | 5.98         | 0.06 | 0.06 | 2.98         | 6.57                        | 30.84          | Ha2          |
| 33       | 0.53 | 4.55 | 5.08         | 0.05 | 0.05 | 2.64         | 11.39                       | 28.87          | Ib           |
| 34       | 0.74 | 2.55 | 3.29         | 0.04 | 0.04 | 2.48         | 19.51                       | 27.60          | Ic           |
| 35       | 0.40 | 3 47 | 3.87         | 0.04 | 0.04 | 3.15         | 9.87                        | 26.48          | Ia           |
| 36       | 0.32 | 2.88 | 3.20         | 0.04 | 0.04 | 1.65         | 8.58                        | 22.82          | Ib           |
| 37       | 0.39 | 3.56 | 3.95         | 0.04 | 0.04 | 1.81         | 9.33                        | 25.63          | Ib           |
| 38       | 0.59 | 3.31 | 3.90         | 0.05 | 0.05 | 2.42         | 10.80                       | 27.89          | Ib           |
| 39       | 0.56 | 3.27 | 3.84         | 0.05 | 0.05 | 2.38         | 10.85                       | 26.20          | Ib           |
| 40       | 0.66 | 2 59 | 3 26         | 0.06 | 0.06 | 3.18         | 11 59                       | 22 39          | Ic           |
| 41       | 0.00 | 3 30 | 3 58         | 0.04 | 0.04 | 3.03         | 6.01                        | 25.77          | Ib           |
| 49       | 0.80 | 2 48 | 3 29         | 0.07 | 0.07 | 4.05         | 11.56                       | 22.77          | Ic           |
| 43       | 1 19 | 1.86 | 3.05         | 0.07 | 0.08 | 4.89         | 16.29                       | 17.75          | Ic           |
| 44       | 0.68 | 1.55 | 2.03         | 0.07 | 0.00 | 3.04         | 13.20                       | 15.91          | Io<br>Io     |
| 45       | 9.37 | 0.11 | 2.23         | 0.05 | 0.05 | 8 59         | 15.20                       | 8 45           | Ia           |
| 46       | 0.90 | 0.83 | 1 73         | 0.15 | 0.15 | 9.77         | 16 59                       | 11.83          | Ic           |
| 47       | 1.67 | 0.05 | 1.75<br>9.27 | 0.05 | 0.05 | 4.11<br>9.92 | 30.57                       | 15.40          | Ic           |
| 17<br>48 | 9.99 | 0.70 | 4.37<br>9.98 | 0.05 | 0.05 | 5.20         | 14.02                       | 5.07           | Ic           |
| то<br>40 | 4.44 | 1.25 | 2.20         | 0.10 | 0.10 | 9.04<br>9.70 | 14.00                       | J.07<br>14 51  | IC<br>In     |
| 79<br>50 | 0.09 | 1.55 | 2.23         | 0.03 | 0.03 | 2.79         | 10.03                       | 14.JI<br>91.60 |              |
| 51       | 2.78 | 1.37 | 5.55<br>4.31 | 0.03 | 0.03 | 2.98         | 69.99                       | 26.48          | Ia           |