The response of benthic foraminifera to pollution and environmental stress in Ria de Aveiro (N Portugal)

La respuesta de los foraminíferos bentónicos a la contaminación y el estrés ambiental en la Ría de Aveiro (N de Portugal)


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Abstract

This work evaluates the quality of the sediment in Ria de Aveiro, a coastal lagoon located at N of Portugal that is under strong anthropic influence, and the effects of the contamination on benthic foraminifera. The initial approach for measuring pollution was done through the load pollution index (LPI), based on As, Cd, Cr, Cu, Ni, Pb and Zn concentrations, and determined by total digestion of the sediments (TDS). This information was complemented by conducting a metal fractionation technique (sequential chemical extraction - SCE) in some of the most contaminated samples in order to define the relevance of different metal bearing-phases (exchangeable cations adsorbed by clay and co-precipitated with carbonates, absorbed by organic matter and retained in the mineralogical phase) and to evaluate the toxic heavy metal availability. Multivariable statistical analyses were carried out taking into consideration the geochemical results, as well as the biotic (percentage of species/groups of species; foraminifer abundance and diversity) and abiotic variables, such as sediment content in mud, total organic carbon (TOC) and Eh.

SCE results show that most of the element concentration in the sediments is retained in the resistant mineralogical phase. However, the higher bioavailability of some toxic elements, such as As, Cd, Cu, Hg, Ni, Pb and Zn, found in Laranjo Bay, Aveiro City, Aveiro Harbours and Espinheiro Channel, have a generic negative impact on benthic foraminifera of the Aveiro lagoon. Differential sensitivity of benthic foraminifera to high concentrations of heavy metals may exist. Quinqueloculina seminulum, for instance, seems to be more tolerant to higher bioavailable concentrations of Pb and Cu than Ammonia tepida or Haynesina germanica. Both
species were previously considered to be the most heavy metal-tolerant foraminifer species.

This study confirmed the use of benthic foraminifera as an important tool for the evaluation of the environmental quality of an ecosystem and for monitoring and restoring it.

**Keywords:** toxic elements; geochemical analysis; benthic foraminifera; lagoon system, Ria de Aveiro, N Portugal

Resumen

Este estudio confirmó el uso de los foraminíferos bentónicos como una importante herramienta para la evaluación de la calidad ambiental de los ecosistemas y también para el seguimiento y la restauración.

**Palabras clave:** elementos tóxicos, análisis geoquímicos, foraminíferos bentónicos, sistema lagunar, Ria de Aveiro, N de Portugal

1. Introduction

In the past decades, the degradation of aquatic environments has become a topic of increasing concern among the public. In northern Portugal, the natural features of Ria de Aveiro have been intensely modified, mainly as a result of urbanization and industrial development.

More than 300,000 inhabitants live around the lagoon and its channels. This high concentration of people in such a small area has brought up several environmental problems and contributed to the degradation of the lagoon’s water quality. Industrial and agricultural activities are intense, stressing the local resources, and land development is on the rise around Ria de Aveiro. The main vulnerable areas of the lagoon, from a water quality point of view, seem to be the far end of the main channels, where bioavailability of pollutants is neglected in most of these works. According to Neff (2002), bioavailability is the extent to which a chemical can be absorbed or adsorbed by a living organism through active (biological) or passive (physical or chemical) processes.

The main goals of this study are identifying heavy metal contamination patches caused by anthropic activities in the sediments of the Ria de Aveiro channels and evaluating the effects of higher bioavailable concentrations of heavy metals (determined by sequential chemical extractions using ICP-MS) on benthic foraminifera.
behind water circulation in the Aveiro lagoon. Tides are semidiurnal and are present in the entire lagoon. The tidal current velocities near the entrance can be higher than 2 m/s (Vaz and Dias, 2008; Dias et al., 2000), but they are weak in many of the innermost small canals and mudflats. Winds affect both the hydro-dynamical regime and the mixing processes in the lagoon by generating surface shear stress and waves (Lopes et al., 2006). The lagoon receives freshwater supplied by several rivers and riverine bodies. The main rivers are the Vouga (~50 m$^3$/s average discharge) and the Antuã (~5 m$^3$/s) (Moreira et al., 1993). The river influence is higher in the upper and inner parts of the lagoon (Vaz and Dias, 2008).

3. Materials and methods

3.1. Sampling and sample preparation

A total of 215 grab-samples collected in 2006/07 in the Ria de Aveiro channels using a boat (ZOE I) were analyzed for grain size, heavy metals and microfauna (benthic foraminifera). During the sampling campaigns, the depth was measured with the boat’s sonar and the sites were located with GPS. The surface sediment samples were collected with an adapted Petit Ponar Grab (opening at both extremities). Only the top ~5 cm of sediment were...
retained for analysis. Sediment splits were taken at each site for textural, geochemical and microfaunal (benthic foraminifera) analyses. The sediments sampled for geochemical analysis were immediately frozen on board. The samples collected for foraminifera studies were stored in buffered ethanol stained with Rose Bengal (2 g of Rose Bengal in 1,000 ml of alcohol). Rose Bengal was used to differentiate between living and dead foraminifera (e.g., Murray, 1991).

3.2 Methods

Field parameters

Some environmental parameters, such as temperature, salinity/conductivity, pH and Eh, were measured in bottom water and sediment. Once in the laboratory, the sediment samples for textural and geochemical analysis were dried to constant weight in an oven for about 72 h, at 45°C, and stored for subsequent analysis.

Grain Size Analysis

For the grain size analysis, the dried sediment samples were homogenized and a portion of about 150-250 g was analyzed. The fine fraction was separated from the sand fraction by wet sieving using a 63 µm screen. The sediment fraction coarser than 63 µm was dry sieved through a battery of sieves spaced at 1 phi (ø) unit.

Chemical Analysis

For the geochemical analysis, a split of the sediment fraction finer than 2,000 µm of each sample was milled. The concentrations of 41 chemical elements were determined at ACME Analytical Laboratories, Canada. The analysis was done by ICP-MS analysis after the total digestion of sediment (TDS) with acid (HClO₄–HNO₃–HCl–HF). Concentrations of Al, Fe, P, Zn, Pb, Cr, Cu, As, Ni and Cd were analysed in this work.

Additionally, 17 samples (Laranjo Bay - Lar1, Lar3, Lar5, Lar6; Aveiro Town – C14; Espinheiro Channel – CC3, CC5, CC6, CC17; Ílhavo Channel – C15, C110; lagoon mouth – EM 22; Aveiro Harbours – Lota1, Lota3, CCom1 and CCom2) were chosen in different lagoonal areas for their high heavy metal concentration and submitted to sequential chemical extractions (SCE) in order to assess the element concentration retained by a specific sediment phase or range of phases. SCE were performed using the following procedure: Step 1 – 1.0 g of sample was leached with 10 ml of 0.1 M sodium pyrophosphate (Na₃P₂O₇) for 1 h (adsorbed by organic matter - humic and fulvic compounds). The element concentrations in the other phases were calculated as the difference between the total concentration and the sum of the two steps (1 and 2).

Total organic carbon (TOC) was determined in a portion of bulk sediment from each sample. Samples were dried at 105 °C for 8 h. About 5 g of dry sediment were submitted to loss-on-ignition (LOI) at 450 °C for 8 h (Oliver et al., 2001). TOC values are reported as percentages of dry weight.

Foraminiferal studies

The samples were washed over a sieve of 63 µm mesh. As foraminifera are rare in the dry sediment fraction >500 µm, in the studied area, the sediments fraction 63-500 µm was used to determine the abundance of benthic foraminifera, expressing the number of tests per gram of dry bulk sediment, and also to study the composition of living assemblages. Foraminiferal tests having rose Bengal stained interiors and containing protoplasm were considered living at the time of the collection (e.g. Horton et al., 1999; Murray and Alve, 1999). For the study of benthic foraminifera’s assemblages, samples were split until it was ideally possible to obtain 300 living specimens. In samples with low number of foraminifera the minimum number of 100 living specimens was used in statistical analysis (Fatela and Taborda, 2002). The number of species per sample (S) and Shannon-index (H) values Shannon (1948); H = −Σpi.ln(pi), where pi is the proportion of each species] were employed to identify changes in the diversity of species. Equitability (E) [E= ln(S); S is the number of species per sample] was also analysed. The proportion of living organisms considering the total assemblage also was determined.

Data Analysis

The load pollution index (LPI) defined by Tomlinson et al. (1980) was used in order to estimate the overall pollution level of the samples. This index is based on concentrations determined by TDS through the equation:

$$LPI = \sum_{n=1}^{N-x} EF_n^{1/x}$$

where EF is the enrichment factor defined as EF = Cn/Bn; Cn represents the measured concentration of the metal n and Bn is the background concentration of the metal n; x is the number of metals considered. The x value in this study is 7 and it includes the elements As, Cd, Cr, Cu, Ni, Pb and Zn. Since the background values of these met-
als in the Ria de Aveiro channels are yet unknown, the average of the total concentration of these elements in 87 sediment samples, selected among the results of 215 samples collected in the studied area for their lower concentrations, were used as a reference.

Samples with a low number of living foraminifers were not used in statistical analysis relating biotic and abiotic data. Thus, only a set of 86 samples is being analyzed in this study by multivariable statistical methods, comparing grain size, geochemical characteristics, redox potential and benthic foraminifera living assemblages. Canonical analysis was carried out with the MVSP 3.1@ software package. Principal component analysis was performed using Statistical@ package 7.

In order to eliminate the influence of particle size, the ratio of toxic elements with Al (associated mostly with clay minerals) was determined (As/Al, Cd/Al, Cr/Al, Cu/Al, Ni/Al, Pb/Al and Zn/Al). Although Fe and Al are not considered toxic elements, high concentrations of these chemical elements can also be markers of anthropogenic activity. Abiotic and biotic data used in canonical analysis were transformed using log_2.

4. Results

4.1. Sedimentological and geochemical analyses

Sedimentary samples were collected at water depths varying between 0.5-30 m. Water temperatures varied between 15-26°C and salinity between 6-34. Temperature variability depends on tidal phase and season. Lower salinities were measured in inner lagoonal areas near the fresh water sources. In sediments, Eh values ranged between -12 and -408 mV, and pH between 6.0-9.9. The lower pH values are generally found in the innermost areas of the lagoon. Results analyzed in this work are included in appendix 1. Maximum, minimum and medium values of each variable are presented in this appendix.

Sediment grain size is heterogeneous in the studied area. The sediment content in fine fraction (<63µm) reaches about 98% (Fig. 2). TOC content in dry sediments ranges between 0.2-12% (Fig. 2). Coarser sediments with low TOC content are common in the most hydrodynamic and deeper areas of the navigable channels. Finer sediments richer in TOC were found in intertidal and mud flat parts under the influence of lower hydrodynamic conditions. In these areas, lower Eh values were found in general.

Concentrations of Al, As, Cd, Cr, Cu, Fe, Ni, P, Pb and Zn increase significantly in some zones of Ria de Aveiro, such as: Laranjo Bay (Murtosa Channel), Aveiro Town and Aveiro Harbours, where the values for the load pollution index are higher (Fig. 3).

SCE results show that, in the 17 studied sites, most of the concentration of the major elements, such as Al and Fe, are retained in the resistant mineralogical phase. Lead, Cu, Ni and As concentrations are also included mostly in the resistant mineralogical phase (Fig. 4). However, relatively high concentrations of Zn and Cd are bioavailable (Fig. 5), being adsorbed by clay minerals and organic matter and co-precipitated with carbonates.

Total bioavailable concentrations determined by SCE of As, Cd, Cu, Ni, Pb and Zn, all of which are considered toxic elements, are plotted in Fig. 6. This plot shows that Zn is the toxic element with the highest bioavailable concentration in the area. The bioavailable concentrations of As, Cd, Cu, Ni, Pb and Zn are higher in Laranjo Bay, due to the Chemical Industrial Complex of Estarreja, and in...
Aveiro City, because of the legacy of past industrial activities, such as ceramics and glass, according to Martins et al. (2010). In Espinheiro Channel (near Cacia’s Industrial area, which houses a pulp mill factory), relatively high bioavailable concentrations of As, Cu, Pb and Zn were found. However, this area was not identified by LPI as a critically contaminated zone.

4.2. Benthic foraminifera analysis

About 195 living benthic foraminifera species were recognized in Ria de Aveiro The list of species was included in appendix 1, as well the percentage of the most frequent species. 

Benthic foraminifera results showed that only very few specimens have dimensions larger than 500 μm in this area. The living benthic foraminifera abundance (n./g) is lower than ≈825 (Fig. 7). Foraminifera density decreases in gravel sandy and sandy sediments found in areas affected by stronger currents, and in low-salinity waters. Living foraminifera are also rare in calmer zones where
the deposition of muddy sediments is continuous, such as in the west side of Mira Channel (near the lagoon entrance) and in hypohaline waters located at inner lagoonal areas connected with the rivers and riverine bodies, where diversity and equitability tend to decrease. The number of species per sample (S) is <28 (Fig. 7), Shannon index values (H) are <2.85 and equitability (E) values are <1.37.

The living foraminifera assemblages are comprised mainly of hyaline carbonated specimens. Most of the lagoon channel assemblages are dominated by *Haynesina germanica* (<79%), *Ammonia tepida* (<73%) and *Elphidium* spp. (<64%; including species such as *E. gerthi*, *E. articulatum*, *E. excavatum*, *E. crispum* and *E. complanatum*). In the sandy sediments of the lagoon entrance under active currents, one can find species such as *Lobatula lobatula* (<14%; Fig. 8), *Cibicides ungerianus* (<20%), *Planorbulina mediterranensis* (<39%; Fig. 8) and *Gavelinopsis praegeri* (<5%). In this area, at the bottom of the navigable channels, where currents are strong, “attached” agglutinated species can be found, such as *Lepidodeuterammina ochracea* (<52%; Fig. 8), *Tiphotrocha concava* (<33%; Fig. 8), *Remaneica helgolandica* (<13%), *Septotrochammina gonzalezi* (<11%) and *Trochammina haynesi* (<5%). *Cribrostomoides jeffreysi* (<5%) and *Reophax dentaliformis* (<3%) are also found in areas located near the lagoon entrance, but in zones characterized by calmer hydrodynamic conditions. Bolivinids can be also found there (<66%), represented mostly by *Bolivina ordinaria* (<62%; Fig. 8) and *Bolivina pseudoplicata* (<13%), *Nonionella stella* (<18%; Fig. 8) and buliminids (<15%; mostly comprised of *Bulimina elongata/gibba* and *Buliminella elegantissima*). This group is more abundant in muddy sediments deposited in protected areas (by harbour structures), under lower current velocity. Miliolids with porcelanous tests (represented mostly by *Quinqueloculina seminulum*; <47%), reach higher proportions, in general, under active currents, especially near the lagoon mouth and in Aveiro city.

Fig. 5. – Concentrations of Zn and Cd (SCE) retained in the resistant mineralogical phase (Res Min Phase) of the sediments, associated with exchangeable cations, adsorbed by clay minerals (Clay & Carb.) and associated with organic matter (OM) are represented with different patterns. Stations with higher available concentrations: Laranjo Bay – Lar1, Lar3, Lar5, Lar6; Aveiro Town – C14; Espinheiro Channel – CC3, CC5, CC6, CC17. Other locations: Ílhavo Channel – C15, C10; lagoon mouth – EM22; Aveiro Harbours – Lota1, Lota3, CCom1 and CCom2.

Fig. 5. – Las concentraciones de Zn y Cd (SCE), retenido en la fase de mineralógica resistente (Res Min Phase) de los sedimentos, asociadas con cationes intercambiables, adsorbido por los minerales de arcilla (Clay & Carb.) y asociados con la materia orgánica (OM), están representadas con diferentes patrones. Estaciones con concentraciones disponibles más altas: Bahía de Laranjo – Lar1, Lar3, Lar5, Lar6; Ciudad de Aveiro – C14; Canal de Espinheiro – CC3, CC5, CC6, CC17. Otras localidades: Canal de Ílhavo – C15, C10; entrada de la laguna – EM22; Puerto de Aveiro – Lota1, Lota3, CCom1 y CCom2.
Fig. 6. – Total available concentrations (ug.kg$^{-1}$) of Zn, Cu, Pb, As, Ni and Cd (adsorbed by clay and organic matter and co–precipitated with carbonates) in the sediments of sites with higher available concentrations: Laranjo Bay – Lar1, Lar3, Lar5, Lar6; Aveiro Town – C14; Espinheiro Channel – CC3, CC5, CC6 and CC17. Other locations: Ílhavo Channel – CI5, CI10; lagoon mouth – E 22; Aveiro Harbours – Lota1, Lota3, CCom1 and CCom3. A logarithmic scale was applied on the y–axis.

Fig. 6. – Las concentraciones totales disponibles (ug.kg$^{-1}$) de Zn, Cu, Pb, As, Cd y Ni (adsorbido por la arcilla y materia orgánica y co–precipitado con carbonatos) en los sedimentos de los lugares con concentraciones disponibles más altas: Bahía de Laranjo – Lar1, Lar3, Lar5, Lar6; Ciudad de Aveiro – C14; Canal de Espinheiro – CC3, CC5, CC6, CC17. Otras localidades: Canal de Ílhavo – CI5, CI10; entrada de la laguna – EM22; Puerto de Aveiro – Lota1, Lota3, CCom1 y CCom2. En el eje Y se aplicó una escala logarítmica.

Fig. 7. – Maps of distribution of living foraminifera abundance (n./g) and number of species per sample (S) in the studied area. The values range is indicated in the figure. The values of living foraminifera abundance were converted by Log$_{25}$, aiming at to obtain a more clear idea of graphic representation. Dimension of grey balls are proportional to values of each site.

Fig. 7. – Mapas de distribución de la abundancia de foraminíferos vivos (n./g) y del número de especies por muestra (S) en el área estudiada. El rango de valores se indica en la figura. Los valores de abundancia de foraminíferos vivos fueron convertidos por Log$_{25}$, con el objetivo de obtener una idea más clara de la representación gráfica. Las dimensiones de las bolas de color gris son proporcionales a los valores de cada sitio.
channels. The proportion of Trochammina inflata (<35%) and Miliammina fusca (<11%) increases in low-salinity waters of inner lagoonal areas. The minimum relative abundance of all these species is zero, thus the higher values were indicated.

4.3. Data analysis

Figure 9 displays the results of the canonical analysis. This analysis includes values for fine fraction (%), TOC (%), Al concentrations, ratios of As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Ni/Al, Pb/Al and Zn/Al (geochemical data analyzed by TDS), and percentages of the most abundant living species/groups of benthic foraminifera (considering their percentage and occurrence in order to avoid statistical redundancy), in the area, such as H. germanica, A. tepida, miliolids, agglutinated foraminifera, Elphidium spp. and B. elongata/gibba. Canonical analysis: i) separates fine fraction (Fines), Al concentrations and the values of the ratios As/Al, Cd/Al, Cr/Al, Cu/Al, Fe/Al, Ni/Al, P/Al, Pb/Al and Zn/Al from most of the biological variables. However, H. germanica and A. tepida distribution is explained by the same axis, as well as Elphidium spp., which displays a lower correlation to the other variables; ii) bolivinids and B. elongata/gibba are joined with TOC and Eh (x -1; i.e., negative Eh values); these species are known to be associated with high flux of organic matter and to survive in low oxygenated environments, where the stress caused by predation and competition is reduced (Bernhard and Sen Gupta, 1999). iii) miliolids and agglutinated species are together with Pb/Al.

Correlations between the distribution of the total bioavailable concentration of As, Cd, Cu, Ni, Pb and Zn, the main species/group of species percentage (A. tepida, H. germanica, bolivinids, buliminids, miliolids, Elphidium spp., agglutinated spp.) and Shannon index values (H), used as an index of diversity, were submitted to principal components analysis (PCA). PCA results considering the first two factors, which explain most of data variability (0.53%), are plotted in Fig. 10. The first factor is more associated with metal concentration and the second one with foraminifera. Table 1 displays Pearson correlations between these variables.

5. Discussion

Values for foraminifera abundance, diversity and equitability are in general low in Ría de Aveiro, when compared with some shelf environments (Martins et al., 2006; 2007). Diversity values are typical of estuarine environments (as was described by, for instance, Debenay et al., 2006; Murray, 1991). One or two species comprise most of the living assemblages in most of the studied sites. These data reveal high environmental stress for foraminifera leading to a prevalence of high species dominance in the area. Several kinds of stressors, including current velocities (described by Vaz and Dias, 2008; Dias et al., 2003, 2000, 1999) that cause sediment remobiliza-
Another limiting factor for the foraminifera of Aveiro lagoon is salinity. Ria de Aveiro is a polyhaline system. Several species found in the studied samples have positive significant correlations with salinity, i.e., they are more common in lagoonal areas under high marine influence, such as: *B. elongata/gibba*, *B. ordinaria*, *B. pseudoduplicata*, *C. ungerianus*, *E. gerthi*, *E. complanatum*, *G. praegeri*, *L. lobatula*, *L. ochracea*, *P. mediterranensis*, *T. concava*, *S. gonzalezi* and *T. haynesi*. Most of the lagoon-al sites are dominated by *A. tepida* and *H. germanica*. *Q. seminulum* is spread over many lagoonal areas influenced by tides. This species is common in shelf marine and lagoonal hypo to hypersaline waters (Murray, 1991). In the inner lagoonal areas, located near the freshwater sources, the salinity varies considerably throughout the year. In these areas, agglutinated species increase, including, for instance, *Trochammina inflata* and *M. fusca*. These species are characteristic of the low salt marshes in numerous estuaries (e.g. Barbero et al., 2004; Edwards et al., 2004; Ruiz et al., 2004); they are able to live in areas with higher erratic values of salinity. Thus, in the study area, salinity has a strong influence on benthic foraminifera assemblage composition and, in hypohaline waters, on their abundance and diversity.

Potential redox was used in this work as an indirect measure of oxygenation in the surface sediments (in the first ≈5 cm of the sedimentary column). More negative values of Eh are, in general, related to lower oxic environments. Low oxic conditions are established in fine-grained sediments rich in organic carbon due to anaerobic degradation of organic matter and difficult oxygen renovation of pore waters. Most of the species/groups of species analyzed in this work have low correlation with Eh values. Water in Ria de Aveiro is frequently renewed. Tides are semidiurnal, with an average range, at the inlet, of about 2 m, and maximum and minimum ranges of 3.2 m (spring tide) and 0.6 m (neap tide), respectively (Dias et al., 2000). The tidal prism of the lagoon, for (maximum) spring tide and (minimum) neap tide, is estimated as $136.7 \times 10^6 \text{ m}^3$ and $34.9 \times 10^6 \text{ m}^3$, respectively (Lopes Fig. 9. – Canonical analysis based on abiotic and biotic data (transformed by log$_e$): Eh, Fines (fine fraction, <63 µm) and TOC percentage, concentrations of Al, values of ratios Cu/Al, Pb/Al, Zn/Al, Ni/Al, Fe/Al, As/Al, P/Al, Cr/Al (geochemical data analysed by TDS), and percentage of living *H. germanica* (H.germ.), *A. tepida* (A.tep.), miliolids (Mil.), agglutinated (Agglut.), *Elphidium* spp. (Elph.), bolivinids (Bol.) and *B. elongata/gibba* (B.elon).
jects (such as shells, vegetables, shingle), like *Ammotium salsum, Arenoparrella mexicana, L. ochracea, C. unge- rianus, L. lobatula, G. praegeri, T. haynesi, P. mediter- ranensis* and *R. helgolandica.* Other species are infaunal and can inhabit relatively deep levels of the sediments (e.g., at depths >4 cm below the surface, according to Rathburn and Corliss, 1994), such as *M. fusca, Jadam- mina macrescens, A. mexicana* and *Haplophragmoides wilberti.* Intermediate to deep infaunal species (according to the terminology of Rathburn and Corliss, 1994) can be affected by low oxygen levels. Therefore, individuals can migrate through the sedimentary column and occupy aerated habitats on surface sediments, avoiding more severe living conditions. Some other species can live in low oxic habitats (e.g., Diz and Francés, 2008; Bernhard and Sen Gupta, 1999; Rathburn and Corliss, 1994). Thus, depressed oxygen levels in the sediments below the surface may not affect many foraminifera in this system.

Is a high concentration of heavy metals disturbing the foraminifers of Ria de Aveiro? LPI values based on As, Cd, Cr, Cu, Ni, Pb and Zn concentrations (obtained by TDS) allowed the identification of three main areas with higher heavy metal concentration: Laranjo Bay (Mur- tosa Channel), Aveiro Town and Aveiro Harbours. In general, the highest concentrations occur in protected areas and in muddy sediments, where concentrations of Al essentially associated with the occurrence of phyllosilicates are higher.

The water is, in general, renewed in most of the lagoon due to semidiurnal tides. According to Dias et al. (2001), the particle residence time is less than 2 days at the central area of the lagoon, at the beginning of the Mira and Ílhavo channels, and extending to almost half of the S.
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Table 1 – Correlation between the total bioavailable concentrations of As, Cu, Ni, Zn, Pb and Cd (adsorbed by clay and organic matter and co–precipitated with carbonates) and Shannon index values (H), A. tepida (A.tep.), Bulimina spp. (Bulim.), Bolivina spp. (Boliv.), H. germanica (H.germ.), miliolids (Milioli.), Elphidium spp. (Elph.), aglutinated spp. (Agglut.). Significant correlations (p > 0.50) are marked in bold.

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Tabla 1 – Correlación entre las concentraciones totales biodisponibles de As, Cu, Ni, Zn, Pb y Cd (absorbido por la arcilla y materia orgánica y co–precipitado con carbonatos) y los valores de índice de Shannon (H), A. tepida (A.tep.), Bolivina spp. (Boliv.), H. germanica (H.germ.), miliolidos (Milioli.), Elphidium spp. (Elph.), especies aglutinadas (Agglut.). Las correlaciones significativas (p> 0.50) aparecen en negrita.

Jacinto and Espinheiro channels. But in some regions particles hardly escape when released into the flood, and, in a few places, none escaped (e.g., the far end of the Mira Channel and the dendritic channels close to Varela in the northern area of the lagoon). Thus, the areas where the particle residence time is higher and where cohesive sediments are deposited can act as sinks of anthropogenic pollutants. The impact driven by urbanization and industrialization, as well as the consequent increased geochemical forcing in this system, tend to be clearer in parts where muddy sediments are deposited, under low hydrodynamic conditions.

Canonical analysis highlighted that higher concentrations of toxic elements (determined by TDS) are adverse factors for benthic foraminifera of Ria de Aveiro. But also lead us to think that species such as H. germanica and A. tepida should tolerate higher level of stress caused by these pollutants. A. tepida has been considered one of the most tolerant species to high heavy metal concentration and is used as a bio-indicator of pollution of anthropized marine sediments (Ferraro et al., 2006). H. germanica was also considered a bio-indicator of pollution by metals (Frontalini et al., 2011; Romano et al., 2008) and of pollution by metals and hydrocarbons (Armynot du Châtelet et al., 2004).

However, canonical analysis results also suggest that agglutinated foraminifera and miliolids are more tolerant to high concentrations of Pb. Agglutinated foraminifera reach higher abundance near the lagoon mouth where spots of Pb pollution caused by fuel used for navigation were found. In this area, species such as L. ochracea, T. concava, R. helgolandica, S. gonzalezi and T. haynesi are very common. These species were frequently found adhered to sand particles and are probably able to track the movement of sediments under active current activity. Thus, they may not be too affected by high concentrations of Pb in this area, where the sediment mobility should be strong. Miliolids, represented mostly by Q. seminulum, are common near the Ria mouth, but also in some Aveiro channels, more specifically, in two areas with distinct hydrodynamic characteristics, where higher Pb concentrations were found.

We tried to confirm these results studying the correlation between total bioavailable concentration of the selected elements (obtained by SCE) and the most abundant living species/groups of benthic foraminifera in most of the 17 samples. Geochemical results revealed that most of the concentration of As, Cd, Cu, Ni, Pb and Zn is retained in the mineralogical resistant phase. However, in the most contaminated areas, such as Laranjo Bay (Murtosa Channel), Aveiro Town and Aveiro Harbours, a high total bioavailable concentration of As, Cd, Cu, Ni, Pb and Zn was found. In Espinheiro Channel, an area with relatively low LPI values, significant bioavailable concentrations of heavy metals were also found.
PCA (Fig. 10) and Pearson correlations (Table 1) evidence that higher bioavailable concentrations of As, Cd, Cu, Ni, Pb and Zn generally prevents the development of large benthic foraminifera communities in the Ria de Aveiro. *A. tepida*, *H. germanica* and *Elphidium* spp. should be more resistant to higher bioavailable concentrations of heavy metals than bolivinids, buliminids and agglutinated foraminifera, for example. However, a differential sensitivity to pollutants may exist among the different species/groups of species of foraminifera. Our results suggest that, contrary to the opinion of Rao and Rao (1979), miliolids in Ria de Aveiro, represented mostly by *Q. seminulum*, may be more tolerant to higher bioavailable concentrations of Cu and Pb than *A. tepida*, *H. germanica* and *Elphidium* spp.

6. Conclusion

LPI values can be used as a first approach to identify polluted areas. Measurement of the sedimentary total concentrations of toxic elements is useful as a general index of contamination, but may provide inadequate or little information about their availability, mobility or toxicity for the living beings. Most of the elemental concentrations are retained in the mineralogical resistant phase, i.e., they don’t affect the biota. Results presented in this work show that SCE analyses are important to evaluate the real degree of sediment contamination and their influence on benthic organisms, namely on benthic foraminifera. Areas with relatively low concentrations of heavy metals can have relatively high concentrations of bioavailable toxic elements.

Thus, the identification of the most tolerant species can change, if we consider the sedimentary total concentrations of toxic elements or the bioavailable concentrations of heavy metals (SCE). Foraminifera are generally affected by high element concentrations, but some species may have differential sensitivities. *A. tepida*, *H. germanica* and *Elphidium* spp. may be more tolerant to high bioavailable concentrations of toxic elements than, for instance, bolivinids and buliminids. However, *Q. seminulum* may be more tolerant to pollution caused by higher bioavailable concentrations of Pb and Cu than *A. tepida*, *H. germanica* and *Elphidium* spp.

Sequential chemical extraction may provide a more correct evaluation of pollution degree by heavy metals.

Acknowledgements

The authors would like to thank Sandra Donnici and an anonymous reviewer for collaborating on the improvement of this work, and Prof. João Dias (principal investigator of EMERA project) and Isabel Abrantes for collaboration in field work. The authors would like to thank Cristina Freitas, Rui Marques and Paulo Miranda for the technical support. This work was financed by the FCT (Portugal), through the EMERA Project (POCTI/ECM/59958/2004), and by the Geobiotec Research Centre, of Aveiro University.

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**Apendix 1.-**

Living benthic Foraminifera species identified in the studied samples

*Acerulina inhaerens* Schultze, 1854

*Adelosina partschi* (d’Orbigny, 1846)

*Ammonia beccarii* (Linne, 1758)

*Ammonia tepida* (Cushman, 1926)

*Ammotium salsum* (Cushman & Brönnimann, 1948)

*Arenoparrella mexicana* (Kornfeld, 1919)

*Balticammina pseudomacrescens* Bronnimann, Lutze & Whittaker, 1989

*Bolivina compacta* Sidebottom, 1905

*Bolivina difformis* (Williamson, 1858)

*Bolivina doniezi* Cushman & Wickenden, 1929

*Bolivina goessi* Cushman, 1922

*Bolivina limbata var. abbreviata* Heron-Allen & Earland, 1924

*Bolivina ordinaria* Pfeleger & Parker, 1952

*Bolivina pseudoplicata* Heron-Allen & Earland, 1930

*Bolivina skagerrakensis* Ovæle & Nigam, 1985

*Bolivina variabilis* (Williamson, 1858)

*Brizalina striatula* (Cushman, 1922)

*Brizalina subaenaria* Cushman, 1922

*Brizalina subspatheulata* (Boomgurt, 1949)

*Brizalina translocens* Pfeleger & Parker, 1951

*Buccella cf.* B. parkerae Anderson, 1953

*Bulimina aculeata* d’Orbigny, 1826

*Bulimina elongata* d’Orbigny, 1846

*Bulimina gibba Forbush, 1905

*Bulimina marginata* d’Orbigny, 1839

*Buliminella elegantissima* (d’Orbigny, 1839)

*Buliminella subtaeniata* var. *taeniata* Cushman, 1927

*Cancris auriculus* (Fichtel & Moll, 1798)

*Cassidulina crassa* (d’Orbigny, 1846)

*Cassidulina laevigata* d’Orbigny, 1826 + *C. carinata* (Silvestri, 1896)

*Cassidulina minutia* Cushman, 1933

*Cassidulina teretis* Tappan, 1951

*Cassidulinoidea bradyi* (Norman, 1881)
Leptohalysis catella
Lepidodeuterammina ochracea
Lenticulina
Lenticulina orbicularis
Lenticulina atlantica
Laticarinina altocamerata
Laryngosigma hyalascidia
Lamarckina haliotidea
Lagenosolenia seguenziana
Lagenoselenia
Lagena perlucida
Lachlanella undulata
Haplophragmoides manilaensis
Haplophragmoides canariensis
Hanzawaia nitidula
Guttulina lactea
Glomospira gordialis (Jones & Parker, 1860)
Globocassidulina subglobosa
Globobulimina auriculata
Gavelinopsis praegeri
Fursenkoina sp.
Fissurina spp.
Fissurina globosocaudata
Fissurina globosa
Fissurina densifasciataformis
Favulina hexagona
Eponides terebra Cushman, 1933
Eoeponidella nanoconica
Elphidium williamsoni
Elphidium spp.
Elphidium oceanensis
Elphidium jenseni
Elphidium gerthi
Elphidium excavatum
Elphidium earlandi
Elphidium crispum
Elphidium advenum
Edentostomina sp.
Dyocibicides biserialis
Discorbis villardeboanus
Discorbis parkeri
Discorbis orbicularis
Discorbis mira
Disborbis
Deuterammina eddystonensis
Deuterammina celtica
Cribrostomoides subturbinata
Cribrostomoides jeffreysi
Cribroeponides criborepandus
Cornuspira involvens
Cornuloculina balkwilli
Cibicides ungerianus
246

cf. spp.

D. clara (Montagu, 1803)
Buchner, 1940

Bandy, 1953

Williamson, 1848

Fichtel & Moll, 1798

Reuss, 1850

Reuss, 1850

Seguenza, 1862

d'Orbigny, 1846

Barker, 1960

Fornasini, 1886

Kennett 1967

Asano & Uchio, 1951

Bryan, 1881

Andersen, 1953

Valvulineria bradyana
Trochammina globigeriniformis
Trochammina adaperta
Trifarina angulosa
Tiphotrocha comprimata
Textularia truncata
Stainforthia loeblichi
Stainforthia fusiformis
Stainforthia feylingi
Stainforthia complanata
Spiroloculina rotundata
Spiroloculina lucida
Spiroloculina excavata
Spirillina vivipara
Septotrochammina gonzalezi
Septloculina tortuosa
Scherochorella moniliforme
Sahulia conica
Rosalina millettii
Rosalina micens
Rosalina araucana
Reophax dentaliniformis
Reophax curtus
Remaneica plicata
Remaneica helgolandica
Quinqueloculina villafranca
Quinqueloculina poeyana
Quinqueloculina oblonga
Quinqueloculina lata
Quinqueloculina lamarckiana
Quinqueloculina auberiana
Pyrgo depressa
Quinqueloculina aknertiana
Quinqueloculina aubersoniensis
Quinqueloculina culpabilis
Quinqueloculina laevigata
Quinqueloculina lamarekiana
Quinqueloculina lauri
Quinqueloculina oblonga (Montagu, 1803)
Quinqueloculina poeyana (D'Orbigny, 1840)
Quinqueloculina seminulum
Quinqueloculina spp.
Quinqueloculina vil Johanke Le Calvez, 1958
Rectungulineria phelegri Le Calvez, 1959
Remaneica helgolandica Rhumbler, 1938
Remaneica plicata (Terquem, 1876)
Reophax curtus Cushman, 1920
Reophax dentaliformis (Bradly 1881)
Rosalin araucana (D'Orbigny, 1839)
Rosalin globularis (D'Orbigny, 1826)
Rosalin micans (Cushman, 1933)
Rosalin milletti (Wright, 1911)
Rosalin williamsonii (Chapman & Parr, 1932)
Rotaliinioides signum (Wells, 1985)
Sahulia conica (D'Orbigny, 1840)
Schrochetridolea moniliforme (Siddall, 1886)
Septiloculina tortuosa El-Nakhil, 1990
Septiloculina gonzalezi (Seiglie, 1964)
Siphonaperta aspera (D'Orbigny, 1826)
Spirillina vivipara Ehrenberg var. runiana Heron-Allen & Earland, 1930
Spirillina vivipara Ehrenberg, 1843
Spiroloculina excavata (D'Orbigny, 1846)
Spiroloculina lucida Cushman & Todd, 1944
Spiroloculina rotundata (D'Orbigny, 1826)
Spiroplectinella earlandi (Parker, 1952)
Stainforthia complanata (Egger, 1895)
Stainforthia fusiiformis (Williamson, 1858)
Stainforthia loeblichi (Feiling, 1934)
Textularia lateralis Lalicker, 1935
Textularia truncata Högland, 1947
Tiphrotrocha comprimata (Cushman & Brönnimann, 1948)
Tiphrotrocha concava Seiglie, 1964
Trifarina angulosa (Williamson, 1858)
Triloculina bermudezii Acosta, 1940
Trochammina adaperta Rhumbler, 1938
Trochammina globigeriniformis (Parker & Jones) var. pygmaea Högland, 1947
Trochammina haynesi (Atkinson, 1969)
Trochammina inflata (Montagu, 1808)
Valvulineria bradyana (Fornasini, 1900)
Wiesnerella auriculata (Egger, 1893)