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Trace metals on the Algarve coast, II: Bioaccumulation in mussels *Mytilus galloprovincialis* (Lamarck, 1819)

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ABSTRACT

Cadmium, copper, iron, manganese, nickel and zinc concentrations were determined by atomic absorption spectrophotometry in samples of soft tissues of the mussel *Mytilus galloprovincialis* (Lamarck, 1819), collected from 19 sampling points on the Algarve Coast (southern Portugal).

Of all the sampling points, Portimão showed the highest metal concentrations in mussel tissues. Metal concentrations increased near urban centres and sources of industrial effluents. Consequently, the areas influenced by the Arade River, the Guadiana estuary and the Formosa Ria lagoon presented the highest metal concentrations. Metal concentrations in mussels from the west coast of the Algarve were higher than in those from the east coast. Our findings indicate that Cd and Cu concentrations in mussels from the different sampling points have increased over the last 10 years, while Fe, Mn and Ni concentrations along the Algarve Coast have fallen. These results are discussed in relation to the variation of human impact, some environmental factors, and other natural phenomena.

Key words: Mussels, trace metals, southern coast of Portugal.

RESUMEN

Metales traza en la franja costera del Algarve, II: bioacumulación en mejillones* Mytilus galloprovincialis *(Lamarck, 1819)

Las concentraciones de cadmio, cobre, hierro, manganeso, níquel y zinc fueron determinadas por espectrofotometría de absorción atómica en muestras de tejidos de mejillones Mytilus galloprovincialis *(Lamarck, 1819), obtenidas en 19 puntos de muestreo en la costa del Algarve (sur de Portugal).*

Entre todos los puntos de muestreo, Portimão mostró la concentración más alta de metales en los tejidos de mejillón. Las concentraciones de metales se incrementan cerca de los núcleos urbanos y efluentes industriales. Consecuentemente, las áreas de influencia del río Arade, el estuario del Guadiana y el sistema lagunar Ría Formosa presentaron las más altas concentraciones de metales. Las concentraciones de metales en mejillones procedentes de la costa oeste del Algarve son mayores que las procedentes de la costa este. Los datos mostraron que las concentraciones de Cd y Cu en los mejillones procedentes de los diferentes puntos de muestreo han aumentado en los últimos diez años, mientras las concentraciones de Fe, Mn y Ni disminuyeron a lo largo de toda la costa. Los resultados han sido discutidos en relación con las variaciones de diversos factores ambientales, la influencia humana y la existencia de fenómenos naturales.

Palabras clave: *Mejillón, metales traza, costa sur de Portugal.*

INTRODUCTION

The Algarve Coast of southern Portugal runs along the Atlantic Ocean between 37° 35' and 36° 58' N, and 7° 25' and 9° 00' W, and is 135 km long from its eastern border with Spain, marked by the Guadiana River, to the western margin on the Atlantic Ocean (figure 1). Apart from the Guadiana River, two major aquatic systems exist: the Arade River and the largest lagoon on the Portuguese coast, the Formosa Ria. In addition to being a major tourist centre, the Algarve has an important fish and shellfish industry, whose total catch represents approximately 20 % of all Portuguese fisheries.

The coastline has been under constant urban pressure over the last 15 years due to this tourist development and consequent environmental degradation, which has started to have an economic impact on shellfish production and even the tourism industry itself. The population, which is concentrated in the coastal zone, increases more than 10-fold over the summer, which aggravates the environmental problems due to the lack of sewage treatment facilities. Streams, rivers and estuarine systems along the coast also contribute anthropogenic inputs. Wastewater effluents have been identified as one of the most important sources of pollution loading on the Algarve coast. One aspect of this environmental degradation is pollution by metals that are bioaccumulated by marine organisms, with serious public health implications (Phillips and Rainbow, 1993).

Biomonitoring of metal loads has been conducted using organisms that are sedentary, have a wide geographical distribution, and accumulate metals in a manner that reflects the environmental conditions. Bivalve molluscs, and in particular *Mytilus* spp., have been successfully utilised as biomonitors for coastal water quality monitoring. The Mussel Watch Programme (Goldberg, *et al.*, 1978) is based on the chemical analysis of contaminants in the soft tissues of these molluscs.

Following the outline of the Mussel Watch Programme, the purpose of the present study was to use the mussel *Mytilus galloprovincialis* (Lamarck, 1819) as a biomonitor on the Algarve Coast.

MATERIALS AND METHODS

Nineteen sites were selected along the Algarve coast (figure 1), where samples of *M. galloprovincialis* were collected. Thirty mussels (45-55 mm, 1.08-2.66 g dry weight) were collected from the same intertidal depth during a spring tide. The specimens were all in the pre-spawning period, with 91 % of them in maturation stage III (Lubet, 1959; Lucas, 1965). Mussels were depurated for 24 h to eliminate gut contents prior to their analysis for metals. The specimens were opened carefully by cutting the adductor muscle, and the soft tissues were dissected out. The tissues were pooled into groups of five individuals, after discarding the shell, byssus and cavity liquor.

The samples were dried in an oven at 80 °C and digested with nitric acid, following the procedure described by Bryan *et al.* (1985). Metal concentrations (Cd, Cu, Fe, Mn, Ni and Zn) were determined using an atomic absorption spectrophotometer (VARIAN-SpectrAA20). Analysis of the TORT I lobster hepatopancreas reference material (National

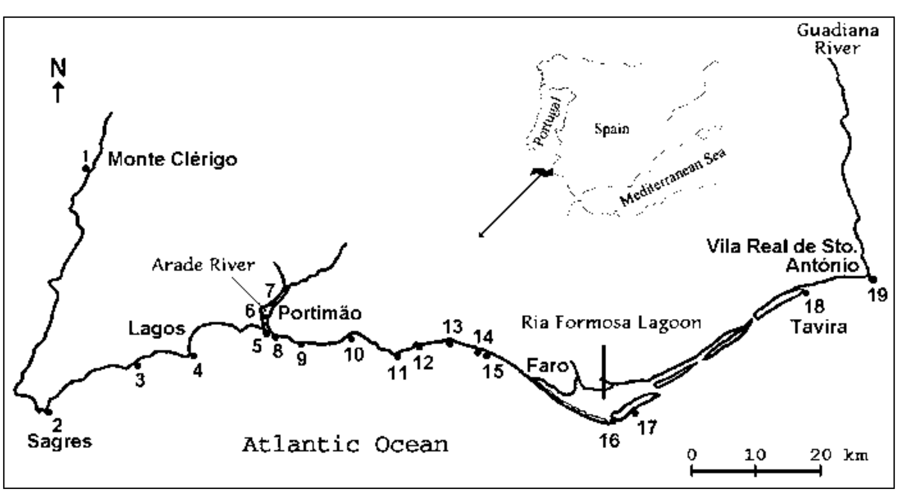

Figure 1. Sampling points along the Algarve coast

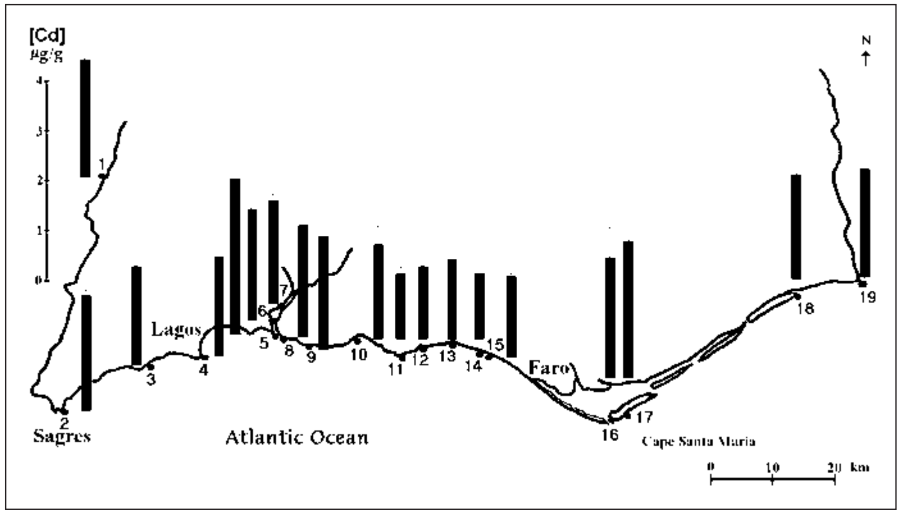

Figure 2. Spatial distribution of Cd concentrations (means ± standard deviations mg g^{-1} dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

Research, Canada) were carried out to validate the metal analysis. The metal concentrations detected in the reference material are within the confidence intervals [(1 – α) × 100] of the respective registered values. The concentrations of all metals are expressed in µg g^{-1} dry weight of soft tissue.

To test significant differences ($p < 0.05$) between a specific pair of treatment means, the parametric Tukey test was used. The statistical procedure also included a numeric classification method, cluster analysis (CA) using the UPGMA (unweighted pair-group method arithmetic averages) applied in the Q-mode (grouping the variable stations according to metal concentrations), and an ordination method, principal component analysis (PCA). For the latter, a correlation coefficients matrix was used instead of the original data. Both CA and PCA were performed with Numerical Taxonomy and Multivariate Analysis System (NTSYS-PC) software.

RESULTS

Cadmium concentrations (mean ± standard deviation) in the whole soft tissues of *M. galloprovincialis* collected along the southern coast of Portugal are presented in figure 2. Cadmium concentrations in the mussels ranged from 1.3 to 3.1 µg g^{-1} dry weight, the highest concentrations being found at stations 5, 16 and 17. These concentrations were significantly different from all the other sampling points ($p < 0.05$). In comparison with the other metal concentrations determined in mussels of the Algarve, copper levels (figure 3) did not show much spatial variability (4.8-7.0 µg g^{-1}). However, mussels from station 19 (which was located in one of the major estuaries directly influenced by mining effluents) presented the highest Cu concentrations, and these were significantly different from the concentrations at the other sampling points ($p < 0.05$).

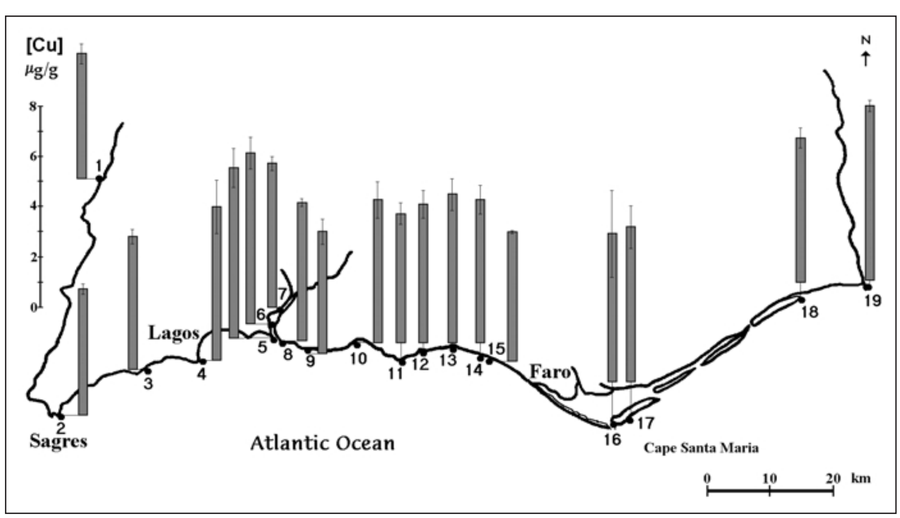

Figure 3. Spatial distribution of Cu concentrations (means ± standard deviations mg g^{-1} dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

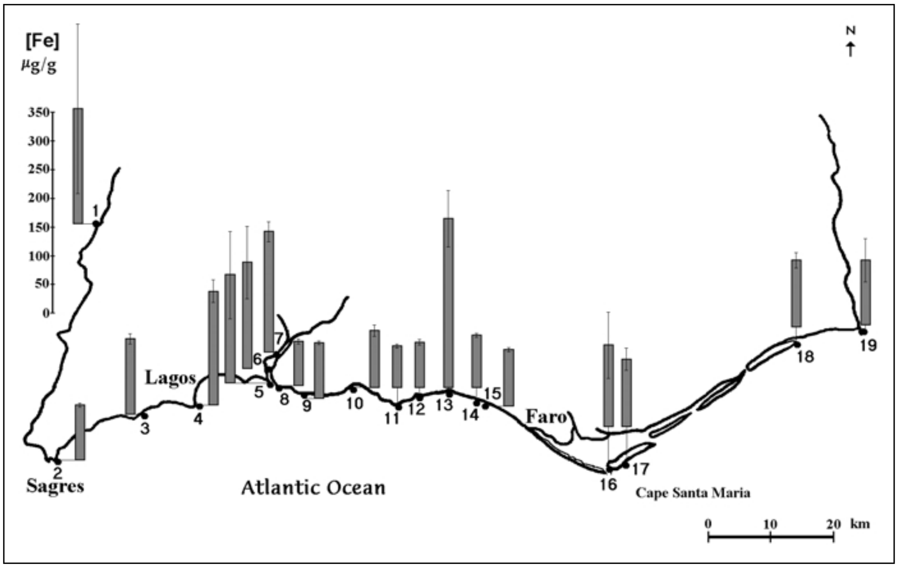

Figure 4. Spatial distribution of Fe concentrations (means ± standard deviations mg g^{-1} dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

Iron concentrations (figure 4) ranged from 72 to 294 µg g^{-1} and Mn concentrations (figure 5) from 3.1 to 15.5 µg g^{-1}. Iron and Mn concentration levels exhibited a similar spatial distribution along the Algarve coast. The application of the Tukey test to these results suggested that Fe concentrations at stations 4, 5, 6, 7 and 13 were significantly different from the others ($p < 0.05$). Similarly, mussels from stations 4, 5, 6, 7 and 19 exhibited Mn concentrations significantly different from the other sampling points.

Nickel concentrations obtained for the mussels sampled ranged from 0.37 to 0.77 µg g^{-1} (figure 6). The highest Ni concentrations were detected at the intermediate part of the coast (between stations 3 and 10, and at station 13).

In contrast with Cu concentrations, Zn concentrations in the mussels showed higher variability (189-398 µg g^{-1}) (figure 7), although no significant differences were detected among the sampling points (ANOVA, $p < 0.05$). These results are related to the heterogeneity of the variances, a problem known as heteroscedasticity (Zar, 1996; Hernández *et al.*, 1992).

The CA in Q mode for all metal concentrations (figure 8) showed that the mussels are divided into two main groups. The first includes samples 1 to 10, and the second, samples 11 to 19. The CA results were confirmed by the application of PCA (figure 9). PC1 represented 45 % of the total variation, whereas PC2 included approximately 24 %. The PC1 component can be interpreted in terms of the similarity between sampling locations and their influence by fresh water or seawater. The PC2 component is related to the geographical distribution of the sampling stations.

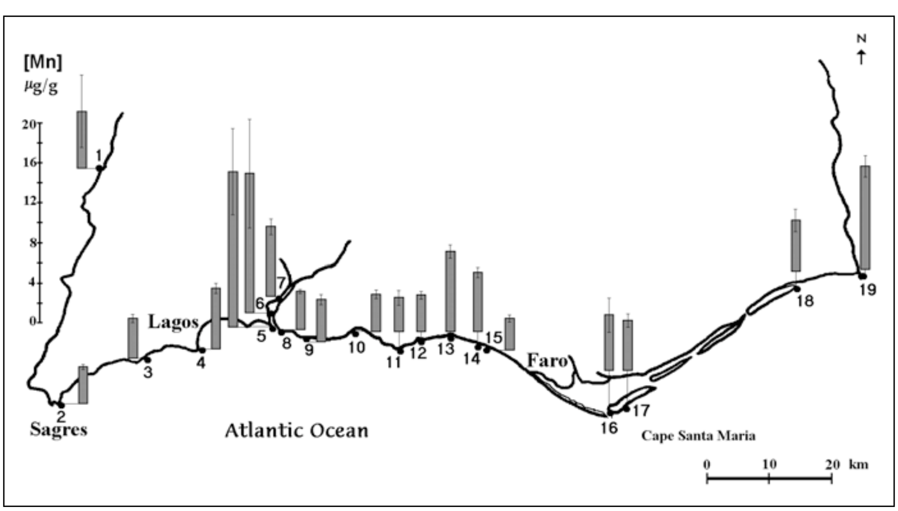

Figure 5. Spatial distribution of Mn concentrations (means ± standard deviations mg g^{-1} dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

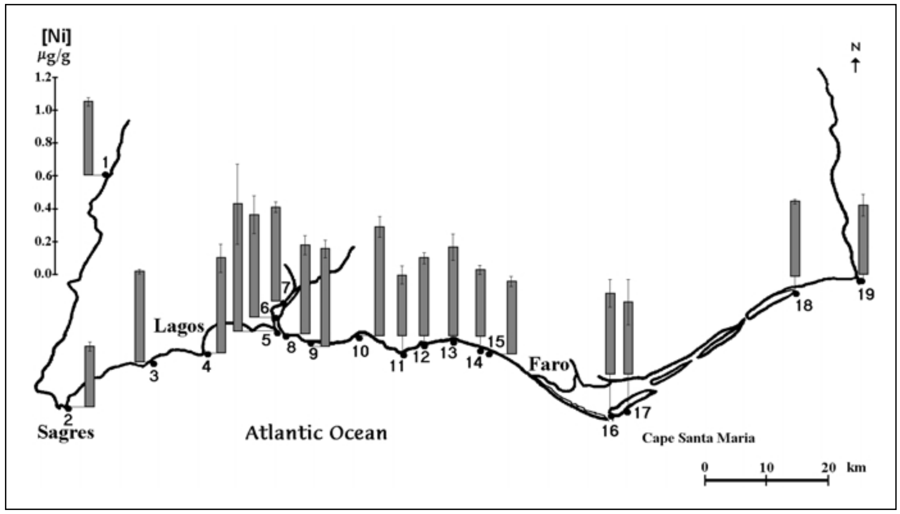

Figure 6. Spatial distribution of Ni concentrations (means ± standard deviations mg g–1 dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

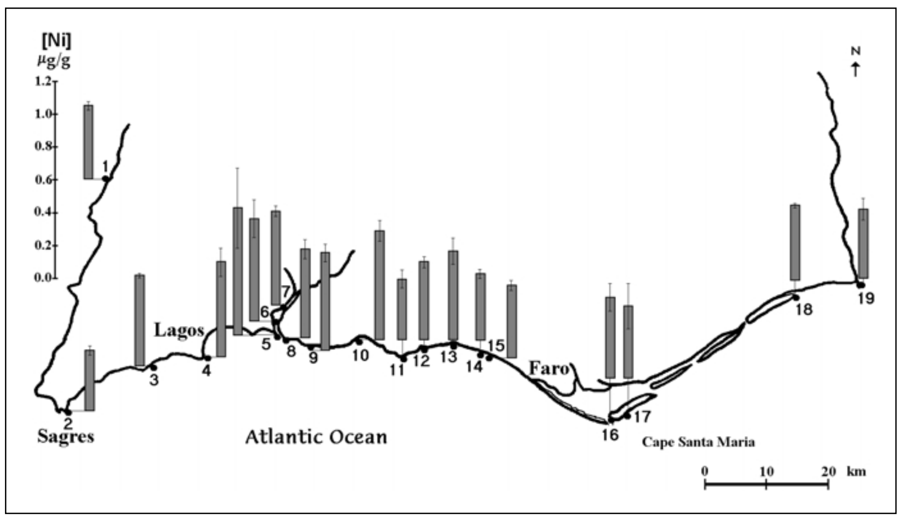

Figure 7. Spatial distribution of Zn concentrations (means ± standard deviations mg g–1 dry weight) in the whole soft tissues of *M. galloprovincialis* along the Algarve coast

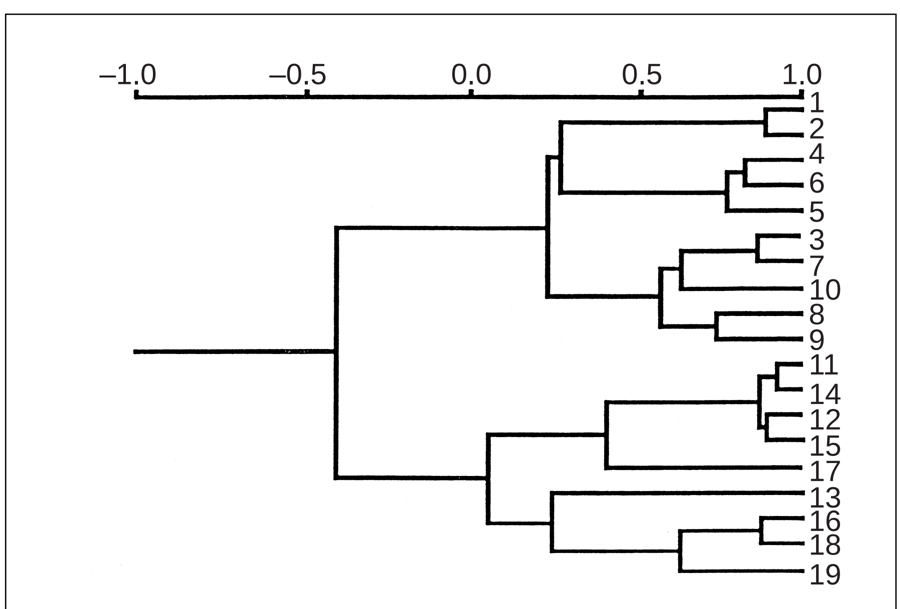

Figure 8. Cluster analysis: Q-mode dendogram with UPGMA

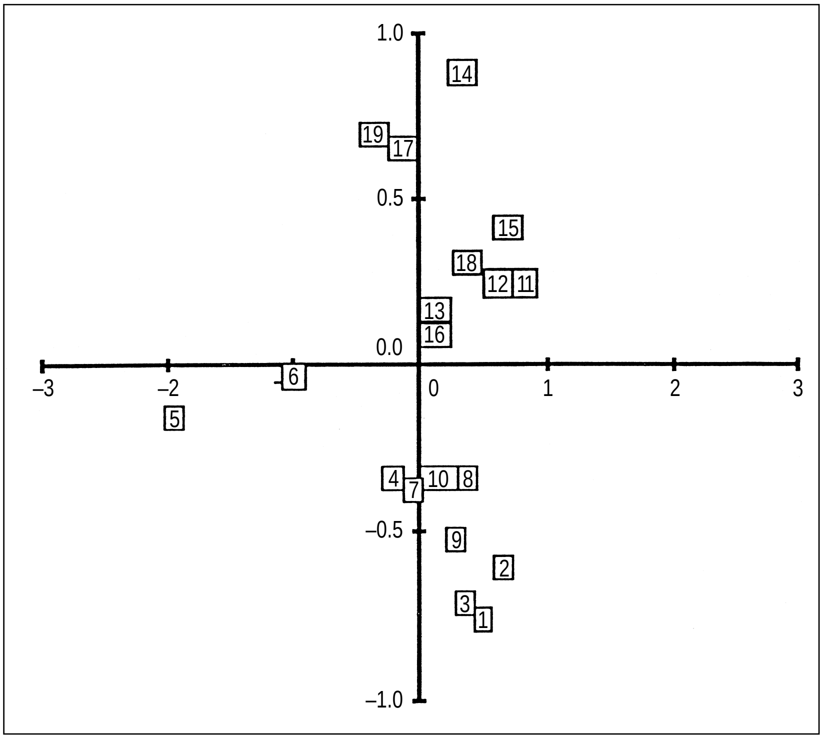

Figure 9. Principal component analysis of metal concentrations in mussels

DISCUSSION

The data reveal a significant increase of metal levels in zones directly affected by urban areas and industrial effluents. Metal concentrations in mussels were also higher in areas directly influenced by freshwater inputs, including the Arade River (stations 5, 6 and 7), the coastal lagoon known as the Ria Formosa (stations 16 and 17), and the estuary of the Guadiana River (station 19). The highest metal concentrations were obtained along the Arade River (station 5) at a site which is affected by sewage and industrial inputs.

The metal concentrations found were generally similar to those obtained by other authors for mussels collected in different geographical areas (Davies and Pirie, 1980; Gault, Tolland and Parker, 1983; Rogério and Vale, 1984; Bargagli, Baldi and Leonzio, 1985; Bryan *et al.*, 1985; Vale *et al.*, 1985; Cortesão, Mendes and Vale, 1986; Martincic, Stoeppler and Branica, 1987; Lobel *et al.*, 1990; Hamilton, 1991). Cadmium and Zn concentrations were mostly higher than those obtained by Vale *et al.* (1985) for the same area 10 years ago; this could be related to the recent development of industry and tourism. However, Fe, Mn and Ni concentrations showed a significant decrease over the last 10 years. In fact, Fe, Mn and Ni are trace-element constituents of the Algarve sediments (Boski *et al.*, in this volume), and one of the major input sources of these metals on the adjacent coastline is land runoff originated by rainfall. The reduction in Fe and Mn concentrations found in the present study could be related to a significant decrease in rainfall (accumulated mean values of precipitation) recorded recently in this region (Anon., 1994a), with a consequent drop in land runoff.

The application of the CA and PCA to metal concentrations in the soft tissues of *M. galloprovincialis* showed a significant difference between mussels from the east coast (stations 1 to 10) and the west coast (stations 11 to 19). With the exception of Zn, mussels collected from the west coast showed higher metal concentrations than those from the east coast. Zinc concentrations showed less consistent variations. Similar results were obtained previously by Hernández *et al.* (1992). Apart from anthropogenic sources, there could be other effects responsible for changes in metal concentrations, e.g. natural upwelling, which is known to occur on the west coast of Portugal (Anon., 1982).

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