

Baseline

Edited by Bruce J. Richardson

The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline—The New Format and Content' (*Mar. Pollut. Bull.* **42**, 703–704).

Distribution of mercury in the upper sediments from a polluted area (Ria de Aveiro, Portugal)

E. Ramalhosa^a, E. Pereira^a, C. Vale^b, M. Válega^{a,*}, A.C. Duarte^a

^a Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

^b National Institute of Agronomy and Fishery Research, Av. de Brasília, 1449-006 Lisboa, Portugal

It is well known that chlor-alkali industries using mercury as a cathode are an important source of this heavy metal to aquatic environments. Once discharged into rivers, lakes or coastal waters, mercury accumulates in sediments and in the aquatic food web (Gonzalez, 1991). Both elemental mercury and its compounds are noxious to all living organisms, and are bioaccumulative and persistent.

Metal concentrations in sediments usually exceed those of the overlying water column. As a consequence, metals originating from human activities can often be identified more readily by analysis of sediments than by the quantification of metal concentrations present in water (Haynes et al., 1995). Sediments also integrate the temporal variability that characterizes metals originating from human sources. However, metals may be remobilized during the early stages of post-depositional transformations of the sediment (Gobeil and Cossa, 1993).

Ria de Aveiro is a long, narrow, coastal lagoon, of 43 km² wet area with a single, artificially maintained connection to the sea (Fig. 1). The coastal plain around the lagoon supports an intensive, diversified agriculture, a variety of heavy and light industries and a population

of about half a million people, a part of which discharge their untreated or partially treated sewage into the lagoon (Lucas et al., 1986). An extensive web of islands and channels make water circulation inside the lagoon difficult and complex, thus allowing the spread of any conservative contaminants before they are discharged into the coastal waters through the single sea mouth. One such contaminant is the mercury, released by a chlor-alkali plant into one of the remotest branches of the lagoon—Estarreja Channel (Fig. 1) (Hall et al., 1988). The Channel ends in a basin (Laranjo Basin) where most of the discharged mercury settles. Laranjo Basin has an area of about 1.5 km² and is totally emptied in most ebb tides. The average volume of water exported with each tidal cycle may be around 2 km³ (Lucas et al., 1986).

This work reports levels of Hg, Fe and Mn and sulphides in the upper sediments of the Laranjo Basin, and examines the influence of these elements on the distribution of mercury.

Short sediment cores (10 cm) were collected by hand at sites A, B and C of Ria de Aveiro (Fig. 1). Cores were sampled in March, May, June 1996 and April 1997. The sediments were sliced in situ at the following depths: 0–2, 2–4, 8–10, 14–16, 24–26, 34–36, 44–46, 54–56, 64–66 and 94–96 mm. The samples were rapidly transferred to vials which were placed under nitrogen atmosphere and frozen. In the laboratory, part of the sediments samples

* Corresponding author. Tel.: +351 234 370 737; fax: +351 234 370 084.

E-mail address: mvallega@dq.ua.pt (M. Válega).

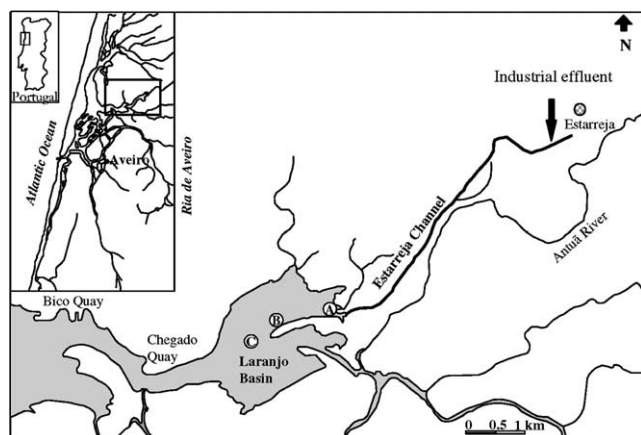


Fig. 1. Sampling Stations in the Laranjo Basin in Ria de Aveiro.

were air dried at room temperature, oven dried at 70 °C for 24 h and homogenized.

Total mercury content was measured by digestion with HNO_3 4 mol l^{-1} and HCl 0.7 mol l^{-1} ; 50 ml of acid solution was added to accurately weighed 0.5 g of dry sediment in duplicate. The digestion was performed in borosilicate glass beakers overnight at room temperature; then, they were heated in a sand bath at 60–70 °C for 2 h. Mercury was determined by cold vapour atomic absorption spectrometry (CV-AAS), using the one-step amalgamation method (Perkin Elmer, model 3030B, coupled to a MHS-20 hydride system). The system was calibrated with acidified standards.

Mercury associated with sulphides was measured by extraction with HCl 3 mol l^{-1} . A volume of 30 ml of HCl was added to 30 mg of dry sediment. The Erlenmeyer flasks were shaken (Burrel, model 75) for 30 min at room temperature (approximately 20 °C). The extraction solution was separated from the solid residue by centrifugation at 6000 rpm for 30 min (B. Braun, model sigma 4–10). The liquid was decanted and analysed as described before, but without the amalgamation step.

Iron and manganese oxides were determined by extraction of 50 g of dry sediment with 20 ml of hydroxylammonium-acetic acid solution (0.1 mol l^{-1} , pH 2) for 16 h at room temperature. Continuous mechanical agitation (Burrel, model 75) was maintained during the extraction. The extraction solution was separated from the solid residue by centrifugation at 6000 rpm for 30 min (B. Braun, model Sigma 4–10). The liquid was decanted and analysed by flame atomic absorption spectrometry (F-AAS), using acidified standards (Perkin Elmer, model 2280).

AVS in sediments was based on the acid reduction of the sulphur compounds to H_2S . The H_2S was collected in NaOH (pH 10–11, 20 ml) and measured by polarography (Analyser PAR, 264 A). Approximately 50 mg of frozen sediment was accurately weighed in an aluminium boat and added to 10 ml of HCl 3 mol l^{-1} . The reac-

tion time was 40 min. The general procedure used to obtain the voltammograms was as follows: 5 ml aliquot of supporting electrolyte (NaCl 36 g l^{-1} in NaOH , pH 10–11) solution was placed in a voltametric cell and purged with nitrogen for 1 min. Then, the require volume of sample solution or of standard Na_2S was added and the solution was purged for 3 min. A 15 s equilibration time at -0.2 V was established before the negative scan was initiated. When further volumes of standard solution were added to the solution in the cell, the mixture was deoxygenated for 0.5 min before carrying out further voltammetry. The standardisation of the solution of Na_2S was performed by a titration with a solution of iodine, previously standardised with a potassium thiosulphate solution. Since potassium thiosulphate cannot be considered an appropriate primary standard, this solution had to be standardised by a potassium iodate solution. The accuracy and precision of the method used to determine total mercury in the sediments was evaluated by a reference material of estuarine sediments (CRM 277) (Griepink and Muntau, 1988). The mean concentrations of mercury and the standard deviation obtained for the reference material was 1.73 ± 0.04 $\mu\text{g g}^{-1}$ dry weight of sediment; the coefficient of variation was 2.5% in 10 determinations. The certified value was 1.77 ± 0.03 $\mu\text{g g}^{-1}$.

The vertical distribution of mercury in the solid phase of the sediments of the three sampled stations is shown in Fig. 2.

At stations A and B, located near the Estarreja Channel, mercury concentrations were much higher than those recorded at station C, located at the central part of the Laranjo Basin (Fig. 1). In Station C, metal concentrations were never higher than 0.04 mmol kg^{-1} , but in cores A and B values up to 0.36 mmol kg^{-1} were measured. The different values between stations are related to the discharge of the liquid effluent enriched in mercury from the chlor-alkali factory in the Estarreja Channel (Lucas et al., 1986; Hall et al., 1987; Pereira et al., 1995). The results suggest that most of the mercury is incorporated in the sediments that are settled at the entrance of the basin. The morphology of the area should also contribute to these depositional preferences. Previous studies have shown that suspended particles in the Estarreja Channel are enriched in mercury (Pereira et al., 1995), indicating its rapid association with the particulate fraction which seems to be the main vehicle for the transport of mercury to the basin (Pereira et al., 1998). The analysis of deeper sediments cores (Pereira et al., 1997) has indicated an increment of mercury when the factory started to produce, and a decrease in the upper sediment layers due to the reduction of the industrial mercury contamination. The cores in the present study showed an increase of mercury with depth. This may also reflect the temporal changes in the rate at which mercury has been added to the Laranjo Basin, but it is not independent of geochemical aspects.

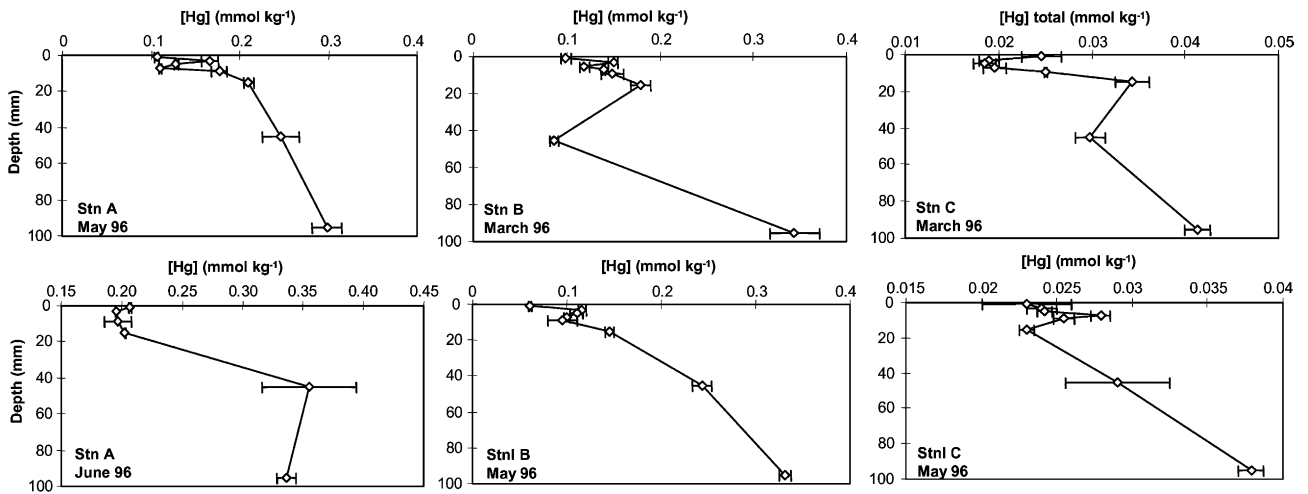


Fig. 2. Vertical profiles of total mercury (mmol kg^{-1}) in sediment cores A, B and C collected from the Laranjo Basin (horizontal bars represents standard deviation).

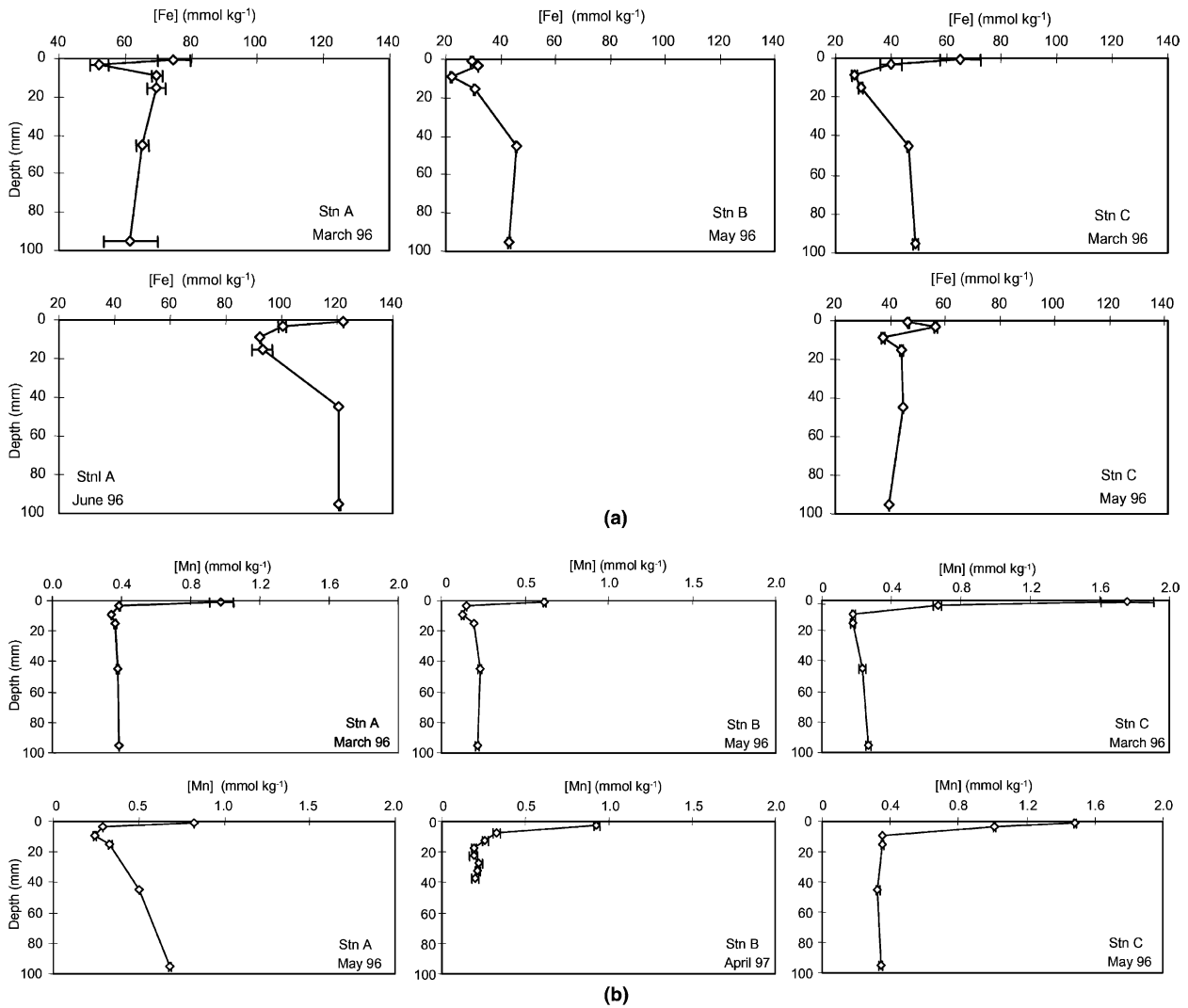


Fig. 3. (a) Vertical profiles of iron (mmol kg^{-1}) extracted with hydroxylammonium-acetic acid solution from sediment at station A, B and C. (b) Vertical profiles of manganese (mmol kg^{-1}) extracted with hydroxylammonium-acetic acid solution from sediment at station A, B and C.

The concentrations of manganese and iron extracted by a reducing solution of hydroxylammonium-acetic acid solution from sediment layers of core A, B and C are shown in Fig. 3a and b. The maximum iron concentrations measured were around 50–120 mmol kg⁻¹ in station A and around 27–62 mmol kg⁻¹ in station C. The manganese profiles indicate the precipitation of manganese oxides very close to the sediment surface, the first 0.5 and 1 cm. The iron oxides are formed at about the same layers. The increase of extracted iron below 2 cm is explained by the fact that acid digestion also solubilizes amorphous iron sulphides (Allen et al., 1993), which seems to be performed close to the upper sediment layers. The formation of insoluble sulphides was proved by the digestion of sediments with a 3 mol l⁻¹ HCl solution (Fig. 4). The precipitation of mercury sulphides must be very effective due to the low value of the solubility product ($K_{sp}(\text{HgS}) = 10^{-53}$) (D'Itri, 1990).

The AVS profiles (Fig. 5) show a sharp gradient with depth and the concentration in core A (151 mmol kg⁻¹) was higher than that in core C (72 mmol kg⁻¹), as found for iron.

In terms of sediment reactivity, two zones can be distinguished: the topmost layers where iron and manga-

Table 1

Minimum and maximum concentrations of total mercury (mmol kg⁻¹) in sediment cores collected at station A, B and C, sliced with a fine spatial resolution

Depth (mm)	[Hg] at A (mmol kg ⁻¹)	[Hg] at B (mmol kg ⁻¹)	[Hg] at C (mmol kg ⁻¹)
1	0.086–0.21	0.061–0.10	0.023–0.062
3	0.12–0.20	0.12–0.15	0.019–0.059
5	0.13–0.15	0.11–0.12	0.018–0.024
7	0.11–0.15	0.10–0.14	0.020–0.028
9	0.15–0.20	0.096–0.15	0.025–0.066
15	0.18–0.21	0.14–0.18	0.023–0.068

nese oxides are formed and a zone rich in sulphide. Both oxides and sulphides chemistries may interfere considerably with the mercury diagenesis.

The mercury concentration in the topmost sediment layers showed a spatial variability among the surveyed stations (Table 1). This lack of uniformity may be attributed to natural variability associated with the physical mixing of the sediments by organisms, to the proximity and temporal changes of the mercury anthropogenic source and eventually to post-depositional mobilisation of mercury.

In spite of the variability, the concentrations of extracted mercury with a 3 mol l⁻¹ HCl solution usually

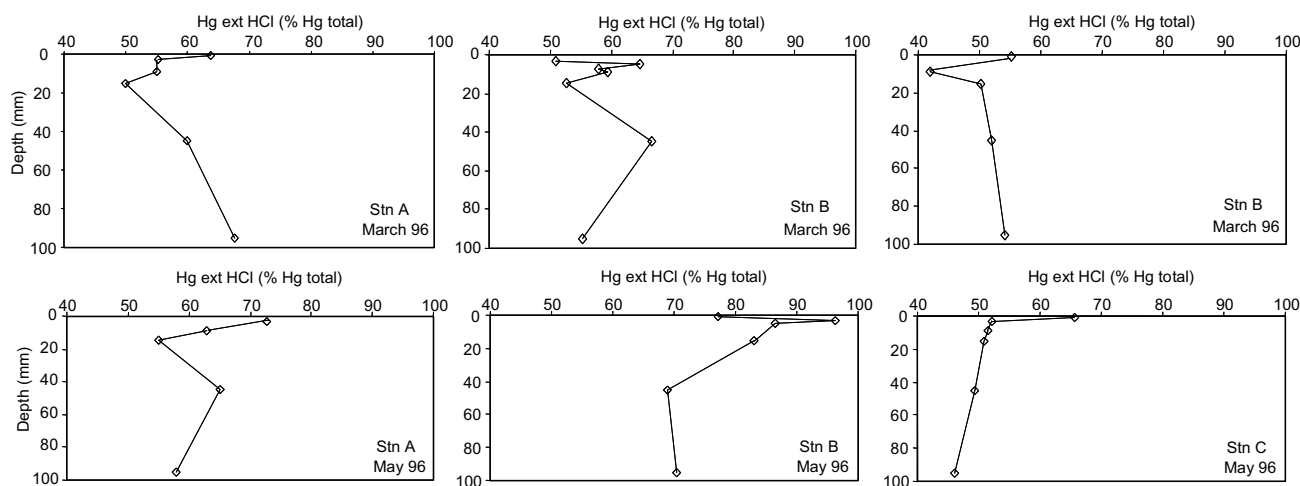


Fig. 4. Vertical profiles of mercury (% of total Hg) extracted with 3 mol l⁻¹ HCl solution from sediments at station A, B and C.

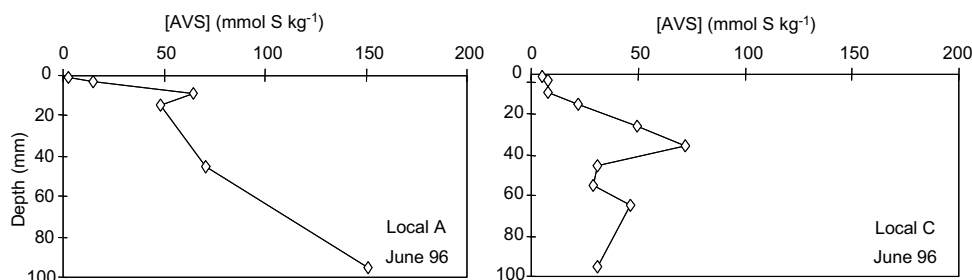


Fig. 5. Vertical profiles of AVS ($\mu\text{mol S kg}^{-1}$) extracted with 3 mol l⁻¹ HCl solution from sediments at station A, B and C.

present a defined depth variation pattern. The profile of the percentage of mercury extracted is high in the oxic/suboxic zone, and then decreases presenting a minimum of acid soluble mercury at levels where manganese and iron oxides are destroyed, and increase with depth.

The increase of extracted mercury with depth clearly indicates its incorporation in insoluble sulphide forms, which may constitute an efficient trap for mercury in the sediments.

References

- Allen, H.E., Fu, G., Deng, B., 1993. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environmental Toxicology Chemistry* 12, 1441–1453.
- D'Itri, F.M., 1990. The biomethylation and cycling of selected metals and metalloids in aquatic sediments. In: Baudo, R., Giesy, J.P., Muntau, H. (Eds.), *Sediments: Chemistry and Toxicity of In-place Pollutants*. Lewis Publishers, Michigan, pp. 163–214.
- Gobeil, C., Cossa, D., 1993. Mercury in sediments and sediment pore water in the Lurentian trough. *Canadian Journal of Fisheries and Aquatic Sciences* 50, 1794–1800.
- Gonzalez, H., 1991. Mercury pollution caused by a chlor-alkali plant. *Water, Air and Soil Pollution* 56, 83–93.
- Griepink, B., Muntau, H., 1988. Commission European Community. Rep. Eur. 11850 EN, pp. 49–65.
- Hall, A., Duarte, A.C., Caldeira, M.T.M., Lucas, M.F., 1987. Sources and sinks of mercury in the coastal lagoon of Aveiro, Portugal. *The Science of the Total Environment* 64, 75–87.
- Hall, A., Duarte, A.C., Oliveira, J.B., Lucas, M.F.B., 1988. Particulate mercury in the coastal area of Aveiro, Portugal. *Heavy Metals in Hydrological Cycle*, 507–512.
- Haynes, D., Toohey, D., Clarke, D., Marney, D., 1995. Temporal and spatial variation in concentrations of trace metals in coastal sediments from the Ninety Mile Beach, Victoria, Australia. *Marine Pollution Bulletin* 30, 414–418.
- Lucas, M.F., Caldeira, M.T., Hall, A., Duarte, A.C., Lima, C., 1986. Distribution of mercury in the sediments and fishes of the Lagoon of Aveiro, Portugal. *Water, Science and Technology* 18, 141–148.
- Pereira, M.E., Duarte, A.C., Millward, G.E., 1995. Seasonal variability in mercury inputs into the Ria de Aveiro, Portugal. *Netherlands Journal of Aquatic Ecology* 29, 291–296.
- Pereira, M.E., Duarte, A.C., Millward, G.E., Abreu, S.N., Reis, M.C., 1997. Distribution of mercury and other heavy metals in the Ria de Aveiro. *Química Analítica I*, S31–S35.
- Pereira, M.E., Duarte, A.C., Millward, G.E., Vale, C., Abreu, S.N., 1998. Tidal export of particulate mercury from the most contaminated area of Aveiro's Lagoon, Portugal. *The Science of the Total Environment* 213, 157–163.

0025-326X/\$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2005.02.043

Trace metal concentrations in coastal marine waters of the central Mediterranean

L. Manfra^{a,b}, A. Accornero^{a,*}

^a *University Parthenope, Department of Environmental Sciences, 80133 Naples, Italy*

^b *ICRAM—Central Institute for Applied Marine Research, 00166 Rome, Italy*

Urban and industrial activities in coastal areas introduce significant amounts of pollutants (including trace metals) into the marine environment. Unfortunately, monitoring data are lacking in most regions where anthropogenic activities are well developed, and especially in the Mediterranean (Cruzado, 1985). This paper reports the concentrations of six heavy metals (Zn, Cu, Mn, Pb, Ni and Cd) in surface marine waters of the southern Tyrrhenian and Adriatic seas. Three coastal areas were selected for sampling, in proximity of the Campania (22 stations), Apulia (22 stations) and Albania (7 stations) shorelines, with most stations located

at a distance of 500 m from the coast and a few stations situated on inshore–offshore transects, in correspondence of 'critical points' such as river mouths and harbors (Fig. 1).

Few and sparse heavy metal data are available for these areas, all referring to sediments (Ferretti et al., 1988; Viel and Zurlini, 1988; Çelo et al., 1999; Cicero et al., 2000; Ianni et al., 2002) and biota (Storelli et al., 2001; Conti and Cecchetti, 2003; Lionetto et al., 2003).

The determination of heavy metal concentrations in seawater may represent a useful tool to evaluate the quality of the marine environment and can elucidate the mechanisms of pollutant transfer among abiotic compartments and biota. Seawater metal analyses are, however, complex to carry out, due to the strong 'matrix effect' produced by salts and oxides present in seawater that may cause interference with the determination of low concentrations of metallic compounds (Chapple

* Corresponding author. Tel.: +39 081 5476573; fax: +39 081 5513679.

E-mail addresses: l.manfra@icram.org (L. Manfra), accornero@uniparthenope.it (A. Accornero).