CADMIUM AND LEAD LEVELS IN THE RIA FORMOSA

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INTRODUCTION

The Ria Formosa lagoon is a natural system of great economic importance to the local fishing industry. 80% of the bivalves produced in the whole of Portugal come from this area and this represents an annual value of about 2 billion escudos.

Sewage and industrial wastewater enter the lagoon at several sites and these contribute to the Heavy Metal (H.M.) pollution of the lagoon.

This study was carried out in order to understand the general trends and the local details of the occurrence of the H.M. in the lagoon.

Trace elements such as cadmium and lead are not conservative in seawater unlike many of the major elements in the marine environment.

Their distribution and behaviour are controlled by biological and geochemical processes as well as tidal processes.

The H.M. can exist in solution as different species some of which can have deleterious effects in the marine environment.

The speciation of HM is an important factor governing their chemical reactivity, bioavailability and toxicity.

SAMPLING

Four stations in the Faro channel were sampled during the month of June. These are shown on the map (figure 1).

Fig.1.Sampling stations in Ria Formosa

The samples were collected using a PVC Go-Flo sampling bottle. The bottle was previously washed with 10% HNO3 and deionised water.

Samples were taken from two depths: 1m below the surface; and 1m below the depth at which the secchi disk was no longer visible. Since no light penetrates to the later depth the biological activity of photosynthetic organisms is expected to be much lower than in the surface sample.

The samples were stored in polyethylene bottles wich were previously treated with 10% HNO3 and deionized water then rinsed three times withe some amount of the sample.

Other samples were filtered on board with a 0.45um Millipore AH filter to remove suspended solids.

All samples were stored at 4.C until the analyses were carried out.

EXPERIMENTAL

Anodic stripping voltammetry has been shown to be useful for trace metals analyses in seawater. Sample handling and pretreatment have been minimized, thereby reducing sources of contamination as well as retaining the chemical integrity of the natural system.

Most of the methods used for the determination of trace metals in seawater are based on the use of Atomic Absorption Spectrophotometry (AAS). A preconcentration technique is used prior to analysis, introducing the possibility of contamination during the manipulation of the sample.

Reagents

Standard 10^{-3} M solutions of Cd(II) and Pb(II) were prepared from $CdCl_2 . 2 \, 1/2H_2O$ and $Pb(NO_3)_2$. Fresh solutions (10^{-6} M) were obtained daily by dilution.

HCl and HNO_3 were suprapur reagent grade (Merck).

Equipment

Anodic Stripping Voltammetry in Differential Pulse Mode (DPASV) was performed using a Metrohm Polarograph composed of a processeur VA 646 and a Post Cell. The cell was equiped with a platinum wire counter electrode, an Ag/AgCl reference electrode (sat.KCl) and a multimode electrode working as an Hanging Mercury Drop Electrode (HMDE).

The experimental conditions were:

- deposition time: 300 s
- rest period: 30 s
- reduction potential: -900 mV
- pulse height: 50mV
- scan rate: 10.0 mv/s

During the electrodeposition of the metals the sample was continously stirred at a speed of 500 rpm and the mercury drop area was 2.3 mm2.

Concentrations were measured by the standard addition method.

RESULTS

The voltammograms of cadmium and lead of a seawater sample of the Ria (station n.3) are presented in fig.2a and 2b(standard addition of 500pg of Pb).
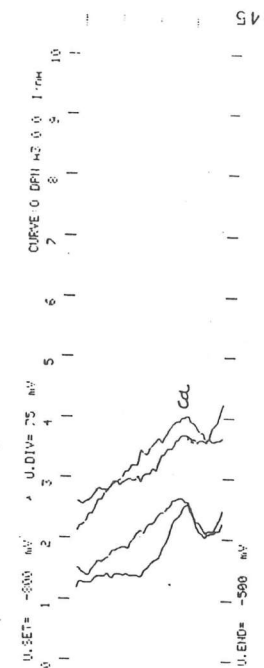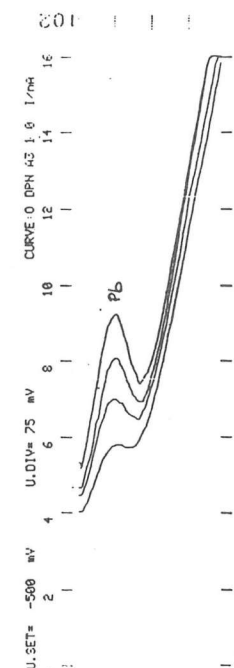

Fig.2a   Fig.2b

Table I shows the salinity and mean concentrations of labile cadmium and lead for each station during this survey.

TABLE 1

STATION Point	Depth m	Labile Cd ng/l	Labile Pb* ng/l	Salinity %.
2	1	n.d.	27.5	36.80
3	1	n.d.	30.0	36.45
3	4.5	n.d.	20.5	36.47
4	1	n.d.	42.0	36.20
5	1	n.d.	24.0	35.85
5	6.5	n.d.	13.0	35.87

n.d.- not detected
* - mean values.S_r (%) between 15 and 20.

The data obtained for cadmium in all samples were below 1ng/l, although the deposition time was 15 minutes.

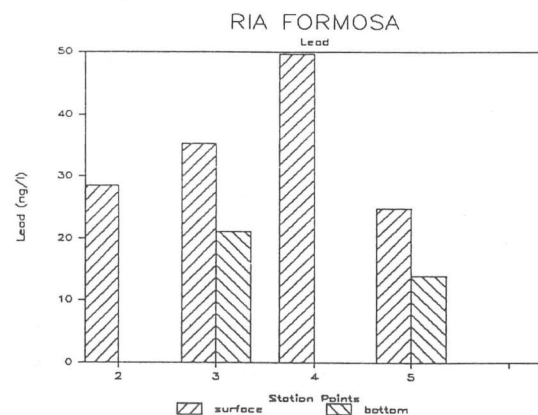The spatial distribution of labile lead in Faro Channel is presented in figure 3.

Fig.3.Concentrations of labile lead in samples from stations of Fig.1.

DISCUSSION

The data presented are only for the first month of sampling of a 12 month project. It is not possible to draw many conclusions at this early stage. It seems, however, that the boat traffic to and from the harbour in the lagoon may give rise to the high values of lead detected at station n.4.

With respect to cadmium it is our intention to try to use a mercury film electrode (MFE) but this has not been possible as yet.

The samples filtered on board for the determination of dissolved lead were contaminated probably by the boat engine exhaust fumes.

It is also our intention to determine the total content of these metals by oxidizing the organic matter content with nitric acid.

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