

Distribution of Heavy Metals in the Coastal Waters of  
Tuscany

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S u m m a r y

The distribution of Zn, Cd, Pb and Cu in the coastal waters of Tuscany (Italy) is reported. Measurements were carried out by differential pulse anodic stripping voltammetry at natural and lower pH values.

R é s u m é

On décrit la distribution du Zn, du Cd, du Pb et du Cu dans les eaux côtières de Toscane (Italie). Les mesures ont été effectuées par redissolution anodique combinée à la voltamétrie impulsionnelle différentielle, toutes au pH naturel et à des valeurs plus basses.

A series of samples were collected from April to September 1978 along the Tuscan coast (Italy) between the estuaries of the Arno and Cecina rivers to measure the concentrations of dissolved heavy metals (Zn, Cd, Pb, Cu) in sea water. Sampling was made monthly at 10 stations 1 mile from the coast and at 1-2 meter depths. Differential

pulse anodic stripping voltammetry was used with a hanging mercury drop electrode.

Measurements were carried out at both natural and lower pH values. The results are summarized in the table. The data refer to unfiltered samples. The mean concentrations found are in agreement with the few data available in literature (1), in particular with those of Capelli (2). Ours are mostly higher than those reported by Nürnberg (3). This is probably due to the fact that our sampling stations were between the estuaries of the Arno and Cecina rivers into which many industries discharge and where the Port of Livorno is situated.

It can be observed that the mean concentrations of metals are lower (equal in the case of Cd) than those considered of minimal risk (4).

The greatest concentration variations were obtained for zinc, which, in some cases (not reported in the table), reached maximum values of 180  $\mu\text{g}/\text{l}$ . These cases could be due to antropogenic sources but we cannot exclude occasional sample contamination.

Wide variations were also observed for cadmium. The levels range from low values, difficult to measure in our experimental conditions ( $< 0.05 \mu\text{g}/\text{l}$ ), to a maximum of 0,6  $\mu\text{g}/\text{l}$  which is higher than the minimal risk concentration (4).

Also percent differences between the concentrations at pH 8 and lower pH values are reported in the table.

These differences could be due to dissolved organic compounds, labile at low pH values (5). In this way we could get indirect information about the complexing capacity of sea water examined.

Metal	pH	Mean	Range	at natural pH
		$\mu\text{g}/\text{l}$	$\mu\text{g}/\text{l}$	
Zn	6	12,9	3,4-20	60-70
Cd	2,7	0,2	0,05-0,6	100
Pb	2,7	3	1-4,7	20-30
Cu	2,7	2,8	0,8-4	50-60

Concentrations of dissolved heavy metals and percentage present at natural pH.

#### REFERENCES

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#### DISCUSSION

##### Questions and comments:

1. What precautions did you make to avoid pH change during the deaeration of the sample during the measurements?  
(L. Sipos, Yugoslavia)
  - No precautions were taken. In agreement with other authors we considered the measurements at "natural pH" if no chemicals were added to the sample. Although as you say, the deaeration causes a pH variation of about 0.5.
2. Avez-vous, dans votre Laboratoire, effectué quelques essais de correlations voltammetry/A.A.?  
Les resultats exprimés par voltametrie sont interfeuriors à ceux exprimes par A.A. (R. Pucci, Monaco).
  - Unfortunately we have no experience with the A.A.S. From the literature it is known that different results are obtained using the two techniques. In any case it may be observed that the differences could depend on a different chemical treatment of samples. This fact could be responsible for both the different speciation of metal and the different risk of contamination.
3. Comment on the results of Nürnberg's group (Nürnberg, Mart, Valenta) is that only on the shipping routs and close to the big ports a peak in heavy metal concentration (Pb, Cd) is observed, and the high concentration of trace metals is not constant like in your case.  
(B. Raspor, Yugoslavia)

- Our results are mostly higher than the mean levels, but not in respect to the peaks, reported by Nürnberg et al. It must be considered that:
  - 1) Our data refer to unfiltered samples and so they contain particulate matter too.
  - 2) Our sampling stations were both between the estuaries of two polluted rivers and near the Port of Livorno.
  - 3) The tract of coast examined by Nürnberg is at least twenty times larger than ours and so that it is difficult to compare results.
- 4. As Dr. Patterson from Pasadena, USA, pointed out, it is very easy to contaminate water samples for Pb measurements. Taking this into consideration your Pb values seem to be too high. (R. Fukai, Monaco).
- If we consider that air is probably the main cause of lead pollution in sea water, it is obvious that the first sea waters layers contain more lead than the deeper ones. Even though our samples were collected at one meter depth. The high values found could also be ascribed to further contamination after sampling.

