

Chemical Oceanography
Concentrations of Cd, Pb and Cu in Ligurian and
Tyrrhenian Coastal Waters

H.W.Nürnberg, L.Mart, P.Valenta

Institute of Chemistry
Institute 4 Applied Physical Chemistry
Nuclear Research Centre (KFA), Juelich
Federal Republic of Germany

Summary: The concentrations of Cd, Pb and Cu in the dissolved state have been determined along the Ligurian and Tyrrhenian coast at 225 sampling stations by differential pulse anodic stripping voltammetry.

Résumé: On a déterminé le long de la côte Ligurienne et Tyrrhénienne à 225 stations les concentrations de Cd, Pb et Cu dans l'état dissolu, utilisant la méthode de redissolution anodique combinée avec la polarographie impulsionnelle différentielle.

In an extended systematic field study during May/June 1976 the concentration levels of dissolved Cd, Pb and Cu have been determined along the Ligurian and Tyrrhenian coast (from Ventimiglia to south of Ostia) at 225 sampling stations. Surface water samples were taken usually 100 m off the shore yet at several locations also profiles offshore up to 3 km were pursued. The results are summarized in the table. The average range found is for Cd and Cu somewhat lower and for Pb a factor 5 to 10 higher than the overall average values given in a recent compilation (1) for the whole sea (Cd 0.02; Cu 1.0; Pb 0.02 $\mu\text{g}/\text{l}$). The highest values corresponding to significant pollution have been recorded along the shipping routes to the big ports (Genoa and to a smaller degree La Spezia). On the other hand in areas rich in algae and/or particulate matter the particularly low concentrations are observed indicating trapping of the heavy metals due to uptake by organisms and chemisorption or incorporation by particulate matter while in areas of very clear water the elevated concentration ranges are frequent. This behaviour reflects tendencies of a general self regulation mechanism with respect to the level of dissolved heavy metals provided polluted coastal waters contain due to the local situation also sufficient scavenging inorganic or biological material, for instance in river estuaries. Furthermore one observes in the vicinity of a river mouth on both sides usually low heavy metal levels a result to be attributed to a physical effect, i.e. the dilution with unpolluted water streaming from offshore waters to the shore and the result of upwhirling of particulate matter

due to the initiation of back currents. It is to be emphasized that the respective concentration levels for the three studied metals are frequently not strictly correlated in their height at a given sampling station suggesting that specific pollution sources will be operative. Along the offshore profiles frequently no significant alteration in heavy metal concentration exists although for some sampling points a small trend of decrease was noticeable.

The samples have been filtrated within 3 to 4 hours (0.45 μ filter) to separate from the particulate matter and the filtrated solution was then acidified with HCl (Merck, suprapur) to pH 2. Subsequently the concentrations of Cd, Pb and Cu were determined simultaneously (12 samples per day) by differential pulse anodic stripping voltammetry at a glassy carbon electrode coated with a thin mercury film (100 to 1000 Å thickness) in situ during the cathodic deposition stage under rotation (1500 rpm) of the electrode. Special precautions to avoid adsorption losses by utilizing conditioned polyethylene containers and teflon cells and to exclude contamination assured reliable accuracy and high precision of the data having only a RSD of \pm 8 % for Cd and Pb and \pm 15 % for Cu. Details of the method have been published elsewhere(2). From the methodological viewpoint the study emphasizes the particular potentialities of the polarographic approach to obtain by suitable techniques highly accurate and reliable data on heavy metals present in sea water at the ultra trace level (3).

Levels of dissolved heavy metals in $\mu\text{g}/\text{kg}$ ($n_{\text{total}} = 225$)

Metal	Low	Elevated	High	Average
Cd	0.005 - 0.009 (n=59)	0.021 - 0.05 (n=33)	0.051 - 0.452 (n=9)	0.01 - 0.02 (n=121)
Pb	0.018 - 0.09 (n=86)	0.21 - 0.5 (n=34)	0.51 - 2.42 (n=9)	0.1 - 0.2 (n=98)
Cu	0.13 - 0.19 (n=7)	0.55 - 1.0 (n=58)	1.1 - 3.6 (n=45)	0.2 - 0.5 (n=111)

n number of sampling stations

References:

- (1) M. Bernhard, A. Zattera, in E.A. Pearson, E. De Fraja Frangipane eds., "Marine Pollution and Marine Disposal" Pergamon Press, London 1975, pp.195-300
- (2) H.W. Nürnberg, P. Valenta, L. Mart, B. Raspor, L. Sipos, "The Polarographic Approach to the Determination and Speciation of Toxic Trace Metals in the Marine Environment", Z. Anal. Chem., in press
- (3) H.W. Nürnberg, P. Valenta, "Polarography and Voltammetry in Marine Chemistry" in E.D. Goldberg, ed., "The Nature of Sea Water", Dahlem Konferenzen, Berlin 1975, pp. 87-136

DISCUSSION

Questions and comments:

1. What is the influence of preparation of samples on measurements at very low concentration levels (adsorption of heavy metals on seston, pH change due to vacuum, etc.)? (M. BRANICA, Yugoslavia).
 - The elimination or sufficient suppression of error sources due to contamination or adsorption losses at utilized labware by first purification and subsequent conditioning of all utilized labware are described in detail in the submitted paper. Adsorption on seston has not yet been studied but is a topic on our future research schedule. The problem of pH-change due to vacuum did not arise in our studies as samples were processed within 5 hours after sampling by filtration and subsequent acidification to pH 2. Within first 5 hours no alterations in sea water samples occurred as extended tests had established.
2. Is it necessary to filter the samples to remove particulates, i.e. why do not use ultracentrifugation to avoid pH changes and adsorption of metals on filters? (D.L. ELDER, Monaco).
 - Ultracentrifugation might be a good alternative approach to separate from suspended particulate matter. Yet there is no problem of adsorption on filters as properly conditioned filters were utilized. As then all potential adsorption sites are occupied by divalent ions of the ionic macro components (Mg^{2+} , Ca^{2+}) of sea water adsorption of the studied trace metals is ruled out. It is questionable if pH-changes to pH 2 should be avoided if one is interested in the total dissolved content of the studied trace metals. That fraction which is strongly chelated will be only released and thus become accessible to voltammetric determination if pH is adjusted to 2 or less.

3. Do you know if there is any evidence concerning the role of humic acid materials in dissolution of metals?

(D.L. ELDER, Monaco).

- No evidence yet, but we are working on this important problems.

4. What are the determination limits for Cd and Pb?

(C. PAPADOPOULOV, Greece).

- Determination limits for Cd are 10^{-3} ug/liter or 10^{-3} ppb, for Pb $5 \cdot 10^{-3}$ ug/liter or $5 \cdot 10^{-3}$ ppb with a R.S.D. 20%. However, in the range 0.2 to 0.02 ppb precision is even better and R.S.D. is less than 8%.

5. What were the error-bars in the profiles of metal concentrations that you have presented us?

(D. ZAFIROPOULOS, Greece).

- The relative standard deviation (R.S.D.) is 8% for Cd and Pb, and 15% for Cu.

6. Have you collected and analyzed biota from your sampling network and, if so, how do the levels in these organisms correlated with those in the dissolved and particulate phases in the surrounding seawater? (S.W. FOWLER, Monaco).

- In the first part of our study we have only investigated the dissolved content of the studied trace metals. Levels at particulate matter are under investigation at present. Studies on the level in selected organisms are scheduled for the near future.

7. What is the mean value of the mass of particulate matter? Is the fraction of particulate cadmium important?

(P. GUEGUENIAT, France).

- This subjects are under investigation at present. Our first topic was to establish an extended survey of reliable data on the truly dissolved content of the studied trace metals in the investigated coastal waters.
8. Have you parallely investigated influences of maximal concentrations of metals founded in the sea water on organisms, especially juvenile stages of marine invertebrates?
(Č. LUCU, Yugoslavia).
- In the first part our studies were restricted to the dissolved content of the studied trace metals in the investigated coastal waters. Contents of marine organisms are on the future schedule of our research project.

