

Dissolved copper speciation in the coastal waters of Alexandria Region

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Speciation studies attempt to differentiate between the chemical forms and distribution of metal species in dissolved, colloidal and particulate phases. The distinction between dissolved and particulate forms by filtration through 0.45 μm is generally accepted. The dissolved fraction includes truly dissolved material plus colloidal fraction. Metals could also be classified according to their rate of reaction with a dissolved ligand as well as the extent of stability of their complex with this ligand. Metals bioavailability and biogeochemical cycles are influenced mainly by their interaction with dissolved organic matter which in turn is a reflection of the impact of man's activity on the environment.

The aim of the present study is to apply the cathodic stripping voltammetry (CSV) technique for the determination of dissolved copper species in several coastal marine environments differing in their exposure to the amount of metal discharged. The labile fraction of the metal is that species measured by CSV in untreated filtered sample including all inorganic complexes and a certain proportion of organically associated metal. The total dissolved metal is those species detected in U.V. irradiated (4 hours, 1 KW mercury lamp) and acidified (pH 2.5 ± 0.1) samples. This includes the summation of the metal present as free, inorganically complexed, organically complexed and colloiddally associated metal species.

Samples were collected during low and high landbased sources discharge periods from three different locations covering the coastal waters of Alexandria region. These environments are subjected to agricultural, industrial and sewage runoff. Samples were collected in precleaned polyethylene bottles, filtered after collection by pressure and stored frozen between sampling and analysis. Analyses were carried out at pH 7.8 ± 0.4 using HEPES buffer and Oxine as a chelator (VAN den BERG, 1986). A PAR 174A Polarograph was used with a PAR 303A SMDE in conjunction with a Ag/AgCl reference and a platinum wire counter electrodes. Collection was performed at -1.0 V for 1 minute while scanning started from -0.3 V. Scanning parameters were: DPCSV, pulse rate 10 s, scan rate 10 mV s⁻¹, pulse amplitude 25 mV. The reduction current was recorded on a x-y recorder. Calibration was achieved using the standard addition technique. Additional analyses for salinity, DOC and TSM were made.

The average labile and total dissolved copper concentrations in the coastal waters of Alexandria, presented in Table 1, are higher than normal values expected in coastal waters. At the high salinity region i.e. offshore stations, labile Cu showed small changes (Figure 1). However, a significant increase in the non-labile Cu fraction was observed opposite to discharge points especially when salinity drops below 30 during high flow period. This increase coincided with the increase in DOC ($r = 0.8755$, $p < 0.001$) and suspended matter ($r = 0.7301$, $p < 0.01$) concentrations. Such a relation suggests the removal of Cu from solution through complexation by either organic matter and/or adsorption onto solids at the turbidity maximum zones. Agricultural rather than industrial and sewage discharges seemed to be the major source for dissolved Cu to the coastal waters. The use of copper sulphate in controlling algal blooms in the Nile delta lakes may be the possible explanation for this source. A high degree of copper complexation was observed at the dumping site for domestic and sewage discharge.

TABLE 1. Average labile and total Cu in Alexandria coastal waters.

Survey	Labile		Total		Non-labile	
	mean	range	mean	range	mean	range
High flow	30±9	18.5-49.7	49±17	24.0-83.5	19±8	5.5-33.8
Low flow	15±8	6.5-34.1	20±11	9.0-40.2	5±3	2.5- 6.1



From the TDCu and salinity regression: $\text{TCu} = -2.15 \text{S} + 117.9$ (high flow) and $\text{TCu} = 0.0995 \text{S} + 17.98$ (low flow), the extrapolated TCu concentrations at salinity zero would be 118 and 18 nM for high and low flow periods, respectively. Such values are inconsistent with those reported at the Nile delta lakes-sea mixing zone i.e. 66 and 10 nM, respectively.

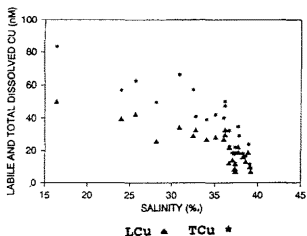


Figure 1. LCu and TCu vs. Salinity.

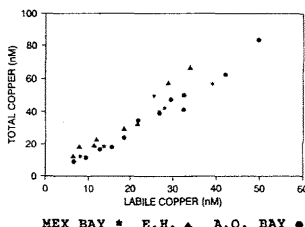


Figure 2. LCu against TCu.

The labile and total dissolved copper are linearly related (Figure 2). The LCu/TCu ratio was obtained for each zone from a plot of LCu values against those of TCu. The ratio ranged between 0.502 ± 0.03 and 0.608 ± 0.05 . This ratio indicated that a range of 89 to 96.4% of the TDCu would be organically complexed. Such a value emphasizes the importance of organic copper complexation in the coastal waters of Alexandria. Reported percentages of bound Cu of the total ranges from 30-50% (BATLEY & FLORENCE, 1976); 70-100% (SUGAI & HEALY, 1978); 94-98% (VAN den BERG, 1984) for coastal waters and <10-35% (DONAT *et al.*, 1986) for oceanic waters. The mean $\log \alpha_{\text{CuL}}$ determined in this study was 4.86 ± 0.97 , a value which is higher compared to previous studies ex: 3.14 for Irish Sea (VAN den BERG, 1984), 2.39-2.72 for Liverpool bay (NIMMO *et al.*, 1989) and 3.95 for Guanabara bay (VAN den BERG & REBELLO, 1986) indicating either high ligand concentration and/or high stability constant.

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