

## SPECIATION OF SOME TRACE METALS (Fe, Cu, AND Cd) IN EL-MEX BAY WATERS, ALEXANDRIA, EGYPT

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**ABSTRACT:** Surface- and bottom-water samples were collected from October 1996 to August 1997 to study levels of iron, copper, and cadmium species in their dissolved labile as well as non-labile and particulate forms in the waters of El-Mex Bay. The results showed that the non-labile concentration of the metals was generally more abundant than that of the labile form: its content reached more than 90% of the total dissolved metal for Cu and more than 80% for Fe. The particulate form was almost at the level of the labile form. The annual concentration of the trace metals of the labile form was  $13 \mu\text{g l}^{-1}$  for Fe;  $3 \mu\text{g l}^{-1}$  for Cu, and  $1.2 \mu\text{g l}^{-1}$  for Cd in the surface- and bottom-waters.

**KEY WORDS:** El-Mex Bay, Speciation, Labile, Non-labile, Particulate, Trace metals.

### INTRODUCTION

There is much data in the literature on metal concentrations in natural waters. Surprisingly, most is on the "dissolved metals". These were extracted from water samples either by chelating resin (chelex-100) or solvent extraction (APDC-MIBK) techniques (Riley and Taylor, 1968; Martin, 1972). According to Abdullah *et al.* (1976) the dissolved metal is present in labile and non-labile forms. There is little information on the non-labile form. Speciation of different soluble metal fractions can also be classified according to size (Stumm and Bilinski, 1972; Guy and Chakrabarti, 1975).

The simplest is the hydrated metal ion. Such ions may form loose electrostatic associations with anions to form ion pairs. Stronger binding is demonstrated by organometallic compounds ranging in complexity from simple amino acid complexity to those formed with humic substances. The latter in the predominant form of dissolved organic matter in natural waters (Rashid and Leonard, 1973).

The present work is an attempt to determine the levels of the different forms of the trace metals (Fe, Cu, and Cd) in their dissolved labile (unstable) and non-labile (stable) complex forms as well as those in the particulate form.

### MATERIALS AND METHODS

#### Area of study

The water samples were collected from a nearly coastal bay area called El-Mex Bay. It lies west of Alexandria between  $29^{\circ}45'$  and  $29^{\circ}54'E$  and  $31^{\circ}07'$  and  $31^{\circ}15'N$  (Fig. 1). It is an area about 12 km, extending between El-Agamy Head land at the west and the western harbour at the east, with a mean depth of 10 m.

The Bay receives a very large amount of agricultural drainage waters at a rate of six million  $\text{m}^3 \text{d}^{-1}$  through the Umum drain. It also receives considerable amounts of untreated

industrial waters from the Alexandria Iron and Steel Factory, a chlor-alkali plant, a cement factory and tanneries as well as oil product contaminants from the Alexandria Petroleum Company.

Water characterization of El-Mex Bay was studied by several authors (e.g., El-Rayis *et al.*, 1984, 1996; Aboul Dahab *et al.*, 1984; El-Gindy *et al.*, 1986; Said *et al.*, 1991; and Emara and Shriadah, 1991).

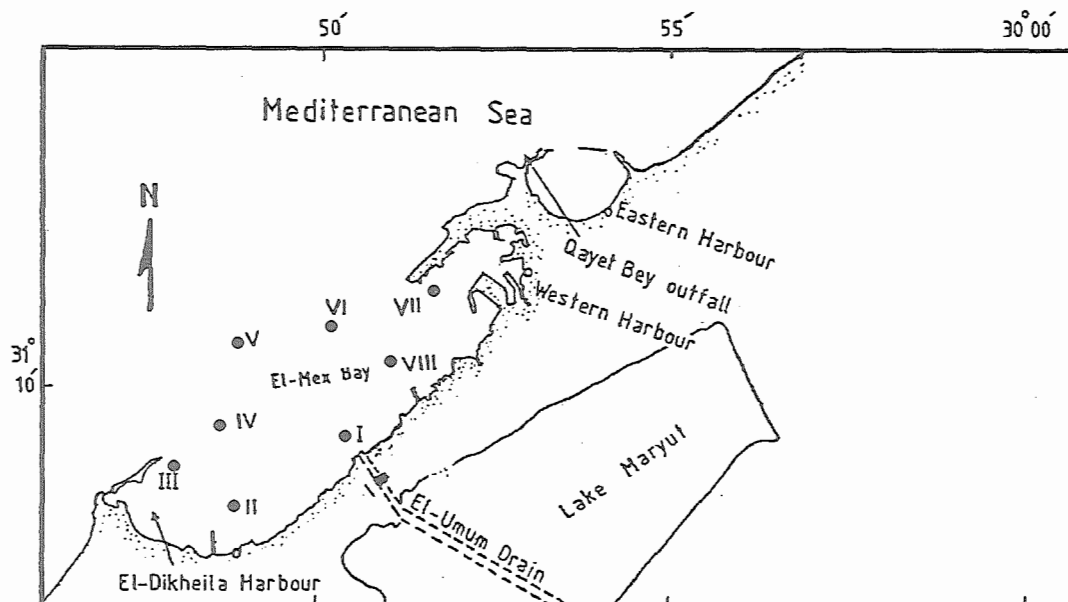


Fig. 1. Position of sampling stations in the area investigated.

#### Sampling and analysis

El-Mex Bay surface- and bottom-water samples were seasonally collected from October 1996 to August 1997. The samples were placed in acid pre-cleaned polyethylene Niskin bottles. The eight collection stations, shown in figure 1, represent different parts of the Bay.

**Particulate metals:** In the laboratory, the water samples were filtered through  $0.45\mu\text{M}$  membrane filters to separate the particulate phase from the soluble phase of the metals (Smith *et al.*, 1981). Then, the suspended matter retained on the filters was washed with deionized distilled water and dried at room temperature. Total suspended matter was calculated before dissolution using the acids HF,  $\text{HClO}_4$  and  $\text{HNO}_3$  in Teflon beakers. The solution was then evaporated to near dryness according to the method of Van Loon (1982) and redissolved in 0.1 M HCl acid.

#### Dissolved metals:

**Total filterable metals:** Total dissolved Fe, Cu, and Cd were determined from part of the filtered sample after gentle boiling (100 ml) and adding 1 ml concentrated  $\text{HNO}_3$  in a Teflon beaker (Van Loon, 1982). The sample was concentrated by evaporation to near dryness; 2 ml HCl and 1 ml  $\text{HNO}_3$  were added, and it was reevaporated to near dryness.

again. Redissolution of the residual used 0.1 M HCl acid.

**Labile metal:** The other part of the filterable sample (1L) was allowed to pass through a glass column containing the chelating resin (Chelex-100) at a rate of  $\approx 5 \text{ ml min}^{-1}$ . The column was then washed with 30 ml of water before eluting the chelated with 70 ml 2N  $\text{HNO}_3$  acid in a Teflon beaker. The elute was evaporated to near dryness at low temperature and the dry residue dissolved with 6 N  $\text{HNO}_3$  (Riley and Taylor, 1968). The labile form includes the free ionic forms plus any labile complexes whose stability constant is less than metal with resin (Abdullah *et al.*, 1976; Förstner and Wittmann, 1981).

**Non-labile metal:** The non-labile metal, strongly bound organic and inorganic, is calculated by determining the difference between total filterable metal and labile metal (Mtf-Mie). All trace metal concentrations were determined using a flame atomic absorption spectrophotometer (Perkin Elmer 2380).

The precision of the analytical method was determined by analysis of six replicate samples of stripped seawater spiked with concentrations of different metals ( $5 \mu\text{g l}^{-1}$ ), giving values of Cd 4%, 5% Cu, and 3% Fe. The accuracy of the preconcentrated technique of dissolved metals was checked by spiking 5 liters of sea-water, previously stripped of all metals by chelex resin with different concentrations of 1, 2, 4, 6 and  $8 \mu\text{g l}^{-1}$ ; the spiked samples were passed through the resin. The results showed 4% deviation from the certified values.

The chemical and physical characteristics of the water samples were determined according to Grasshoff (1976) for dissolved oxygen, FAO (1975) for oxidisable organic matter, salinity using a salinometer (Model RS-7C) and pH by a digital pH-meter (Orient Research Model 201).

## RESULTS AND DISCUSSION

### General water characteristics

The seasonal range and average values of the different physical and chemical water sample parameters of El-Mex Bay are shown in Table 1.

**Salinity:** The results showed that the surface water salinity ranged between 3.77‰ at the outlet of the Umum drain (Site 1) and 39.61‰ (Site VII), with an annual mean of 19.06‰. The bottom water salinity was between 9.80‰ (Site V) and 41.68‰ (Site VIII), with an annual mean of 30.77‰. The maximum and minimum values occurred in April and October. The salinity of the surface water was less than the bottom water. This reflects the effect of the Umum drainage waters. El-Rayis *et al.* (1984) and El-Gindy *et al.* (1986) observed that El-Mex Bay surface-water is brackish and over lies a deeper saline layer during most of the year.

**Organic matter (OM):** Large variations in organic content were found between the surface- and bottom-waters and during the different seasons. The surface-water was highly enriched with organic matter, particularly near and in front of the Umum drain, Site 1 ( $12.16 \text{ mg O}_2 \text{ l}^{-1}$ ) and Site II ( $13.6 \text{ mg O}_2 \text{ l}^{-1}$ ), respectively. Obviously, this source is the

Table 1. Seasonal range and mean of El-Mex Bay water samples from October 1996 to August 1997.

Parameter	Autumn (Oct.)		Winter (Feb.)		Spring (Apr.)		Summer (Aug.)		Annual Mean	
	range	mean±S.D	range	mean±S.D	range	mean±S.D	range	mean±S.D		
Salinity (%)	S	3.77-22.93	14.99±7.21	6.15-34.37	21.24±9.29	5.65-39.61	22.81±5.54	5.26-24.61	17.19±8.12	19.06
	B	9.8-31.73	21.5±7.41	27.64-34.84	33.09±2.95	27.51-41.68	35.31±1.35	31.24-34.93	33.17±1.14	
pH	S	7.42-8.56	8.02±0.21	7.42-8.55	7.92±0.22	7.29-7.79	7.53±0.16	7.54-8.18	7.78±0.18	7.81
	B	7.71-8.22	8.0±0.27	8.06-8.39	8.17±0.21	7.49-7.84	7.71±0.12	7.83-8.09	7.99±0.13	
Organic Matter (mg O <sub>2</sub> /l)	S	1.64-3.44	2.28±0.57	0.34-4.71	2.29±1.32	7.04-13.6	10.2±2.63	1.6-3.68	2.38±2.24	4.29
	B	1.68-3.04	2.58±0.52	0.34-1.68	0.86±1.71	6.24-7.36	5.73±2.81	0.16-1.44	0.72±2.27	
Suspended Matter (mg/l)	S	14-70	31.88±18.46	8.0-24.0	13.63±5.61	10.0-24.0	17.75±6.09	12.9-30.6	17.56±5.26	20.21
	B	14-49	32.83±14.96	6.0-22.0	16.83±6.37	27.0-45.0	31.16±5.44	18.4-32.7	23.68±7.05	
Dissolved Oxygen (ml O <sub>2</sub> /l)	S	1.49-7.39	4.62±6.99	0.89-5.15	3.47±2.40	0.45-7.17	4.23±1.7	1.12-7.39	3.42±1.22	3.94
	B	3.29-6.72	4.78±5.78	4.70-5.37	5.19±3.10	2.46-5.38	4.39±1.6	4.93-6.94	5.30±0.46	

S=surface; B=bottom

main supply of organic matter to the Bay. The maximum average organic content was 10.2 mg O<sub>2</sub>l<sup>-1</sup> in the surface water in spring and 5.73 mg O<sub>2</sub>l<sup>-1</sup> in the bottom water during the same period, while the minimum value was 0.16 mg O<sub>2</sub>l<sup>-1</sup> in the bottom water in summer at Site VIII.

**Dissolved oxygen (DO):** It is worthy to mention that some stations (Sites I, II) had low values of dissolved oxygen, between 0.45 and 2.69 ml O<sub>2</sub>l<sup>-1</sup>, while others (Site VI) had high ones, (7.39 ml O<sub>2</sub>l<sup>-1</sup>).

#### Speciation of trace metals:

The seasonal mean concentrations of metal species as well as the regional average values in the surface and bottom waters of the studied area are shown in Figures 2 and 3.

#### Particulate trace metals

The distribution of both Fe and Cu particulates tends to increase in October and decrease in the other months. The highest mean value of Cu particulate ranged from 4.76±2.93 µg.l<sup>-1</sup> in the surface-water to 2.30±2.69 µg.l<sup>-1</sup> in the bottom-water, while the highest average content of Fe reached 248.9±153 in the surface- and 95.90±23.39 in the bottom-water (Fig. 3).

The regional average content of the Fe and Cu particulates, shown in figure 2, indicates that the highest concentrations of these metals were at Sites I and II. This may be attributed to the discharges from the El-Mex pumping station. Their distribution decreased away from the outfalls. The regional distribution of the average values of Cd particulate revealed that the large concentrations were in the eastern side of the Bay as well as Sites III and IV. This is perhaps due to the effect of the adjacent polluted area of the western harbour. Cadmium particulate decreased around the estuarine region, Sites I and II. This could be due to the large amounts of waste water. Site V had the lowest value of Cd particulate, 0.70±0.25 µg.l<sup>-1</sup> in the surface- and 0.56±0.35 µg.l<sup>-1</sup> in the bottom waters (Fig. 2).

The regional distribution of Fe and Cd particulates had the same trend: large values were found in the surface water with lesser ones at the bottom water. Conversely, except for few samples, this was the reversed for the Cu particulate, at Sites VI, VII, and VIII (Fig. 2). This is perhaps due to the biological influence that may be considered a major pathway for the transfer of trace metals. Previous work showed that Cd concentration in plankton is about 1100 times greater in the western harbour than in the seawater of El-Mex Bay (El-Rayis *et al.*, 1997).

#### Dissolved metals

**Labile metals:** Figure 2 shows the regional mean values of the labile trace metals, Cu, Fe, and Cd. The labile Cu was fluctuated between 1.91±1.73 µgl<sup>-1</sup> at Site V and 3.35±2.14 µgl<sup>-1</sup> at Site I at the surface-water. Its concentrations in the bottom water ranged between 2.78±1.51 µgl<sup>-1</sup> and 6.42±6.19 µgl<sup>-1</sup> at Sites V and VI, respectively.

The distribution of labile Fe was similar to the labile Cu in that the high values were found in the bottom-water. Surface labile Fe concentrations ranged between 5.14±4.22 µgl<sup>-1</sup> at Site II and 16.89±18.06 µgl<sup>-1</sup> at Site VII. Maximum labile Fe content in the

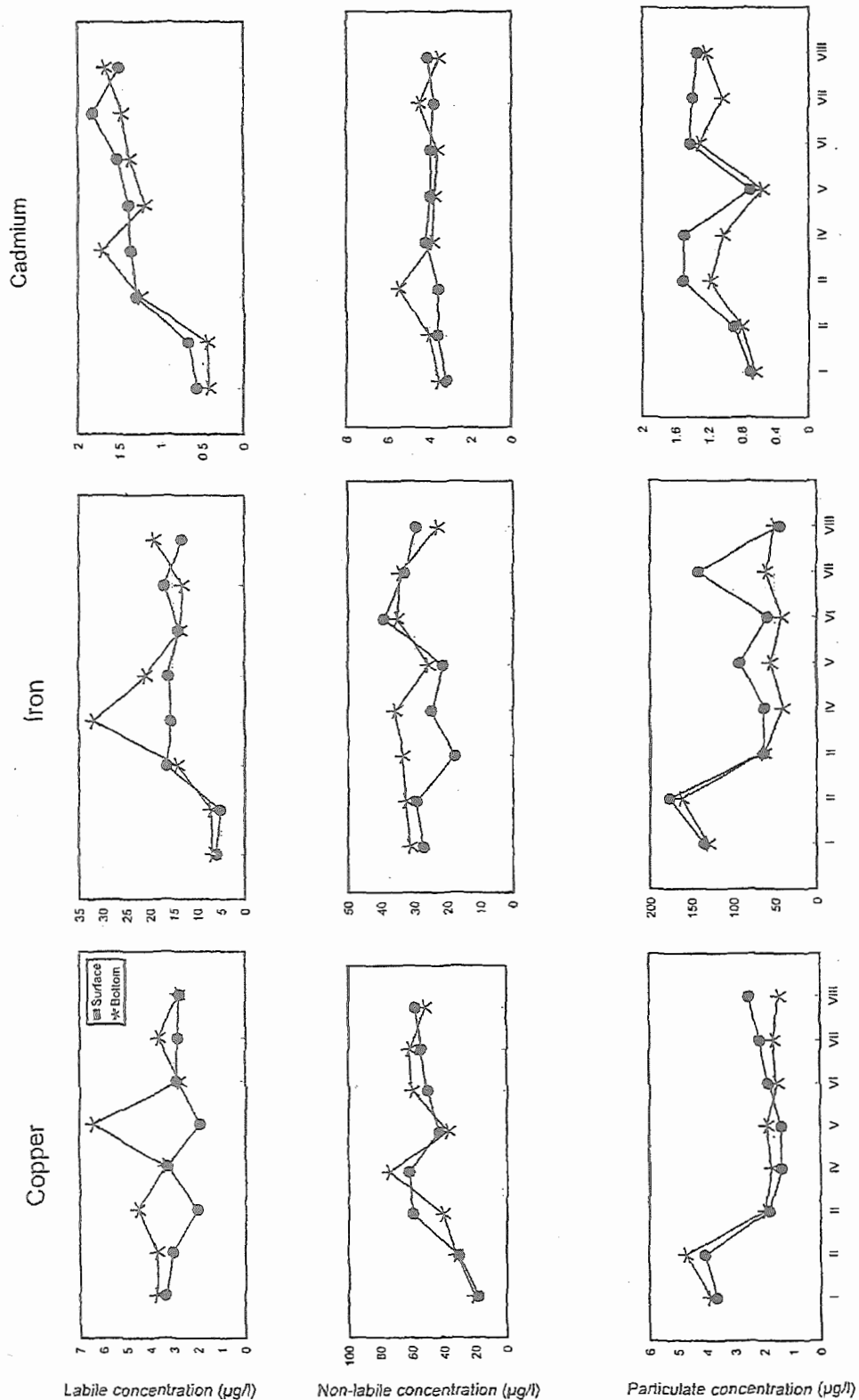


Fig. 2. Regional variations (average values) of different metal species ( $\mu\text{g/l}$ ) of El-Mex Bay water samples from October 1996 to August 1997.

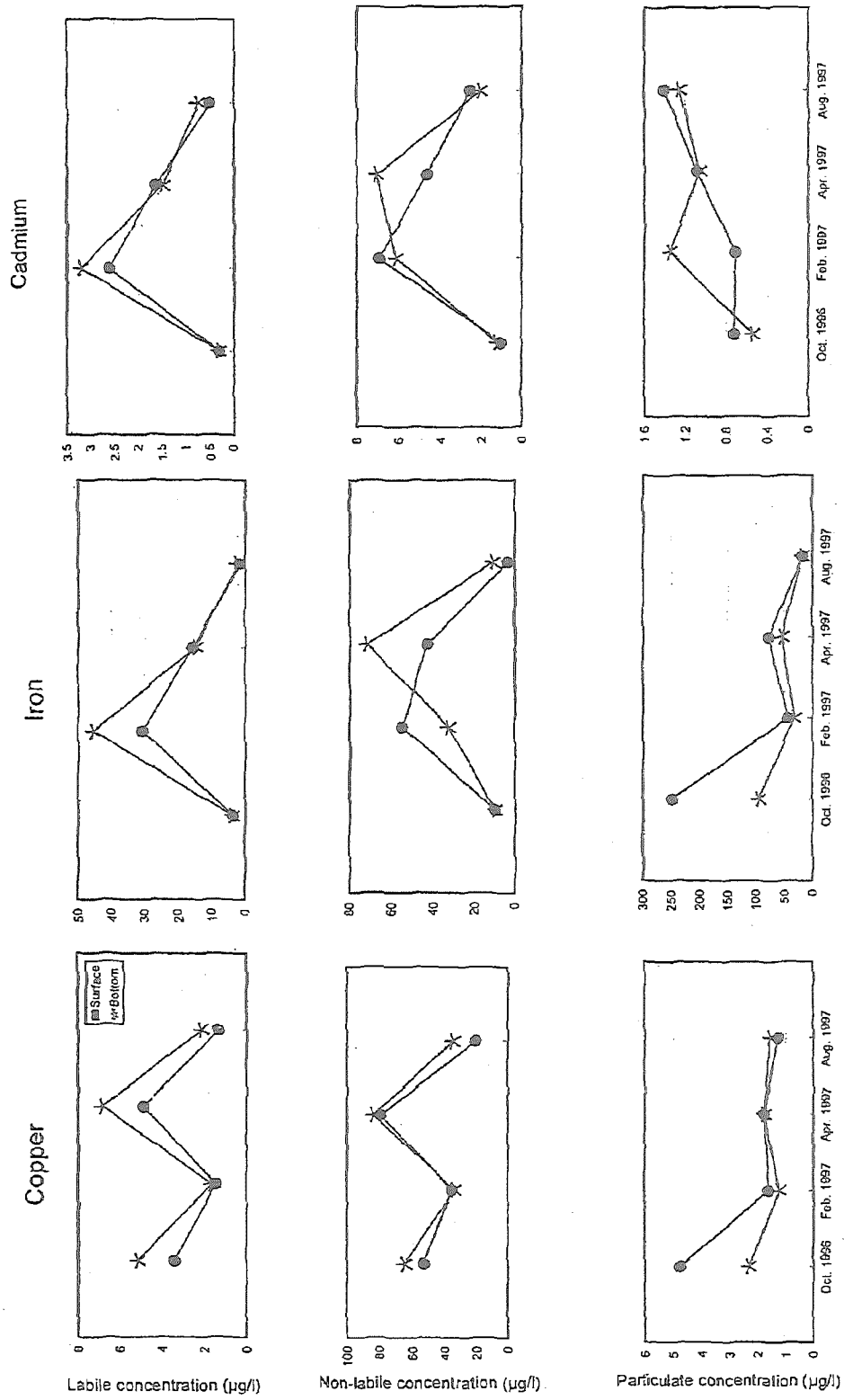


Fig. 3. Seasonal variations (average values) of different metal species (µg/l) of El-Mex Bay water samples from October 1996 to August 1997.

bottom water was at Site V ( $20.94 \pm 31.67 \mu\text{g l}^{-1}$ ) and the minimum at Site I ( $6.82 \pm 2.41 \mu\text{g l}^{-1}$ ).

The average values of labile Cd were slightly different for surface- and bottom-waters. Its concentration ranged between  $0.56 \pm 0.31 \mu\text{g l}^{-1}$  at Site I and  $1.82 \pm 2.01 \mu\text{g l}^{-1}$  at Site VII at the surface-water, while in the bottom-water, the labile Cd content ranged between  $0.42 \pm 0.23 \mu\text{g l}^{-1}$  at Site I and  $1.71 \pm 1.43 \mu\text{g l}^{-1}$  at Site IV. Previous studies showed that the content of dissolved Cd in the western harbour ranged between 1.2 and  $7.9 \mu\text{g l}^{-1}$  (Tayel *et al.*, 1997).

Figure 2 shows that the remarkable increase in the concentrations of the different species of Cd towards the seawater (Site VII) was due to the effect of the adjacent polluted area of the western harbour. The decrease around the estuarine region was due to dilution by large amounts of agriculture wastewater. The same trend of dissolved Cd was observed by Abdel Moniem *et al.* (1994).

Monthly variations of labile metals content in the investigated area showed that the labile Cu at the surface is higher than that at the bottom at all months (Fig. 3). The labile Cu content ranged between  $1.33 \pm 0.49 \mu\text{g l}^{-1}$  in August and  $4.88 \pm 1.83 \mu\text{g l}^{-1}$  in April at the surface and from  $1.65 \pm 0.28 \mu\text{g l}^{-1}$  in February to  $6.81 \pm 3.03 \mu\text{g l}^{-1}$  in April at the bottom.

The monthly average variations of labile Fe and Cd are similar. The results in Fig. 3 revealed that the highest content is found in February ( $30.6 \pm 12.96 \mu\text{g l}^{-1}$  for Fe and  $2.61 \pm 1.18 \mu\text{g l}^{-1}$  for Cd) in the surface-water and  $45.22 \pm 13.81 \mu\text{g l}^{-1}$  for Fe and  $3.2 \pm 0.46 \mu\text{g l}^{-1}$  for Cd in the bottom-water. Their lowest content was found in August in both surface- and bottom waters.

The results revealed that the relative percentage of the labile-Fe phase ranged between 0.1 and 20% of the total dissolved iron. The labile Cu form ranged between 1.7 and 10% of the total dissolved in surface- and bottom-waters, except for some water samples where the labile-Cu reached to 15 and 26% of the total (Site I) in winter and summer, respectively, and to 44% (Site V) in the autumn.

**Non-Labile metals:** The monthly variations of the non-labile metals (Fe and Cd) indicate that February and April have the highest content, while October and August have the lowest values at the surface and bottom waters (Fig. 3).

There is an increase of non-labile Cu content in the surface and bottom waters in October and April and a decrease in February and August.

The monthly average content of the non-labile trace metals in the surface-water of the investigated area ranged between  $3.45 \pm 2.88$  and  $54.74 \pm 20.15 \mu\text{g l}^{-1}$  for Fe,  $20.61 \pm 37.70$  and  $79.24 \pm 18.70 \mu\text{g l}^{-1}$  for Cu, and  $1.05 \pm 0.44$  and  $6.93 \pm 1.91 \mu\text{g l}^{-1}$  for Cd.

The level of the non-labile form reached values as high as 80% for those of the total dissolved Fe; more than 90% of the total dissolved Cu was presented in this form. El-Rayis *et al.* (1996 and 1997) noted that the area that lies west of the drain outlet is enriched with Fe and that a considerably higher concentration of Cu is found near the outlet of the western harbour. The large concentration of non-labile Cu may be due to the effect of dissolved organic matter such as humic and fulvic acids. Windom *et al.* (1991) showed that a considerable amount of Cu is ponded into the dissolved organic matter.



## CONCLUSIONS

The El-Mex Bay region receives very large amounts of wastewater, which affects the water quality. The present study shows the seasonal as well as regional distribution and variations of Fe, Cu, and Cd in El-Mex Bay waters. These forms include labile as well as non-labile and particulate metals.

In general, the distribution of trace metals may be arranged in the following order: non-labile > labile > particulate for Cu and Cd while the distribution content of Fe forms followed the order: particulate-Fe > non-labile-Fe > labile-Fe.

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