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The Distribution of Chromium, Copper, Cadmium and Lead in Areas of Multi-Polluting Factors of Alexandria

By

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Abstract

Sea water samples were collected from El-Mex Bay and Eastern Harbour during the period from November 1987 to January 1989. The samples were analysed for chromium, copper, cadmium and lead using Atomic Absorption Spectrophotometer. The concentrations varied as follows; Cr ND-0.90 ug. 1-1, Cu 0.31-23.84 ug. 1-1, Cd 0.12-18.60 ug. 1-1 and Pb 0.04-7.76 ug. 1-1. Against expectation, El-Mex Bay, a multipolluted area of Alexandria, gave generally lower metal levels (Cr, Cd and Pb) than the Eastern Harbour, which is mainly affected by sewage wastes. Concentrations of chromium declined linearly through the wide salinity range (5.83-39.47) of El-Mex Bay, as well as the narrow range (38.51-39.10) of the bottom water of the Eastern Harbour. Well oxygenated bottom waters showed a tendency to concetrate Cu and Pb in El-Mex Bay and only Cu in the Eastern Harbour than the less oxygenated waters.

The copper concentrations in the Eastern Harbour and chromium in El-Mex Bay are correlated with oxidizable organic matter (r = 0.57, 0.74 respectively), suggesting that complexation may play an important role in distribution of these elements.

Inroduction

Previous investigations on the levels of heavy metals in the waters of the Eastern Harbour and El-Mex Bay (El-Sayed 1981, Aboul Dahab **et al.**, 1984; Emara and Shriadah 1990) have shown that both areas are genreally Polluted. The Eastern Harbour is affected by the major outfall at Kayet Bay which discharges an average amount of 230,000 m³ per day of wastes, in addition to 7 minor outfalls inside the harbour. The shipyard which is located at the northwestern edge of the harbour, gives additional source of metals to the harbour.El-Mex Bay, west of Alexandria, recieves mixed agricultural run-off (Umum Drain, 4.8-9.5 x 106 m3 d-1) and industrial wastes from chloro-alkali plant, tanneries and slaughterhouse. It also receives airborne particles from the fumes of adjacent industrial plants including a cement factory. The bay is probably contaminated by petroleum products from Al-Alamien oil field and from Suez Mediterranean pipeline terminal (SUMED).

The aim of the present study was to investigate the distribution and fluxes of Cr, Cu, Cd and Pb in the study areas, Cr and Pb have not been investigated before in the Eastern Harbour.

Materials and Methods

Sea water samples were collected monthly from 8 stations in the Eastern Harbour (November 1987 - September 1988) and bimonthly from 7 stations in El-Mex Bay (Fig. 1) from January 1988 - January 1989. Surface and bottom water samples (2 liters) were filtered through a 0.45 um Millipore. Metals in the filtered sea water were preconcentrated using APDC-MIBK extraction procedure and back extraction into an acidic aqueous solution. The final acidic extracts were analyzed with a Varian Atomic Absorption (Model 1250) Spectrophotometer. The precision for replicate samples was between 5 and 10% of the lowest values determind in this study. A detailed description of the method is given by Boniforti **et al.** (1984). Dissolved oxygen, hydrogen sulphide and salinity were analysed according to Grasshoff (1976), and oxidizable organic matter by the method of Ellis **et al.**, (1946).

Results and Discussion

The concentration of heavy metals varied as follows: Cr, ND-0,90 ug 1-1, Cu 0.31-32.84 ug l^{-1}, Cd 0.12-18.60 ug 1-1 and Pb 0.04-7.76 ug 1-1. The mean concentration of heavy metals studied in the Eastern Harbour and El-Mex Bay are shown in Table 1. The high coefficient of variation shown for most metals reflects the wide variations in the concentrations of these metals in different months. There was no distinct differences between the surface and the bottom values except for Cu which revealed higher levels in the bottom water of El-Mex Bay. The Eastern Harbour which is mainly affected by sewage, exhibited higher levels of Cr (1.5 times), Cd (1.3 times) and Pb (1.2 times) compared with El-Mex Bay. Dissolved trace metals varied considerably throughout the two areas and the concentrations were higher at stations 1, 3, 5, 6 in El-Mex Bay and stations VI, VII, VIII in Eastern Harbour, which are closest to the major sources of pollution.

The relationship between heavy metals and dissolved oxygen (Fig. 2) showed that copper in both areas and lead in El-Mex Bay increased in well oxygenated water. In addition, dissolved copper decreased to a minimum concentration (0.55-2.65 ug 1-1) in areas with high hydrogen sulphide content (1.78-2. 33 mg 1-1) and the concentration at the bottom was higher by a factor of 48 compared to the surface values.

Lead showed analogous behaviour in El-Mex Bay (Fig. 3), but its concentration at the low and high levels of hydrogen sulphide was considerably low. In contrast with the observation of Aboul Dahab **et al.** (1984), the surface concentration of Pb remained lower everywhere except at a few stations (Table 1). On the other hand, Cd and Pb in El-Mex and the Eastern Harbour respectively, showed linear increase with increasing concentration of hydrogen sulphide (r = 0.70, 0.51), indicating the tendency of these metals to concentrate in water with low oxygen content. This condition may indicate the release of Cd and Pb from the bottom sediments in poorly oxygenated waters and their adsorption in well oxygenated waters.

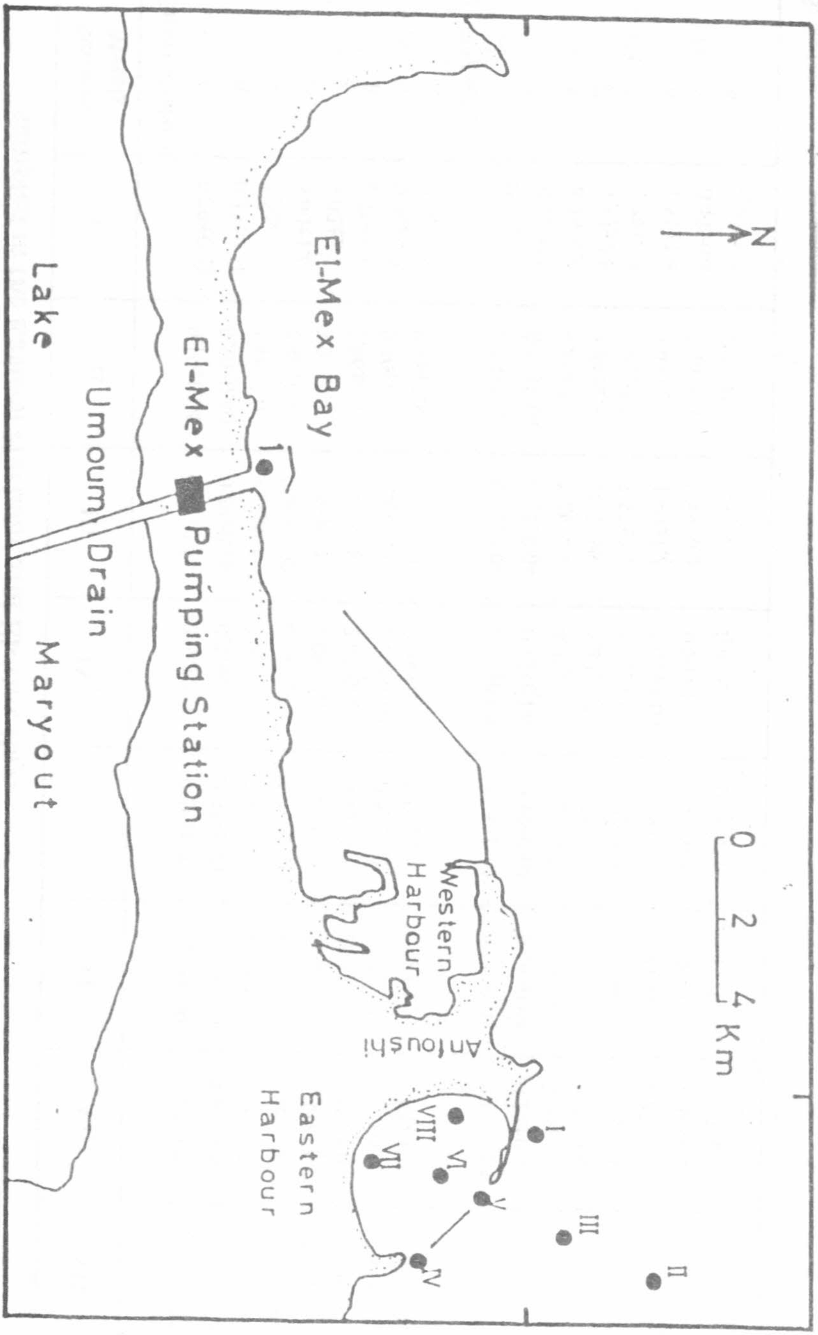

Fig. (1)
Area of investigation

Table 1: Mean and standard deviation (±) of concentration of dissolved heavy metals (ug 1-1) at the stations sampled in the Eastern Harbour and El-Mex Bay.

Stations Metals	I	II	III	IV	V	VI	VII	VIII	Mean
Eastern Haebour									
Cr S	0.29±0.23	0.10±0.04	0.31±0.26	0.24±0.14	0.28±0.24	0.28±0.09	0.37±0.26	0.18±0.07	0.26±0.1
B	0.33±0.16	0.50±0.40	0.29±0.18	0.31±0.24	0.05±0.01	0.27±0.10	0.36±0.26	0.13±0.02	0.28±0.1
Cu S	3.52±2.3	3.46±2.0	3.29±2-6	3.04±2.2	2.60±1.7	4.46±3.2	2.56±1.0	4.20±3.2	3.39±0.7
B	3.00±1.6	2.40±0.9	2.86±1.02	4.84±2.73	4.08±3.2	3.13±0.6	3.48±1.6	6.01±3.9	3.72±1.2
Cd S	2.02±2.2	3.21±4.2	1.06±0.2	1.09±0.8	2.22±1.1	3.68±5.7	1.34±1.0	2.48±1.6	2.14±0.9
B	1.53±1.3	1.06±0.5	1.47±0.6	2.03±2.2	4.42±6.3	2.25±2.0	2.19±1.0	1.69±1.2	2.08±1.0
Pb S	0.30±0.2	0.30±0.2	1.09±1.0	0.29±0.10	0.54±0.2	1.57±2.7	0.30±0.10	0.46±0.2	0.61±0.4
B	0.39±0.3	0.76±100	0.38±0.1	0.38±0.2	0.58±0.4	0.38±0.2	0.58±0.3	0.42±0.3	0.48±0.1
1- El Mex Bay									
Cr S	0.37±0.1	0.15±0.04	0.19±0.08	0.13±0.02	0.15±0.03	0.11±0.04	0.14±0.04		0.18±0.090.
B	0.22±0.1	0.17±0.04	0.11±0.04	0.12±0.06	0.19±0.04	0.14±0.04	0.22±0.1		0.17±0.05
Cu S	6.76±4.9	4.96±3.9	5.28±2.7	4.42±3.1	6.05±2.7	7.7±6.9	3.90±1.9		0.58±1.3
B	4.83±2.8	4.84±2.8	10.20±6.2	6.89±3.2	8.75±3.7	7.28±3.2	5.75±3.97		6.93±2.0
Cd S	0.79±0.4	1.01±0.7	2.55±3.1	1.11±1.0	3.22±5.5	1.19±0.8	1.16±0.8		1.58±0.9
B	1.51±1.4	1.48±2.1	1.49±1.3	1.41±1.03	3.78±3.4	1.4±0.8	0.83±0.5		1.7±0.9
Pb S	0.47±0.4	0.24±0.1	0.49±0.3	0.20±0.1	0.43±0.4	0.98±1.6	0.44±0.2		0.46±0.2
B	0.31±0.1	0.33±0.2	0.4±0.5	0.41±0.5	0.84±0.6	0.55±0.3	0.32±0.2		0.46±0.2

S: Surface
B: Bottom

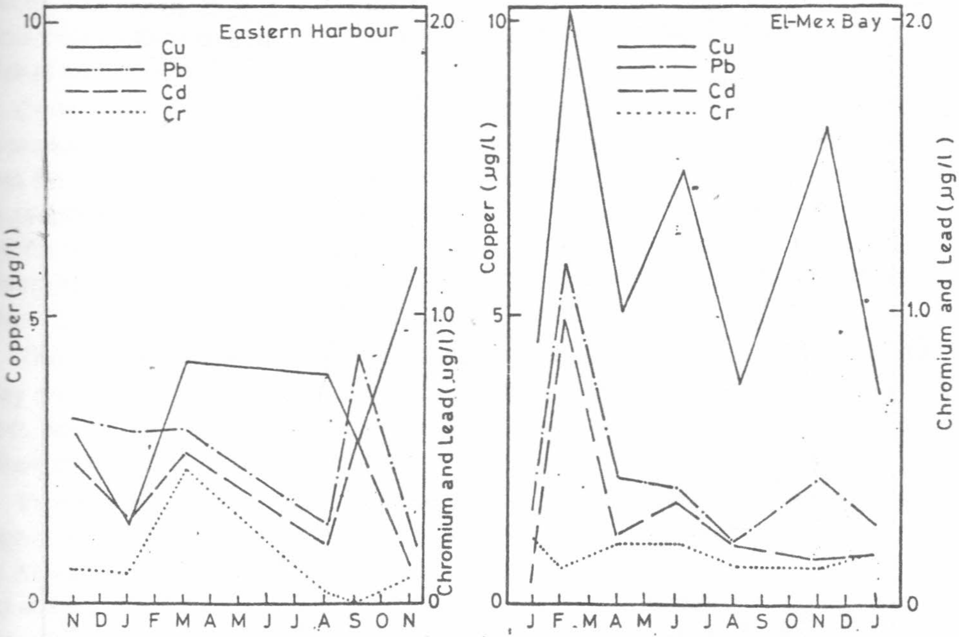

Fig. (2)

Dissolved oxygen - trace metals (Cu & Pb) relationship in the Eastern Harbour and El-Mex Bay waters.

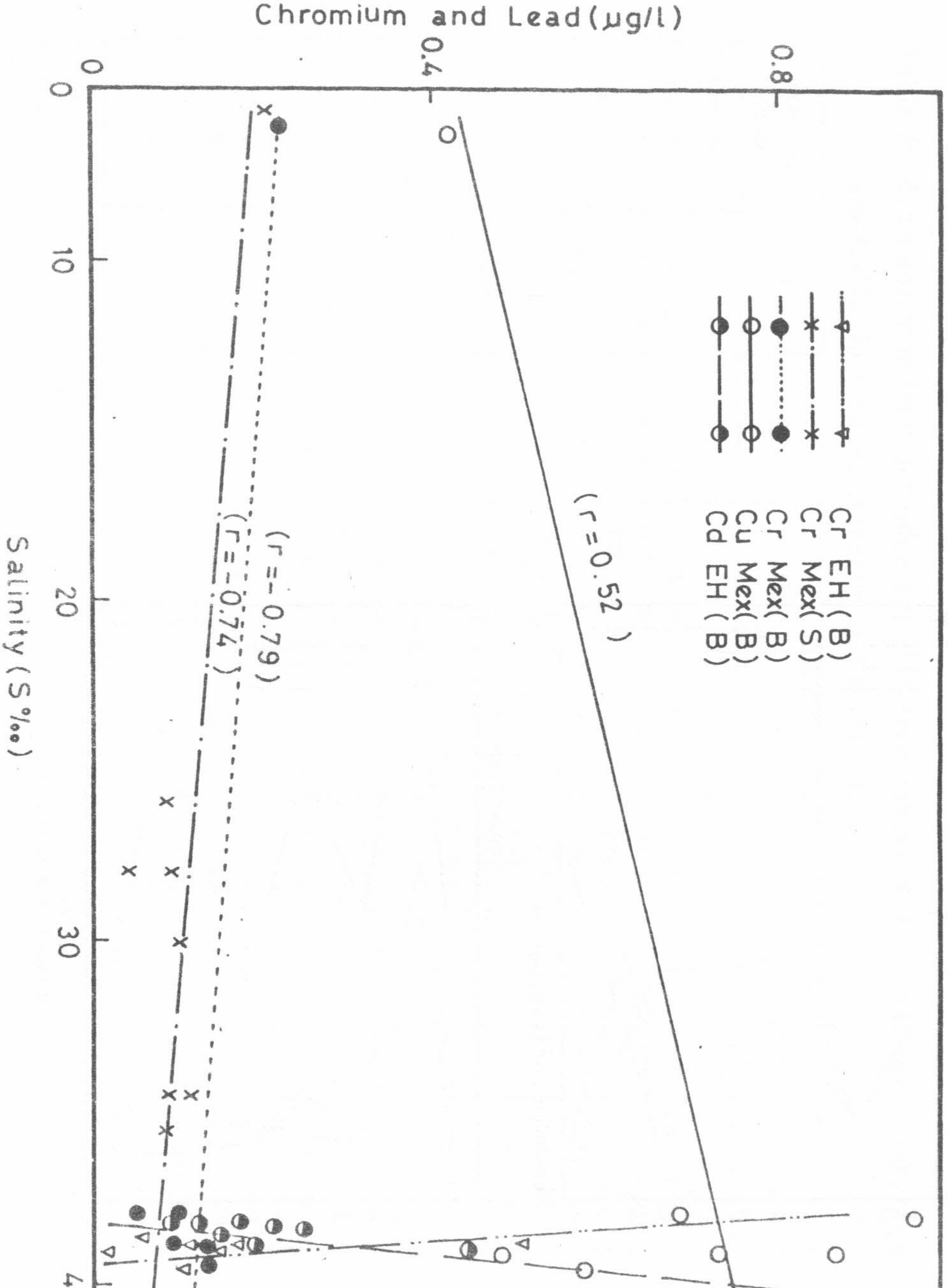

Fig. (3)

Hydrogen Sulphide-trace metals (Cd, Cu & Pb) relationships in the Eastern Harbour and El-Mex Bay waters.

Geochemical processes may influence concentrations of heavy metals in the investigated area. Concentration of dissolved Cr decline in a linear fashion throughout the wide salinity range (5.83-39.47) of El-Mex Bay, as well as the narrow range (38.51-39.10) in the bottom water of the Eastern Harbour (Fig. 4). Furthermore, discharging of fresh water from Umum Drain showed also significant correlation with Cr (r = 0.44) rather than, with other metals. Copper and Cadmium showed a tendency to increase linearly with salinity in the bottom water of the investigated area, while lead showed insignificant relationship with salinity.

Monthly variations of heavy metals (Fig. 5a,b) showed a substantial increase in February and March than in other months except Cr, which was more affected by fresh water discharging into El-Mex Bay. This increase may be attributed to the effect of winter agitation of bottom sediments rich in heavy metals. In addition, the similar pattern of variations observed for the metals Cu, Pb and Cu, Cd in El-Mex Bay is further confirmed by the strong correlations existed between these metals (r = 0.76 and 0.69, respectively). The case was somewhat different in the Eastern Harbour, where a good negative correlation between Cr and both Cu (r = -0.68) and Cd (r = -0.58) was found. This indicates that appearance of local high concentration for one metal by possible contamination does not necessarily correlate with high values for other metals (Fukal and Huynh-Ngoc, 1976).

Comparison of the values in the present study with concentrations reported by other workers in the Mediterranean Sea (Table 2), suggests that the current levels of Cu and Pb fall within the ranges given by Spivack (1981) and Branica (1976) for the west to middle Mediterranean and North Adriatic Sea respectively. Earlier results from Alexandria waters given by Aboul Dahab **et al.**, (1984) are lower than the present ones. Measurements from the Gulf of Gera in the eastern Aegean Sea yielded 30 times as much Cr and 4.6 times as much Pb (Scoullos **et al.**, 1982).

The copper concentrations in the Eastern Harbour as well as chromium in El-Mex Bay are significantly, correlated with oxidizable organic matter (r = 0.57, 0.84 respectivel), which may suggest that complexation plays an important role in distribution of these elements (Samuel and Phillips, 1988).

In conclusion, the eastern harbour which is mainly affected by sewage exhibited higher levels of Cr, Cd and Pb than El-Mex Bay which represent a multi-polluted area of Alexandria. The concentration of Cu and Pb (Mex Bay) increases in well oxygenated waters, while Cd (Mex Bay) and Pb (EH) showed a tendency to concentrate in water with low oxygen content.

Concentrations of Cr decline in a linear fashion throughout the wide salinity range of El-Mex Bay, as well as the narrow range in the bottom water of the EH. With the exception of Cr, the concentrations of heavy metals showed generally more elevated values in winter months.

The concentrations of Cu (EH) and Cr (Mex Bay) are correlated with oxidizable organic matter, which may suggest that complexation play an important role in distribution of these metals.

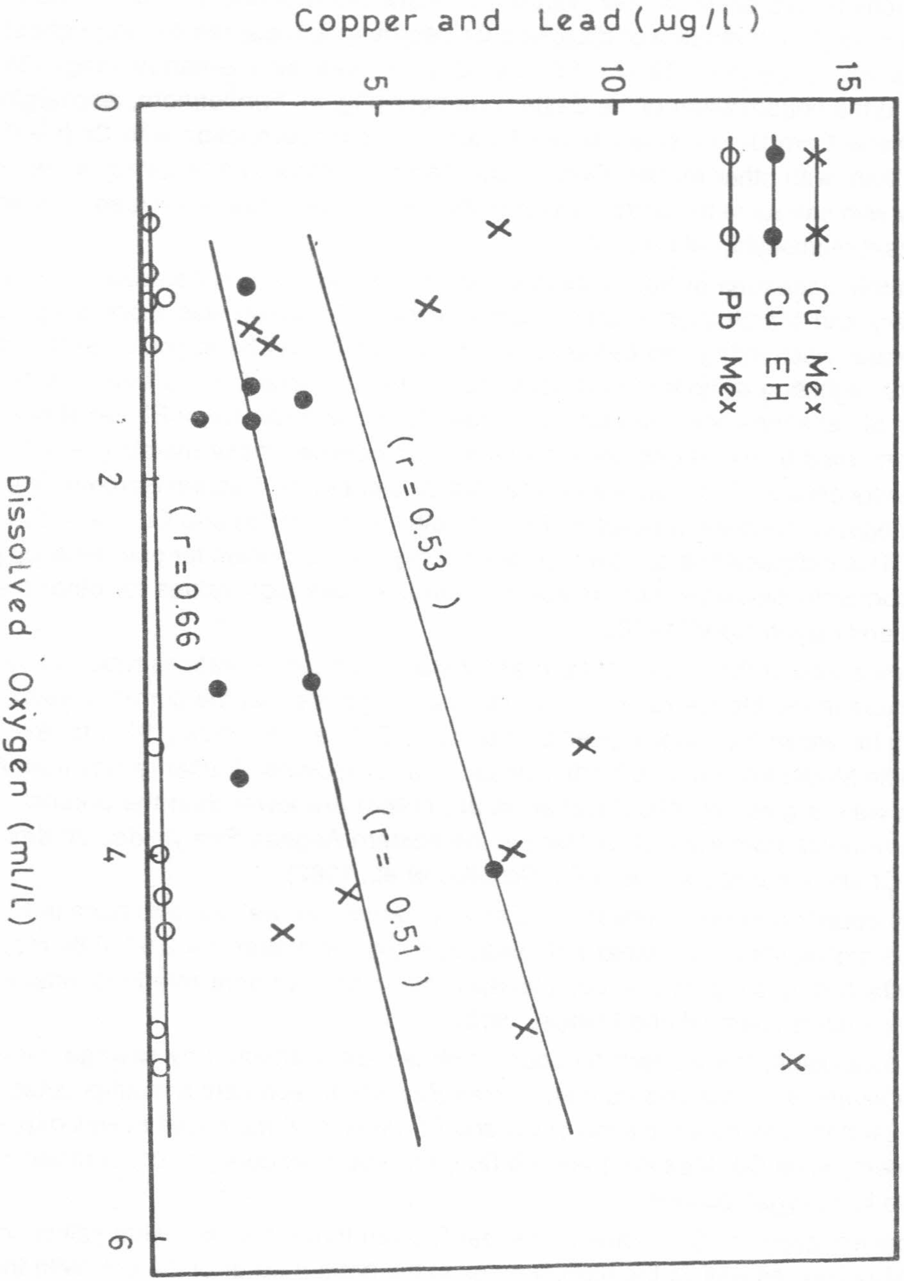

Fig. (4)

Plots of the average trace-metal (Cr & Pb) concentrations versus salinity in sea water from the Eastern Harbour and El-Mex Bay (S: Surface & B: Bottom).

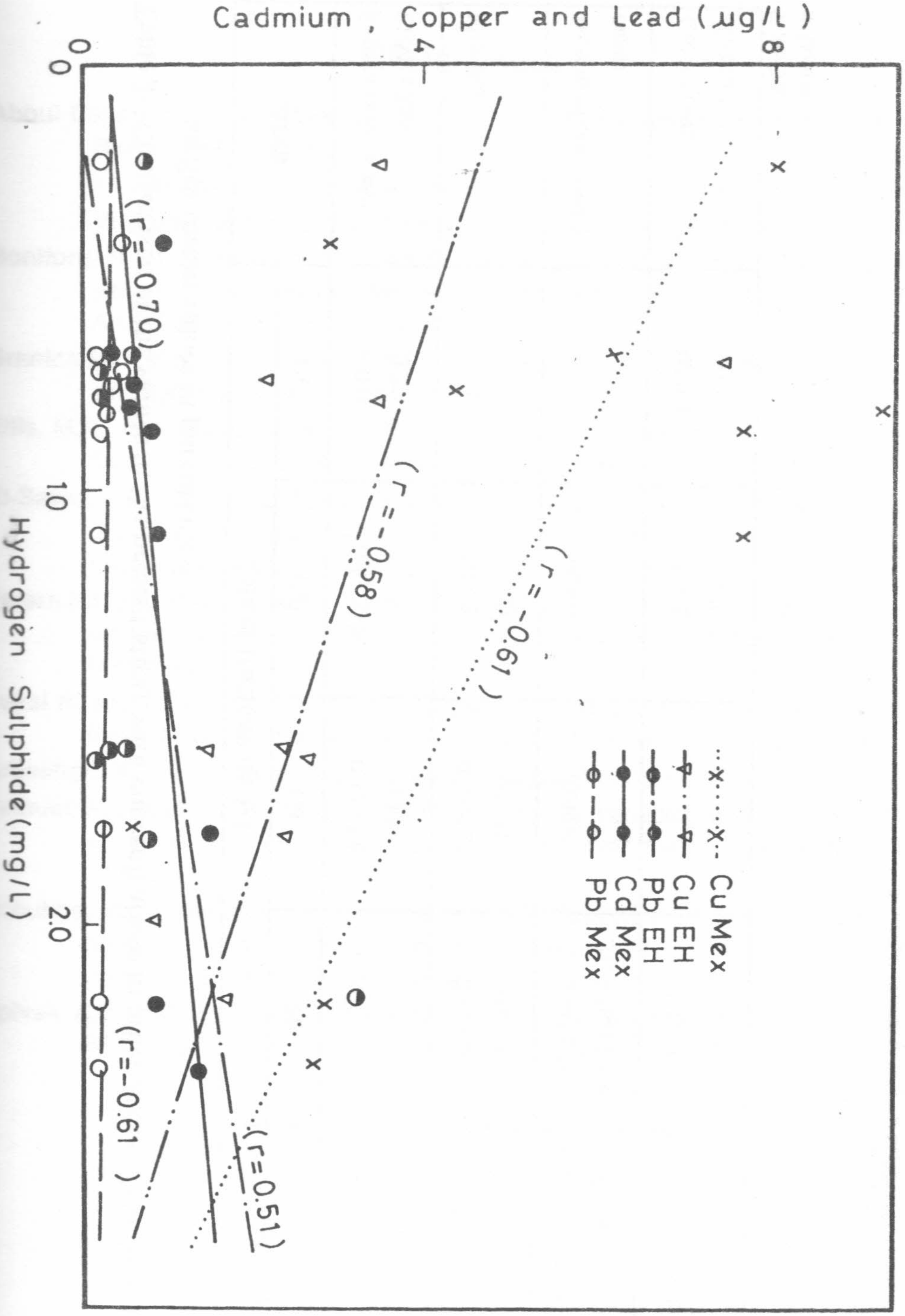

Fig. (5)

Monthly variation of trace-metals in the Eastern Harbour and El-Mex Bay.

Table 2: Comparison of the values in the present study with concentrations in other areas of the Mediterranean Sea (mean values in parentheses)

Area	Concentrations ug 1-1				Reference
	Cr	Cu	Cd	Pb	
Eastern harbour and El-Mex Bay	nd-0.90 (0.22)	0.31-23.8 (4.9)	0.12-18.6 (1.88)	0.04-7.80 (0.5)	Present study
Mex Bay	_	1.17-4.2 (2.1)	0.09-0.21 (0.15)	0.12-0.2 (0.17)	Aboul Dahab et al. (1984)
West to Middle Mediterranean	_	(4.45)*	(0.49)*	2.0-48.0** N. Adriatic Sea	* Spivak (1981) ** Branica (1978)
Culf of Gera (Greece)	4.2-9.5 (6.65)	1.0-2.7 (1.7)	_	1.4-4.1 (2.3)	Scoullos et al.. (1982)

S: Surface
B: Bottom

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