Concentration Level of some Dissolved Trace metals in Mediterranean Coastal water N-W- Egypt.

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Abstract

Surface and bottom seawater samples were collected during three seasonal cruises; spring, summer 2008 and winter 2009 from 10 perpendicular sectors along the western part of the Egyptian Mediterranean coast. Dissolved trace metals (Zn, Cu, Pb and Cd) were determined to investigate their distribution patterns and comparing their levels with the minimal and hazardous concentrations. The concentrations of Zn, Cu, Pb and Cd, were scattered in the ranges: (ND–49.87 μgL^{-1}; mean 10.20$\pm$7.67 μgL^{-1}), (0.27–72.46 μgL^{-1}; mean 12.10$\pm$16.99 μgL^{-1}), (0.04–29.77 μgL^{-1}; mean 7.26$\pm$5.34 μgL^{-1}) and, (0.19–6.41 μgL^{-1}; mean 0.73$\pm$0.61 μgL^{-1}), respectively. The results revealed a wide range of variation and regional irregularities. It is also indicated significant higher concentration of Zn and Cu compared to Pb and Cd. The study revealed that the mean concentrations of the metals examined here are higher than those either reported for the Mediterranean Sea water or of typical of open ocean water. However, in most of studied seasons they are at levels lower than the minimal risk concentrations reported by WQC (1972). In all cases the average concentrations of trace elements in the investigated area are far from the hazardous concentrations.

Keywords: Trace metals, South East Mediterranean Sea, N-W-Egypt

1. Introduction

Rapid growth of industry and a tremendous increase in the world population have resulted in environmental pollution (Akar *et al.,* 2009). Water pollution is a serious problem and heavy metals are common pollutants in water that threaten human health and environmental quality (Guo *et al.,* 2008). The presence of heavy metals in aquatic environment has been of major concern because of their toxicity to many life forms and tendency for bioaccumulation in the food chain even in relatively low concentrations (Mansri *et al.,* 2009 and Akar *et al.,* 2009). Since the majority of heavy metals do not degrade into harmless end products, their concentrations must be reduced to acceptable levels, and therefore constantly monitored. The Mediterranean Sea is a concentration basin in an arid zone, where evaporation exceeds precipitation and runoff. To compensate for the negative water balance, Atlantic water enters the Mediterranean Sea through Gibraltar Straight, where two distinct layers separated at about 150 m are recognized. These are Atlantic water upper inflow of low temperature and low salinity exceed the out flowing more saline subsurface Mediterranean water which originates mainly in the Eastern Mediterranean water (Halim *et al.,* 1995). The Atlantic water moves eastwards as a surface flow along the North African coast. It continues eastward to reach the Levantine Basin through the strait of Crete. Along the Egyptian coast it is overstepped by the Mediterranean surface water of higher temperature and salinity (Morcos, 1972). The Atlantic water is finally entrapped in the large Marsa Matrouh anti–cyclonic gyre (Ozsoy, 1989). The classical description of circulation of the Eastern Mediterranean Basin depicts a large cyclonic gyre between Cyprus and the Egyptian coast with a smooth flow between the surface and 500 m in all seasons. However, the oceanographic regime of the Mediterranean coast of Egypt falls under the influence of a number of factors which are determined mostly by its geographic position. The Atlantic water entering the Mediterranean is one of the factors determining the system of the currents in this area, which can be traced in the upper layers along the coast of Egypt. Egyptian coasts of the Mediterranean Sea are exposed to different sources of pollution particularly of freshwater origin. The main sources are Nile River and the northern lakes of Egypt, as well as agricultural effluents and sewage drains, in addition, the impact of several industrial effluents especially the biggest industrial areas at Alexandria and Port Said. On the other hand, the eastern and western of the Mediterranean coasts of Egypt are mainly subjected to the tourist activities; therefore, many studies were conducted to measure the levels of pollutants particularly heavy metals along the Mediterranean Sea of Egypt (Shriadah and Emara, 1993; El-Sammak and Abou El-Kassium, 1999; Aboul Naga *et al*., 2002; El-Rayis and Abdallah, 2005; El-Moselhy and Hamed, 2006; Shakweer *et al.,* 2006).

The main purpose of the present study is to investigate the distribution patterns of dissolved trace metals (Zn, Cu, Pb and Cd) along the western part of the Mediterranean coast of Egypt and comparing their concentrations with the minimal and hazardous concentrations.

2. Material and methods

2.1. Sampling and analysis

Water samples were collected along the west of the Mediterranean coast of Egypt (Figure 1) as a part of the environmental development research plan of the National Institute of Oceanography and fisheries (NIOF). A research vessel belonging to the institute was used for sampling through three trips along the coast within the period between spring 2008 and winter 2009. The area of study was represented by perpendicular sections as shown in Figure1. Surface and bottom water samples from each section were collected using Niskin bottle (5 liters capacity) at 5 and 200 meter depth, respectively. The samples were kept in polyethylene Jerry cans, prewashed with acid and rinsed with metal-free water. The sample was filtered through membranes filter paper, 0.45 μm pore size (Millipore). The filtrated sample was allowed to pass through a glass column packed with chelating resin "Chelex-100", mesh size (40-60 μm) in ammonium form at a rate of 5 ml/min.to preconcentrate the dissolved metals (Riley and Taylor, 1968; Abdullah and Royle, 1974). The metals on the resin were then eluted with 70 ml of 2N HNO_3 and 10 ml DDW. The eluted and the washing were collected in Teflon cubs, and then evaporated on a ceramic hot plate at about 70°C to near dryness. The residue was re-dissolved in1ml of 6N HNO_3 and the volume was completed to 25 ml using DDW, and then transferred into a plastic vial. All chemicals used were pure analytical grade and Milli-Q water was used throughout the study. All glassware used were soaked in detergent, rinsed with water, soaked in 10% HNO_3 for 5 d, rinsed with Milli-Q water and kept in the oven at 110 ∘C until needed. In order to make the column ready to use, the column was further washed with 100 ml DDW, 30 ml of 2N purified NH_4OH and then 100 ml of DDW. For preparation of reagent blank and standard solution, five liters of seawater sample have been allowed to flow twice in the same manner throughout the (Chelex-100) column. A part of free seawater metal was used for the reagent blank and the other was used for spiking with known concentration of metals for the preparation of standard solution for the calibration. The concentrations of the mentioned trace metals in the acidic extracts were measured using AAS (Shimadzu Atomic Absorption Spectrophotometer-AA-6800 with auto sampler Shimadzu ASC 6100, Japan).

2.2. Method validation and quality control studies

Validation of the method and quality control samples were done using a reference material (NASS-5, National Research of Council of Canada) and applying the computerized 4.3 quality system program provided by DANIDA from VKI. The limits of detection (μgL⁻¹) were calculated by six determinations (duplicate measurements) in one batch of synthetic seawater. The detection limits were 0.009, 0.030, 0.007, and 0.009 μgL⁻¹ for Zn, Cu, Pb and Cd, respectively. Precision was determined by three replicate analyses of one sample and expressed as a coefficient of variation (CV), and the results of the precision agreed within 10 %. The accuracy of the pre-concentrated technique of dissolved trace-metal determination was evaluated by spiking 1L of natural seawater (previously stripped of all trace metals) using certified reference material (NASS-5, solution). The spiked samples were extracted using the previous technique and the metal concentrations were determined. The recovery of spiked metals was 95, 90, and 91 for Zn, Cu, Pb and 91 % for Cd respectively. The results for the analysis of trace metals in the reference material are shown in Table 1.

3. Results and Discussion

Dissolved trace metals and bioavailability are a complex function of many factors, including the total concentration of metals, mineralogy, pH, redox potential, temperature, biota, total organic matter, suspended particulate content, water volume and water velocity, duration of water, wind transport, and removal from the atmosphere by rainfall. The range and the average concentrations of trace metals (Zn, Cu, Pb, and Cd) in the water samples collected from the Mediterranean Sea N-W of Egypt in the three successive cruises spring, summer (2008) and winter 2009 are given in Tables (2,3,4 and 5), respectively.

3.1. Temperature and Salinity Distribution

The results of temperature and salinity recorded in the study area at the same time revealed horizontal distribution of water temperature at 5 m, ranged from 19.0 - 22.5 °C in spring 2008. The near bottom distribution of water temperature shows the prevailing of depth effect, where it continuously decreases seaward, opposite the autumn season where the longitudinal variation prevails. It decreases from 22.5 °C to 15 °C near bottom in the open sea. The 5 m horizontal distribution of water temperature in summer 2008 ranged from 27.8 to 30.8 °C. The 5 m distribution of water salinity shows a homohaline 5m layer of about 38.8 in the west increasing to 39.2. In the coastal area, the water salinity decreases due to coastal runoff, namely; Mersa-Matruh. For near bottom salinity distribution, it is locally changed with a general increase in the eastward direction.
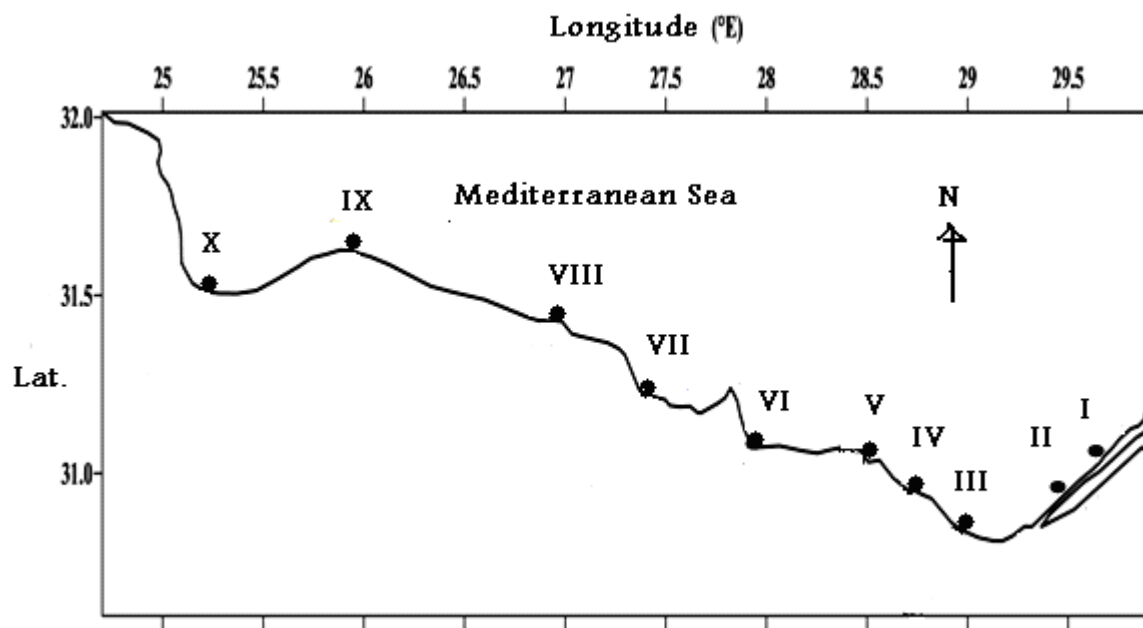
Figure 1: Sampling location

Table 1: Concentrations in µgL^{-1} (mean ± SD) for different metals in the reference materials (NASS-5, national research of council of Canada)

Metal	Found	Certified
Zn	0.099±0.042	0.102±0.039
Cu	0.301±0.061	0.297±0.046
Pb	0.010±0.006	0.008±0.005
Cd	0.028±0.004	0.023±0.003

Table 2: Range, mean & standard deviation of dissolved zinc (µgL−1) in surface and bottom water along the western part of the Mediterranean

Season	Depth (m)	Range&Mean	El Mex	Sidi Kerir	EL Hammam	Alamaen	EL Dabaa	Foka	Alm El Room	Marsa Matrouh	Sidi Barani	El Saloum
Spring 2008	5 m	Range	*	7.97	3.32–7.54	6.66–23.62	13.88–23.45	3.07	10.35–21.93	15.26	9.40–24.16	16.13–34.07
		Mean	*	*	5.93±2.28	17.43±9.36	20.23±5.50	*	17.31±6.14	*	18.37±7.88	25.62±9.02
	200 m	Range	5.97–7.09	12.38–20.34	2.38–22.88	9.96–24.31	15.24–25.96	10.00–23.15	5.97–13.49	22.30	2.87–16.78	2.96–24.49
		Mean	6.53±0.79	16.36±5.63	9.50±11.59	18.60±7.61	20.89±5.38	16.58±9.30	9.43±3.80	*	9.54±6.97	12.17±11.10
Summer 2008	5 m	Range	7.05–13.85	12.88–14.16	12.26–15.33	3.63–14.42	10.03–16.99	8.93–13.66	6.26–13.11	6.09–8.82	0.58–12.11	4.69–7.75
		Mean	10.45±4.81	13.44±0.66	13.88±1.54	9.02±7.63	13.79±3.51	11.00±2.42	9.25±3.50	7.46±1.93	5.63±5.90	6.22±2.16
	200 m	Range	8.80–11.30	9.22–12.30	10.12–14.21	5.85–12.51	15.07–16.36	9.56–13.53	3.39–11.98	5.80–49.87	2.92–13.32	2.93–16.49
		Mean	10.05±1.76	11.10±1.65	12.45±2.10	10.12±3.71	15.51±0.73	12.04±2.16	7.32±4.34	21.75±24.42	7.83±5.22	11.97±7.83
Winter 2009	5 m	Range	4.27–7.86	3.50–5.50	3.25–5.59	7.61	ND–8.48	2.83–4.17	ND–3.90	5.00–5.13	4.00–4.76	ND–4.57
		Mean	6.34±1.86	4.50±1.41	4.29±1.19	*	3.50±4.43	3.50±0.95	1.95±2.76	5.06±0.09	4.38±0.54	2.28±3.23
	200 m	Range	0.51–5.11	0.23–6.86	2.17–6.82	3.93–5.22	1.17–3.30	5.44	4.17–5.61	1.63–6.97	6.03	0.21–0.23
		Mean	3.55±2.64	4.15±3.48	5.20±2.63	4.58±0.91	2.47±1.14	*	4.89±1.02	4.30±3.78	*	0.22±0.01
Seasonal Mean	5 m	Mean	8.44	8.97	8.03	13.23	12.51	8.17	9.5	6.26	9.46	11.37
	200 m	Mean	6.70	10.54	9.05	11.1	12.96	14.31	7.21	13.03	8.69	8.12

Table 3: Range, mean & standard deviation of dissolved copper (µgL-1) in surface and bottom water along the western part of the Mediterranean

Season	Depth (m)	Range&Mean	El Mex	Sidi Kerir	EL Hammam	Alamaen	El Dabaa	Foka	Alm El Room	Marsa Matrouh	Sidi Barani	El Saloum
Spring 2008	5 m	Range	2.35–3.76	7.97	2.26–4.95	2.71–63.28	3.25–65.39	3.20	6.08–52.23	4.74	1.94–61.33	4.24–72.46
		Mean	3.21±0.76	*	3.70±1.36	24.92±33.36	42.81±34.37	*	22.30±25.95	*	37.67±31.48	40.42±34.30
	200 m	Range	10.03–13.24	6.59–48.78	4.13–63.45	3.26–56.07	5.84–60.65	2.97–64.05	2.57–7.86	58.07	4.46–27.13	4.07–29.55
		Mean	11.64±2.27	27.69±29.83	24.39±33.83	36.40±28.86	40.18±29.92	33.51±43.19	5.76±2.81	*	12.06±13.05	12.92±14.41
Summer 2008	5 m	Range	2.15–4.05	2.32–32.19	2.68–25.08	7.09–26.99	4.37–6.45	1.80–5.58	3.22–3.60	4.61–9.37	1.53–11.95	2.11–7.02
		Mean	3.10±1.34	12.32±17.21	12.13±11.60	17.04±14.07	5.37±1.04	4.20±2.09	3.47±0.22	6.99±3.36	5.18±5.87	4.56±3.47
	200 m	Range	1.79–3.56	2.03–3.44	4.60–12.47	3.03–5.40	4.76–5.03	2.18–6.86	2.41–3.98	8.30–27.07	3.16–5.26	2.88–3.21
		Mean	2.67±1.25	2.89±0.75	7.96±4.06	4.17±1.19	4.90±0.14	4.38±2.35	3.35±0.83	14.59±10.81	4.03±1.09	3.08±0.17
Winter 2009	5 m	Range	0.27–7.97	7.99–11.00	0.34–8.66	1.88	5.69–10.48	0.43–2.88	3.62–5.80	7.98–10.13	8.73–9.25	6.16–7.46
		Mean	2.97±4.33	9.49±2.13	5.46±4.48	*	8.30±2.42	1.65±1.73	4.71±1.54	9.05±1.52	8.99±0.37	6.81±0.92
	200 m	Range	8.26–12.31	3.62–11.40	6.85–8.15	6.29–10.71	4.37–5.50	7.38	8.05–13.01	2.80–10.87	6.96	9.62–12.05
		Mean	10.28±6.27	6.56±4.22	7.45±0.66	8.50±3.13	5.10±0.63	*	10.53±3.51	6.83±5.71	*	10.83±1.72
Seasonal Mean	5 m	Mean	3.09	10.91	7.10	20.98	18.83	2.93	10.16	8.02	17.28	17.26
	200 m	Mean	8.20	12.38	13.27	16.36	16.73	18.95	6.55	10.71	8.05	8.94

Table (4): Range, mean & standard deviation of dissolved lead (µgL-1) in surface and bottom water along the western part of the Mediterranean

Season	Depth (m)	Range&Mean	El Mex	Sidi Kerir	EL Hammam	Alamaen	ElDabaa	Foka	Alm El Room	Marsa Matrouh	Sidi Barani	El Saloum
Spring 2008	5 m	Range	9.29–9.85	8.33	8.26–10.19	4.22–11.42	5.64–11.84	8.74	8.91–11.04	8.60	8.40–11.46	7.50–18.24
		Mean	9.63±0.30	*	9.29±0.97	8.85±4.02	8.46±3.14	*	10.23±1.15	*	9.56±1.66	12.31±5.46
	200 m	Range	8.91–9.87	8.14–10.10	10.35–11.30	9.32–12.89	4.88–14.79	10.69–12.30	7.42–10.65	10.09	8.66–29.77	8.60–14.02
		Mean	9.39±0.68	9.12±1.39	10.72±0.51	10.55±2.03	9.44±5.00	11.50±1.14	8.89±1.64	*	16.02±11.92	11.52±2.73
Summer 2008	5 m	Range	5.05–7.07	0.07–0.12	5.91–14.88	8.27–9.62	5.53–18.88	0.05–0.10	0.06–0.09	0.07–0.08	0.04–0.10	0.08–0.09
		Mean	6.06±1.43	0.10±0.03	9.51±4.74	8.95±0.95	14.19±7.51	0.07±0.02	0.08±0.01	0.07±0.01	0.07±0.03	0.09±0.01
	200 m	Range	4.80–6.28	0.06–0.07	0.11–11.32	4.96–17.06	5.08–19.54	0.07–0.07	0.06–0.10	0.07–1.04	0.05–16.05	0.08–0.20
		Mean	5.54±1.05	0.06±0.01	7.52±6.42	9.22±6.79	10.15±8.14	0.07±0	0.08±0.02	0.39±0.56	5.42±9.20	0.14±0.06
Winter 2009	5 m	Range	5.47–9.82	6.81–12.19	9.56–14.82	6.01	1.96–9.64	6.21–7.11	7.17–8.49	6.26–8.26	7.09–8.34	7.43–10.02
		Mean	7.76±2.18	9.50±3.80	12.98±2.96	*	6.50±4.03	6.66±0.64	7.83±0.93	7.26±1.41	7.72±0.88	8.73±1.83
	200 m	Range	5.74–8.39	3.37–7.15	7.25–26.47	4.20–9.62	6.21–6.69	7.51	10.39–12.66	6.56–7.86	7.58	4.80–5.53
		Mean	7.19±1.35	5.79±2.10	14.04±10.78	6.91±3.83	6.51±0.26	*	11.52±1.60	7.21±0.91	*	5.16±0.52
Seasonal Mean	5 m	Mean	7.82	4.80	10.59	8.90	9.72	3.37	6.05	3.67	5.78	7.04
	200 m	Mean	7.37	4.99	10.76	8.89	8.70	5.79	6.83	3.80	10.72	5.61

Table (5): Range, mean & standard deviation of dissolved cadmium (µgL-1) in surface and bottom water along the western part of the Mediterranean

Season	Depth (m)	Range&Mean	El Mex	Sidi Kerir	EL Hammam	Alamaen	El Dabaa	Foka	Alm El Room	Marsa Matrouh	Sidi Barani	El Saloum
Spring 2008	5 m	Range	0.77–0.87	0.68	0.56–0.66	0.21–0.53	0.50–0.64	0.66	0.76–0.83	0.53	0.39–0.68	0.56–1.28
		Mean	0.80±0.06	*	0.62±0.06	0.39±0.16	0.58±0.07	*	0.80±0.03	*	0.53±0.15	0.80±0.42
	200 m	Range	0.66–0.88	0.46–0.58	0.38–0.74	0.59–0.87	0.32–0.65	0.58–0.88	0.59–0.73	0.42	0.50–0.69	0.53–0.77
		Mean	0.77±0.16	0.52±0.09	0.59±0.19	0.71±0.14	0.52±0.18	0.73±0.21	0.65±0.07	*	0.58±0.10	0.68±0.13
Summer 2008	5 m	Range	0.26–0.38	0.32–0.69	0.61–1.18	0.85–2.13	0.96–1.14	0.26–0.37	0.33–0.49	0.55–0.59	0.62–0.77	0.35–0.50
		Mean	0.32±0.09	0.50±0.19	0.97±0.31	1.49±0.90	1.06±0.09	0.33±0.06	0.42±0.08	0.57±0.04	0.68±0.08	0.42±0.10
	200 m	Range	0.39–0.62	0.20–0.26	0.50–0.70	0.64–2.39	0.98–1.40	0.32–0.48	0.41–0.58	0.51–6.41	0.39–1.70	0.47–0.85
		Mean	0.50±0.16	0.23±0.03	0.63±0.11	1.23±1.01	1.13±0.23	0.39±0.08	0.48±0.09	2.48±3.41	1.16±0.68	0.65±0.19
Winter 2009	5 m	Range	0.37–1.25	0.84–1.28	0.38–0.94	0.34	0.47–0.65	0.49–1.16	0.55–2.39	0.19–0.88	0.67–2.40	0.34–0.43
		Mean	0.71±0.47	1.06±0.31	0.70±0.29	*	0.55±0.10	0.83±0.48	1.47±1.30	0.53±0.49	1.54±1.22	0.39±0.06
	200 m	Range	0.59–0.82	0.38–0.81	0.48–0.79	0.47–1.85	0.34–0.47	1.37	0.41–0.69	0.41–1.00	0.66	0.59–0.76
		Mean	0.70±0.11	0.57±0.22	0.68±0.18	1.16±0.97	0.42±0.07	*	0.55±0.20	0.71±0.42	*	0.67±0.12
Seasonal Mean	5 m	Mean	0.61	0.78	0.76	0.94	0.73	0.58	0.90	0.55	0.92	0.54
	200 m	Mean	0.66	0.44	0.63	1.03	0.69	0.56	0.56	1.60	0.87	0.67

Table 6. Concentrations of trace metals (µgL⁻¹) in western area of the Mediterranean Sea compared to the Present study

Location	Zn	Cu	Pb	Cd	Reference
Mediterranean west area (Egypt)	ND-34.07	0.27-72.46	0.04-18.88	0.19-2.40	Present study
El Mex Bay		1.84-11.71			Faragallah et $al.$, 2010
El Mex Bay	20.79-59.29	3.69-4.90	2.65-6.14	0.66-6.45	Abdallah, 2008
El Mex Bay	22.0	3.80	0.60	0.16	Abou El Dahab, 1985
Mediterranean west area	5.89-51-62	1.92-60.26	7.72-16.73	1.06-5.74	Shakweer et $al.$, 2006
Mediterranean East area	0.91-90.33	1.73-30.76	3.22-13.18	0.64-6.13	Shakweer et $al.$, 2006
Mediterranean	65.0	3.21	6.02	0.42	El-Moselhy and Hamed, 006
Mediterranean Sea (Coastal water)	0.86-7.40	0.30-0.83	0.53-10.31		Okbah and Nasr 2006
Eastern harbor	1.0-39.8	0.6-12.2	0.4-18.8	ND-2.5	El-Nady, 1996
Abu-Qir Bay	0.4-117	0.3-4.17	2.64-54.0	ND-4.3	El-Nady, 1996
Suez Canal (Bitter Lakes)	1.38-30.45	0.22-10.79	3.11-60.95	0.99-4.59	El-Naggar, 2009
Red Sea (off shore)	0.13-1.17	0.07-0.29	0.02-0.68	0.02-.078	Shriadah et $al.$, 2004
Balaton lake	0.73	0.49	0.14	0.002	Nguyen et $al.$,2005
Bahrain	2.99	0.2	0.14	0.13	Al Sayed et $al.$,1994
Oceanic waters	5.00	3.00	0.03	0.05	WQC 1972
Minimal risk	20	10	10	2.2	WQC 1972
Hazardous risk	100	50	50		WQC 1972

3.2. The Levels of Metal Concentration

3.2.1. Zinc (Zn):

Zinc is essential and beneficial elements in human growth and it is plant micronutrient, being an important constituent in the formation of enzymes and nucleic acid synthesis (Kouadio and Trefry, 1987). From Table 2 and Figure 2, in the surface water, the variations of zinc concentrations were from ND - 34.1, 0.6 – 16.9 and ND - 8.5 µgL⁻¹ in spring, summer and winter, respectively. However, in the bottom water, the respective seasonal concentrations varied between 2.4 - 25.9, 2.9 -49.9, and 0.2- 6.9 µgL⁻¹ .

In general, the concentrations of Zn in most surface samples were lower than in the bottom waters at many stations. The higher values in bottom water may be related to zinc release from sediment to the above water layer (Abdel-Moati, 1985). The relatively lower concentration at surface layer is due to the intense biological consumption by phytoplankton in the euphotic layer, suggesting that Zn exhibited a vertical type distribution (Burton and Slatham, 1990). Table 6 shows a comparison between the average concentrations of Zn for the surface water and the bottom water with the minimal and hazardous concentrations. It is obvious that in all cases the average concentrations of Zn are less than the hazardous risk concentration (100 µgL⁻¹).

3.2.2. Copper (Cu):

In aquatic environment copper can exist in three broad categories mainly particulate, colloidal and soluble. The dissolved phase could contain both the free ions as well as copper complexed to organic or inorganic ligand. Binding of copper to humic acid and other organic compounds can be very strong. So that a large portions of dissolved copper is often organically complexed (Allen and Hansen, 1996). The concentration of copper is regulated by the dissolved organic matter and its transport will be controlled by organic matter mobility and influenced by biological and geological processes (Hasle and Abdullah, 1981). Desorption of copper from sediment into the bulk water depends on pH, salinity and the presence of natural or synthetic chelating agents. The regional and seasonal distributions of the average concentration of Cu in the study area are shown in Table 3 and Figure 3. The seasonal variations of Cu concentrations were found in the ranges of 1.94 – 72.46, 1.53 – 32.19 and 0.27 – 11.00 µgL⁻¹ in the surface water during, spring, summer and winter, respectively. However, for the bottom water the Cu concentrations varied between 2.57 – 64.05, 1.79 – 27.07 and 2.80 – 13.01 µgL⁻¹ during the above mentioned seasons, respectively.

High contents of Cu were measured during spring and summer seasons, probably due to high evaporation rate with the increase of water and air temperatures during hot seasons (Abdo, 1998), and due to the release of Cu from sediment to overlying water. On the other hand, the minimum values recorded during winter may be attributed to chelation of copper by aquatic organisms or other artificial compounds deposited on the bottom sediment (Abdo,1998), or due to the adsorption of copper by humic materials and deposited to the bottom sediments (Abdo, 2002). The concentration and mean values of Cu (Table 3) revealed irregular variation regard to sampling stations.

Table 6 shows the comparison between the average concentrations of Cu for the surface and the bottom water layers with the minimal and hazardous concentrations. According to WQC (1972), the average concentration of Cu exceeds the minimal risk (10 µgL⁻¹) during spring in the area under investigation. The Cu concentrations exceed the hazardous concentration (50 µgL⁻¹ in bottom sample at Marsa Matrouh region in

spring season, this may attribute to anthropogenic source (Table 3).

3.2.3. Lead (Pb):

Coastal waters can receive significant inputs of lead from industry, sewage and natural mineralization of the watersheds. Lead exists in seawater as a combination of precipitation equilibrium and complexation with organic and inorganic ligands. The minimum, maximum and average concentrations of Pb in water along the western area of the Mediterranean coast of Egypt are given in Table 4. The regional distributions of Pb concentrations were presented in Figure 4.

The seasonal variations of lead concentrations gave values in the ranges 4.22- 18.24, 0.04 – 18.88 and 1.96 – 14.82 μgL^{-1} in the surface water during spring and summer (2008) and winter 2009, respectively. For the bottom waters the concentrations were fluctuated in the ranges of 4.88 – 29.77, 0.05 – 19.54 and 3.37 – 26.47 μgL^{-1} during the mentioned seasons, respectively. The high values during winter and spring may be attributed to the decaying of plankton and precipitation of organic matter associated with lead to the sediments (Abdo, 2002). However, the increase of lead concentrations during summer seasons is mainly attributed to the mobilization of lead from the sediment to the above water due to the microbial activities, the degradation of organic matter liberated during hot seasons and the formation of organo lead compounds (Goher, 1998). The seasonal vertical distribution pattern of Pb in surface and bottom waters is shown in Figure 4. The concentration ranges and mean values of Pb revealed a small range of variation and irregularities with regard to sampling stations. Table 6 shows the comparison between the average concentrations of Pb for the surface water and for the bottom water with the minimal and hazardous concentrations. According to WQC (1972), the average concentration of Pb exceeds the minimal risk (10 μgL^{-1}) in spring with the investigated area.

3.2.4. Cadmium (Cd):

The atmospheric fallout of Cd to marine waters represents a major input of Cd at global level (Nriagu and Pacyno, 1988). Cd interacts with organic matter found in natural waters including amino acids, hydroxyl and carboxylic acids of aliphatic and aromatic nature. Cadmium may exist in water as the hydrated ion or as organic complexes with humic acids (OECD, 1994). Much of the Cd entering freshwater from industrial

sources and atmospheric deposition may be rapidly adsorbed by particulate matter and thus sediment may be a significant sink for Cd emitted to the aquatic environment (WHO, 1992).

The variation of Cd concentrations in the surface and bottom water samples from the investigated area is summarized in Table 5. The seasonal variations of Cd concentrations were in the ranges of 0.21 – 1.28, 0.26 – 2.13 and 0.19 –2.48 μgL^{-1} in the surface water during spring, summer (2008) and winter 2009, respectively. For the bottom water the cadmium contents are fluctuated between 0.32–0.88, 0.20–2.41 and 0.34–1.85 μgL^{-1} during the above seasons, respectively. The seasonal vertical distribution pattern of Cd in surface and bottom waters is shown in Figure 5.

Table 6 shows the comparison between the average concentrations of Cd for the surface water and for the bottom water with the minimal and hazardous concentrations. Generally, the average concentrations of Cd were lesser than the minimal risk concentration (2.2 μgL^{-1}). However, the absolute value of Cd concentrations exceeded the minimal risk at bottom water of Marsa Matrouh (6.41 μgL^{-1}) in summer and at Sidi Brany region for the surface water samples in winter (2.40 μgL^{-1}).

In general, from the above average concentrations of the metals in spring ,summer (2008) and winter 2009 were (10.20±7.67μg/l); (12.10±16.99 μgL^{-1}); (7.26±5. μgL^{-1}l) and (0.73±0.61 μgL^{-1}) for Zn, Cu, Pb and Cd, respectively. So it is cleared that, Egyptian coastal water of the western part of the Mediterranean Sea showed similar concentrations for all studied metals than the typical open ocean water concentration reported by WQC (1972). However, in most seasons it is lower than the minimal risk concentrations and in all cases it is far from the hazardous concentrations reported by WQC (1972).

Comparing the concentrations found here for surface water with those reported in the literature (Table 6), It is concluded, that the concentrations observed here are comparable with those recorded by most workers in the Mediterranean Sea and they gave higher values than those found by others in different areas.

Investigations of the correlation between the metals revealed strong association between Zn and Cu (*r= 0.88, n=27 at P* <0.05) and between Cd and Pb (*r= 0.73, n=27 at P* <0.05). This reflects that the two pairs of the metals (Cu and Zn) and (Cd and Pb) have the same behavior and the same source of pollution.
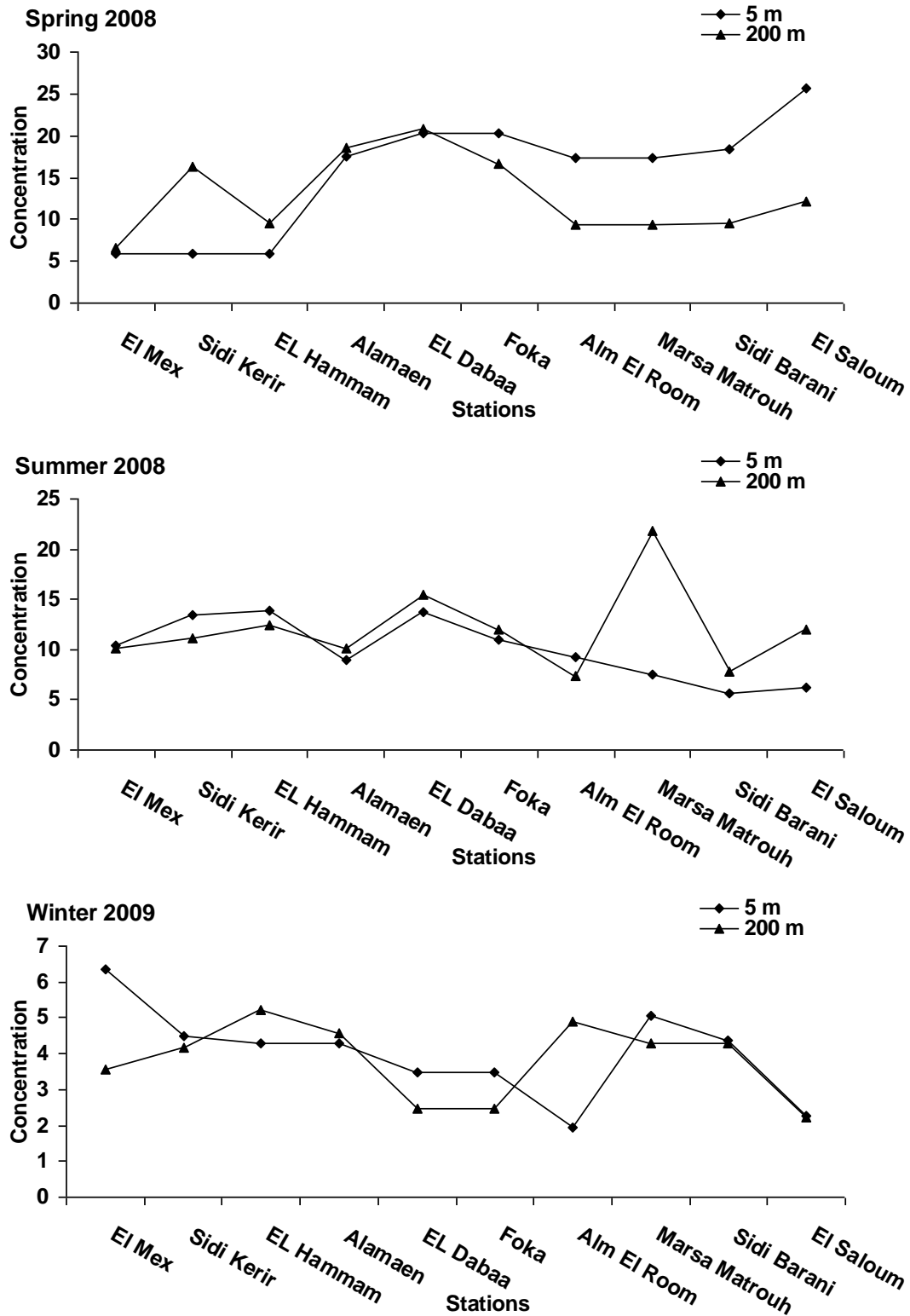
Figure 2. Concentration Level of Zn (µgL^{-1}) in Mediterranean Coastal water N-W- Egypt.
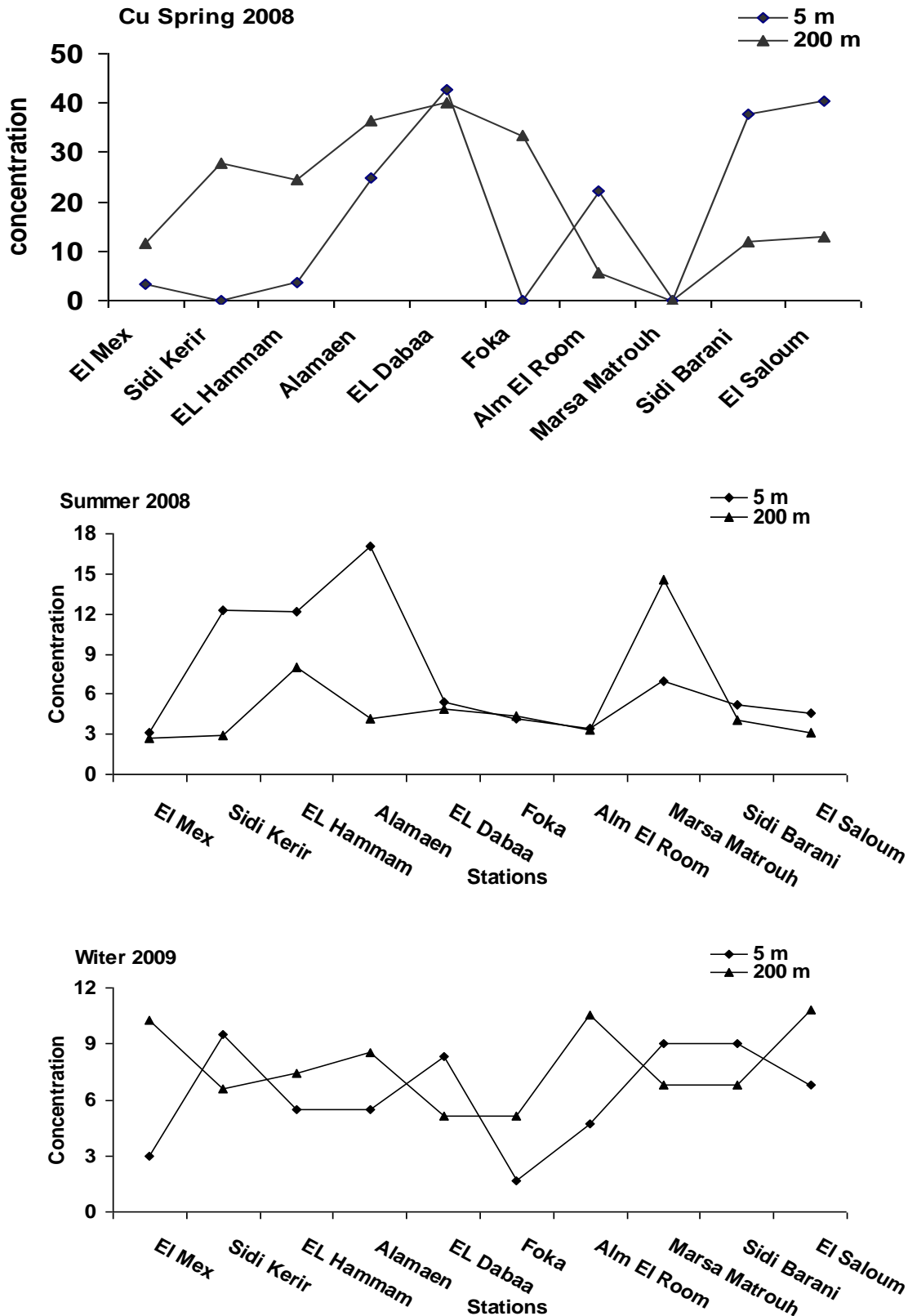
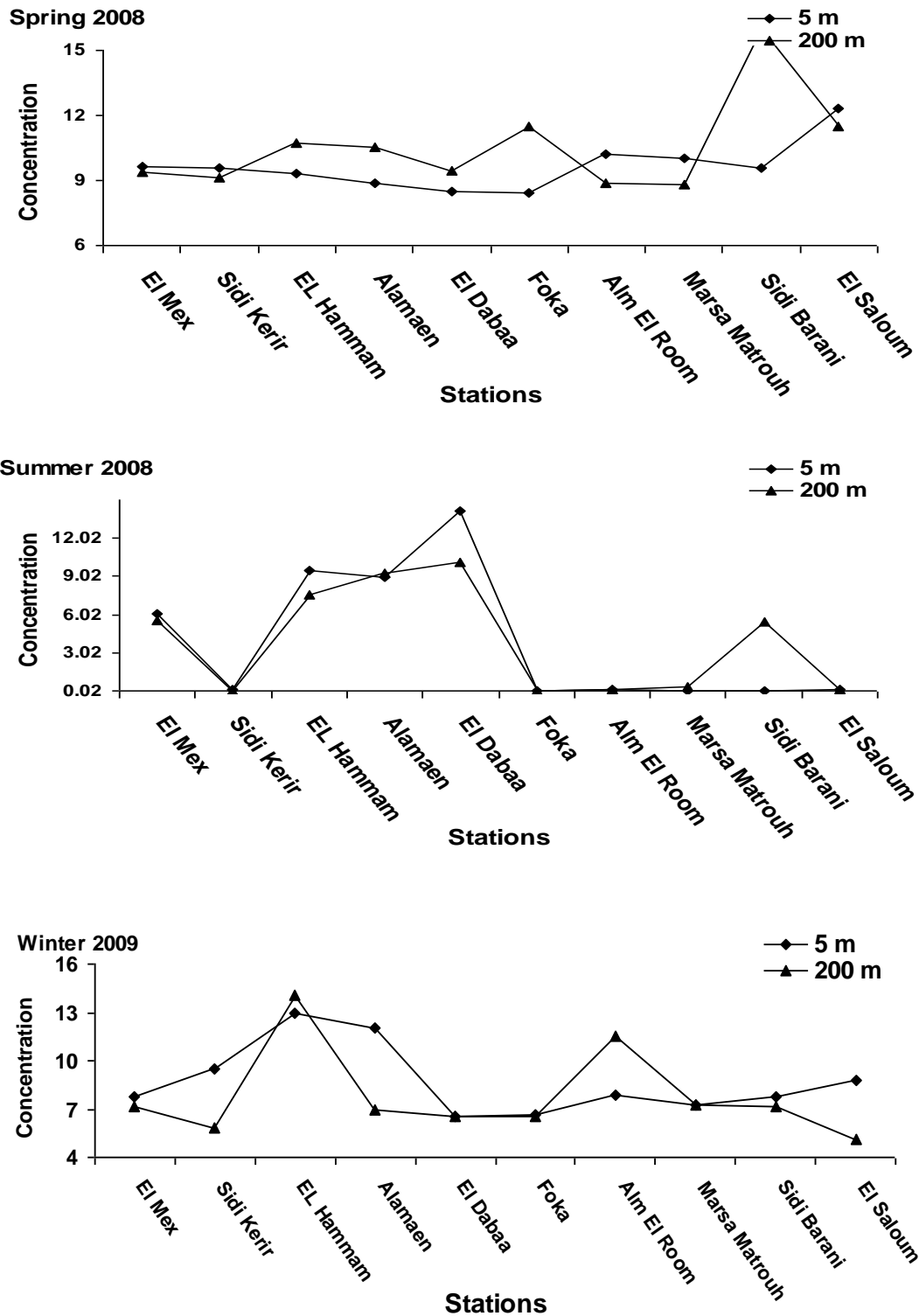Figure3. Concentration Level of Cu (μgL^{-1}) in Mediterranean Coastal water N-W- Egypt

Figure 4. Concentration Level of Pb (μgL^{-1}) in Mediterranean Coastal   water N-W- Egypt
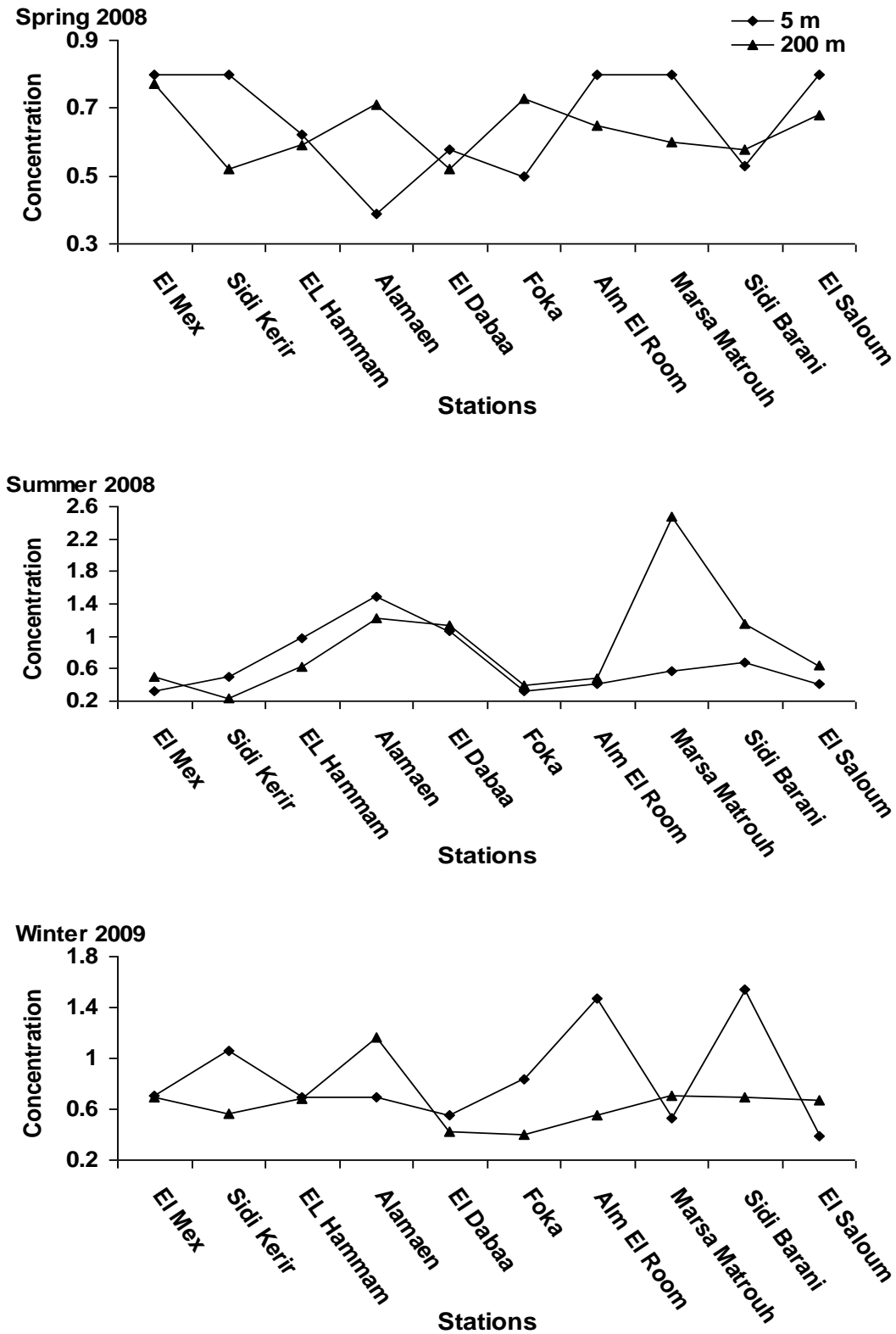
Figure 5. Concentration Level of Cd (μgL^{-1}) in MediterraneanCoastal   water N-W- Egypt

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مستوى تركيز بعض العناصر الشحيحة الذائبة فى المياة الساحلية للبحر المتوسط-مصر

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تم جمع عينات من المياه السطحية والعميقة خلال ثلاث رحلات موسمية الربيع والصيف والشتاء 2008 2009 من 10 قطاعات عمودي على طول الجزء الغربي من ساحل البحر المتوسط من المكس الى السلوم . تم تقدير بعض العناصر الشحيحة الذائبة (الزنك والنحاس والرصاص والكادميوم) لدراسة توزيع هذه العناصر و مقارنة مستوياتها مع التراكيز الخطرة و الحد الأدنى المسموح به.

وقد تراوحت التركيزات للزنك و الرصاص والنحاس والكادميوم في الحدود التالية : (بدون تاريخ - 49.87) ميكروجرام/لتر بمتوسط 10،20 ± 7،67 ميكروجرام/لتر (، 0،27-72،46)ميكروجرام/لتر بمتوسط 12،10 ± 16،99 ميكروجرام/لتر) و(0.04- 29.77) ميكروجرام/لتر بمتوسط 7.26± 5.34 ميكروجرام/لتر) و(0.19- 6.41) ميكروجرام/لتر بمتوسط 0.73 ±0.61 ميكروجرام/لتر) علىالتوالى. واظهرت النتائج وجود مدى واسع من اتغيرات فى التراكيز ترجع الى الاختلاف ا لمكانية. كما توضح النتائج أيضا وجود تركيز عالى من الزنك والنحاس بالمقارنة بالرصاص والكادميوم. وكشفت الدراسة أن تركيزات هذه العناصر كانت أعلى من تلك التي ذكرت سواء لمياه البحر المتوسط أو من مياه المحيطات المفتوحة. ومع ذلك فان العناصر التى تم دراستها تقع فى مستويات أقل من الحد الأدنى من المخاطر التي سجلت فى WQC 1972. وبصفة عامة فان متوسطات تركيزات العناصر الشحيحة الذائبة في المنطقة لا تزال بعيدة عن حدود التركيزات الخطرة.