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HEAVY METALS CONCENTRATION IN SOME FISH TISSUES FROM SOUTH MEDITERRANEAN WATERS, EGYPT

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ABSTRACT

The concentrations of nine heavy metals (Cd, Co, Cu, Fe, Hg, Mn, Ni, Pd and Zn) were determined in five common fish namely: Sigana-Batata (*Siganus rivulatus*), Bouri (*Mugil capito*), and Balamita bed (*Scomber unicolor*) from the open sea, facing to Lake Edku, and Bolti Akhdar (*Tilapia zillii*) and Karmout (*Clarias lazera*) from Lake Edku. Three metals (Co, Ni and Pd) were not yet detected in the studied fish species during the four seasons. The average concentrations of the other heavy metals analyzed exhibited the following decreasing order: Fe > Zn > Mn > Cd > Cu > Hg. The concentrations of Cu and Zn were lower than the Effect Range-Low (ERL) for all studied fish, while the other metals (Fe, Mn, Cd and Hg) were ranging from over the ERL and under the Effect Range-Median (ERM). These results suggest that the fish collected from open sea and Lake Edku might be considered relatively unpolluted with heavy metals. The metal pollution index (MPI) for most studied fish fluctuated between the calculated MPI for ERL and ERM. However, MPI recorded for summer showed the highest value over other seasons in the studied fish samples.

INTRODUCTION

Estuaries and coastal zones, particularly near large population centers, are of concern as they receive the largest discharges of chemical contamination due to source proximity. Confined bays and brackish Lakes are often the most ecologically vulnerable and sensitive area. Toxic compounds can affect productivity, reproduction and survival of marine organisms and can be hazardous to human health. Coastal monitoring programs are valuable for assessing the current state of coastal environments, for determining trends in contaminants over space and time, and for identifying potential sources of contamination to prevent future problems.

Heavy metals, which are important pollutants in coastal waters, represent potential toxic substances associated with run-off. In the water column, they are known to be mainly associated with sediments and suspended particulate organic matter (Saouter *et al*., 1993). Metals contaminants can enter the environment in excess amounts from industrial and mining effluents, from the combustion of fossil fuels, discharge of sewage and sewage sludge; also from fertilizer and pesticide residues (Forstner and Wittmann 1979). Pathways for metal input to the marine environment include transport via rivers and streams, direct discharge and atmospheric fallout are well known. Over a few decades, there has been growing interest to determine heavy metal levels in the marine environment and attention was drawn to find out concentration level of public food supplies particularly fish. Therefore, metal body loads of aquatic biota are often measured and used to evaluate ecological risks and potential sublethal effects (Bryan *et al*., 1980 & 1985; Phillips, 1980 & 1990; Phillips and Rainbow, 1993; Rainbow, 1995; Kalay & Canli, 1999).

The aim of this study is to determine heavy metal concentrations (Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb and Zn) in the muscle of fishes namely: Sigana-Batata (*Siganus rivulatus*), Bouri (*Mugil capito*), and Balamita bed (*Scomber unicolor*) from the open sea facing to Lake Edku and Bolti Akhdar (*Tilapia zillii*) and Armout (*Clarias lazera*) from Lake Edku, South Mediterranean Sea, Egypt (Figure 1). These fish species are very common food items for Egyptians and live in different ecological habitats and different feeding behavior (Table 1).

MATERIAL AND METHODS

Fish specimens of Sigana-Batata (*Siganus rivulatus*), Bouri (*Mugil capito*), Bolti Akhdar (*Tilapia zillii*), Armout (*Clarias lazera*) and Balamita bed (*Scomber unicolor*) were collected seasonally from autumn 2001 to summer 2002 from the South Mediterranean Sea and Lake Edku, by local fishermen. Ten fish were obtained from each species and were packed in ice and brought to the laboratory on the same day. Tissues of the examined fish were dissected, using clean equipment and put in petridishes and transferred into an oven set to 50 °C to dry. Drying continued until all the wet tissues reached to a constant weight. Dry tissue samples (triplicate each 0.2 g) were put into digestion flasks followed by addition of 5 ml nitric acid (Merck), 2 ml perchloric acid and heated at 90 °C until all the materials were dissolved. After digestion, the digested samples were diluted with deionized water, filtered and completed, using deionized water to 10 ml. The resulting solutions were analyzed, using flame atomic absorption spectrophotometer (Perkin Elmer, Model 2380). The results were expressed in $mg.kg^{-1}$ dry wt. (UNEP/FAO/IAEA/IOC, 1984). Metal concentrations are reported on dry weight basis, rather than wet weight to provide a more accurate measure of metal load, since water content in biota varies with species, age and condition.

Reagents of analytical grade were utilized for the blanks and calibration curves. Precision was checked against standard reference material provided by the National Research Council of Canada (DORM-1 for dogfish) and was within the range of certified values with 96% recovery for all metals studied.

The absorption wavelength and detection limits were as follows: 228.8 nm and 0.06 $mg\,kg^{-1}$ for Cd; 240.7 nm and 0.05 $mg\,kg^{-1}$ for Co; 324.7 nm and 0.06 $mg\,kg^{-1}$ for Cu; 248.3 nm and 0.8 $mg\,kg^{-1}$ for Fe; 279.5 nm and 0.7 $mg\,kg^{-1}$ for Mn; 232.0 nm and 0.09 $mg\,kg^{-1}$ for Ni; 217.0 nm and 0.8 $mg\,kg^{-1}$ for Pb; 213.9 nm and 0.7 $mg\,kg^{-1}$ for Zn, respectively.

Mercury analysis was conducted, using cold vapor atomic absorption (SOLAAR 32). In which 0.2 g of the homogenized dry sample was weighed accurately into a previously pre-cleaned Teflon vial, 5 ml of HNO_3 and 2 ml of perchloric acid were added and the mixture was heated at 50 °C, until all the materials were dissolved. After cooling to room temperature, the volume was diluted, by using bi-distilled water, filtered and completed to 25 ml; then subjected to Hg-determination with triplicate analysis (UNEP/IAEA 1984). To evaluate the accuracy and precision of the analytical methodology, reference material DORM-2 (provided by EIMP-IAEA) was run parallel with the samples. The recovery rate was 96% for total Hg. A check standard and blank were run after every seven samples. Detection limit for Hg was 0.008 $mg\,kg^{-1}$. All calculations were carried out on a Microsoft Excel program for Win XP 2002.

RESULTS AND DISCUSSION

The results of heavy metals in the different fish species collected during the four seasons from the open sea and Lake Edku, south Mediterranean Sea are presented in Table 2. Heavy metal concentrations ranged between 0.44 to 1.86 for Cu, 21.01 to 49.0 for Zn, 16.14 to 33.58 for Mn, 143.34 to 2439.16 for Fe, 0.92 to 3.19 for Cd and 0.05 to 1.61 mg kg^{-1} dry wt. for Hg, while Co, Ni and Pd were not detected in all studied samples.

Cadmium concentrations in fish tissues were elevated with some variations between species, where the highest concentrations were 3.19 ± 0.53 in autumn and 2.53 ± 0.42 in Spring in *Clarias lazera*, while Cd was not detected in winter. The concentrations of Cd were higher than ERL (1.2mg kg^{-1}) and lower than ERM (9.6mg kg^{-1}) for all studied samples except for *Siganus rivulatus* collected in autumn and *Clarias* collected in winter. The concentrations of Cd recorded in this study were lower than these recorded from Lake Edku (Table 3) (Emara, 1982) and about two to four times more than these from Lake Mariut (Saad *et al.* 1981), but lesser than these reported for the North Pacific, USA (Miao *et al.* 2001). However, this study showed lower Cd content in Lake Edku during the last twenty years. Kilgour (1991) indicated that fish with a close relationship with sediment, show relatively high body concentration of Cd, although uptake from water higher than uptake from sediment for fishes which do not burrow.

Mercury was greatly elevated than ERL (0.15 mg kg^{-1}) for most of the studied samples except for *Mugil capito*, which recorded low concentration than ERL, while, *Tilapia zillii* recorded Hg concentrations over ERM (0.71 mg kg^{-1}) for samples collected in summer and autumn. Meanwhile, *Clarias lazera* recorded slightly elevated Hg than ERM in winter samples. This may be due to industrial and municipal wastes, which come from different factories constructed near Abu-Qir, (e.g. El-Ahlia-paper factory, Rakta paper factory, Abu-Qir fertilizers factory) beside the Electric Power Station and El-Amria (Abu-Qir) Drain.

The concentrations of iron were fluctuated between 143.34 ± 22.68 to 2439 ± 1387 mg kg^{-1}. The highest concentration of Fe was present in Balamita (*Scomber unicolor*) during summer and the lowest was recorded for *Tilapia zillii* in autumn. However, summer samples recorded higher iron concentrations for all studied samples, while the lowest iron concentrations recorded for samples collected from open sea and Lake Edku were reported in winter and autumn, respectively.

Copper concentrations exhibited low values for all studied samples collected from both open sea and Lake Edku ranging between 0.44 ± 0.09 and 1.86 ± 0.14 mg kg^{-1}, which are much lower than ERL (34 mg kg^{-1}). The Cu concentrations recorded in this study were much lower than that recorded by Shakweer (1993) for Lake Edku and one third of that recorded by El-Moselhy (1996) for Alexandria and Red Sea (Table 3), which may indicate a remarkable decrease in Cu content during the last few years for Lake Edku.

Manganese concentrations in fish tissues varied between 16.31 ± 0.98 and 33.58 ± 0.74 mg kg^{-1}. The higher concentrations of Mn were recorded in summer samples collected from the open sea and in spring samples from Lake Edku. Zn concentrations fluctuated between 21.01 ± 2.38 and 49 ± 4.33 mg kg^{-1} which were much lower than ERL (150 mg kg^{-1}). However, Zn and Fe may vary between different fish species as a result of their biological needs (Quazi *et al.*, 1995). It is generally agreed that heavy metal uptake occurs mainly from water, food and sediment, however, effectiveness of metal uptake from these sources may differ in relation to ecological needs, metabolism of fish contamination gradient of water, food and sediments as well as other factors such as temperature (Health, 1987; Langston, 1990; Roesijadi and Robinson, 1994). Canli and Furness (1995) also showed that tissue distribution of metals in the Norway Lobster, *Nephross navegicus* differed significantly owing to the uptake from food and from seawater.

The significant correlation (at $p<0.05$) between metal concentrations in fish tissues were studied between seasons and species. The results of summer, autumn and spring samples showed no correlation between the metal concentrations, while in winter samples, a positive correlation was noted between Cu and Zn ($r = 0.89$, $p = 0.04$) and a negative correlation between Fe and Zn ($r = -0.92$, $p = 0.02$). The correlations of heavy metal concentrations for each species separately recorded no correlation for *Mugil capito* and *Tilapia zillii*, while *Siganus rivulatus* showed a negative correlation between Cd and Zn ($r = -0.98$, $p = 0.02$) and a positive correlation between Cu and Zn ($r = 0.96$, $p = 0.03$), *Scomber unicolor* showed only a positive correlation between Cd and Zn ($r = 0.999$, $p = 0.007$), and *Clarias lazera* showed a negative correlation between Mn and Fe ($r = -0.98$, $p = 0.01$). However, the correlation between the 113 parameters showed only a moderate correlation between Fe and Hg ($r = 0.56$, $p = 0.015$).

The principle component factor analysis (PCFA) was preformed on the 113 heavy metals values using Varimax Normalized. The PCF analysis, at its simplest, can be regarded simply as an ordination technique, for reducing multivariate data into fewer dimensions. PCF analysis transforms an original set of N variables into a net set of N principle components. The transformation is such that the first and second components almost invariably account for a far proportion of the total value (Davis *et al.*, 1973; Hopke, 1983; Meglen, 1992). Figure 2 shows the spatial distribution of the different elements with respect to both factor 1 and factor 2 which explain 89.99% of the total variance with data variations of 33.11% for factor 1 and 56.81% for factor 2. Both factor 1 and 2 lie on their positive side Cd, Mn, Fe and Zn. On the other hand, factor 2 loads Hg on its positive side, where its loads lie on the negative side of factor 1 with a high (0.92) and low (–0.18) values, respectively. The statistical analysis indicates that the distribution pattern of Hg (Factor 2) is very different from that of the other metals. Point sources as they exist for the other analysed heavy metals do not exist or are of subordinate importance for this metal. The clustering of the other metals (Cd, Cu, Mn and Zn) together may indicate the syngestic sources of these metals.

The overall metal contents of fish tissues at the sites investigated in this study were compared, using the metal pollution index (MPI) calculated with the formula (Usero *et al.*, 1996 and 1997):

$$MPI = (Cd \times Cu \times Fe \times Hg \times Mn \times Zn)^{1/6}$$

MPI ratios ranged between 0.92 for *Tilapia zillii* in autumn samples to 3.72 for *Scomber unicolor* in summer samples. Moreover, MPI were higher in summer samples for all species (Table 2). However, heavy metal concentrations recorded in this study were lower than the maximum acceptable limits shown in Table 4, indicating that, the five fish species examined in this study can be considered unpolluted with heavy metals.

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Table 1. Common and scientific names, food, location and length of fish samples.

Common name	Scientific name	Length	Feeding	Loction
Sigana-Batata	*Siganus rivulatus*	17 - 20	Herbivorous[a]	Open Sea
Bouri	*Mugil capito*	20 - 25	Omnivorous[b]	Open Sea
Balamita beda	*Scomber unicolor*	25-30	Carnivorous[c]	Open Sea
Karmout	*Clarias lazera*	40 - 45	Carnivorous[d]	Lake Edku
Bolti	*Tilapia zillii*	15-17	Omnivorous[e]	Lake Edku

a: Feeds on brown, red and green algae; b: Feeds on minute bottom-living organisms or on algae floating near the surface, also on organic matter contained in mud and sand; c: Feeds mostly on clupeoid fishes, particulary sardinellas; d: feeds on small fishes; e: Feeds on algae and small fishes

Table 2. Heavy metals concentration (mg kg^{-1} of dry weight) in fish samples collected from south Mediterranean Sea.

Species	Season	Cd	Co	Cu	Fe	Hg	Ni	Mn	Pd	Zn	MPI
Siganus rivulatus	Summer	1.39 ± 0.09	ND	0.67 ± 0.14	388.1± 53.83	1.61	ND	25.39 ± 1.95	ND	49 ± 4.33	2.07
	Autumn	0.92 ± 0.05	ND	0.82 ± 0.18	242.44 ± 71.39	0.05	ND	19.41 ± 1.31	ND	33.04 ± 40.5	1.07
	Winter	1.65 ± 1.17	ND	0.66 ± 0.08	236.53 ± 22.99	0.32	ND	19.08 ± 1.47	ND	29.36 ± 1.78	1.39
	Spring	2.31 ± 1.12	ND	0.61 ± 0.10	329.66 ± 51.43	0.10	ND	21.01 ± 2.38	ND	21.01 ± 2.38	1.22
Mugil capito	Summer	1.52 ± 0.10	ND	1.19 ± 0.85	272.58 ± 48.64	0.13	ND	25.00 ± 0.86	ND	37.12 ± 11.3	1.49
	Autumn	2.04 ± 1.01	ND	1.86 ± 0.14	281.14 ± 23.40	0.06	ND	33.58 ± 0.74	ND	33.82 ± 3.64	1.45
	Winter	1.78 ± 0.00	ND	0.48 ± 0.12	189.97 ± 11.39	0.11	ND	19.59 ± 3.31	ND	31.20 ± 1.87	1.02
	Spring	1.26 ± 0.27	ND	1.07 ± 0.27	343.81 ± 23.64	0.07	ND	16.31 ± 0.98	ND	29.83 ± 9.78	1.15
Scomber unicolor	Summer	1.36 ± 2.06	ND	1.31 ± 0.11	2439.16 ± 1387	1.40	ND	33.37 ± 0.91	ND	39.16 ± 7.92	3.72
	Autumn	2.04 ± 1.01	ND	0.77 ± 0.16	256.22 ± 24.54	0.50	ND	32.64 ± 1.41	ND	36.86 ± 2.03	1.80
	Winter	1.69 ± 0.94	ND	0.44 ± 0.09	248.43 ± 14.84	0.62	ND	16.19 ± 2.08	ND	28.95 ± 0.27	1.41
	Spring	NA	NA	NA	NA	NA	NA	NA	NA	NA	
Tilapia zillii	Summer	1.36 ± 0.48	ND	0.89 ± 0.19	517.65 ± 1425.8	0.86	ND	17.21 ± 2.18	ND	29.87 ± 4.55	2.28
	Autumn	1.80 ± 0.03	ND	0.50 ± 0.10	143.34 ± 22.68	0.76	ND	17.11 ± 1.91	ND	33.73 ± 2.36	0.92
	Winter	2.28 ± 0.95	ND	0.77 ± 0.15	166.82 ± 7.81	0.35	ND	17.50 ± 2.06	ND	33.85 ± 5.60	1.44
	Spring	2.28 ± 0.79	ND	0.91 ± 0.26	276.99 ± 55.06	0.10	ND	20.48 ± 4.41	ND	27.92 ± 2.44	1.34
Claris lazera	Summer	1.65 ± 0.76	ND	1.04 ± 0.02	460.98 ± 43.21	0.16	ND	16.14 ± 0.24	ND	42.68 ± 3.54	1.57
	Autumn	3.19 ± 0.53	ND	1.17 ± 0.43	153.47 ± 24.90	0.29	ND	17.07 ± 4.99	ND	48.06 ± 11.48	1.19
	Winter	ND	ND	0.86 ± 0.09	180.27 ± 11.92	0.72	ND	18.03 ± 2.28	ND	34.82 ± 2.91	1.37
	Spring	2.53 ± 0.42	ND	1.06 ± 0.18	220.82 ± 7.93	0.19	ND	18.98 ± 2.19	ND	38.66 ± 0.27	1.41
ERL		1.2	NA	34	NA	0.15	20.9	NA	46.7	150	
ERM		9.6	NA	270	NA	0.71	51.6	NA	218	410	

ND: Not detected, NA: Not available; MPI: Metal pollution index calculated for wet weight; ERL: Effect Range Low; ERM: Effect Range Median.

Table 3. Heavy metal concentrations (mg kg^{-1} dry weight) in fish tissues from the literature.

Location	Cd	Cr	Cu	Hg	Pb	Zn	references
1	0.61-1.43	1.10-2.07	2.26-6.15	na	4.43-9.11	18.0-33.4	Kalay *et al*. (1999)
2	1.2-15.3	1.7-24	4.0-343	0.1-0.42	9.3-56.5	79-301	Miao *et al*. (2001)
3	0.2-0.9	1.9-30	1.9-440	na	0.8-2.2	12-650	Cohen *et al*. (2001)
4	0.25-0.55	na	4.15-14.6	na	1.25-4.5	na	Edwarda *et al*. (2000)
5	0.13	na	3.74	na	2.86	27.4	El-Moselhy (1996)
6	0.15-0.20	na	1.25-4.45	na	1.23-1.86	13.6-24.9	El-Moselhy (1996)
7	0.75	na	18.7	na	na	38.6	Saad *et al*. (1981)
8	na	na	9.69	0.41	na	20.14	Niazzy *et al*. (1995)
8	4.5-6.0	na	na	na	na	na	Emara (1982)
8	NA	na	89.3	na	na	132.48	Shakweer (1993)
9	0.65	na	2.99	na	2.74	76.28	El-Moselhy (1993)

1 = Turkey; 2 = USA, North Pacific Ocean; 3 = California coastal Wetlands; 4 = South Australia;
5 = Alexandria; 6 = Red Sea; 7 = Lake Mariut; 8 = Lake Edku; 9 = Suez Gulf; na = not available.

Table 4: Maximum acceptable limits (mg/kg) of some heavy metals

Metal	mg/kg	Referance
Cd	0.04	EPA (1995) (safety level in fish tissue)
	5	CEFAS (1997); BOE (1991)
	10	NHMRC (1987); EEC (1979)
Cu	100	MAFF (1956); BOE (1991)
	350	NHMRC (1987)
Zn	250	Ministry of Food (1953)
	750	NHMRC (1987)
Pb	25	BOE (1991)
	50	Great Britain-Parliament (1979)

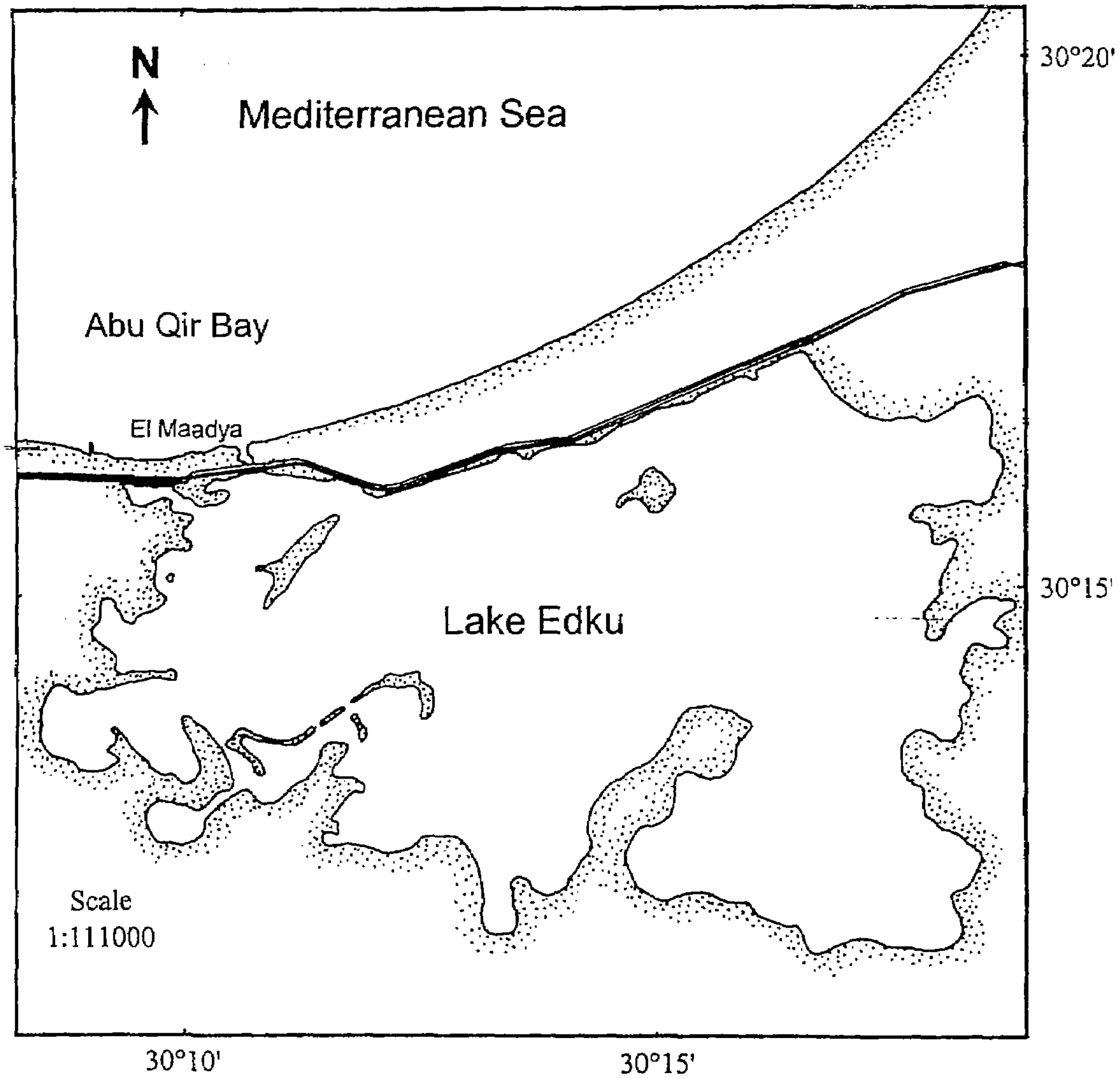

Figure 1. Map of Lake Edku and Abu Qir Bay, Egypt showing locations of study area.

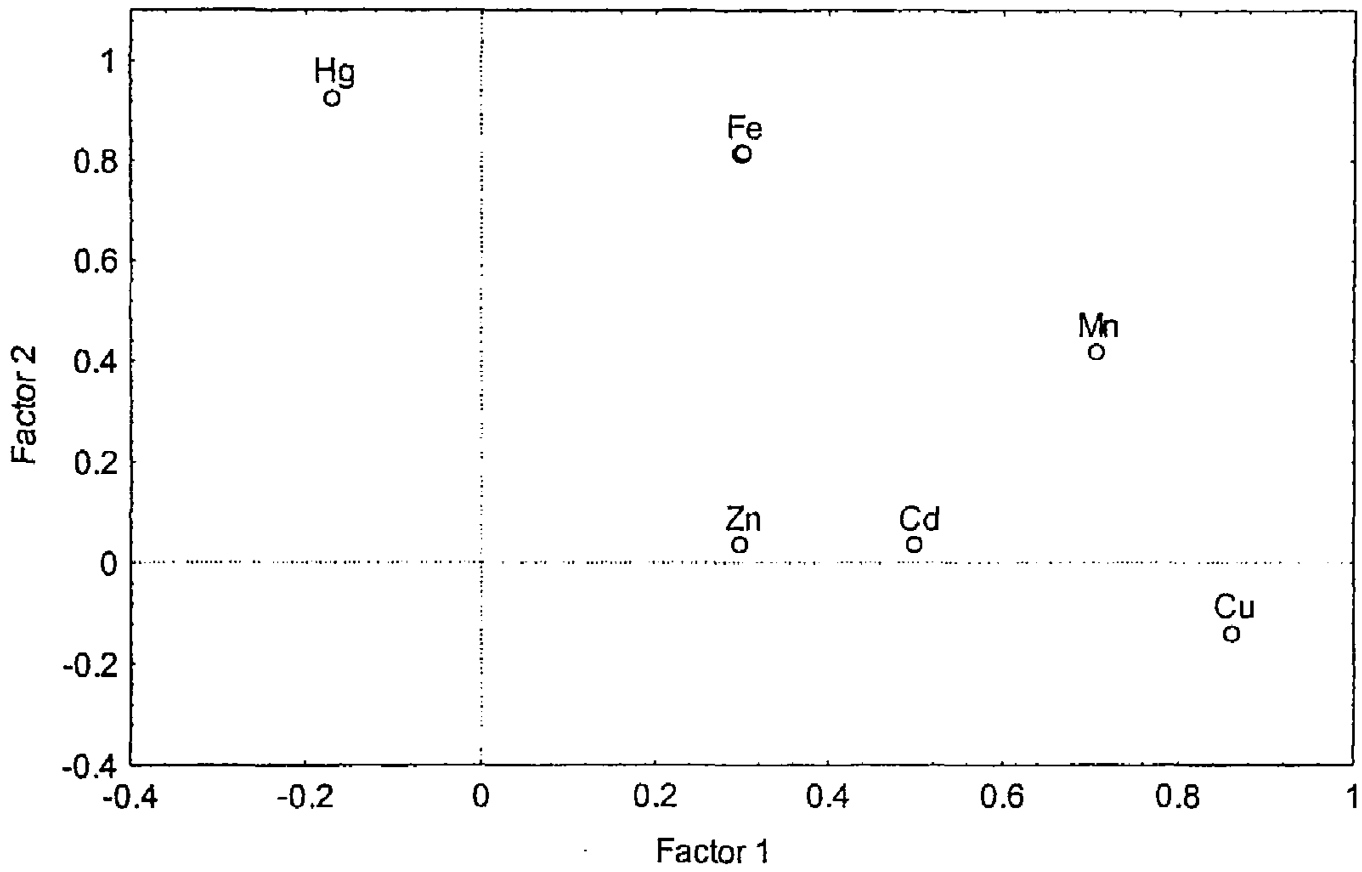

Figure 2. Principle component factor analysis (Varimax Normalized) association of different elements with respect to factor 1 and 2.