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Chemistry and Ecology

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Okbah, Mohamed A. and Nasr, Samir M.(2006) 'Dissolved trace-metal concentrations along the Mediterranean Sea, to the north of the Nile Delta Region, Egypt', Chemistry and Ecology, 22: 2, 125 – 135 To link to this Article: DOI: 10.1080/02757540600579268 URL: http://dx.doi.org/10.1080/02757540600579268

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Dissolved trace-metal concentrations along the Mediterranean Sea, to the north of the Nile Delta Region, Egypt

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(Received 27 May 2005; in final form 12 January 2006)

This work focuses on four marine sites of the Mediterranean Sea, north of the Nile Delta, Egypt. Surface-water samples were collected seasonally during 2003. The aim of this study is to assess the levels of some dissolved trace metals (Fe, Mn, Zn, Cu, and Pb) in two environmental conditions. The metal concentrations in the coastal zone were in the following ranges: $11.92-30.45 \,\mu$ gl⁻¹ for Fe, 5.79- $17.36 \,\mu g l^{-1}$ for Mn, 0.87–7.80 $\mu g l^{-1}$ for Zn, 0.40–1.87 $\mu g l^{-1}$ for Cu, and 1.53–10.31 $\mu g l^{-1}$ for Pb. In the sites with continental water input (mixing zone), the metals were scattered in the following ranges: Fe (19.72–60.33 μ g l⁻¹), Mn (12.63–35.60 μ g l⁻¹), Zn (2.67–22.00), Cu (0.83–8.10 μ g l⁻¹), and Pb (1.72–29.7 μ gl⁻¹). The results for the metal concentrations showed a remarkable decrease in the levels of the different metals going from the estuaries and outlets into the coastal sea water. Generally, the levels of the metals in the two zones are higher than the background levels of the unpolluted area. A comparison of the trace-metal levels in the coastal zone of the Mediterranean Sea north of Nile Delta with the minimal risk concentration (reported by water-quality criteria, WQC) showed a significantly lower content at the coastal area of the Mediterranean sea of Egypt. The study also indicated that the impact of anthropogenic inputs was limited in the distribution of the metals, except that the Pb content was slightly higher in the area of the mixing zone than that reported for WQC. The relationships between the different trace-metal concentrations and the other parameters (salinity, chlorophyll a and suspended particulate matter) were discussed, and the simple regressions between them were evaluated.

Keywords: Trace metals; Estuaries; Nile Delta; Mediterranean Sea

1. Introduction

The coastal Delta Lakes (Mariut, Edku, El Burullus, and El Manzalah) form a transitional zone between land and the Mediterranean Sea. These lakes are influenced by the climatic conditions of the southeastern Mediterranean Sea, with the highest turbidity coinciding with agitation of bottom sediment by strong wind action in these shallow lakes. These constitute the most productive natural system in Egypt, and most of their water comes from polluted agricultural drains as well as industrial wastewater and sewage [1]. The lakes are the final reservoir of large amount of untreated wastewater which is released directly into the Mediterranean Sea.

Chemistry and Ecology ISSN 0275-7540 print/ISSN 1029-0370 online © 2006 Taylor & Francis http://www.tandf.co.uk/journals DOI: 10.1080/02757540600579268

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All of this waste dumped into the sea could have an adverse effect on both marine organisms and water quality. The other regions in the present study were the Rosetta and Damiatta estuaries, which have been studied by many investigators; these estuaries also control the Nile water discharge into the Mediterranean Sea. The maximum discharge from the Rosetta estuary occurs in January ($1487 \times 10^6 \text{ m}^3$) and the minimum during November [2]. The bottom of the estuary in the inner part is mainly black mud enriched with organic matter with a distinct smell of H₂S gas reflecting the discharge of organic waste [2].

Some trace metals are essential for aquatic organisms (Fe, Mn, Cu, and Zn), but they are in toxic form when natural levels are exceeded to higher abnormal concentrations [3]; other metals such as Pb and Cd are not essential and have a toxic effect. Trace-metal accumulation and occurrence in the Egyptian coastal regions of the Mediterranean Sea waters and the estuaries of Nile River (Rosetta and Damitta estuaries) as well as the outlets of El-Burullus and El-Gamil have been studied [4–7]. The aim of the present work is to study the levels of several trace-metal concentrations in the coastal and mixing zones of the Mediterranean Sea in front of the Nile Delta (Egypt).

2. Materials and method

2.1 Sampling and analytical methodology

Eight surface-water samples were collected seasonally in the coastal and mixing zones of the study area in January (winter), April (spring), July (summer), and November (autumn) 2003. These samples were collected in four regions of the Mediterranean Sea coast of Egypt (figure 1): (1) Rosetta estuary (stations I and V), (2) El-Burullus outlet (stations II and VI), (3) Damitta estuary (stations III and VII), and (4) El-Manzalah outlet (stations IV and VIII). Water samples were collected from below the surface (0.5 m) using a Niskin bottle sampler in previously acid-washed polyethylene bottles. The pH of the water samples was determined using a portable pH meter. Salinity was determined using a Beckman induction salinometer (Model RS-7C). Chlorophyll *a* and suspended particulate materials were determined according to Strickland and Parsons [8].



Figure 1. Map of sampling stations.

Table 1. Concentrations (mean \pm S.D., μ g l⁻¹) for different metals in the reference material (NASS-5, National Research Council of Canada).

| Metal | Found | Certified |
|----------------------------|--|---|
| Fe Mn Zn Cu Pb | $\begin{array}{c} 0.197 \pm 0.025 \\ 0.910 \pm 0.070 \\ 0.098 \pm 0.047 \\ 0.305 \pm 0.055 \\ 0.010 \pm 0.005 \end{array}$ | $\begin{array}{c} 0.207 \pm 0.035 \\ 0.919 \pm 0.057 \\ 0.102 \pm 0.0.39 \\ 0.297 \pm 0.046 \\ 0.008 \pm 0.005 \end{array}$ |
| | | |

Extraction, analyses, and measurements of trace metals were carried out according to Martin [9]. A 750 ml water sample was filtered as soon as possible after collection through a previously acid-washed 0.45 μ M membrane filter. The pH of the filtrates was adjusted to 4–5 with 6 N HCl [9, 10]. The metals in the samples were extracted from the filtrate using solvent extraction (APDC-MIBK) as a chelating agent for the metals. The metals were complexed with ammonium pyrolidine dithiocarbmate (APDC; C₅H₁₂N₂S₂) and extracted into methylisobutylketone (MIBK; (CH₃)₂CHCH₂COCH₃)). Back-extraction into an acidic aqueous solution was done by shaking the extract with 35 ml of 1% HCl [10]. The concentration of different metals (Fe, Mn, Zn, Cu, and Pb) in the final acidic extracts was measured using a GBC-932 Ver. 1.1 atomic absorption spectrophotometer in the flame mode.

2.2 Method validation and quality control studies

Validation of the method and sample quality control 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 [11]. All reagents used were of analytical grades, and Milli-Q water was used throughout the study. All glassware used were soaked in detergent, rinsed with water, soaked in 10% HNO3 for 5 d, rinsed with Milli-Q water and kept in the oven at 110 °C until needed. The limits of detection ($\mu g l^{-1}$) were calculated by six determinations (duplicate measurements) in one batch of synthetic sea water. The detection limits were 0.045, 0.009, 0.008, 0.007, and 0.03 μ g l⁻¹ for Fe, Zn, Mn, Pb, and Cu, 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 750 ml of natural sea water (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 metal spiked were 90% for Cu, 91% for Pb, 105% for Mn, 91% for Fe, and 95% for Zn. The results for the analysis of trace metals in the reference material are shown in table 1.

3. Results and discussion

3.1 Physical and chemical characteristics of the Nile Delta region

The pH value was measured in water from the study area; the coastal zone water was on the alkaline side, pH > 8, and ranged from 8.04 to 8.27 (table 2), while the mixing zone showed lower pH values (7.45–7.95) than the coastal zone. The salinity was found to decrease from the coastal to the mixing zone, ranging from 32.54 ± 1.56 to 37.19 ± 0.43

|) | |
|-----|--|
| 95 | |
| 78 | |
| 12 | |
| .60 | |
| 32 | |
| | |

| Table 2. | Mean \pm S.D. of trace-metal concentrations (μ g l ⁻¹ | ¹), pH, S‰, Chl <i>a</i> and suspended particulate matter in the coastal and mixing zones of the Mediterranean Sea north of |
|----------|---|---|
| | | the Nile Delta, Egypt (January to November 2003). |

| | | Metals | | | | | | | | | |
|---------------------------|---------|-------------------|------------------|-----------------|-----------------|-----------------|-------------------|-----------|-------------------|------------------------|------------------------------|
| | | Fe | Mn | Zn | Cu | Ni | Pb | pН | S ‰ | $Chl a (\mu g 1^{-1})$ | SPM (mg 1 ⁻¹) |
| Stations of | Ι | 14.91 ± 4.73 | 8.83 ± 1.89 | 2.02 ± 0.65 | 0.87 ± 0.32 | 1.44 ± 0.29 | 6.09 ± 3.20 | 7.82-8.05 | 36.55 ± 0.88 | 3.80 ± 1.93 | 23.61 ± 0.95 |
| coastal zone | II | 20.16 ± 6.19 | 10.78 ± 2.75 | 3.22 ± 2.54 | 0.81 ± 0.53 | 1.07 ± 0.24 | 3.34 ± 3.25 | 7.95-8.12 | 36.42 ± 9.91 | 2.55 ± 1.56 | 29.66 ± 7.78 |
| | III | 15.08 ± 2.39 | 9.88 ± 2.58 | 3.35 ± 1.32 | 0.95 ± 0.70 | 0.79 ± 0.95 | 2.98 ± 2.01 | 8.05-8.17 | 37.19 ± 0.43 | 6.52 ± 1.59 | 45.21 ± 8.12 |
| | IV | 21.56 ± 5.48 | 13.49 ± 4.49 | 2.42 ± 1.93 | 1.07 ± 0.47 | 0.99 ± 0.24 | 3.82 ± 2.97 | 8.15-8.21 | 32.54 ± 1.56 | 13.50 ± 2.35 | 48.96 ± 12.60 |
| | Annual | 17.93 ± 4.69 | 10.75 ± 2.93 | 2.75 ± 1.36 | 0.93 ± 0.35 | 1.07 ± 0.43 | 3.34 ± 2.86 | 7.82-8.21 | 35.70 ± 2.23 | 6.59 ± 5.21 | 36.86 ± 7.32 |
| | average | | | | | | | | | | |
| Stations of mixed zone | V | 30.66 ± 10.38 | 16.15 ± 5.08 | 6.88 ± 2.05 | 1.83 ± 0.27 | 2.96 ± 1.02 | 22.98 ± 17.60 | 7.45-8.05 | 23.16 ± 30.06 | 11.35 ± 15.32 | 34.30 ± 43.21 |
| | VI | 36.10 ± 4.06 | 22.32 ± 7.99 | 13.23 ± 7.02 | 2.53 ± 1.72 | 2.76 ± 0.75 | 9.54 ± 9.17 | 7.56-8.45 | 10.41 ± 20.72 | 35.90 ± 92.41 | 102.0 ± 165.00 |
| | VII | 26.03 ± 3.81 | 18.82 ± 4.06 | 9.40 ± 3.29 | 1.60 ± 1.12 | 2.32 ± 0.71 | 14.64 ± 9.43 | 7.63-8.13 | 15.85 ± 19.54 | 7.56 ± 20.64 | 47.50 ± 70.68 |
| | VIIII | 44.08 ± 10.92 | 20.69 ± 4.69 | 6.77 ± 3.55 | 3.21 ± 2.73 | 2.05 ± 0.41 | 6.71 ± 5.03 | 7.51-8.16 | 5.62 ± 7.87 | 58.25 ± 95.82 | 125.4 ± 160.50 |
| | Annual | 34.22 ± 7.29 | 19.49 ± 5.46 | 9.70 ± 3.98 | 2.29 ± 1.52 | 2.47 ± 0.72 | 15.02 ± 10.31 | 7.51-8.45 | 13.76 ± 7.85 | 28.30 ± 10.54 | 76.45 ± 15.60 |
| | average | | | | | | | | | | |

PSU and 5.62 ± 2.87 to 23.16 ± 3.06 PSU, respectively. The concentration of chlorophyll *a* (Chl *a*) changed between 2.55 ± 1.56 and $13.50 \pm 2.35 \,\mu g \,l^{-1}$ for the coastal zone and between 7.56 ± 2.64 and $58.25 \pm 13.82 \,\mu g \,l^{-1}$ for the mixing zone. The data for suspended particulate matter (SPM) showed wide regional variations in their distribution patterns ranging from 23.61 ± 0.95 to $48.96 \pm 12.60 \,\text{mg} \,l^{-1}$ in the coastal zone and from 34.30 ± 10.21 to $125.40 \pm 16.50 \,\text{mg} \,l^{-1}$ in the mixing zone. Higher concentrations of Chl *a* and SPM and a lower salinity were measured in the mixing zone than in the coastal zone (stations I, II, III, and IV) and these variations were due to the effect of the anthropogenic inputs, mainly composed of agricultural effluents from the drains as well as industrial and sewage waste water.

3.2 Distribution of trace metals

Dissolved trace metals and bioavailability are a complex function of many factors, including the total concentration of metals, mineralogy, pH, redox potential, temperature, total organic matter, suspended particulate content, volume water and water velocity, duration of water, wind transport, and removal from the atmosphere by rainfall.

3.2.1 Iron (Fe) and manganese (Mn). The regional distribution of dissolved Fe and Mn concentrations in the study area is presented in figure 2. The dissolved Fe in the coastal water zone fluctuated between $11.92 \,\mu g \, l^{-1}$ at station I (in spring) and $30.45 \,\mu g \, l^{-1}$ at station II (in winter), while the concentrations in the mixing zone ranged from $19.72 \,\mu g \, l^{-1}$ at station V (in spring) to $60.33 \,\mu g \, l^{-1}$ at station VIII (in summer). The levels of dissolved Mn (figure 2) showed a wide variability for the coastal water and the mixing zone. The variation of dissolved



Figure 2. Dissolved Fe and Mn concentrations $(\mu g/l)$ in the coastal and mixing zones.

Mn concentration in the coastal zone ranged between $5.79 \,\mu g \, l^{-1}$ at station I (in spring) and $17.36 \,\mu g \, l^{-1}$ at station IV (in autumn), while the Mn concentration was approximately twoto threefold higher in the mixing zone than in the coastal zone, ranging from $12.63 \,\mu g \, l^{-1}$ at station V (in spring) to $35.6 \,\mu g \, l^{-1}$ at station VI (in the autumn). The high levels of dissolved Fe and Mn are related to the influence of drainage water. There was a tendency towards decreasing iron and manganese concentrations in the coastal zone at stations I, II, III, and IV. It is clear from the results that the dissolved Fe and Mn concentrations in the coastal zone is much lower than those recorded in the mixing zone. This may be related to the physical mixing of estuarine and marine water, which leads to a continuous decrease in trace-metal content of sea water in front of the Nile Delta with increasing salinity. The relationship between salinity ($S, \%_0$) and both Fe and Mn showed negative correlations (r = -0.761, -0.517, respectively), indicating a decrease in Fe and Mn from the low to the higher salinity. The decrease in dissolved Fe and Mn with increasing salinity appears to be explicable by the oxidation of Fe_{II} to Fe (OH)₃ and/or decrease in Fe(OH)₃ solubility at increased pH [12].

Fe =
$$47.193 - 0.755 \ S\%_o$$
 $r = -0.761, p < 0.05$
Mn = $23.217 - 0.289 \ S\%_o$ $r = -0.517, p < 0.05$.

The annual mean value of Fe was $17.93 \pm 4.69 \,\mu g l^{-1}$ in the coastal zone (table 2); this value increased twice $(34.22 \pm 7.29 \,\mu g l^{-1})$ in the mixing zone. However, a good correlation was observed between dissolved Fe concentrations and both Chl *a* and suspended matter (r = -0.715 and 0.713, respectively). The annual mean concentration of dissolved Mn showed a high variability (table 2) for the investigated area, ranging from $10.75 \pm 2.93 \,\mu g l^{-1}$ in the coastal zone to $19.49 \pm 5.46 \,\mu g l^{-1}$ for the mixing zone.

Seasonal variability of dissolved Fe and Mn revealed elevated values in winter and summer period. This may be explained as a result of the effect of winter agitation of the bottom sediments, which have high metal concentrations. This could be confirmed by the relationship between the concentration of both dissolved Fe and Mn with the values of SM, or suspended particulate matter (r = 0.713, 0.527, respectively) in the winter season.

Fe =
$$13.692 - 0.199$$
 SM $r = 0.713, p < 0.05$
Mn = $9.938 - 0.084$ SM $r = 0.527, p < 0.05$.

Another factor that should be considered is the low uptake of metals by phytoplankton in winter and autumn as low levels of Chl *a* were recorded in the winter and autumn. On the other hand, in the summer, the decomposition of organic matter and release of metals might explain the high content of trace metals in the aquatic system [13]. The levels of Chl *a* revealed significant correlations with both Fe and Mn content. This may suggest that Fe and Mn are important elements in the biogeochemical cycle of phytoplankton growth. This is clear from the simple linear regression equations for Chl *a* and both Fe and Mn.

Fe =
$$19.772 + 0.301$$
 Chl a $r = -0.715$, $p < 0.05$
Mn = $12.343 - 0.132$ Chl a $r = -0.553$, $p < 0.05$.

Generally, the levels of dissolved Fe and Mn were higher in the coastal area of the Mediterranean Sea (increasing by eight- and 20-fold, respectively) than those reported by Martin and Whitfield [14] and was lower than the minimal risk concentration reported for water-quality criteria (WQC) [15]. **3.2.2** Copper (Cu) and zinc (Zn). The regional variations in dissolved Cu in the investigated area are reported in figure 3. In the sites in the mixing zone, the absolute values of Cu content fluctuated between $0.83 \,\mu g \, l^{-1}$ at station VII in spring and $8.10 \,\mu g \, l^{-1}$ at station VIII in summer. In the coastal zone, the values ranged between a minimum of $0.40 \,\mu g \, l^{-1}$ in spring (at stations II and IV) and a maximum of $1.87 \,\mu g \, l^{-1}$ in summer at station IV. The annual average concentrations of dissolved Cu in the investigated area were relatively high in the sites of the mixing zone, $2.29 \pm 1.52 \,\mu g \, l^{-1}$ (table 2) and decreased in the coastal zone ($0.93 \pm 0.35 \,\mu g \, l^{-1}$).



Figure 3. Dissolved Cu, Zn and Pb concentrations $(\mu g/l)$ in the coastal and mixing zones.

The concentration of dissolved Zn at the sites of the mixing zone and the coastal zone are shown in figure 3. The mean values revealed a wide variation with regard to the coastal and mixing zones. The distribution pattern of dissolved Zn indicates a significantly lower concentration in the coastal zone. The annual variations of dissolved Zn concentration ranged between $2.75 \pm 1.36 \,\mu g \, l^{-1}$ for the coastal zone and $9.70 \pm 3.98 \,\mu g \, l^{-1}$ for mixing zone stations.

The high rate of organic matter decomposition in the summer season is the main reason for the increasing dissolved Cu and Zn concentrations in this period. On the other hand, the low levels of dissolved Cu and Zn in spring season may be related to several factors. Generally, the biological factors seem to have a strong influence on bioaccumulation of the metals. Abdel-Moati [16] suggested that the biological uptake is the main factor controlling the removal mechanisms of dissolved Cu. In the study area, phytoplankton play an important role in the distribution of the dissolved metals; directly, through the uptake of dissolved metals (negative correlations between Ch1-*a* and both Cu and Zn), and indirectly by increasing the pH, followed by a transition of dissolved Cu and Zn to the particulate form.

Cu =
$$1.66 + 0.0132$$
 Chl a $r = -0.658$, $p < 0.05$
Zn = $2.14 + 0.178$ Chl a $r = -0.461$, $p < 0.05$.

The flocculation process with humic substances could be playing an important role in the removal of dissolved Cu and Zn. The results recorded by Abdel-Moati [16] showed that 20% of dissolved Cu was removed during the mixing process in the Rosetta estuary. More than 40% of dissolved Cu in some rivers was removed through this process [17]. Positive correlation was found between dissolved Fe concentration and both dissolved Cu and Zn concentrations. This reflects the role of Fe in scavenging other metals, and the solubilities of Cu and Zn are affected strongly by the solubility of Fe.

Cu =
$$1.001 + 0.415$$
 Fe $r = 0.413$, $p < 0.05$
Zn = $2.239 + 0.130$ Fe $r = 0.340$, $p < 0.05$.

The results of dissolved Cu and Zn at stations VI and VIII (representing the outlets of El-Burullus and El-Manzalah Lakes) were higher than those recorded at stations V and VII (Rosetta and Damitta estuaries). The source of trace-metal pollution in these lakes is mainly the drains (agricultural and industrial wastes) which pour into the lakes [18]. Abdel-Moati and El-Sammak [19] reported that Cu and Zn levels have increased in Lake Manzalah sediments over the last 10 yr by nearly 60% for Cu and nearly doubled for Zn. The data for dissolved Cu and Zn concentrations in this study of the coastal zone revealed levels similar to those reported by Martin and Whitfield [14], and lower values were observed in the mixing zone compared with those found in the literature [20, 21].

3.2.3 Lead (Pb). The regional variations of dissolved Pb content in the present study showed a decreasing trend from the mixing zone stations to the coastal zone (figure 3). The seasonal distribution of dissolved Pb concentration in the coastal zone ranged between $1.53 \ \mu g l^{-1}$ in summer at station II and $10.31 \ \mu g l^{-1}$ in winter at station I. Generally, the data showed elevated levels of dissolved Pb content in the mixing zone stations, with values ranging from $1.72 \ \mu g l^{-1}$ in spring at station VI to $29.7 \ \mu g l^{-1}$ in winter at station V (figure 3). This may be due to the effect of the increasing rate of brackish-water discharges at station V; the maximum discharge occurs in January ($1487 \times 10^6 \ m^3$). In addition, the bottom of the estuary is composed of black mud enriched with organic waste [2]. Another important factor is fossil fuels and trash, which is burned without any emission control systems. Pb also may reach the

| Location | Fe | Mn | Zn | Cu | Ni | Pb | References | |
|-------------------------------|-------------|------------|-------------|-------------|-------------|-------------|---------------------------------|--|
| Coastal water | | | | | | | | |
| Mediterranean Sea (Egypt) | 11.92-30.45 | 5.79-17.36 | 0.86-7.40 | 0.30-0.83 | 0.51 - 2.90 | 0.53-10.31 | Present study | |
| Eastern Harbour and | | | | | | | | |
| El-Mex Bey (Egypt) | - | - | - | 4.9 | - | 0.5 | Shriadah and Emara [22] | |
| Red Sea (Egypt) offshore | 0.56 - 4.4 | 0.06-0.21 | 0.13-1.17 | 0.07-0.29 | 0.05-0.21 | 0.02 - 0.68 | Shriadah et al. [17] | |
| Red Sea (coast, Egypt) | 16.2 | 0.83 | _ | 5.1 | _ | _ | Saad and Kandeel [23] | |
| Red Sea (Jeddah, KSA) | _ | - | 6-14 | 4.9 | _ | 1.1-27 | Hamza and Amireh [24] | |
| Arabian Gulf (Bahrain) | 0.01 - 0.08 | 0.03-0.13 | 0.03-11.25 | 0.03-0.38 | 0.13-0.53 | 0.03-0.23 | Al-Sayed et al. [18] | |
| South Agean (Greece) | _ | 0.13-29.12 | _ | 0.16-15.21 | 0.55-15.98 | 0.23-9.22 | Voutsinou-Talladour et al. [16] | |
| El-Mex Bey (Egypt) | 13.0 | - | - | 3.0 | _ | - | Okbah [25] | |
| Island waters | | | | | | | | |
| Estuaries and outlets (Egypt) | 19.72-60.3 | 12.36-35.6 | 2.67 - 22.0 | 0.56 - 1.67 | 1.43-3.73 | 1.72-59.7 | Present study | |
| River Nile (Egypt) | 2.5 | 0.46 | 8.18 | 1.3 | - | - | El-Rayis and Saad [5] | |
| Lake Mariut (Egypt) | 42.5 | _ | 18.3 | 10.6 | _ | _ | Saad and Fahmy [26] | |
| Ora River (Nigeria) | 124.7 | 450 | 7.5 | 8 | _ | 5 | Mombeshora et al. [27] | |
| Lake Victoria (Kenya) | - | 50-3276 | 25-125 | 5-57.0 | - | 7–93.6 | FAO [19] | |
| Background | | | | | | | | |
| Rivers | 40.0 | 7.0 | 20.0 | 7.0 | _ | 0.3 | Burton and Liss [28] | |
| Coastal waters | 2.0 | 0.4 | 2.5 | 1.0 | - | 0.03 | Martin and Whitfield [29] | |
| Minimal Risk Concentration | 50 | 20 | 20 | 10 | 2 | 10 | WQC [20] | |

Table 3. Dissolved trace-metal concentrations ($\mu g l^{-1}$) in inland and coastal waters compared with the reported values.

Dissolved trace-metal concentrations along the Mediterranean Sea

| | pH | S‰ | Chl a | SPM | Fe | Mn | Zn | Cu | Ni | Pb |
|-------|--------|--------|--------|--------|-------|-------|-------|--------|-------|----|
| pН | 0 | | | | | | | | | |
| S‰ | -0.244 | 0 | | | | | | | | |
| Chl a | 0.298 | -0.765 | 0 | | | | | | | |
| SPM | 0.324 | -0.795 | 0.894 | 0 | | | | | | |
| Fe | 0.117 | -0.761 | 0.713 | 0.713 | 0 | | | | | |
| Mn | 0.011 | -0.517 | 0.553 | 0.527 | 0.664 | 0 | | | | |
| Zn | 0.050 | -0.371 | 0.261 | 0.317 | 0.356 | 0.663 | 0 | | | |
| Cu | 0.100 | -0.226 | 0.358 | 0.173 | 0.413 | 0.355 | 0.013 | 0 | | |
| Ni | 0.191 | -0.299 | 0.262 | 0.359 | 0.294 | 0.253 | 0.439 | -0.268 | 0 | |
| Pb | 0.035 | -0.205 | -0.125 | -0.027 | 0.347 | 0.137 | 0.259 | -0.181 | 0.433 | 0 |
| | | | | | | | | | | |

Table 4. Correlation matrix.

atmosphere, as it is often disposed of in the area. Abdel-Moati [16] suggested that trace-metal desorption from solid material (suspended particles and sediments) in estuarine environments may be an important process for introducing dissolved metals to the water system; stirring bottom sediments also could enhance metal transfer to overlying waters, thus enriching their concentrations in the water body. Rosetta estuarine particles are markedly enriched in Pb [16]; This is illustrated from the local effects of domestic and industrial discharge (Rosetta town).

The results for Pb concentration reported in the literature (table 3) show that the concentrations observed here are much higher than those recorded in the Eastern Harbour, El-Max Bay, Arabian Gulf, and the Red Sea [22–25] and are similar to those of the south Agean, Greece [21]. In general, the data for dissolved Pb concentration in this study were increased 100-fold in comparison with those reported by Martin and Whitfield [14] in the coastal waters. On the other hand, dissolved Pb in the coastal zone of the Mediterranean Sea of Egypt is lower than the minimal risk concentration reported by WQC [16]. In the mixing zone of the study area, dissolved Pb is much lower than the values for Lake Victoria and higher than the Ora River [20, 26].

3.3 Correlation matrix

The correlation matrix for the different trace metals in the present study showed that there were no significant correlations for some pairs of trace metals (table 4). The correlation of Ni and Pb with Cu was poor (r < 0.2) and between Mn and both Ni and Pb (r = 0.2 and 0.06, respectively), thus indicating that a local high concentration for one metal as a result of possible contamination does not necessarily indicate high values for other metals [13]. This also reflects different sources and different biogeochemical behaviours [23]. On the other hand, good positive correlations (P < 0.05) were found between several pairs of trace metals. Most of the significant relationships were Fe and Cu (r = 0.76), Mn and Zn (0.66), Mn and Fe (0.66); Mn and Cu (r = 0.53); Zn and Ni (0.42); as well as Fe and Zn (0.33). These might indicate the important role of iron and manganese as a common sink for trace elements such as Cu and Zn.

4. Conclusion

In comparison with the background values in the literature, the levels of the metals (Fe, Mn, Zn, and Cu) in the two environmental conditions, mixing and coastal zones of the Mediterranean Sea in front of the Nile Delta were slightly high. The impact of anthropogenic input

from the mixing zone on trace-metal distribution along the coastal zone was limited. The dissolved Pb concentrations in this study were increased 100-fold compared with those reported in the coastal waters. On the other hand, this level lies within the minimal risk content reported by WQC.

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