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CHEMICAL AVAILABILITY AND TRANSFORMATIONS OF TRACE METALS (Fe, Mn, Zn, Co AND Ni) IN LAKE MARYUT SEDIMENTS, ALEXANDRIA, EGYPT

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Laboratory experiments were performed to predict the fate and transformation of trace metals (iron, manganese, zinc, cobalt, nickel) associated with polluted sediments. Three sediment samples from Lake Maryut were collected. After an incubation period of about 168 hr, the different chemical forms of the metals were determined under oxidizing and reducing condition. The results showed that a large quantity of manganese was converted from the oxide fraction to the more exchangeable and water-soluble fractions, while iron, zinc, cobalt and nickel associated with the Mn-oxide form were increased. The relative percentage of metals, including the water-soluble exchangeable and organic forms, constituted < 10% of the total amount for iron, < 16% for manganese, 25% for zinc, 63% for nickel and 35% for cobalt.

Also, the results showed that the metals bound with organic materials followed the order: nickel > cobalt > zinc > iron > manganese.

Keywords: Lake Maryut sediments; trace metals availability; transformation

INTRODUCTION

Lake Maryut is one of the Nile Delta Lakes situated along the Mediterranean coast of Egypt at latitude 31° 10' N and longitude 29° 55' E.

Lake Characterization

This is a closed, very shallow lake, situated to the south of Alexandria. It has an area of about 63 km² and a mean depth of about 1 m. The lake is divided by artificial embankments into four basins (Fig. 1).

In recent years, Lake Maryut is considered as an oxidation pond for Alexandria waste water and agriculture wastes, discharged to it by the newly constructed plant stations. The lake has been subjected to various anthropogenic activities.

In 1993, the East and West treatment plants began to treat Alexandria waste water. Both are primary treatment plants and they discharge their final effluents into the lake. The physico-chemical characteristics of the waste water of these plants were studied previously by Mourad (1994).

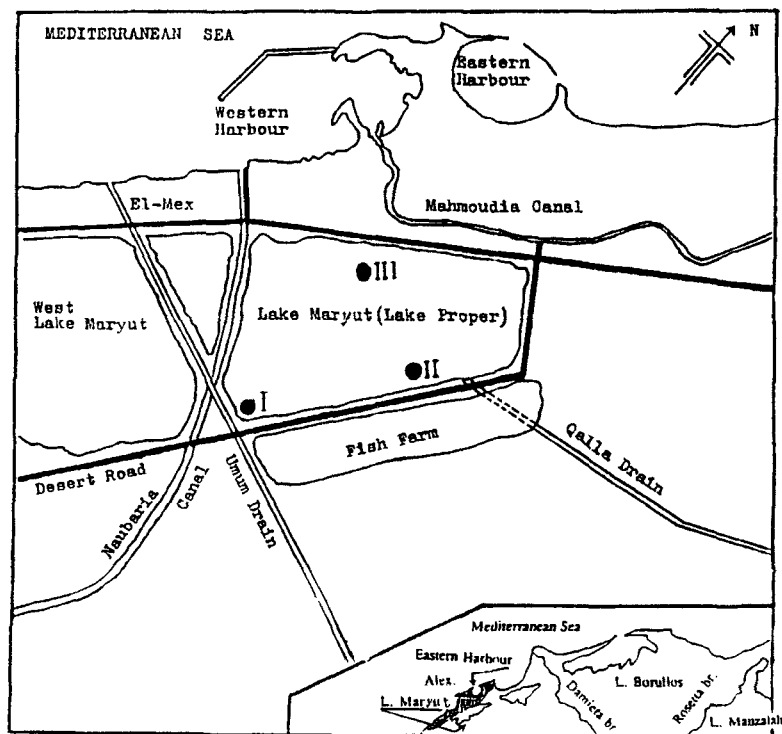


FIGURE 1 Lake Maryut and sampling sites.

Previous work conducted on Lake Maryut showed that dissolved oxygen was between zero to 6.36 mg. O₂ l⁻¹ and hydrogen sulphide between 0.84 to 47.98 mg l⁻¹ (Okbah, 1995). Complete depletion of oxygen was seen and may be due to the oxygen consumption in the decomposition of organic matter and in oxidation of chemicals from the polluted effluent. Organic matter was generally present in high concentrations in the water and fluctuated between 30.1 and 74.3 mg O₂ l⁻¹ and organic materials in the lake water are mainly produced through the decomposition of the discharged domestic and industrial wastes and the decaying planktonic organisms.

Today the lake has become heavily polluted with heavy metals derived from domestic, industrial and agricultural wastes (Okbah, 1995). Besides a knowledge of the total heavy metal content of the sediment, it is essential to have information on the mobility and transformation, in order to estimate the danger to the environment. The transformation of heavy metals in sediments is strongly influenced by the pH, redox potential, clay minerals and organic matter, all of which can significantly influence the solubilization or retention of heavy metals. The concentration of heavy metals varies with time and the chemistry of manganese and iron which seem to control the solubility of other heavy metals (Kedziorek and Bourg, 1995). The sediment-bound contaminants range from water-soluble and exchangeable forms, which are available to aquatic organisms, to elements bound within the crystal structure of clay and silicate minerals, which under normal conditions are unavailable for biological uptake (Lindau and Hossner, 1982). Contaminants may also be associated with organic matter, sulphide, carbonates and iron and manganese hydrous oxides that are potentially available to soil organisms (Shuman, 1979). Previous research has demonstrated that pH and oxidation reduction of sediment water systems regulate the chemical form and mobility of heavy metals (Gambrell *et al.*, 1977). Multistep sequential extraction schemes provide a more complete picture for predicting the heavy metal fate, distribution and transformation. Various forms of elements in sediment are now more important for assessing the availability of possible pollutants and waste materials. The microelements are especially important because slight changes in availability can cause these elements to become either toxic by contamination of food chain, or deficient for micro-organisms and plants.

The aim of this study was to evaluate the magnitude of the different forms of metals in the sediment and to assess their transformation with various chemical forms in sediment-water system after an incubation period (about 168 hr) in laboratory conditions.

MATERIAL AND METHODS

1. Sampling and Methods of Analysis

Three sediment samples (Fig. 1) were collected from Eastern Lake Maryut using a modified Ekman bottom sampler. In the laboratory the samples were spread over glass sheets and left to dry in the air. The air dried samples were disaggregated with the fingers, crushed and passed through a 1 mm sieve. The sample was divided into two portions.

The first portion was prepared for determination of the total elemental analysis using digestion with an acid mixture, $\text{HNO}_3/\text{HClO}_4/\text{HF}$, as 3:2:1 (Oregioni and Aston, 1984). Total calcium carbonates were measured volumetrically as percent CaCO_3 by a simple water calcimeter apparatus (Black, 1965). The second portion was subjected to laboratory studies and sequential extraction as shown in Figure 2.

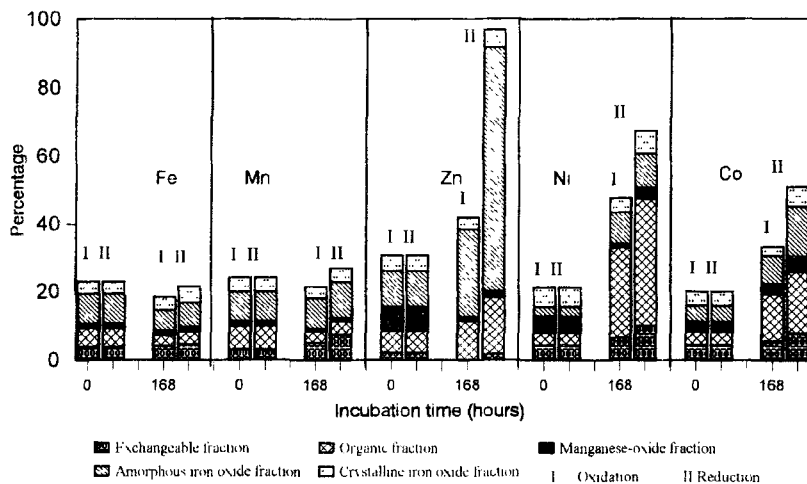


FIGURE 2 Trends of trace metals concentration extracted by different reagents with time at station I.

The physical and chemical analysis of samples (Tab. I), showed that they differed in texture and organic carbon.

2. Incubation Experiment

Duplicate sediment samples (30 gm of each) were put into 250 ml glass bottles, to obtain flooded conditions, and 90 ml deionized distilled water was added to the sediment samples. The bottles were closed with screw stoppers and were stirred by shaking on a rotary shaker at 200 rpm for one hour to maintain homogeneous suspension, and then left to stand at room temperature.

An oxidized condition was maintained by continuously passing air into the suspension using an air compressor. A reduced medium was maintained by passing nitrogen gas to replace the air in the flask. The redox potential (Eh) and pH were recorded at zero time and after 168 hr. The pH and Eh of the suspension were measured by placing platinum or glass electrode and calomel electrode in the solution of each sample.

The bottles were swirled until all the sediment was suspended and opened to take 10 ml from each sample and this was centrifuged (5000 rpm for 30 min at room temperature) to separate the water-soluble trace metals (fraction 1).

A further set of samples were submitted to the sequential extraction techniques described by many investigators (Sims and Patrick, 1978; Chao, 1972; Shuman, 1982; Prohic and Kniewald, 1987; and Martin *et al.*, 1987). Six steps of a sequential fractionation scheme (Fig. 2) was used to partition the metals into water soluble trace metals; exchangeable; organically bound; manganese oxides bound; amorphous iron oxides and crystalline iron oxides.

Trace metals were determined using Atomic Absorption Spectrophotometry (Unicam SP 1900).

3. Chemical Fractionation

Sequential leaching techniques were used according to the previous studies. The principal operationally defined host components associated with each fraction in the sequential technique and the reagents used to effect the stage separations.

The water-soluble fraction (stage 1) was obtained by taking 10 ml of suspension from each sample and centrifuged to separate this fraction.

TABLE I Properties of sediments used for the laboratory studies (after Okbah, 1995)

Site	Grain size (%)			Org. carbon %	CaCO ₃ %	Texture	Total concentration ($\mu\text{g g}^{-1}$)					
	Sand	Silt	Clay				Fe	Mn	Zn	Co	Ni	
I	26.0	5.0	69.0	2.306	23.5	Clay	8906	1191	148	188	134	
II	14.0	45.0	41.0	6.384	16.0	Silt-Clay	6953	976	84	156	83	
III	53.0	11.0	36	3.376	28.0	Sand-Clay	6445	738	424	187	100	

One gram wet sediment from stage 1 was used to perform the fractionation procedure (Tab. II).

RESULTS AND DISCUSSION

After an incubation period (168 hr), significant changes were observed in the concentrations of trace metals associated with their different forms. Both redox potential Eh and change of pH had marked effects on manganese transformation.

It is clear that the highest redox potential affected on the amount of manganese in the Mn-oxide fraction, extracted by $\text{NH}_2\text{OH}\cdot\text{HCl}$. A decrease in the redox potential (from -16 at Site II to -205 at Site III) caused a marked transformation of the Mn-oxide form to the water soluble and exchangeable fractions. Figures 2, 3 and 4 showed that a small decrease in the pH value sufficed to convert the Mn-oxide fraction to the more exchangeable and water soluble fractions, especially in reduced condition. Although, manganese and other trace metals were solubilized at low pH and Eh, a large part of the solubilized manganese did not remain water-soluble, but became associated with the exchangeable fraction. Generally, large amounts of manganese associated with the exchangeable and water soluble fractions increased with an increased incubation time.

TABLE II The sequential extraction techniques of different fractions

<i>Fraction phase Stage</i>	<i>Reagents</i>	<i>pH</i>	<i>Shaking (h)</i>	<i>Reference</i>
2- Exchangeable cations	20 ml 1 M ammonium acetate	7	3	Prohic and Kniewald (1987)
3- Organic fraction	50 ml 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	10	8	Alexandrova (1960) Sims <i>et al.</i> (1979)
4- Mn-oxides fraction	50 ml 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$	2	0.5	Chao (1972)
5- Amorphous iron oxides	50 ml 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4 + 0.2 \text{ M } \text{C}_2\text{O}_4\text{H}_2$	3	4	Shuman (1985)
6- Crystalline iron oxides	50 ml 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4 + 0.1 \text{ M } \text{ascorbic acid}$	3	0.5	Shuman (1985)

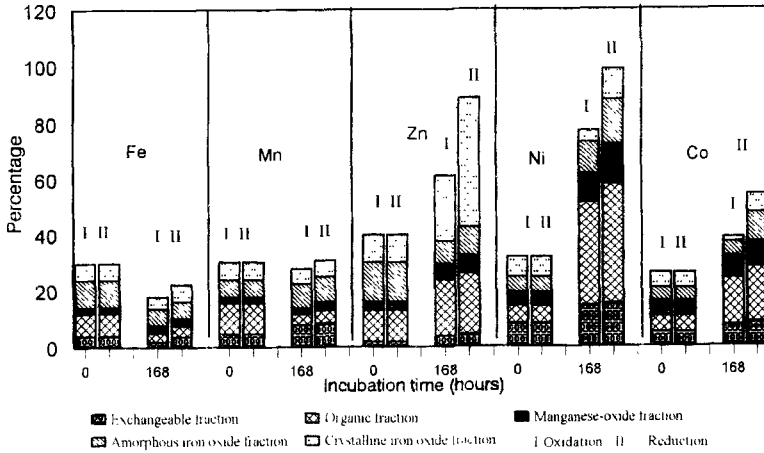


FIGURE 3 Trends of trace metals concentration extracted by different reagents with time at station II.

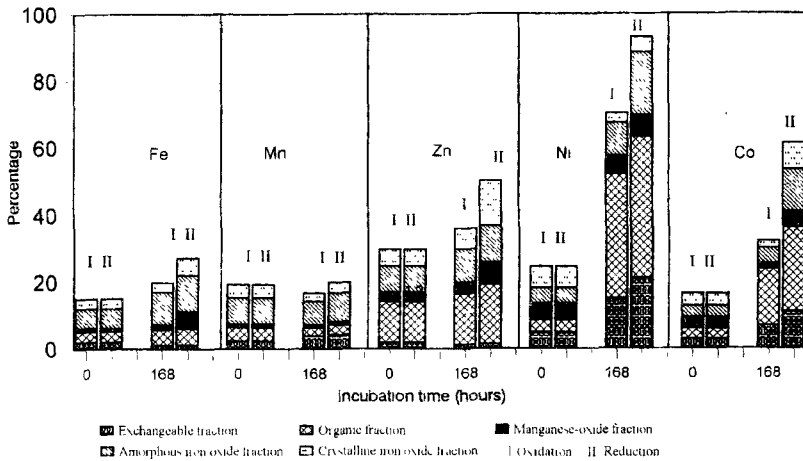


FIGURE 4 Trends of trace metals concentration extracted by different reagents with time at station III.

Also, the results revealed that the greater amount of manganese associated with the organic fraction decreased through the incubation period, manganese behaviour associated with the crystalline Fe-oxide has the same trend as organically bound material. In contrast, the amount of manganese bound to amorphous iron oxide increased.

The results indicated that the amount of iron, zinc, cobalt and nickel associated with the Mn-oxide form was increased possibly affected with the decrease in the Eh and pH. Also, a greater amount of cobalt and nickel were bound to the exchangeable form.

The fate and distribution of trace metals (iron, zinc, cobalt and nickel) among the water-soluble fraction at the end of incubation period were decreased or increased; these may be influenced by many factors, including the relative concentration of metals, differences in energies of adsorption on colloid surface and differences in the capacity of metals to form highly stable complexes with organic matter (Sims and Patrick, 1978).

Manganese in the exchangeable fraction represents 8% of the total amount, results seen with the other studies. Shata *et al.* (1993) found that manganese content of the exchangeable fraction of the sediment of Khor Kalabsha is relatively low (4–8%). Manganese in the exchangeable form was less than 1% of the total (Okbah, 1991).

Saoud *et al.* (1986) showed that the increase of manganese among water-soluble and exchangeable fractions was very high, accompanied by a significant decrease in the content of the easily reducible manganese (Mn-oxide fraction).

Previous studies conducted by Gotoh and Patrick (1972) at pH's 6, 7 and 8 stated that the conversion of reducible manganese to water soluble and exchangeable forms took place at redox potentials of +200 to +300 mv.

The amounts of zinc, nickel and cobalt extracted by sodium pyrophosphate solution were found to be very high compared with those of iron and manganese attributed to the organic phase in the extraction sequence (Figs. 2,3 and 4). This may be due to the decomposition of organic compounds produced in the sediment-water system, in that reducing conditions are brought about by microbial reduction. The microbiological processes have a great influence on the transformation of these metals. Chelating compounds produced in sediment-water system may react with metal ions and alter the redox reaction of sediment trace metals. Schnitzer and Khan (1972) showed that the metals, nickel, cobalt, zinc, iron and manganese, formed complexes with humic substances and that the order of stabilities of the different metal complexes followed the order: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$

The present study (Figs. 1, 2 and 3) showed that the relative percentage of metals associated with the organic fraction can be arranged in the following order: nickel > cobalt > zinc > iron > manganese.

Shata *et al.* (1993) found that the manganese bound to the organic fraction was 8.8%, iron 5.2% and zinc 18.5% of the total concentration. El-Deek (1995) showed that the organic bound fraction ranged from 0.08–8% for iron and 2.6–24.4% for manganese.

The relative percentage of all five trace metals after about 168 hr extracted from the three samples including the summation of three fractions to represent the water-soluble, exchangeable and organic fractions constituted < 10% of the total amount of iron, < 16% for manganese, 25% for zinc, 63% for nickel and 35% for cobalt. Elsokkary and Müller (1990) showed that about 54% of the total nickel is of non-lithogenous origin (exchangeable + carbonate + easily reducible + moderately reducible + organic/sulphide) of the Nile Delta sediments. Zinc fractionation of the samples (Figs. 2, 3 and 4) showed that major amounts of zinc were associated with the crystalline iron oxide fraction at Site II and associated with amorphous iron oxide at Site I, and a greater amount was found in the residual fraction at Site III. Also, the slight change in pH of the sediment at Site II, it appears relatively higher amount of zinc in the exchangeable and organic fractions. Kuo and Baker (1980) reported that the solubility and exchangeability of zinc in soil increased with decrease in soil pH. Previous studies (Gambrell *et al.*, 1980) showed that the total dissolved and exchangeable levels of zinc were greatest at pH 5.0 and decreased to undetectable levels at pH 8.0. Under strongly reduced conditions (–150 mv), levels of exchangeable zinc were lower than under more oxidized conditions, and agrees with those reported here (Figs. 2 and 4). The decrease in the exchangeable zinc fraction in sediments of Sites I and III may be due to its precipitation as zinc carbonate (Mandal and Biswapati, 1986), and increases in the acidified ammonium oxalate fraction caused a slight increase in the amount of zinc associated with the crystalline iron oxides fractions at Site I compared with the two sites due to the transformation of the crystalline oxides to poorly ordered amorphous forms, resulting in release of a part of the zinc bound in the crystalline form and its adsorption by the amorphous oxides (Iu *et al.*, 1981). Kuo *et al.* (1983) suggested that zinc and

manganese were more strongly associated with amorphous iron oxides with only small amounts being occluded in crystalline iron oxides.

Extractable zinc, which represents the organic complexed form, varied from 16% (Site I), 19% (Site III) to 21% (Site II) of the total amount. This appeared to vary directly with organic carbon content of the sediments (Tab. I).

Figures 2, 3 and 4 show relatively higher percentage of zinc, nickel and cobalt released by hydroxylamine hydrochloride and oxalate solution fractions under reducing conditions. If we are able to compare between the metal concentrations in oxidizing and reducing medium, the results revealed the important role of oxides and hydroxides minerals in the sediment samples from scavenging zinc, cobalt and nickel.

The total percentage of these fractions solublized by $\text{NH}_2\text{OH}\cdot\text{HCl}$ and oxalate solution for each metal are followed the order:

zinc > nickel > cobalt at Site II

zinc > cobalt > nickel at Site I

zinc > nickel > cobalt at Site III

We can arrange these metals according to their solubility by water-soluble, ammonium acetate and $\text{Na}_4\text{P}_2\text{O}_7$, following the order nickel > cobalt > zinc of the three samples. We suggest that a greater importance of adsorption with respect to co-precipitation as the mechanism responsible for the scavenging of trace metals in the anoxic sediments.

CONCLUSION

The distribution of manganese, iron, zinc, nickel and cobalt in lake Maryut among the different chemical phases revealed that:

1. At reduced conditions and with a small decrease in the pH value was able to convert the manganese oxide fraction to exchangeable and water soluble fractions, while the organic-bound fraction of manganese is decreased.
2. Greater amount of cobalt and nickel are found in exchangeable and water soluble fractions through an incubation time (168 hr).

3. Highest relative percentage of zinc, nickel and cobalt found in the organic bound fraction after the incubation time. These reflect the important role of organic compounds produced in the aquatic environment on the mobile and transformation of zinc, nickel and cobalt followed the order nickel > cobalt > zinc.
4. The results represent the important role of iron and manganese oxides and hydroxides in the sediments for scavenging trace metals zinc > nickel > cobalt at Sites II and III.
5. The results showed that higher levels of metals (nickel, cobalt and zinc) are found in non-lithogenous materials and these can affected the aquatic organisms (plant and animals). Also, it is clear that the humic substances (extracted with $\text{Na}_4\text{P}_2\text{O}_7$) have the capacity of binding substantial metals and thus they can exert considerable control over the supply and availability of nutrient elements to the environment.

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