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Total Dissolved Zinc and Total Particulate Zinc in Nozha Hydrodrome

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ABSTRACT: The Hydrodrome, covering area of 5.04 km^2 and average depth of 2.11 m, became polluted in recent years from the feeding contaminated Nile water. Surface water samples were collected monthly from this lake for studying seasonal distribution of Total Dissolved Zinc (TDZn), Total Suspended Matter (TSM) and Total Particulate Zinc (TPZn). The high amounts of TSM affected the distribution of TDZn. The behavior of Zn was generally governed with pH variations, influencing adsorption/desorption processes. The relative increase in TDZn in the lake compared with earlier data illustrates the effects of heavy metal pollution in recent years. The maximum average TDZn value at the location of breeding ducks coincided possibly with the erosion factors working on the large over floating metallic constructions built for this activity. The large amounts of organic matter derived from duck wastes containing TDZn participate in the increase in TDZn through phytoplankton recycling. The zonal distribution of TSM in the lake was limited. The feeding canal seemed to be not the main source of TSM, confirming existence of another source of TSM for the lake. The TSM peaks in spring and summer prove the biogenic TSM origin. It seemed that most of Zn in the lake, especially the inorganic forms, reached its water via anthropogenic sources and TPZn dominated the TDZn. A positive regression equation existed between TSM and TPZn; TSM = 24.483 ± 4.27 + 0.04 ± 0.02 TPZn ($r = 0.354$, $p < 0.013$). This illustrates that the bulk of TSM was composed of TPZn plus other contributors. The seasonal TPZn peak in April in the lake and its feeding waters increased the annual mean concentration for the lake. The very high TPZn scored in April in front of the feeding canal reflected these spring peaks and mostly resulted from garbage wastes and letter dumped into the uncovered feeding canal.

INTRODUCTION

Trace metals play a considerable role in the sea, although they contribute negligibly to the total salt content of seawater. According to Chester 2000, rock weathering, atmospheric deposition and pollution releasing trace metals are the main sources of metals into the surface waters. Considerable amounts of metals, originating from pollution activities or physical processes, enter the coastal aquatic environments through rivers (Gesamp/UNESCO, 1994). The path of trace metals from sources to seawaters and then to sediments depend on their chemical state in the marine environment. Zinc is essential for the growth of marine organisms; its uptake from the aquatic environment by organisms is one of the possible processes of it removal (Scoullos, 1980). It also serves as an activator in some enzymatic reactions and as a factor for the enzyme carbonic anhydrase. Bruland (1980) observed a linear relationship between zinc and reactive silicate and suggested that zinc is removed as a trace constituent of some biogenic carrier phase. Abdel-Moati (1985) observed a positive correlation between zinc and reactive silicate in Lake Manzalah, the largest northern Nile Delta lake, indicating that some of the zinc may be included in the biological processes and attributed the zinc increment in summer to the peak of phytoplankton in this season. However, zinc becomes toxic when present in high levels in the aquatic environment. Heavy metals enter the marine environment through weathering of the earth's crust and human activities, mainly via municipal and industrial wastes.

A research project was conducted on the geochemical behavior of zinc in two Egyptian coastal ecosystems subjected to different sources and types of runoff. The present study, a part of this pioneer project, deals with local and seasonal distribution of TDZn, TSM and TPZn in the Nozha Hydrodrome, an artificial coastal Egyptian lake.

STUDY AREA

Nozha Hydrodrome is a nearly rounded freshwater body of 5.0 km^2 surface area. The average water depth is 2.1 m and the maximum depth is 3.8 m. It receives its water from the Nile via Mahmoudia Canal through a Feeding Canal. In 1939, the Hydrodrome was separated artificially from Lake Mariut located at its eastern side by an embankment and its sides are reinforced with concrete. The lake is used as a fish farm for the Nile fishes and at its western region, a large buoyant ducks breeding project has been established. The surplus water of the lake is discharged via an outlet located opposite to the inlet (Figure 1).

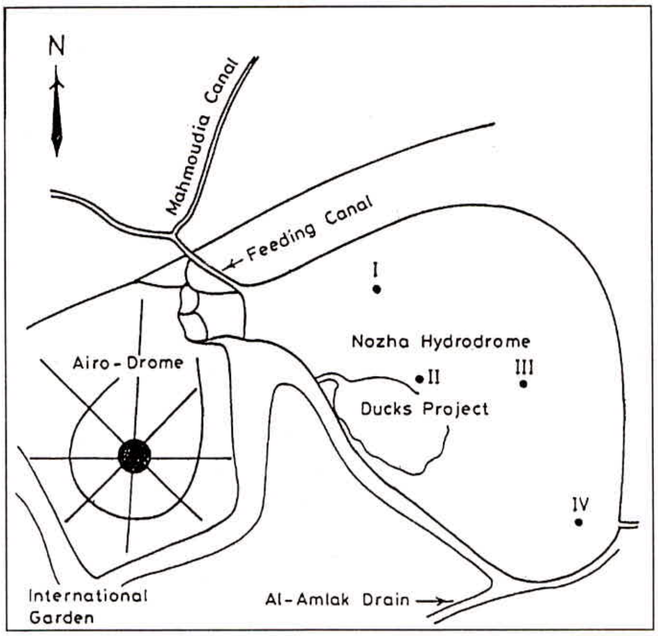

Fig. 1: Map of the Nozha Hydrodrome showing position of stations

MATERIAL AND METHODS

Water sampling was carried out four stations selected at different regions in the lake (Figure 1). Station I represents the water imported from the Feeding Canal after mixing with the Hydrodrome water. Station II represents the area around the duck breeding project. Station III represents the mid Hydrodrome and station IV the southern part of the lake near the outlet. The Feeding Canal was ceased feeding the lake during July, due to shifting of its water to feed the cultivated surrounding land.

Monthly sampling occurred from the surface water at 30 cm below the surface to avoid floating matter. This sampling was carried out during 12 successive months of 2 following years. Also, water sampling was conducted during the same period from the Feeding Canal to follow up the impact of metal pollution on the lake.

Before filtration of water samples, special standards of cleanliness were adhered to the laboratory. The water samples were filtered, using pre-weighed millipore membrane filter paper (0.45 µm, diameter 47 mm) to separate the dissolved from the particulate zinc fractions and to determine the TSM gravimetrically.

Dissolved zinc was determined by the APDC-MIBK pre-concentration technique. The accuracy of this technique was evaluated by spiking three different 250 ml samples previously chelated (free-metal) lake water. with increments of TRISTOL, MERK STANDARD solution. Spiked samples were chelated using APDC-MIBC method into 5 ml. Concentrations of the concentrated dissolved zinc was measured using A.A.S. and 100% of Accuracy was obtained. Precision was measured by determining the chelated zinc in 250 ml replicate samples (previously stripped of all trace metals by chelation) with an initial concentration of 1 p.p.m. Results showed 1.01 ± 0.098 mean concentration.

Zinc associated with suspended matter was subjected to a chemical leaching technique described by Tessiuer *et al.* (1979). The residue was dissolved in HCl and the volume was made up to 25 ml with ultra pure water for measurement by A.A.S. For determination of the accuracy and precision of the method, the SRM-2704, Bufflo River Sediments, National Insiutute of Standards and Technology Office of St. Ref. materials, USA was used.

RESULTS

Total Dissolved Zinc (TDZn)

The absolute values ranged from 10 $\mu g.l^{-1}$ at station II in July to 239 $\mu g.l^{-1}$ at station II in November. The regional averages varied from a minimum at station I to a maximum at station II, which was mostly similar to those at the other stations. Fluctuations in the regional averages was not significant ($T = 1.661$, $P < 0.195$). The monthly averages varied widely from 13.5 ± 3.5 $\mu g.l^{-1}$ in July to 149.8 ± 83.7 $\mu g.l^{-1}$ in November. Higher monthly averages appeared in winter months. Variations of the monthly averages were statistical significant ($T = 4.319$, $P < 0.001$). Contrary to the conditions in February. April, May, and June the concentrations in the Feeding Canal in autumn and winter were lower than the average monthly values in the lake. The overall concentration of TDZn for the study period reached 59.68 ± 7.85 $\mu g.l^{-1}$ (Table 1).

Total Suspended Mater (TSM)

The absolute values of TSM varied considerably from 1.1 $mg.l^{-1}$ at station III in September to 100 $mg.l^{-1}$ at the same station in March. Variation of the regional averages was limited, varying from 28.3 ± 21.0 $mg.l^{-1}$ at station I to 33.4 ± 26.4 $mg.l^{-1}$ at station IV. The monthly variations ranged markedly from 2.5 ± 1 $mg.l^{-1}$ in September to 79 ± 21 $mg.l^{-1}$ in March. The seasonal distribution was significant ($T = 4.75$, $P < 0.001$).

Table 1: Monthly Variations of Total Dissolved Zinc (μg.l^{-1}) in the Hydrodrome and its Feeding Canal

Stations	*Aug.*	*Sept.*	*Oct.*	*Nov.*	*Dec.*	*Jan.*	*Feb.*	*March*	*April*	*May*	*June*	*July*	*Regional Aevrages ± S.D*
I	45	34	55	43	180	70	26	35	17	30	32	11	48.2 – ± 44.5
II	41	44	76	239+	156	70	46	46	17	19	26	10–	65.8 + ± 67.0
III	62	58	32	186	155	112	27	38	14	30	20	17	62.6 ± 58.0
IV	69	42	25	131	98	166	55	88	21	13	22	61	62.2 ± 49.7
Monthly averages S.D ±	54.3 ± 13.4	44.5 ± 10	47.0 ± 23	149.8 + ± 83.7	147.3 ± 34.8	104.5 ± 45.5	38.5 ± 14.3	51.8 ± 24.6	17.3 ± 2.9	23.0 ± 9	25.0 ± 5	13.5 ± 3.5	59.68 ± 7.85
Feeding Canal	42	29	12–	51	72+	44	45	51	20	28	66	-	41.8 ± 18.4

The annual mean for the study period was 31.53 ± 2.23 mg.l^{-1}. The monthly distribution in the Feeding Canal showed that the main supply of TSM to the lake was not the Feeding Canal, as its values did not exceed the monthly averages in the lake in most months (Table 2).

Total Particulate Zinc (TPZn)

The absolute values varied widely from 11 μg.l^{-1} at station III in September to 1432 μg.l^{-1} at station I in April. The regional averages varied from 132.5 ± 77.0 μg.l^{-1} at station IV to 243.8 ± 3.84.7 μg.l^{-1} at station I. The seasonal averages ranged very widely from 18.0 ± 8.3 μg.l^{-1} in September to 666.5 ± 541.0 μg.l^{-1} in April. The overall and highest values in the Feeding Canal followed the seasonal averages in the lake in the same months. The overall mean for the Feeding Canal (131.45 ± 91.0 μg.l^{-1}) was noticedably lower than that for the lake (Table 3).

Table 2: Monthly Variations of Total Suspended Matter (mg.l^{-1}) in the Hydrodrome and its Feeding Canal

Stations	*Aug.*	*Sept.*	*Oct.*	*Nov.*	*Dec.*	*Jan.*	*Feb.*	*March*	*April*	*May*	*June*	*July*	*Regional Verages ±S.D*
I	2	3.0	16	28.0	12.0	23.1	33	76	52	28	12	48	28.3– ±21.0
II	6	2.5	28	26.7	19.2	15.4	55	52	72	64	24	20	32.0 ±22.9
III	2	1.1–	5	37.5	25.0	23.1	40	100+	56	24	20	56	32.5 ±28.3
IV	2	3.3	10	26.7	23.1	23.1	40	88	68	28	28	60	33.4+ 26.4±
Monthly averages ±S.D	3 ±2	2.5– ±1	15 10±	30.0 ±5	20.0 ±6	21.2 ±4	42 9±	79+ ±21	62 10±	36 19±	21 ±7	46 ±18	31.53 ±2.23
Feeding Canal	4.3	3.3–	10	7.5	8	42	4	64	76+	12	8	-	21.65 ±26.35

Table 3: Monthly Variations of Total Particulate Zinc (μg.l^{-1}) in the Hydrodrome and its Feeding Canal

Stations	*Aug.*	*Sept.*	*Oct.*	*Nov.*	*Dec.*	*Jan.*	*Feb.*	*March*	*April*	*May.*	*June*	*July*	*Regional averages ±S.D*
I	17	30	61	154	181	217	339	140	1432+	164	63	125	243.8+ ±384.7
II	52	15	211	116	122	125	295	133	653	113	87	83	167.1 ±169.2
III	15	11–	29	175	189	193	238	115	359	269	142	127	155.2 ±105.9
IV	14	16	53	189	146	202	204	116	222	221	96	111	132.5– ±77.0
Monthly averages ±S.D.	24.5 ± 18.4	18.0– ± 8.3	88.5 ± 82.8	158.5 ± 31.8	159.5 ± 31.2	184.3 ± 40.7	269.0 ± 60	126.0 ± 13	666.5+ ± 541	192.5 ± 67.4	97.0 ± 33	111.5 ± 20.3	174.65 ± 148.30
Feeding Canal	22	16	29	72	143	207	240	214	268^{+}	110	125	–	131.45 ± 91.00

DISCUSSIONS

Total Dissolved Zinc (TDZn)

The optimum growth of phytoplankton is dependent on the aquatic supply of certain trace elements, such as zinc plus other major elements essential for productivity (Ahdy, 1982). The zinc in aquatic environment may be either adsorbed onto TSM and bottom sediments or desorbed and stay in dissolution form available to consumption by organism. The competition between these two major systems governs the dissolution of trace metals between the solid and aqueous phases.

The high amounts of TSM in the lake water affect the TDZn distribution. The metal behavior is also governed by variations in pH values, affecting adsorption/desorption processes. The annual mean concentration of TDZn found by Ahdy (1982) in the Hydrodrome for samples collected in 1979 ($8.1\ \mu g.l^{-1}$) was about seven times lower than the present overall mean ($59.68 \pm 7.85\ \mu g.l^{-1}$), reflecting the accumulation of zinc in the lake with progress of time. Also the annual mean values of TDZn in most other Egyptian water bodies were markedly lower than the present overall mean, confirming the effect of heavy metal pollution on the Hydrodrome.

The maximum regional average TDZn value was not observed at station I near the Feeding Canal as expected, but at station II (breeding duck area). This might be attributed to the erosion factors working on the large floating metallic construction for the breeding process, the paints used to protect this construction, the effect of fishing boats anchoring there and the large amount of organic matter derived from the duck wastes containing dissolved zinc.

The minimum monthly average value of TDZn in April coincided mainly with zinc consumption by phytoplankton abundant in spring. Zinc seems to have an established biochemical role and sounds likely that the patchiness of its distribution has a biological origin. The well documented correlation between chlorophyll a and TDZn is below as a statistical regression equation:

Chlorophyll-a $mg.m^{-3} = 21.3 \pm 1.7 - (0.05 \pm 0.02)$ TDZn $\mu g.l^{-1}$ ($r = -0.298, p < 0.04$).

When dissolved zinc is substituted by zero in the equation, chlorophyll-a still has a calculated value ($21.3 \pm 1.7\ mg.m^{-3}$). Bruland (1980) stated that zinc is removed as trace constituent by some biogenic carrier phase. Cole (1979) mentioned that zinc is an important requirement in photosynthesis, as an agent in hydrogen transfer.

The TDZn content in the Hydrodrome and its Feeding Canal was always lower than the TPZn, except in August and September. This illustrates the increase in TDZn in the Feeding Canal in these two months.

Total Suspended Matter (TSM)

Clay minerals are the most common component of TSM. The rest is from biogenic origin, living (bacteria, fungi and plankton) and dead (detritus). In TSM the amount of organic matter is comparable or even exceeds that of the organic particulate matter. The composition of TSM reflects its different sources; autochthonous and/or allochthonous.

The zonal distribution of TSM was rather limited, giving a minimum regional average value in front of the Feeding Canal discharges and the maximum in front of the outlet. This canal seemed to be not the main source of TSM to the lake, as its annual average TSM value was lower than the overall mean for the lake (Table 2).

The monthly distribution of TSM in the lake and its Feeding Canal showed that the TSM of this canal exceeded the TSM of the lake only in January and April (Table 2).This proves the existence of an alternative source of TSM for the lake. The peaks in March, April and July confirm the biogenic origin of TSM when vegetation was abundant.

Total Particulate Zinc (TPZn)

Suspended particles in the lake are one of the main pathways by which various dissolved ions may be removed from the water to be incorporated into the lake sediments. The nature and the characteristics of these particles determine to a large extent the type and composition of the sediments. Many other factors affect removal of dissolved ions from the water, such as temperature, chlorosity, particle size, concentration of ions and amount of suspended particles.

The strong positive significant correlation existed between TPZn and TSM ($r = 0.808$, $p < 0.001$) explained the definite contribution shared by TPZn in building up the TSM. Statistical analysis yielded a +ve regression equation between TSM and TPZn in the lake;

TSM $= 24.483 \pm 4.27 + 0.04 \pm 0.02$ TPZn
($r = 0.354, p < 0.013$).

Abdel-Moati pointed that the metal dynamic in the Northern Nile Delta lakes, including the Hydrodrome, is governed by some processes; mostly input from the drainage feeding waters, bottom generation and biological activities of aquatic organisms.

The TPZn dominated in the lake waters giving about 75% of the total zinc concentration. The highest absolute TPZn concentration scored in April in front of the feeding water discharges resulted from the manifold garbage wastes and litter thrown to the uncovered Feeding Canal in that month.

The earlier annual mean value obtained from the study area by Ahdy (1982) was obviously lower than the present overall mean, confirming metal pollution during recent years.

Most of the zinc content in the Hydrodrome, especially the inorganic forms, reached its water trough the anthropogenic sources dumping into the Feeding Canal. The averages and means TPZn in the present study were markedly higher than those found before 12 years from the same lake (Ahdy, 1982) and also from other Egyptian waters bodies, confirming the considerable influence of metal pollution in recent years.

REFERENCES

Abdel-Moati, M.A.R. (1985). "Studies on the chemistry of Lake Manzalah waters, Egypt". *PhD Thesis*, University of Alexandria, Alexandria, Egypt.

Ahdy, M.H (1982). "Distribution of heavy metals in Lake Mariut and the Nozha Hydrodrome and their accumulation in the fish". *MSc Thesis*, University of Alexandria, Alexandria, Egypt.

Bruland, K.W. (1980). "Oceanographic distribution of cadmium, zinc nickel and copper in the North Pacific". *Earth, Planetary Sci., Lettr*, 47: 176–198.

Chester (2000). "*Marine Geochemistry*". 2nd Edit. Black Well Science Ltd.

Cole, G.E. (1979). "*Text book of Limnology*". 2nd edit. C.V. Mosby Comp.

De Haan, F.A.M., Van Riemsdijk, W.H. and Van der Zee, S.E. (1993). "General concepts of soil quality": In Eijsackers, Hamers T., H.G.P. (Eds.). *Integrated soil and sediments research: A Basis for copper protection.* Kluwer Acad. Dordrecht.

GESAMP/UNESCO (1994). "Anthropogenic influences on sediments discharges to the coastal zone and the environmental consequences". *Report and Studies* 52, 4–30.

Gueguen, C., Gilbin, R., Pardos, M. and Dominik, J. (2004). "Water toxicity and metal contamination assessment of a polluted water: The Upper Vistula River (Poland)". *Applied Geochemistry* 19, 153–162.

Scoullos, M. (1980). "Dissolved and particulate zinc in a polluted Mediterranean Bay". *Ves. Journees Etud. Pollut. C.I.E.S.M.* 483–488.

Tessier, A., Campbeil, P.C. and Bisson, M. (1979). "Sequential extraction procedure for the speciation of particulate trace metals". *Anal. Chem.*, 51(7), 844–850.