

## Chemical Assessment of Wadi El-Rayan Lakes-Egypt

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**Abstract:** Wadi El-Rayan depression (southwest of Cairo in the western desert of Egypt) holds two man-made lakes and created as a reservoir for agricultural wastewater. This work presents an attempt to declare the status of water quality including anions, cations, nutrient salts and trace metals (Cd, Pb, Cu, Zn and Fe), besides concentrations of the selected trace metals, organic matter, carbonate and exchangeable nutrient in the lake's sediments. Results revealed that, the major ion ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ) concentrations in the 1<sup>st</sup> lake (588, 452, 401 and 88.82 mg lG<sup>l</sup>, respectively) are less than the 2<sup>nd</sup> (2613, 1018, 796.7 and 393.4 mg lG<sup>l</sup>, respectively) and the condition was governed mainly by; the intrusion of drainage water through El-Wadi Drain. In the 2<sup>nd</sup> lake, the rate of evaporation and the amount of water discharged from the 1<sup>st</sup> are the main factors control these concentrations. Elevated concentrations of trace metals in water and sediments were recorded and often associated with the impacts of urbanization, where site 1 showed the highest average values ( $\mu\text{g gG}^l$ ) of Mn (1560), Zn (369), Cu (91), Pb (81) and Cd (23) in lakes sediment. It was concluded that the discharged wastewaters via El-Wadi Drain contain compounds that can have a detrimental impact on the lakes environment and cause rapid increase in the salinity level, particularly at the 2<sup>nd</sup> lake.

**Key words:** Water quality % Nutrient salts % Trace metals % Lake sediment % Wadi El-Rayan Lakes

### INTRODUCTION

The lakes-wetland complex is a spatially and temporally dynamic system in which the water quality of lakes depends on both weather conditions and polluting parameters. Wadi El-Rayan lakes receive the agricultural wastewater drainage from El-Wadi Drain and vary in their physical and chemical characters [1]. The first Wadi El-Rayan lake is less saline (1.4-1.5 g lG<sup>l</sup>) than the second one (4.5-6.1 g lG<sup>l</sup>), where the salinity increases southward. As a result of increased human activities and the expansion in agriculture, this virgin wetland will be salinized in a much shorter period [2].

Excess nutrient supplies from increased sedimentation due to changes in land use, atmospheric deposition, agricultural fertilizer runoff and other anthropogenic sources, can have adverse effects on wetland ecosystems [3]. Responses may include changes in carbon storage and nutrient retention [4] and shifts in plant community composition [5]. These responses are likely to depend on the magnitude and characteristics of the inputs and the nature of ecosystem nutrient limitation [3]. Internal nutrient loading is therefore important to consider when determining the trophic condition of a

water body [6]. It was reported that, the concentration of common anions in the two lakes water was not significantly different than that reported earlier [7,8], except an increased levels of cyanide and cadmium, indicating human wastes contamination. Nutrients concentrations are higher in the first lake than in the second one [8-10]. This was concurrently with phytoplankton abundance [11,12].

Recent years have witnessed significant attention being paid to the problems of environmental contamination by a wide variety of chemical pollutants, including the trace metals [13]. Trace metal concentrations in the water column is relatively low, but the concentrations in the sediment may be elevated. Low level discharges of a contaminant may meet the water quality criteria, but long-term partitioning to the sediments could result in the accumulation of high loads of pollutants [14]. In same time, it was reported that the second lake of Wadi El-Rayan wetland was more contaminated by trace metals and pesticides than the first [2], where pollutants from agricultural waste including pesticides and fertilizers as well as other effluents of industrial activities and runoffs certainly will pass into the biotic elements of the ecosystem.

The principal objectives of the present study are: 1) examination of the chemical status of the water and sediment in the study area through the quantitatively determination of macro and microelements beside the nutrient salts; 2) studying the impacts of urban development and human interaction on the water and sediment quality; 3) investigation of the water chemistry in the El-Wadi Drain discharged into the 1<sup>st</sup> lake water to assess the level of environmental pollution.

## MATERIALS AND METHODS

**Sampling Site Description:** Wadi El-Rayan is a great depression (703 km<sup>2</sup>) situated in the Western Desert, 40 km southwest of El-Fayum Province. Since 1973, the depression has been used as a water reservoir for agricultural drainage water exceeding the capacity of Lake Qarun. Nowadays, it holds two main lakes, at different elevations, connected by swampy channel. They lie between 30° 20' - 30° 25' E and 29°05' - 29°20' N (Fig. 1).

The first lake of Wadi El-Rayan covers an area of about 53 km<sup>2</sup> at 10 m below the sea level and receives frequent effluent of wastewater from El-Wadi Drain (about 200 million cubic meters of agricultural drainage water are transported annually) [15]. It is completely filled with water and is surrounded by dense vegetation [16]. The surplus water from this lake floods to the second one via the shallow connecting channel.

The 2<sup>nd</sup> lake is larger than the first one (110 km<sup>2</sup> at 18 m below the sea level) with maximum water depth recorded is 33 m. It is changing all the time, where newly flooded areas are continuously added at the southwestern side of the lake. The inflow water to the second lake varied from  $3.66 \times 10^6 \text{ m}^3$  in July to  $17.68 \times 10^6 \text{ m}^3$  in March with a total annual of  $127.2 \times 10^6 \text{ m}^3/\text{year}$  [17].

**Sampling and Analysis:** Seasonal water and sediments samples were collected at six sites, representing different habitats of the lakes during the period from February (winter) to November (autumn) 2006. Six sites (1, 2 & 3) and (4, 5 & 6) were chosen to represent the 1<sup>st</sup> and 2<sup>nd</sup> lake, respectively (Fig. 1). The water samples were collected from the surface at all sites except for 2 and 5 (characterized by high depth), both surface (2S and 5S) and bottom (2B and 5B) water were sampled. The water samples were filled in glass bottles and kept cool on the spot. Sediment samples were collected using an Eckman sampling device. At each site three sub-samples of water and sediments were collected and mixed, to ensure that the sample was representative for this site. The sediments were put in air-sealed plastic bags and kept cool in the

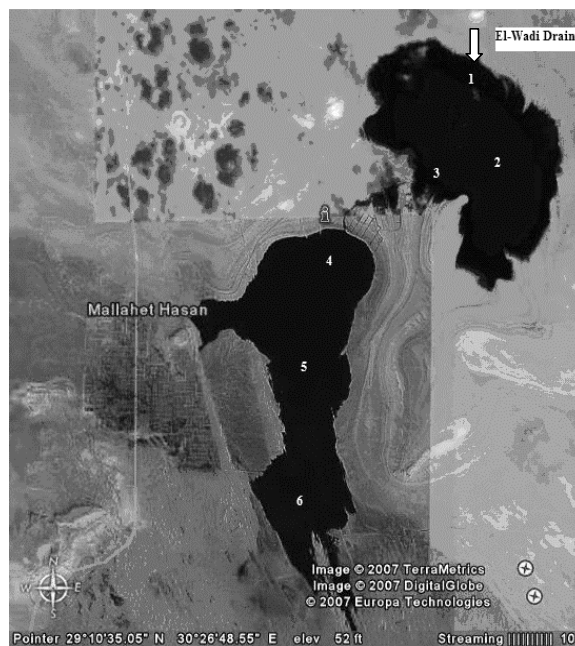


Fig. 1: Map of Wadi El-Rayan Lakes showing sampling sites

field. One additional surface water sample from El-Wadi Drain was collected to study its impacts on the lakes environment.

**Field Measurements:** The electrical conductivity (EC) was measured using a conductivity meter (S.C.T.33 YSI), transparency by Secchi disc, pH by Orion Research Ion Analyzer 399A pH meter and water temperature by an ordinary thermometer.  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  were measured titrimetrically on the spot. Also, dissolved oxygen content (DO) was determined by azide modification method as specified in APHA [18].

**Water Analysis:** Water samples were analyzed for all selected variables, according to procedures specified in APHA [18]. Chemical oxygen demand (COD) was performed by potassium dichromate oxidation and biochemical oxygen demand (BOD) by 5 days incubation methods. Chloride was determined by argentometric and sulphate by gravimetric methods. Sodium and potassium were measured directly using the flame photometer model JENWAY PFP, U.K. Calcium and magnesium were determined by EDTA titrimetric method. Concentrations of nitrite, nitrate, ammonia, orthophosphate (ortho-P) and reactive silicate in water were determined using the colorimetric techniques with formation of reddish purple azo-dye, Cd reduction, phenate, stannous chloride

reduction and molybdosilicate methods, respectively. Total phosphorus (total-P) was measured as reactive phosphate after persulphate digestion. Total Fe, Mn, Zn, Cu, Pb and Cd in water were measured after digestion using an atomic absorption reader (Perkin Elmer 3110 USA) with graphite atomizer HGA-600.

**Sediment Analysis:** For total metals, sediment samples were allowed to defrost, then were air-dried in a circulating oven at 60°C. A total digestion for one gram sediment was carried out according to the method of Jackwerth and Würfels [19]. The solutions were directly analyzed for total Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Fe, Mn and Zn by atomic absorption spectrophotometry (Perkin Elmer 3110 USA), while total Cu, Pb and Cd were analysed by atomic absorption with a graphite atomizer (HGA-600). The organic matter (OM) content was determined by oxidation with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in acidic media [20]. The carbonate content was determined by the method described in ASA [21]. The concentrations of exchangeable ammonia, nitrite and nitrate were measured using the KCl extraction and

quantified directly by indophenol blue, modified Griess-Hosvay and hydrazine-CuSO<sub>4</sub> reduction methods, respectively according to ASA [21].

**Statistical Analysis:** Data of water and sediments samples were tested for significant differences for all variables among different seasons and sites by means of one-way ANOVA. Also the relationship between the different studied variables were assigned by computing the correlation coefficients (r) using Microsoft Excel (2003).

## RESULTS

**Physical and Chemical Properties of Water:** Water temperature exhibited little variance between the sites and reflected the air temperatures, it is varied between 14.18 in December to 28.83 °C in August. The water of the 2<sup>nd</sup> lake was more transparent than the first one; the entrance of the both lakes (sites 1 & 4) sustained the lowest transparency values (Table 1). The pH values were always

Table 1: Ranges of the physical and chemical variables in Wadi El-Rayan Lakes water

Variable	Winter		Spring		Summer		Autumn	
	1 <sup>st</sup> lake	2 <sup>nd</sup> lake	1 <sup>st</sup> lake	2 <sup>nd</sup> lake	1 <sup>st</sup> lake	2 <sup>nd</sup> lake	1 <sup>st</sup> lake	2 <sup>nd</sup> lake
EC (mS cmG <sup>-1</sup> )	2.86-3.04	10.28-14.16	2.66-2.95	12.22-16.20	2.20-2.70	6.50-17.60	245-2.68	6.69-13.82
Transparency(cm)	65-170	80-295	65-175	90-275	80-170	60-300	70-175	110-270
TS (g lG <sup>-1</sup> )	1.68-2.22	8.01-11.99	1.85-1.93	8.98-11.74	1.83-1.87	8.64-11.69	1.86-1.99	6.46-11.80
TDS (g lG <sup>-1</sup> )	1.53-1.94	7.28-11.69	1.63-1.70	8.75-11.46	1.75-1.76	7.50-11.44	1.71-1.75	5.58-11.31
pH	8.32-8.53	8.21-8.42	8.40-8.47	8.19-8.21	8.26-8.33	8.26-8.33	8.10-8.47	7.98-8.35
DO (mg lG <sup>-1</sup> )	10.23-11.60	9.40-13.40	7.60-10.40	9.60-12.00	4.40-9.80	8.40-10.40	10.10-12.10	8.92-13.52
COD (mg lG <sup>-1</sup> )	8.22-9.29	4.62-5.32	6.00-8.00	7.60-8.80	4.36-6.12	3.52-5.08	6.52-8.84	3.92-7.64
BOD (mg lG <sup>-1</sup> )	4.68-4.82	3.96-4.69	3.40-4.30	2.40-4.00	3.40-4.92	2.08-4.80	4.68-5.72	2.76-5.52
CO <sub>3</sub> <sup>2-</sup> (mg lG <sup>-1</sup> )	17.20-20.00	16.20-24.20	16.00-36.00	20.00-44.00	4.00-28.00	8.00-28.00	16.00-20.00	12.00-24.00
HCO <sub>3</sub> <sup>-</sup> (mg lG <sup>-1</sup> )	152.0-158.0	127.8-204.0	128.0-152.0	172.0-328.0	136.0-172.0	152.0-168.0	152.0-164.0	152.0-172.0
Cl <sup>-</sup> (g lG <sup>-1</sup> )	0.729-0.886	1.884-2.961	0.450-0.535	1.110-1.400	0.510-0.530	1.250-3.299	0.449-0.529	2.275-4.540
SO <sub>4</sub> <sup>2-</sup> (g lG <sup>-1</sup> )	0.212-0.231	0.509-0.614	0.505-0.575	1.134-1.252	0.480-0.507	0.817-1.262	0.419-0.606	1.012-1.237
Na <sup>+</sup> (mg lG <sup>-1</sup> )	500.1-529.0	752.30-887.64	335.13-434.76	746.34-841.50	326.07-407.59	483.07-820.61	324.26-405.78	601.42-827.86
K <sup>+</sup> (mg lG <sup>-1</sup> )	19.16-21.65	64.25-96.25	18.92-24.42	62.70-80.30	16.50-22.00	33.00-71.50	16.50-22.44	44.00-68.64
Ca <sup>2+</sup> (mg lG <sup>-1</sup> )	52.14-66.3	88.18-144.29	48.10-52.1	152.3-176.35	33.67-44.89	109.32-126.95	44.09-56.11	104-168.34
Mg <sup>2+</sup> (mg lG <sup>-1</sup> )	48.62-82.65	277.13-377.2	75.36-87.52	254.93-393.82	71.47-75.85	217.33-495.44	121.55-158.02	272.27-505.65
NO <sub>3</sub> <sup>-</sup> (µg lG <sup>-1</sup> )	46.38-89.25	24.36-39.96	18.86-92.57	14.86-26.86	15.43-20.57	20.57-61.42	29.14-109.14	13.14-36.00
NO <sub>2</sub> <sup>-</sup> (µg lG <sup>-1</sup> )	33.25-62.34	6.05-17.38	13.22-132.23	10.20-13.60	2.27-11.33	5.67-90.34	12.09-26.07	7.56-16.25
NH <sub>3</sub> (µg lG <sup>-1</sup> )	425.3-801.6	198.2-310.5	345.0-1014.0	168.0-402.0	216.0-1740.0	69.0-222.0	597.0-861.0	180.0-498.0
Ortho-P (mg lG <sup>-1</sup> )	0.084-0.137	0.051-0.062	0.088-0.158	0.071-0.104	0.085-0.159	0.055-0.084	0.102-0.192	0.048-0.096
Total-P (mg lG <sup>-1</sup> )	0.529-2.254	0.283-0.567	0.400-0.639	0.369-0.556	0.344-0.721	0.434-0.859	0.308-0.409	0.205-0.446
SiO <sub>3</sub> <sup>2-</sup> (mg lG <sup>-1</sup> )	1.60-2.88	2.65-3.83	3.32-5.79	5.38-9.16	4.25-4.57	3.55-5.06	0.47-1.42	1.60-2.33
Fe (µg lG <sup>-1</sup> )	315-831	380-822	361-1502	465-828	275-767	323-387	345-422	340-493
Mn (µg lG <sup>-1</sup> )	32-122	30-104	39-102	55-154	15-65	30-50	22-57	42-54
Zn (µg lG <sup>-1</sup> )	44.0-96.1	52.0-100.0	72.0-81.0	56.0-98.0	29.1-40.0	35.2-48.0	45.0-98.2	55.0-69.0
Cu (µg lG <sup>-1</sup> )	11-24	13-19	43-70	59-73	8-10	18-23	24-54	44-52
Pb (µg lG <sup>-1</sup> )	45-86	47-83	110-135	93-129	38-80	64-97	95-129	82-136
Cd (µg lG <sup>-1</sup> )	8-15	9-20	22-53	39-71	11-20	11-24	19-51	51-61

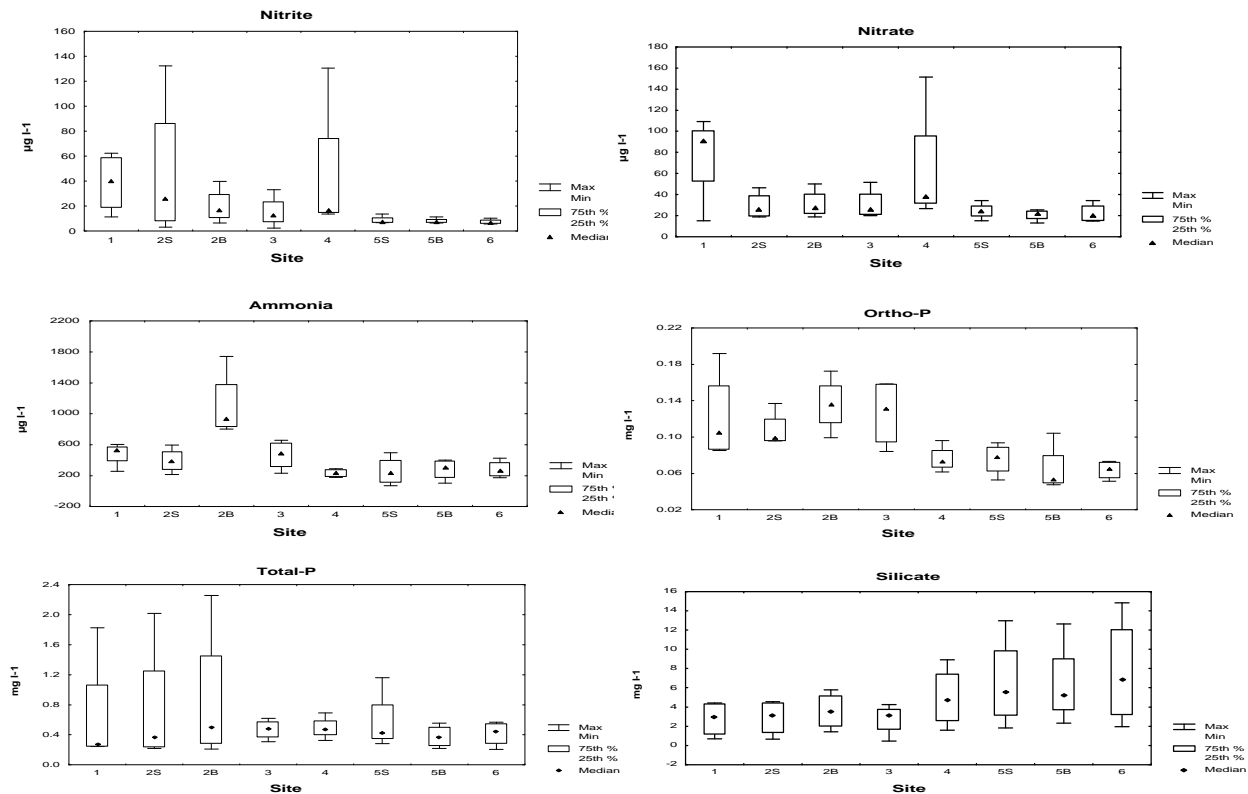


Fig. 2: Multiple box and whisker plots of nutrient salts in lakes water. The central box covers the middle 50% of the data values, between the lower and upper quartiles, while the central point represents the median

in the alkaline side with small local differences without seasonal variations. There was an observed increase in EC, TDS and TS in the 2<sup>nd</sup> lake in comparison with the 1<sup>st</sup> one. In the 2<sup>nd</sup> lake the TDS and TS were usually low in the northern area (site 4). The minimum values of DO were recorded in the bottom samples of the deepest stations of the two lakes (2B, 5B). The COD and BOD showed high values in the 1<sup>st</sup> lake compared with the 2<sup>nd</sup>, with significant ( $P < 0.05$ ) seasonal variations at the both lakes. The anions analysis, showed high chloride and sulphate concentrations in comparison with carbonate and bicarbonate (Table 1). The carbonate values showed large amplitude with random distribution along different seasons and sites. The dominant anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) and major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) showed higher concentrations in the 2<sup>nd</sup> lake than the 1<sup>st</sup> and governed mainly by the intrusion of drainage water through the El-Wadi Drain. On a mass basis, the sodium ion was the dominant cation contribute 71 & 57% for 1<sup>st</sup> and 2<sup>nd</sup> lakes, respectively, followed by  $\text{Mg}^{2+}$  (16 & 28 %) and  $\text{Ca}^{2+}$  (9 & 10%), while  $\text{K}^+$  showed the less percentage (4 & 5%).

The average concentrations of ortho-P, nitrite, nitrate and ammonia in the 1<sup>st</sup> lake sites showed slight increase compared with the 2<sup>nd</sup> lake (Fig. 2). Conversely, the concentrations of silicate showed high values in 2<sup>nd</sup> compared with the 1<sup>st</sup> lake; relatively increase during hot seasons in the two lakes. The variations in Fe concentration showed irregular distribution patterns among sites and seasons for the 1<sup>st</sup> lake, where the maximum values were recorded at the surface of site 2 (1502  $\mu\text{g l}^{-1}$ ) in spring. Mn concentrations showed significant ( $P < 0.05$ ) seasonal trends in the six sites with slight increase in spring especially in the 2<sup>nd</sup> lake, where, the maximum values were recorded in surface and bottom water at site 5 (154 and 153  $\mu\text{g l}^{-1}$ , respectively). Zinc concentrations showed a wide range of variations, where sites 1 (40.0-98.2  $\mu\text{g l}^{-1}$ ) and 4 (48.0-100.0  $\mu\text{g l}^{-1}$ ) maintained the highest values. Copper and lead showed a wide range of variations with high significant ( $P < 0.01$ ) seasonal trends. The two elements showed the highest values in spring and autumn. The average cadmium concentrations for all sites showed high values in the 2<sup>nd</sup> lake with significant ( $P < 0.05$ ) seasonal variation compared with the 1<sup>st</sup>.

Table 2: Summary of sieve test results for Wadi El-Rayan Lakes sediment samples

Site	Depth (m)	Gravel* %	Very coarse	Coarse	Medium	Fine	Very fine	Mud* %	Nomenclature
			sand*%	sand*%	sand*%	sand*%	Sand*%		
1	4.5	1.60	0.70	0.30	0.91	10.20	26.69	59.60	Gravelly sandy mud
2	15.0	0.00	0.00	0.00	0.70	5.46	32.46	61.38	Sandy mud
3	5.0	2.70	5.78	16.03	30.01	22.49	12.27	10.72	Gravelly muddy sand
4	6.0	0.00	0.00	0.00	0.00	19.05	31.44	49.51	Muddy sand
5	21.0	0.82	0.60	0.40	4.20	22.10	29.88	42.00	Gravelly muddy sand
6	8.0	15.40	3.18	13.06	32.09	24.68	7.48	4.11	Muddy gravelly sand

\* Personal communication with Mr. Hassan Farahat (NIOF)

Table 3: Site variations of the studied variables in Wadi El-Rayan Lakes sediment

Variable	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD
		n=4		n=4		n=4		n=4		n=4		n=4
OM (%)	9.26-11.03	9.88±0.82	4.76-8.68	7.49±1.83	1.35-6.08	3.97±2.26	4.59-7.30	5.72±1.32	2.18-8.46	5.32±2.59	0.55-2.27	1.56±0.84
Carbonate (%)	21.36-30.24	26.64±3.87	29.18-43.57	36.15±6.83	22.54-42.30	32.41±9.61	25.74-33.24	29.63±3.08	21.46-28.72	24.89±3.07	19.67-29.11	24.14±3.90
NO <sub>3</sub> (µg gG <sup>1</sup> )	2.31-6.23	3.84±1.75	2.74-5.89	4.55±1.45	9.06-15.37	12.98±2.90	6.89-26.00	12.71±8.92	2.03-11.00	5.16±4.10	2.46-16.17	8.04±5.79
NO <sub>2</sub> (µg gG <sup>1</sup> )	0.340-0.453	0.397±0.056	0.397-1.492	0.845±0.484	0.302-2.569	1.185±0.992	0.264-1.326	0.752±0.442	0.189-1.039	0.482±0.389	0.302-0.718	0.523±0.172
NH <sub>3</sub> (µg gG <sup>1</sup> )	103.9-339.2	241.7±116.0	101.9-318.4	208.2±102.0	72.8-235.1	153.7±81.1	74.5-238.4	160.2±83.2	83.9-248.3	170.9±83.4	31.4-142.4	86.7±46.8
Na <sup>+</sup> (mg gG <sup>1</sup> )	20.35-34.00	28.58±6.06	20.35-35.34	29.18±6.45	25.70-34.27	31.06±3.71	23.56-42.84	32.93±9.23	20.35-49.26	31.24±12.65	21.25-40.25	29.83±8.02
K <sup>+</sup> (mg gG <sup>1</sup> )	4.27-8.50	5.88±1.84	3.59-8.08	6.27±1.90	4.05-12.07	7.90±3.34	3.04-11.98	7.28±4.00	3.96-12.13	7.09±3.70	3.00-6.67	4.47±1.58
Ca <sup>2+</sup> (mg gG <sup>1</sup> )	113.0-245.0	162.5±62.1	129.9-490.0	264.8±160.9	126.7-270.0	215.3±64.0	108.0-413.2	239.8±148.2	97.0-284.4	169.2±83.9	104.9-177.1	140.4±38.2
Ba <sup>2+</sup> (mg gG <sup>1</sup> )	34.44-45.33	40.87±4.99	48.66-97.21	69.80±20.65	46.66-61.11	53.61±6.50	52.77-68.33	60.27±6.92	30.25-68.88	47.14±16.21	27.78-54.44	40.00±13.14
Fe (mg gG <sup>1</sup> )	2.525-2.996	2.834±0.215	2.510-2.960	2.729±0.187	1.876-2.777	2.446±0.396	2.436-2.895	2.723±0.200	1.388-2.995	2.502±0.752	1.258-2.458	1.900±0.517
Mn (µg gG <sup>1</sup> )	868-1560	1197.5±315	593-1179	779.3±273.9	515-659	602.0±67.3	433-1010	658.8±260.1	424-990	646.8±256.5	99-391	198.3±134.6
Zn (µg gG <sup>1</sup> )	96-369	250.3±135.5	86-344	161.8±122.5	55-314	139.8±119.1	86-177	135.3±39.1	49-166	131.5±55.8	28-152	76.0±57.2
Cu (µg gG <sup>1</sup> )	47-91	71.5±18.6	30-44	36.3±6.1	19-31	25.3±5.7	15-58	33.0±19.6	14-46	28.3±13.7	9-14	11.3±2.2
Pb (µg gG <sup>1</sup> )	17-95	60.8±34.7	17-66	42±21.5	9-35	23.5±11.0	11-56	37.8±19.1	10-68	38.8±23.7	9-40	28.8±13.8
Cd (µg gG <sup>1</sup> )	4-23	11.0±8.4	4-19	9.0±6.8	3-10	5.8±3.0	3-9	6.5±2.5	2-8	6.0±2.8	2-8	5.5±2.6

**Sediment Analysis:** Sand and finer materials were predominated along most sites of the two lakes, except for the south side of the 2<sup>nd</sup> lake (Table 2).

The amount of OM present in sediment samples varied spatially ( $P < 0.01$ ) throughout the catchment's. OM content recorded high values at the entrance of El-Wadi Drain effluent, where the average values varied from 3.97 % (site 3) to 9.88 % (site 1) in the 1<sup>st</sup> lake. Carbonate content for lake sediment showed significant ( $P < 0.05$ ) temporal variations and some spatial variation ( $P = 0.084$ ), where summer and autumn showed the highest values. The average carbonate concentration showed higher values in the 1<sup>st</sup> lake in compared with the 2<sup>nd</sup> lake (Table 3). Higher values of nitrate ( $< 10 \mu\text{g gG}^1$  for most sites) are recorded in the lakes sediment than nitrite and showed significant ( $P < 0.05$ ) site variations with some seasonality ( $P = 0.13$ ), where winter and autumn maintained the highest values. The nitrite-nitrogen concentrations are mostly very low ( $< 1 \mu\text{g gG}^1$ ) for most sites and showed significant ( $P < 0.05$ ) seasonal trends, where winter and spring registered the lowest values.

The dominant species of nitrogen in lakes sediment is ammonia that shows a similar pattern to nitrite, but at overall very high levels (Table 3). Ammonia showed high significant ( $P < 0.01$ ) seasonal trends with concentration maxima usually recorded at site 1. The lakes sediments are slightly enriched in Ca<sup>2+</sup>, Ba<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>. Significant differences ( $P < 0.05$ ) were found for levels of Ca<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> between the seasons. Generally the highest values of Na<sup>+</sup> and K<sup>+</sup> were recorded during winter, while Ca<sup>2+</sup> showed maxima concentrations in hot and minima in cold seasons. By evaluating the results obtained on a mass basis, it seems that the concentrations of studied elements in Wadi El-Rayan sediment showed the proportions: Ca<sup>2+</sup> > Ba<sup>2+</sup> > Na<sup>+</sup> > K<sup>+</sup>. Gradual decrease from site 1 to 3 were noted for the levels of Mn, Zn, Cu, Pb and Cd, which showed high values in the 1<sup>st</sup> lake compared with the 2<sup>nd</sup> (Fig. 3). Fe concentrations showed some variability among sites ( $P = 0.06$ ) and seasons ( $P = 0.09$ ). Mn concentrations showed high variability among sites ( $P < 0.01$ ) with no significant seasonal variation, where the highest values were recorded in winter at the two lakes.

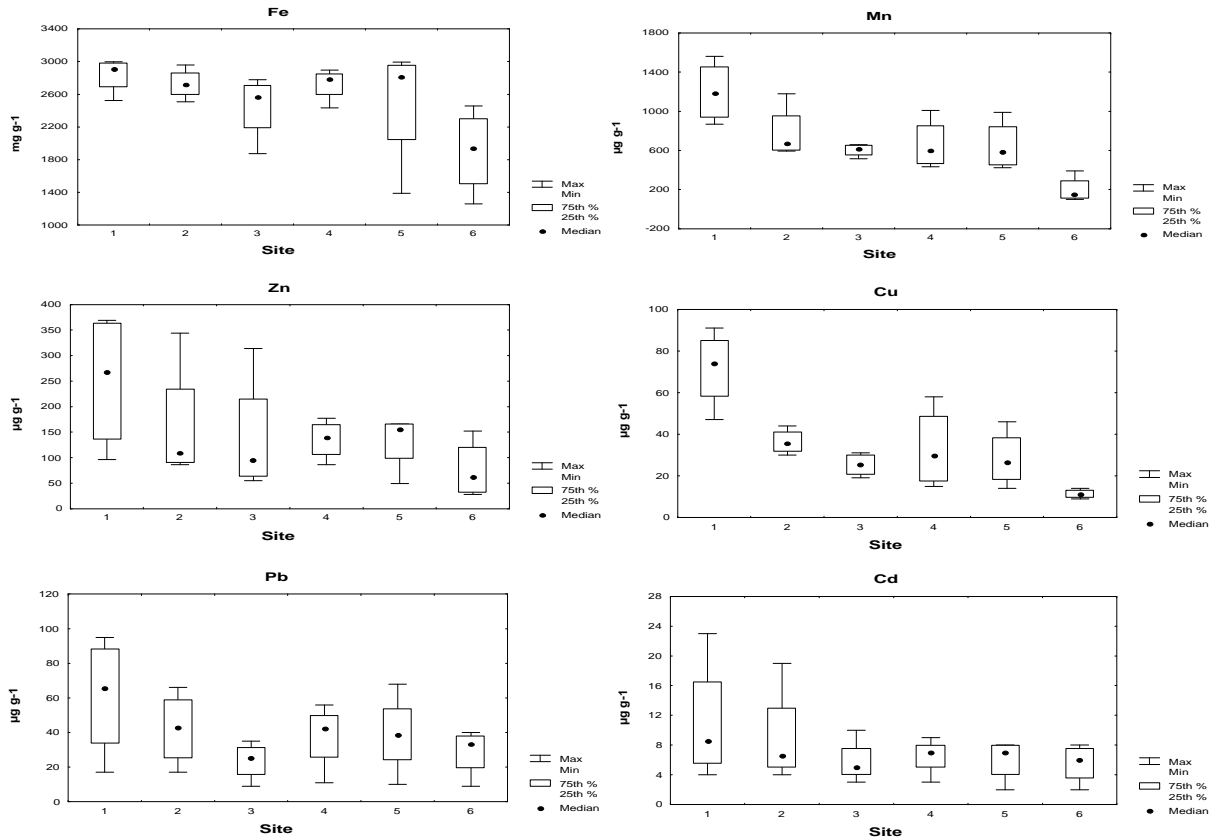


Fig. 3: Multiple box and whisker plots of trace metals in lake sediment. Details as given in Fig. 2.

Table 4: The physical and chemical variables for water samples in El-Wadi drain effluent

Variable	Winter	Spring	Summer	Autumn
TS (g l <sup>-1</sup> )	6.770	1.280	2.598	2.126
pH	8.09	8.20	7.55	8.62
DO (mg l <sup>-1</sup> )	10.00	10.4	5.6	10.62
COD (mg l <sup>-1</sup> )	6.98	7.80	6.32	6.04
BOD (mg l <sup>-1</sup> )	7.25	9.90	6.12	5.06
CO <sub>3</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	3.0	6.0	8.0	2.0
HCO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	232.0	229.0	225.0	230.0
Cl <sup>-</sup> (mg l <sup>-1</sup> )	2425	699	659	1161
SO <sub>4</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	420	722	639	536
Na (mg l <sup>-1</sup> )	870.5	260.2	431.2	361.9
K (mg l <sup>-1</sup> )	41.03	19.54	26.38	22.19
Ca (mg l <sup>-1</sup> )	234.01	152.12	89.87	195.84
Mg (mg l <sup>-1</sup> )	212.1	104.00	76.10	194.12
NO <sub>3</sub> <sup>-</sup> (µg l <sup>-1</sup> )	696.2	356.1	595.6	682.2
NO <sub>2</sub> <sup>-</sup> (µg l <sup>-1</sup> )	409.1	400.5	58.54	111.5
NH <sub>3</sub> (µg l <sup>-1</sup> )	505	1068	323	301
Ortho-P (mg l <sup>-1</sup> )	0.602	0.311	0.345	0.411
Total-P (mg l <sup>-1</sup> )	1.626	0.813	1.194	1.231
SiO <sub>3</sub> <sup>2-</sup> (mg l <sup>-1</sup> )	4.60	10.20	5.79	3.80
Fe (µg l <sup>-1</sup> )	529	1629	409	445
Mn (µg l <sup>-1</sup> )	30	65	34	39
Zn (µg l <sup>-1</sup> )	88	51	49	61
Cu (µg l <sup>-1</sup> )	33	66	25	32
Pb (µg l <sup>-1</sup> )	120	77	80	96
Cd (µg l <sup>-1</sup> )	13	9	11	14

Marked seasonal differences in sediment concentrations were exhibited by Zn and Cd at the two lakes ( $P < 0.05$ ), where autumn showed the minimum values and winter showed the maximum values. Concentration maxima usually occurred at sites 1 and minima at site 3. However, site 6 persistently had the lowest metal levels when differences in sediment texture between locations were taken into account. Cu concentrations showed high significant ( $P < 0.01$ ) site variations, but don't showed any temporal variations. The concentrations of Cu were highest at site 4 for the 2<sup>nd</sup> lake and clearly peaking at site 1 for the 1<sup>st</sup> lake. Pb showed high significant ( $P < 0.01$ ) temporal variation without spatial variation, where autumn recorded the lowest values in the two lakes.

**Water chemistry of El-Wadi Drain:** The results revealed that the effluent of El-Wadi Drain contained low total solid and sulphate values especially in winter, while chloride concentrations recorded the highest value in winter (Table 4). The pH values of the drain effluent were alkaline. However, bicarbonate showed higher values than that recorded in 1<sup>st</sup> lake, The drain effluent are slightly

enriched in  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  where the order of abundance on a mass basis was  $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ . The data from the drain effluent compared with the 1<sup>st</sup> lake data suggest a massive input of nutrients.

## DISCUSSION

A preliminary assessment of water of the two lakes showed that the concentrations of metallic and non-metallic elements in the 2<sup>nd</sup> lake water are higher than the 1<sup>st</sup>. The concentration of major cations and anions in the 1<sup>st</sup> lake are controlled by the intrusion of drainage water through El-Wadi Drain [1]. The rate of evaporation and the amount of water discharged from the 1<sup>st</sup> lake are the main factors control these concentrations in the 2<sup>nd</sup> lake [22]. Due to the increase in waste disposal to Wadi El-Rayan Lakes, TDS levels show a progressive increase, particularly at the 2<sup>nd</sup> lake. TDS had been slightly increased in the 1<sup>st</sup> lake ( $1.74 \text{ g lG}^{-1}$ ) than those recorded by Rabih [23] and Konsowa and Abd Allah [11] ( $1.52$  and  $1.43 \text{ g lG}^{-1}$ , respectively). The 2<sup>nd</sup> lake undergoes an obvious increase (average:  $10.09 \text{ g lG}^{-1}$ ) than those reported by Saleh *et al.* [8], Ramadan and El-Shabrawy [24]; Konsowa [25]; Abd Allah [17] and Abd Allah and Konsowa [12] ( $2.40$ ,  $2.50$ ,  $4.20$ ,  $4.63$  and  $5.68 \text{ g lG}^{-1}$ , respectively). Accordingly, the lakes may be salinized in a short period, particularly the second lake, which may lead to a steady change in its fauna and flora. This is confirmed by the results of El-Shabrawy [15] and Konsowa [26], who reported that the macrobenthos and phytoplankton assemblages in the 2<sup>nd</sup> Wadi El-Rayan Lake sustained great changes.

The increase in the average concentrations of ortho-P, total-P, nitrite, nitrate and ammonia in the 1<sup>st</sup> lake sites and at site 4 through the whole study period may be due to the sewage discharge from El-Wadi Drain which also, reached the 2<sup>nd</sup> lake via connecting channel. These results are in agreement with the findings of Aboul-Ela and Khalil [9]; Saleh *et al.* [8] and Abd El-Karim [22], also these finding confirmed by the finding of Konsowa and Abd Allah [11], Abd Allah and Konsowa [12] and Konsowa [26], who showed that the phytoplankton was much abundant in the 1<sup>st</sup> lake than the 2<sup>nd</sup>. Silicate showed an opposite trends, where the 2<sup>nd</sup> lake harbored the highest numerical density of diatoms than the 1<sup>st</sup> lake [26].

The water from Wadi El-Rayan Lakes appeared to have detectable concentrations of iron, manganese, zinc, copper, lead and cadmium. The obtained results indicated that the selected metals in the 2<sup>nd</sup> lake revealed higher concentrations than the 1<sup>st</sup> according to the increase in

Table 5: Water quality guidelines of metals ( $\mu\text{g lG}^{-1}$ ) for freshwater and saltwater according to USEPA [28]

Metal	Freshwater*		Saltwater		Present results	
	Chronic	Acute	Chronic	Acute	1 <sup>st</sup> lake	2 <sup>nd</sup> lake
Zn	340	340	86	86	29.1-98.2	35.2-100.0
Cu	26	44	3.7	5.8	7.5-65	13-73
Cd	5.6	17	8.8	40	8-53	9-61
Pb	9.5	240	8.5	220	38-135	47.0-136.4

\*The guidelines were calculated at total hardness  $350 \text{ mg lG}^{-1}$

salt concentration, where the competition increases between the cations and metals for binding sites on sediment and as a result metals are driven off into the overlying water [27]. These results are in agreement with the finding of Mansour and Sidky [2], who reported that the 2<sup>nd</sup> water lake was more contaminated by trace metals and pesticides than the first. The present results showed elevated zinc concentrations during all seasons at sites 1 and 4 and sometimes exceeding the chronic guideline cited by USEPA [28] for salt water (Table 5), where Zn are mainly associated with fertilizers and pesticides [29]. However, all Pb and Cd water concentrations in the two lakes showed higher levels than chronic guidelines (Table 5). All the above recorded results can often be attributed to contamination of the drainage water by the domestic municipal waste [2,30]. Where, Cd is present as an impurity in several products, including phosphate fertilizers and detergents [31]. However, many samples contained Cu concentrations exceeding the fresh and saltwater chronic guidelines. This can often be attributed to contamination of the drainage water by Cu, where the agricultural materials are considered one of the main sources of Cu [32]. Accordingly, the lakes water was polluted by trace metals and acts as a slow poison and adversely affects the ecology and thereby harming the flora and fauna and the natural inhabitat. The positive correlations ( $n=16$ ,  $P<0.05$ ) between concentrations Fe/Mn, Cu/Pb, Cu/Cd and Pb/Cd in the 1<sup>st</sup> ( $r=0.60$ ,  $0.88$ ,  $0.79$  &  $0.86$ , respectively) and 2<sup>nd</sup> lakes ( $r=0.63$ ,  $0.78$ ,  $0.88$  &  $0.87$ , respectively) indicated their common origin (agricultural pesticides) [30].

Sediments play an important role in the physical movement, chemical partitioning and biological fate of trace metals [27,33]. Since most anthropogenic contaminants (those associated with human activity) are also associated with clay and silt fractions, the establishment of elevated concentrations of trace metals in sediments can play a key role in detecting the impacts of urbanization and the sources of pollution in aquatic systems [34,35].

Table 6: Quality guidelines of metals ( $\mu\text{g g}^{-1}$ ) for freshwater and marine sediment

Metal	Freshwater (MacDonald <i>et al.</i> [41])		Marine (USEPA [40])		Present results	
	Chronic	Acute	Chronic	Acute	1 <sup>st</sup> lake	2 <sup>nd</sup> lake
Zn	123	315	124	271	55-369	28-177
Cu	35.7	197	18.7	108	19-91	9-58
Cd	0.6	3.5	0.68	4.21	3-23	2-9
Pb	35	91.3	30.2	112	9-95	9-68

The sharp decrease in OM from north to south in the two lakes is related to variations in the quantity and the ability of organic material to move with the sediment within the sedimentation process downstream. The role of OM and sediment grain size in relation to the accumulation of trace metals to the sediment has often been emphasized [36]. These were confirmed by the significant correlation ( $n=24$ ,  $P<0.05$ ) between OM and each of Fe, Mn, Zn, Cu, Pb and Cd ( $r=0.6$ ,  $0.77$ ,  $0.43$ ,  $0.76$ ,  $0.60$  and  $0.43$ , respectively). Also, the increases in trace metals concentrations tend to be associated with finer grained sediments and this can be seen in that the higher trace metals concentrations are found at the sites where finer sediments occur. These also were confirmed by the positive correlation ( $n=6$ ,  $P<0.05$ ) between each of Fe, Mn, Cu and Pb with the percent of fine sand ( $r=0.55$ ,  $0.52$ ,  $0.46$ , &  $0.33$ , respectively) and mud ( $r=0.57$ ,  $0.65$ ,  $0.63$  &  $0.43$ ).

The influence of flow of drainage effluent in the 1<sup>st</sup> lake and the amount of water released to the 2<sup>nd</sup> lake will enhance the spatial and temporal variations in sediment chemistry, with turbulence encouraging oxygenation of the sediment-water interface and influencing rates of sediment nutrient retention and release [37]. Ammonia seemed to be released in greater levels than nitrate and nitrite and clearly showing the overall reducing nature of the bottom sediments. Previous studies performed in a variety of trophic status water bodies have shown that greater amounts of nitrogen ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) are released from sediments under anaerobic conditions as compared to those of aerobic [6,38]. The present study revealed that positive correlation ( $n=24$  at  $P<0.05$ ) was exist between exchangeable ammonia and OM ( $r=0.61$ ), where the decomposition of deposited organic material releases inorganic N compounds which may be returned to the water column [3].

Based on the observed associations, iron and manganese oxides beside OM seem to be the principal carrier phases for transporting the selected metals. These

were confirmed by the significant positive correlation ( $n=24$  at  $P<0.05$ ) between each of Zn, Cu, Pb and Cd with Fe ( $r=0.54$ ,  $0.50$ ,  $0.60$ , &  $0.50$ ) and Mn ( $r=0.70$ ,  $0.91$ ,  $0.60$  &  $0.67$ , respectively). Contamination of surface sediments by trace metals is of potential ecological importance as the sediment-water interface serves as habitat for often abundant and diverse communities [39]. Toxic effects on benthic organisms resulting from trace metals pollution may alter community structure and in turn affect the aquatic ecosystem as a whole [13]. To identify chemicals of potential concern in the lakes sediments, the results were compared to sediment quality guidelines from various sources (Table 6) [40,41]. The levels of Zn, Cu and Pb in most sites exceeded those at which an adverse effect on benthic aquatic life might be expected (chronic values). However, Cd levels in most sites were an order of magnitude more than the acute value. The presence of high metals levels may originate from diffuse anthropogenic inputs from agriculture wastes which were confirmed by the increase in their average concentrations in 1<sup>st</sup> lake compared with the 2<sup>nd</sup> lake. In addition, the presence of these metals in the aquatic ecosystem has far-reaching implications directly to the biota and indirectly to man [42].

It could be concluded that the discharged wastewaters via the El-Wadi Drain contain compounds that can have a detrimental impact on the lakes environment and cause rapid increase in the salinity level, particularly at the 2<sup>nd</sup> lake. Therefore, more investigations and great efforts must be done to find solutions for minimize the increase in salinity and pollutants in this important natural protectorate.

#### ACKNOWLEDGEMENT

The authors wish to express their deepest grateful to Prof. Dr. Mohamed Basuni, Dr. Radwaan Abd-Ellah and Mr. Hassan Farahat for their kind helps.

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