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Assessment of water quality and trace metals in sediment of Southern Marshes.

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Abstract

Water quality surveys were designed and implemented during Dec.2011 to Feb. 2012 at three stations, in the Hor Al-Gebaysh, Al-Bourgah and Harer. Physical and chemical stressors including the natural water quality parameters, dissolved oxygen (DO), temperature, salinity and pH as well as nutrients were studied. The mean ranges of the following parameters were recorded: In Hammar Low value of salinity was 1.24 ppt in spring and higher was 2.11ppt in summer. Al-Bargah low value was 1.41ppt in winter and higher 2.01ppt in summer, while The lower value recorded in Al-Gebayesh was 1.12 ppt in winter but higher value was 1.98 ppt in Autum Air temperature in Al-Gebayesh the range was from 14.82- 36.08°C. Dissolved oxygen concentrations have generally been high. Determination of heavy metals (Pb , Cu and Ni) in three locations Al-Gebaysh, Al-Bourgah and Harer. The result showed that the Al-Bourgah and Harer as the most contaminated site with heavy metal. Levels of Ni in sediment ranged was 112 µg/g d.w in winter 2012,The levels of Pb higher was 41.61 µg/g d.w in Harer and lower 25.23 µg/g d.w in Al-Gebaysh, while Cu metal was 10.21 µg/g d.w in winter in Al-Bourgah to 19.12 µg/g d.w in Harer in summer.

1- Introduction

Wetland is considered a transitional area between land and water (Smith, 1980), it as a half-way world between terrestrial and aquatic ecosystems. It is largely dominated by water and has special type of flora and fauna, which usually undergo time scheduled characteristic changes from hydric to mesic types (Goswami *et al.*, 2010). The quality of water is identified by its physical ،chemical and biological properties. The particular problem in case of water quality monitoring is the complexity associated with analysis a large number of measured variables (Bayacioglu, 2006).

The physical and chemical characters of water are considered as the important principles in the identification of the quality and type of the water for any aquatic system (Abdo, 2005; Salman and Hussain , 2012). Temperature of air and water affect the biological activities of the living organisms in the Southern Marshes like phytoplankton and aquatic plants in which the day light affect the photosynthesis in plants which lead to the increase of biomass in the water body (Beitinger and Fitzpatrick, 1979). On the other hand the dynamics of organic matter in wetland sediments, closely related to biogeo- chemical cycles of nitrogen and phosphorous (Prusty *et al*., 2009). Wetland supports plant species intermediate between true aquatic and terrestrial habitats (Banerjee & Venu, 1994). Several biotic factors affect the occurrence and growth of macrophytes, such as sediment properties (Kim *et al*., 2001), water quality (Mathew *et al*., 2002), temperature and fluctuations in water levels (Ellery *et al*., 2003).

Salinity of the Iraqi southern marshes affected by the air temperature, day light, the amount of rains and also by the input and output of fresh water from the surrounding rivers. Hussain and Grabe (2009) showed that the salinity has increased over time adversely affecting agriculture in southern Iraq. Dissolved oxygen concentrations have generally been high, waters are typically slightly alkaline, and extensive submerged aquatic vegetation facilitates the settling of suspended solids. Nitrates are the predominant form of inorganic nitrogen, and the concentrations were low compared to other water bodies in Iraq. Nutrient limitation experiments indicated that the phytoplankton were nitrogen limited. The salinity can affect some aquatic plants. Al-Kenzawi(2011) found positive relationships for water temperature and salinity with the growth were observed, while negative relationships were observed for water depth, calcium, magnesium, nitrite, nitrate, and phosphate with *Hydrilla verticillata* growth.

Partow (2001) studied the hydrology of the marshes of Iraq and mentioned that less than 10 % of their area remained as functioning marshland by the year 2000, the only remaining marsh was the northern portion of Huwaiza; the other two marshes, Hammar and Central were totally desiccated. After May 2003, water began to return to the marshlands. In 2004, up to 40% of the former marshlands were reflooded. Some of the reflooded areas experienced rapid regrowth of marshland vegetation, other areas are slowly recovering; while some reflooded areas remain barren (Al-Musawi, 2012). Heavy metals distribution and seasonal variation were studied in the re-flooded marshes of the Mesopotamia, southern Iraq studied by (Al-Maarofi *et al*., 2013) and showed that the distribution of heavy metals in Al-Hawizeh and Al-Hammar marshlands were efficient for metals reduction, especially for Ni, while the Central marshland has the major contribution as source to metals. The marsh water is rich in nutrient especially nitrate and phosphate, reflecting high productivity in similar manner to other Iraqi marshes. Results were compared with other studies in the area. The present survey can act as a basis for future monitoring and recovery of the marshland ecosystem. (DouAbul *et al*., 2013).

Most studies were focused upon the physical and chemical parameters, as well as ecological aspects (Al-Saadi *et al*., 1981, Al-Arajy, 1988, Al-Zubaidi, 1985, Al-Lammi, 1986, Qassim, 1986 and Al-Saad and Al-Timari, 1993). Al-Musawi (2009) studied the water quality of Al-Hammar marsh in the south of Iraq. He mentioned that due to unavailability of Iraqi environmental regulations regarding marsh water on the one hand and the lacking of any actual water quality parameter values of such waters prior to desiccation. Al-Saad *et al*.(2010) Studied water quality surveys were designed and implemented during November 2005 to September 2006 at six locations, 4 in the Hor Al-Hammar (Al-Barga, Al-Nagara and Al-Baghdadia 1 and 2) the other two locations in Hor Al-Hwaaiza (Um Al-Warid and Um Al-Neiach) .. While physic-chemical parameters and inorganic nutrient load of water of East Hammer marsh studied by(Al-Abbawy *et al*.,2013) and she showed that the seasonally changes in water depth, that varied between 40-300 cm. Dissolved oxygen values were ranged between 4.54 to 11.2 mg/l, with mean 7.57±1.3 mg/l. The variation in pH values at each season for study area ranged from 7.02 to 8.4, the values of the pH reached top during the summer months and least during winter months

In this research, the variation of some water quality parameters in the southern marsh was studied to find out its efficacy to treat the contamination, and study would provide an understanding about the trace metals in sediment.

2- Materials and Methods

Study site

Water samples were collected from three stations along Iraqi Southern marshes (1) Al-Bargah (2) Al-Gebayesh (3) Harer station ,Figure (1) ,during the period Jan.(2011) to Feb.(2012) .Water samples were transferred to Marine Science Center laboratories and Department of

Biology/College of Science and kept for later chemical analysis .

Parameters like air and water temperature were recorded using Thermometers.PH recorded by using PH meter of the type HANNA HI-9821. Salinity measured by using meter of the type WTW 3301 .Dissolved Oxygen (D.O) recorded by using the method of APHA (1999).

In the laboratory nutrients were determined according to standard methods (APHA, 1999).Nitrites and phosphor were determined according to Bender Schneider and Robinson (1952) which explained by Parson *et al*,(1984).

Sediment samples were collected from stations. Three selected trace metal (Cu, Pb and Ni) were determined, the sediment has been separated by sieving and grinding, samples was done to following procedure described by ROPME (1983) by using nitric acid digestion and Spectrophotometer type Sco.UV-19.

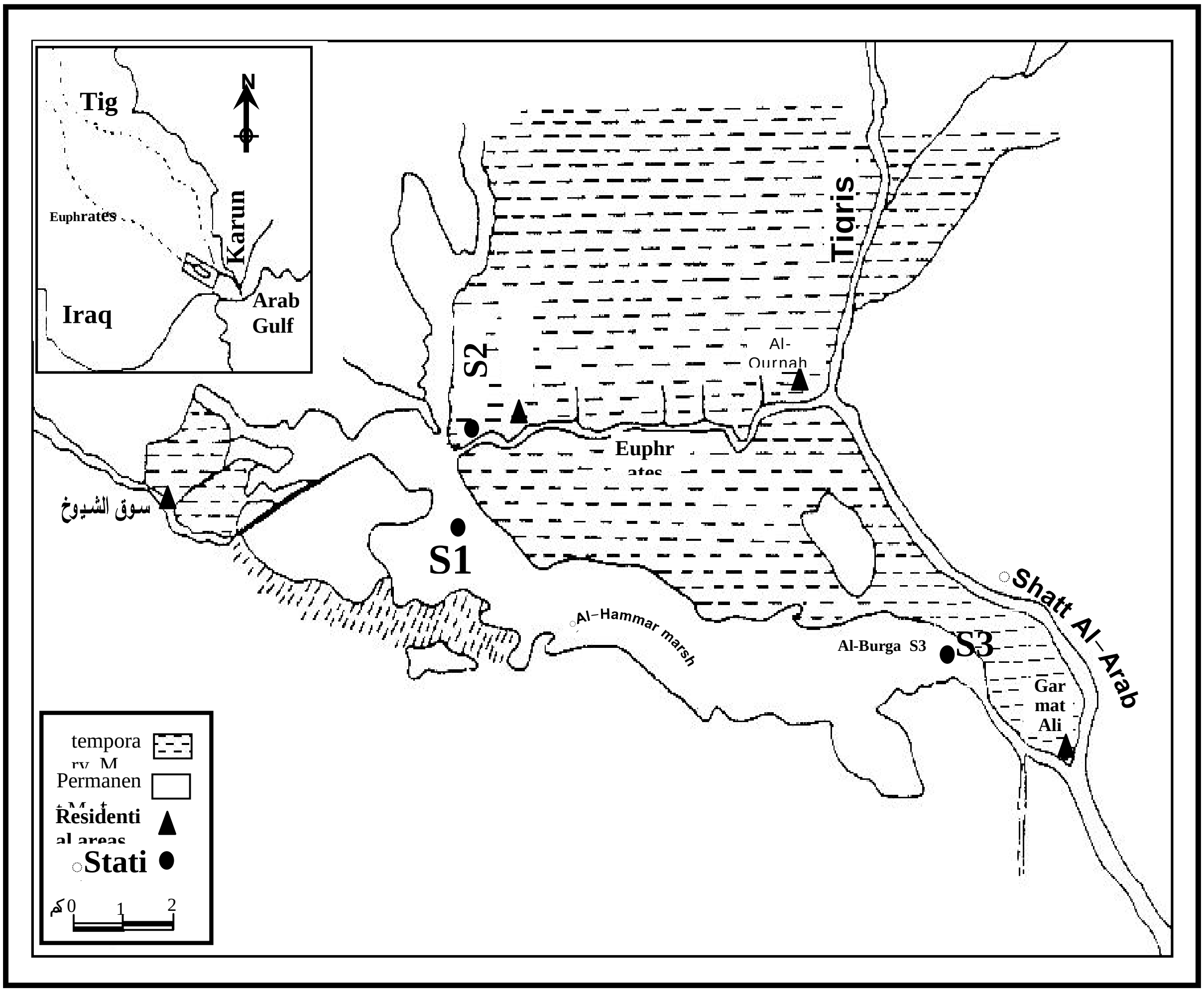


Figure (1) Study area

3- Results and Discussions

Results of the present study showed that the air temperature in all stations were high during summer and low during winter (Tables 1,2, 3,). In Al-Hmmar it ranged from 16.07-36.14 °C (Table 1). While in Al-Barga the range was from 15.92 – 32.18. °C (Tables 2). In Al-Gebayesh the range was from 14.82- 36.08°C (Table 3). Lowest water temperature 9.9°C was recorded in January 1988 in the Al-Hammar marsh (Al-Aaraji, 1988 and Hassen, 1988). No differences were recorded between the temperature at the surface and lower layers within the water column due to shallowness of the water in the marshes (Maulood *et al*., 1979).While (Al-saad *et al*.,,2010) recorded in Al-Barga was from 14.0 – 33.0°C

The pH of water is a measure of the hydrogen ion (H^+) concentration in water; it is an important parameter for describing the state of chemical processes. The pH of all the water samples was up 8.5 except that at Al-Bargah location which was 8.51 in July of summer 2011 Table (2), due to the disposing of municipal wastewater from region treatment plant. The pH has a unique value occurred in the basic side between 7 and 8.5 as those for other Iraqi waters due to the gypsum nature of the bottom and soil of the marshes (Al-Saad *et al*.,2010). Al-Zubidy (1985) has recorded high pH values up to 9.13 in Al-Qurnah marshes and explained that on the basis of increased phytoplankton in the area. pH outside a range of 4-10 can kill fish (Mattews, 1998), while water with pH greater than 8.5 is called hard water; pH value due to many factors such as removal of (CO_2) by photosynthesis through bicarbonate degradation, low primary productivity, reduction of salinity and temperature and decomposition of organic matter (Bragadeeswaran *et al*., 2003).The results in (Table 1,2 and 3) showed that the pH values reduced in summer and autumn . pH values in the marshes should have been related to the CO_2 content. In summer and autumn, increased CO_2 should have reduced pH due to decomposition of organic material same was reported by Banat *et al*.(2006) that lower pH existed in Al-Shafi marsh.

Table (1) Physical and Chemical parameters and nutrient levels of Harer waters during study period

Season	Parameter	Air Temp.C°	Water Temp. C°	PH	Salinity ppt	D.O. µg\l	Nitrate µg\l	Phosphate µg\l
Winter 2011	Dec.	17.52	13.51	7.73	1.37	6.36	4.21	2.11
	Jan.	17.71	13.25	7.92	1.53	7.01	4.13	2.09
	Feb.	18.21	16.03	8.01	1.61	7.08	4.19	1.99
	Average	17.81	14.26	7.88	1.62	6.81	4.17	2.06
Spring 2011	March	23.12	20.81	7.20	1.24	4.59	7.71	0.61
	April	24.81	21.52	7.31	1.64	4.22	7.73	0.51
	May	25.61	22.40	7.93	1.78	4.13	6.81	0.60
	Average	24.51	21.57	7.48	1.52	4.31	7.41	0.61
Summer 2011	June	35.12	32.82	7.53	2.01	4.07	5.32	2.01
	July	36.14	33.12	7.64	2.11	3.92	5.25	1.91
	Aug.	36.02	33.51	7.32	2.07	3.72	4.42	1.80
	Average	35.76	33.15	7.49	2.06	3.90	5.01	1.90
Autumn 2011	Sep.	26.11	23.62	7.81	1.94	4.21	4.98	0.98
	Oct.	24.02	21.13	7.32	1.73	4.76	4.79	0.91
	Nov.	20.81	18.50	7.13	1.63	5.01	4.66	0.99
	Average	23.64	21.09	7.42	1.77	4.66	4.81	0.96
Winter 2012	Dec.	17.03	14.53	8.10	1.71	7.22	4.39	1.87
	Jan.	16.07	13.62	8.36	1.64	7.31	4.27	2.91
	Feb.	18.71	16.21	8.11	1.59	7.18	4.11	2.72
	Average	17.27	14.78	8.19	1.64	7.23	4.42	2.50

Table (2) Physical and Chemical parameters and nutrient levels of Al-Bourgah waters during study period

Season	Parameter	Air Temp.C°	Water Temp. C°	PH	Salinity ppt	D.O. µg\l	Nitrate µg\l	Phosphate µg\l
Winter 2011	Dec.	16.41	13.01	7.82	1.41	8.98	4.01	1.93
	Jan.	15.92	12.17	8.01	1.44	8.41	4.09	1.87
	Feb.	17.22	14.01	8.19	1.50	8.01	3.88	1.98
	Average	16.51	13.06	8.03	1.45	8.46	3.99	1.92
Spring 2011	March	21.13	19.80	7.69	1.51	6.25	4.41	0.51
	April	24.61	21.28	7.91	1.58	6.01	4.16	0.32
	May	25.71	22.38	8.06	1.68	6.44	4.09	0.42
	Average	23.81	21.15	7.88	1.59	6.23	4.22	0.41
Summer 2011	June	31.02	27.35	7.62	1.79	5.61	4.06	1.11
	July	32.18	28.01	7.51	2.01	5.44	4.21	1.87
	Aug.	31.91	29.20	7.21	1.70	5.21	3.98	1.61
	Average	31.67	28.18	7.44	1.83	5.42	4.08	1.53
Autmn 2011	Sep.	26.23	22.13	8.01	1.79	6.01	3.62	0.78
	Oct.	25.01	18.61	7.81	1.63	6.21	3.58	0.64
	Nov.	20.66	16.03	7.62	1.69	6.32	3.49	0.91
	Average	23.96	18.92	7.81	1.73	6.18	3.56	0.77
Winter 2012	Dec.	16.91	12.81	7.41	1.49	8.71	3.91	1.52
	Jan.	16.01	12.01	7.63	1.56	8.36	3.19	1.62
	Feb.	18.09	13.52	7.71	1.58	7.93	3.11	1.14
	Average	17.00	12.78	7.58	1.54	8.33	3.40	1.42

Table (3) Physical and Chemical parameters and nutrient levels of Al-Gebayesh waters during study period

Parameter / Season		Air Temp.C°	Water Temp. C°	PH	Salinity ppt	D.O. µg\l	Nitrate µg\l	Phosphate µg\l
Winter 2011	Dec.	15.11	13.20	7.91	1.61	7.51	4.06	3.01
	Jan.	15.01	13.03	8.01	1.49	7.43	4.13	2.81
	Feb.	16.21	14.07	8.12	1.55	7.18	4.09	2.79
	Average	15.44	13.43	8.01	1.55	7.37	4.09	2.87
Spring 2011	March	20.82	18.51	8.21	1.12	4.91	6.62	0.75
	April	23.21	21.00	8.35	1.14	4.98	6.55	0.71
	May	24.03	22.07	8.17	1.21	5.01	6.69	0.81
	Average	22.68	20.52	8.24	1.15	4.96	6.62	0.75
Summer 2011	June	35.01	32.17	7.64	1.86	4.03	4.12	2.11
	July	35.22	32.81	7.82	1.92	4.01	4.26	2.08
	Aug.	36.08	32.01	7.75	1.81	3.94	4.31	2.01
	Average	35.43	32.33	7.73	1.86	3.99	4.17	2.80
Autmn 2011	Sep.	25.23	23.07	7.52	1.91	4.81	3.21	1.19
	Oct.	23.12	21.03	7.61	1.91	4.93	3.62	1.08
	Nov.	21.30	20.01	7.39	1.98	5.08	3.59	1.06
	Average	23.21	21.37	7.50	1.93	4.94	3.64	1.11
Winter 2012	Dec.	14.82	13.11	8.14	1.75	7.42	4.19	2.91
	Jan.	15.07	12.92	8.22	1.61	7.51	4.22	3.03
	Feb.	17.22	14.97	8.12	1.53	7.32	4.08	3.41
	Average	15.70	13.66	8.16	1.63	7.41	4.13	3.20

Many inorganic ions such as sodium, chloride, magnesium, and calcium are present in surface water. Fig.'s (1, 2 and 3) show the variation of salinity concentrations. In Harer Low was 1.24 in spring and higher 2.11 in summer, Al-Bargah low was 1.41 in winter and higher 2.01 in summer, while in Al-Gebayesh was 1.12 in winter lower and higher 1.98 in Autum was highest. Salinities were generally in the oligohaline (0.5 to 5.0) range from researcher such as Al-Sahaf (1976); Al-Zubaidi (1985); Al-Aarjy (1988)

Al–Rikabi (1992), but low mesohaline salinities were reported from the Harer marsh (Table1).Banat *et al.* (2006) found that spatial and temporal differences existed between parts of Harer marsh . The recorded high values from salinity could be attributed to the low amount of rain full, higher rate of evaporation (Balasubramanian and Kannan, 2005, Asha and Diwakar, 2007).

Table (1,2 and 3) shows the results of dissolved oxygen concentrations of the selected stations. Dissolved oxygen levels varied between 5.21 mg/L in Summer and 8.98 mg/L in winter of Al-Bargah, Al-Gebayesh was 3.94 mg/L in Summer and 7.51mg/L in winter, and Harer was 3.72 mg/L in Summer and 7.31mg/L in winter. Dissolved oxygen (DO) concentrations were generally high in present study compared with DO concentrations ranged from 1.67 mg l^{-1} (Al-Zubaidi 1985) to 11.95 mg l^{-1} (Al-Laami 1986).But the same results found in Maulood *et a*l. (1979) measured 4.2 mg l^{-1} and 5.03 mg l^{-1} and Al-Aarjy (1988) recorded 9.1 mg/L in Al- Chebayesh/Qurna marshes, 8.30 mg l^{-1} in Al-Hammar, and 8.l mg l^{-1} in the Al-Taar marsh during March and April of 1988 .

The higher value of DO which might due to the cumulative effect of higher wind velocity coupled with heavy rain fall and the resultant fresh water mixing (Rajasegar, 2003, Saravanakumar *et al*., 2008), but the low level of dissolved oxygen recorded can be attributed to low density of aquatic plants and phytoplankton (Solai *et al*., 2005), or the sewage discharges from the catchment area are gradually affecting the aquatic life (Addo *et al.,* 2011). Also the minimum mean values of dissolved oxygen were recorded during summer at stations Al-Hammar, and Al-Gebayesh (Tables 1, 2 and 3), because as the temperature increases the oxygen holding capacity of water decreases, which means that temperature plays a major role in the biological processes. Al-Lami (1986) .also noticed many factors affect the concentrations of dissolved oxygen in a water body, among the organic pollution, temperature, light penetration, water movement, availability of plants and nutrients (Al-Musawi, 2012).

The concentration levels of nutrients in the water samples were showed in Table (1, 2 and 3and Figure 1,2).In water; they provide nutrients for the primary producers such as algae, phytoplankton and seaweeds. If the nutrients reach high levels in water exposed to light, algal problems may arise. Fig.'s 1, 2 and 3 show the variation of NO_3 in marsh. There are high levels of NO_3 in the 7.73 µg\l in the spring Harer while in Al-Gebayesh was 6.69 µg\l in the spring, But Al- Bourgah was 4.41 µg\l in spring of No_3. Nitrates and nitrites are veritable indication of the biological pollution in natural water

(Addo *et al*, 2011). The highest nitrate value could be mainly due to the organic materials received from the catchment area (Ashok *et al*., 2008) or through oxidation of ammonia form of nitrogen to nitrite formation (Rajasegar, 2003).(Husian and Grabe, 2009) reported that in Al-Hammar marsh nitrate concentrations were higher than in the Al-Chebayesh marshes (Qurna marshes) and lower in Al-Taar which agree with present study. As well as nitrates characterized by high values especially winter which agree with (Al-Saad *et al*., 2010). Nitrite and nitrate concentrations were depended on the serial microbial transformation which also depends on dissolved oxygen values (Bragadeeswaran, *et al.*, 2003). The result recorded higher values of nitrite during some study seasons could be due to the increase phytoplankton excretion, oxidation of ammonia, reduction of nitrate and bacterial decomposition of planktonic detritus [Asha and Diwakar, 2007, Govindasamy and Kannan,2000), but the low level of nitrite during summer may be due to the increase of salinity present (Sankar,*et al*, 2010).

Phosphorous is a limiting nutrient for algal growth and therefore controls the primary productivity of a water body [Karikari,2007].Fig.'s 1, 2 and 3 show the variation of PO_4 in marsh. There are high levels of PO_4 1.98 in the winter in Al-Bargah while in Al-Gebayesh 3.41 in winter of Po4. But Harer was 2.91 in winter of Po_4 (Figure 3). Phosphate levels were high at Al-Gebayesh marshes while the Harer marsh is characterized by low levels of Po_4. Al-Imarah *et al*. (2006) concluded that the waters of southern Iraqi marshlands are rich in nutrient especially nitrate and phosphate which enhance the growth and billings of aquatic plants and phytoplankton which are necessary for primary productivity in the food chain. The higher concentration of Po_4 was maybe due to the input resulted from city sewage discharge, land drainage and urban run-off (Hassan *et al.*, 2010). Al- Saad *et al*.(2010) recorded during 2004 are little bit higher than those recorded in the previous studies such as (Al-Imarah *et al*., 2006), it was(0.008-1.41 µg at P-PO_4/l) .

Analysis on the presence of heavy metals was performed in sediment sampled in three stations (Fig 4, 5 and 6) shows that the southern part of the study area gives some pollution with trace metals. Levels of Cu in sediment ranged from 10.21 µg/g d.w in winter 2012 in Al-Bourgah to 19.12 µg/g d.w in Harer in summer (Fig.1). The range obtained was higher than the set value as a result agrees with the reason may be due to the concentrations of trace metals are effected by chemical and physical parameters .The contamination with trace metals may determined to the health of the aquatic ecosystem and the rural communities that utilize the marsh water for domestic purposes without any treatment .The sediment pollution with heavy metals, through to be due to different sources such as urban wastes , industrial effluents land washout and boats activities(Al-Yaseri, 2011).

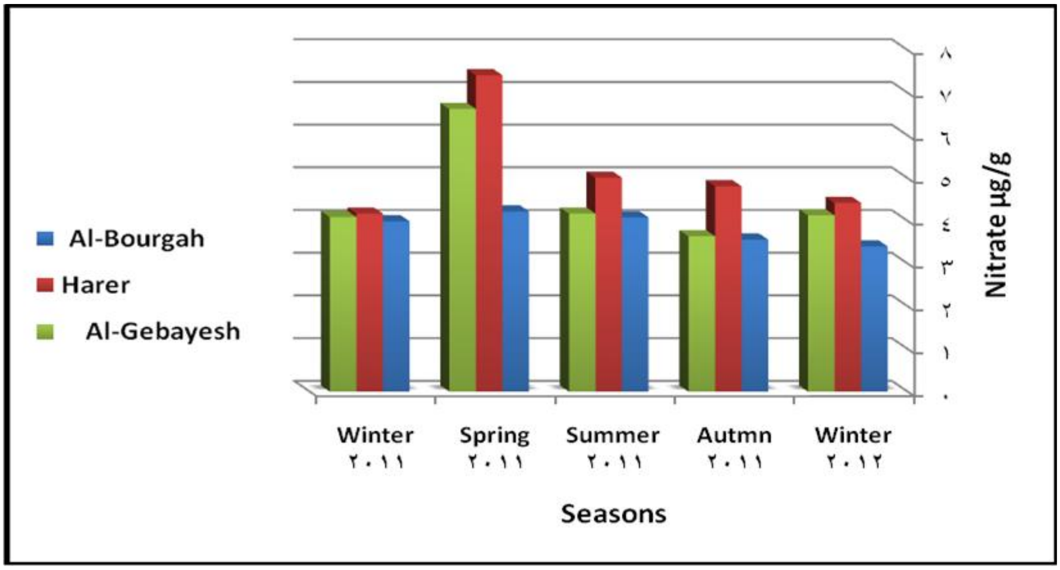


Figure (2) Concentration levels of range nitrate in the water samples.

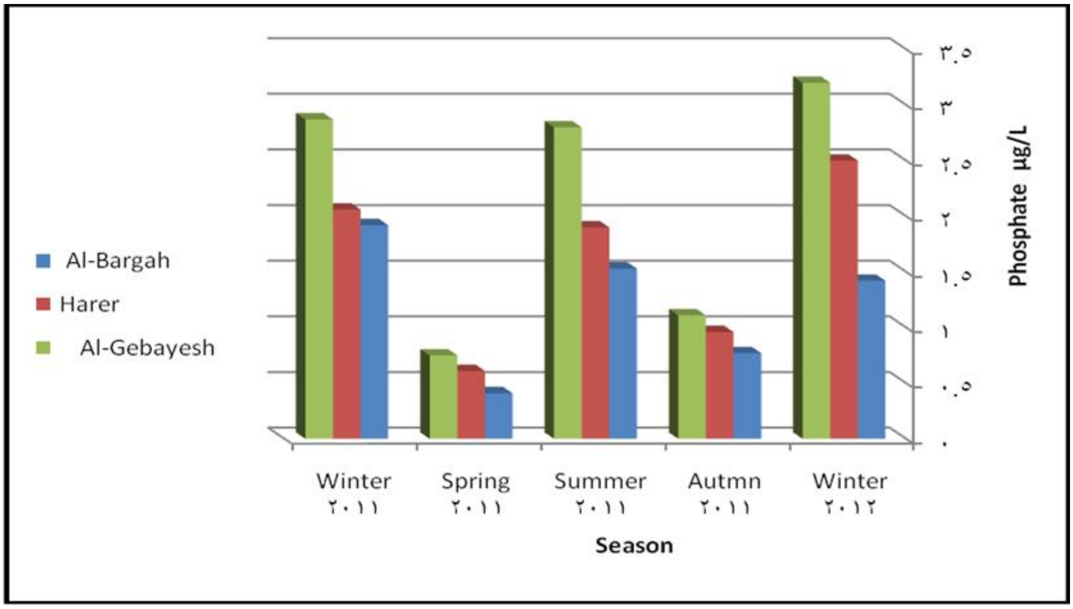
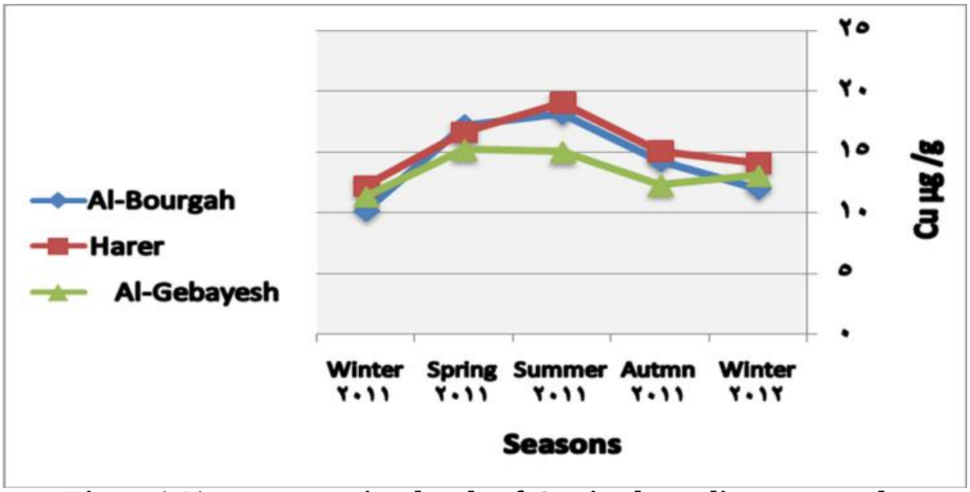
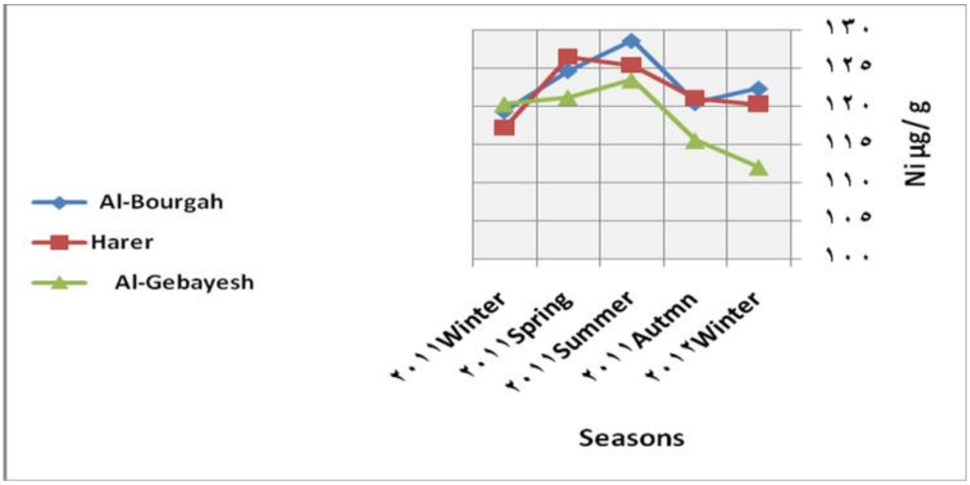


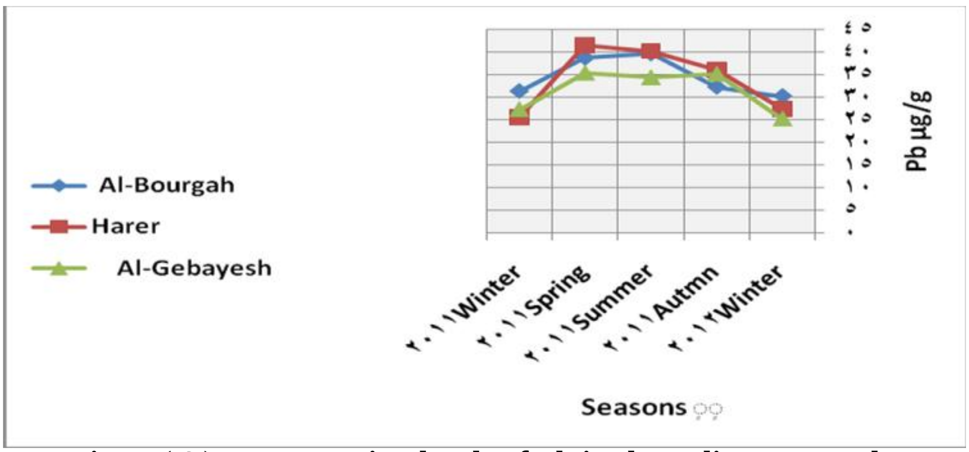
Figure (3) concentration levels of range phosphate in the water samples.



Figure(4) concentration levels of Cu in the sediment samples.



Figure(5) concentration levels of Ni in the sediment samples.



Figure(6) concentration levels of Pb in the sediment samples.

Levels of Ni in sediment ranged from lower in winter 2012 was 112 µg/g d.w and higher in 128.65 µg/g d.w in the range obtained in this study was much higher (DWAF,1996 and Al-Yaseri, 2011) reported that the typical concentration of Ni in unpolluted surface water are given as 5.0 ×10-4 mg/l ,So that the indicating that the waters contaminated .

The levels of Pb obtained in sediment higher in spring 2011 in Harer was 41.61 µg/g d.w and lower 25.23 µg/g d.w in Al-Gebaysh in winter 2012, The values of trace metals obtained in this study exceed the allowable level hence making the water unsuitable for domestic use degrees of temperatures and pH water is influence the solubility and availability of metals, the use of the marsh water for drinking purposes by man and animals could lead to accumulation of the metal with resultant ill- health effects (Al-Yaseri, 2011) . The degrees of temperature effected on the biogeochemical cycle of trace metals (weiner, 2000). As well as the salinity effected on the biogeochemical cycle and leading to a decrease in adsorption capacity of sediment, the concentrations of trace metals are effected by chemical and physical parameters (Wetzel, 2001).

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تقييم نوعية المياه والمعادن النزرة في رواسب الاهوار الجنوبية.

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الخلاصة

تم أجراء عملية لأختبار نوعية المياه في الاهوار الجنوبية العراقية للفترة من ديسمبر 2011 الى فبراير 2012 في ثلاث محطات وهم هور الجبايش والبركة وحرير في هور الحمار. كانت المؤشرات المختبرة هي درجات الحرارة والملوحة والاوكسجين المذاب (DO) فضلا عن الدالة الحامضية. وبينت الدراسة أن الملوحة وجدت أن أقل قيمة لها سجلت في فصل الربيع في منطقة حرير وكانت 1.24جزء بالمليون أما التركيز الاعلى فكان 2.11 جزء بالمليون في فصل الصيف.أما هور الجبايش فكانت أقل قيمة لها كانت 1.12 جزء بالمليون في فصل الشتاء والقيمة الاعلى سجل في فصل الخريف وكانت 1,98 جزء بالمليون. درجات الحرارةسجلت معدلات من 14.82 -36.08 م°. ووجد أرتفاع في تراكيز الاوكسجين المذاب فضلا عن تراكيز عالية من النترات والفوسفات. قيست تراكيز ثلاث من العناصر الثقيلة(الرصاص ، النحاس ، النيكل)في رواسب ماخوذة من مناطق الدراسة من الجزء الجنوبي .أشارت النتائج بان محطتي البركة وحرير الاعلى تاثرا" بالعناصر النزرة من بقية المحطات.