Some of Heavy Elements in Water, Fish and Plant Species from Shatt Al-Arab at Basrah Governorate –Iraq

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Abstract

Current study had done in November 2018 in four stations include two stations in south and another two in north of Shatt Al –Arab of Iraq. The pH value is ranged from 7.85 to 8.89 as well as the electrical conductivity from 2.84 to 3.92 ms/cm while the salinity is ranged from 1.81 to 2.5cPPT and these values were recorded at temperature ranging (14-18.2) ˚C and dissolved oxygen was 6 to 9.22 mg /L. The biological oxygen demined ranged was (1-5) mg/L. This total dissolved heavy elements showed significant differences in water, fish, and plant samples. In water samples, found iron value was in the range of 9.52 to 14.97) mg/L while zinc component value was ranged from 0.48 to 1.11 mg/L, and copper component values ranged between (0.275 -0.848) mg/L. In the all body fish samples, the iron component appeared value ranged from 11.18 to 15.83 mg/kg dry weight while the value of zinc component is ranged of (17.306-74.25) mg /kg dry weight while copper component recorded value ranging of (11.45 - 34) mg / kg dry weight. Further, plant samples contain iron element value ranged from 16.12 to 42.12 mg / kg dry weight while zinc element value ranged between (22.55-142) mg / kg dry weight and copper component recorded values ranging of (65.875-94.5) mg / kg dry weight. However, cadmium and lead elements were not detectable in all plant species.

1. Introduction

Heavy elements pollution of water as dissolved and particulate phase is very important and harmful pollutants of the aquatic environment [1]. Pollution with heavy elements has become a main environmental problem because of its toxicity, non -degradable and constant nature, this leads to their accumulation in plants ,microorganisms, and various aquatic organisms, which, in turn are ,transferred to humans through the food chain and therefore lead to multiple human health problems [2]. Heavy elements called with this name because they have specific gravity more than $5g/cm^3$ and also called trace elements when present in low concentrations at 0.1% in the earth's crust all these influence the health of humans, animals and plants [3].Heavy elements are present in the aquatic environment at very low concentrations when these water bodies are away from origin of pollution, but concentrations may increase as a result of fast growth of populations and different human activities [4]. Heavy elements are one of the most important and dangerous types of pollution which threatens the aquatic environment with its living and non -living components, and therefore affects the living organisms [5]. The concentrations of elements in the natural aquatic ecology are ordinarily, at differing from Nano gram to Microgram per liter, however elements' concentrations in waters caused some problems to the balance of aquatic ecosystem [6].

The elements concentrations may increase above natural levels due to the release of industrial, agricultural, household and other wastes [7]. There are various sources that supply the aquatic environment with heavy elements and different concentrations, and maybe partitioned into two main sources: natural resources and anthropogenic resources [8; 9]. Natural resources include soil washing, weathering of natural mineral rocks, agricultural lands and natural events, which carried by rainwater, flood water to the aquatic environment. Heavy elements also, enter the aquatic environment because of organisms' hydrolysis after death [10; 11]. While the other source of heavy elements is anthropogenic sources, they represent all sources of human activity like fertilizers, industrial waste, agricultural pesticides, textiles, traffic emissions ,weathering of buildings, dyes, the utilization of oil refinery products and atmospheric deposition [12]. Household wastes play an important role in adding heavy elements to the aquatic environment [13]. Some of these elements are essential and necessary to sustain the life of living organisms such as Copper, Zinc, and Iron, which play main roles in the functioning of enzyme systems [14].

On the other hand at higher concentrations become toxic. The other group of biological elements is constrained or non -essential and contains elements that pollute the aquatic environment and harmful to their biota even at low levels to exposure [15]. For example, lead, cadmium and chromium the exposure to them because's serious health effects, including reduced growth with development, cancer disease, organ damage, nervous system damage, and in acute cases lead to death [5;16]. Aims of the study determination of variables properties of water in two locations from the north and south of the Shatt Al-Arab and measurement the concentrations of some which elements in the water, fish and plants with comparison between the north and south of the Shatt Al-Arab.

2. Materials & Methods

2.1 Field of work

Field work and measurements were done in November, 2018, at four stations at Shatt Al _Arab of Iraq. Two stations of Dayr and Al-Sharash, north of the river, and two stations of Al-asmeda and Mhaela river south. Water samples were and supplied with polyethylene bottles, all Fishes samples were collected by fishing nets and stored in the ice box. Plants were collected by plastic bags, all samples done as three replicate.

2.2 Laboratory work and analysis

1- Water temperature (WT: °C), Potential of hydrogen ions (pH), Electrical Conductivity (EC: ms/cm) and Salinity= EC ×0.46:

 were measured in site using Multimeter type (Multi 350 i SET 5).

2-Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD_5)

Winkler method was used to determine the DO and BOD_5. Winkler bottles (transparence) 300 ml were filled with the water to detect the dissolved oxygen level; the oxygen level was fixed at each bottle in the field added 2 ml solution from manganese sulfate, 2 ml solution from alkaline iodide azid, and 2 ml sulfuric acid. Another Winkler bottles (dark) were filled with the water sample to detect the BOD5 values, which were left without fixation and stored in ice box until reaching [17].

2.3 Heavy metals extraction

a- In water:

Followed the method in [17] Sampling was conducted in November 2018 from the intended stations. the water sample is collected from the specified station for the size of 10 liters, then the sample is filtered through the 0.4µm milipore filter paper, then the water samples passing through the filter paper were focused using an ion exchange column containing the SK120 resin in hydrogen form depending on the method and used 50 mL of dilute nitric acid (2 NM) as an eluent rinse of elemental ions Cu + 2, Cd + 2........ etc.) then evaporated the solution at a temperature of 70 ° C to pre-dry, Add 1 milliliter of concentrated nitric acid and 5-10 ions free of water, and store in plastic bottles to measure the concentrations of heavy elements ions Use of atomic absorption spectrum flame device (FAAS) Pye Unicom model SP9.

b- Plants and fish samples

Followed the method [18] to determine the heavy element concentrations.

Samples of plant and fishes were dried in 80C for 24 hours, and then each was sample prepare for chemical analysis as follows: Samples of dried parts in triplicate were digested in mixed sulfuric and perchloric acids (1:1 v: v) then analyzed for Cd, pb, Cu, Fe and Zn according to the standard methods by using Atomic Absorption Spectrophotometer Pye Unicom model SP9.

3. **Results and Discussion**

3.1 Physicals and Chemicals variables

1- Temperature

Water temperature is the most important factors affecting aquatic life. Through its effect on different chemical measurements such as dissolved oxygen in water. The water temperature ranged between (14-18.2) °C (figure 1). The results of the study showed changes between the Northern part and Southern part of the Shatt al-Arab. The temperature of water as recorded the highest value 18.2 in the fertilizer plant and the lowest value in the two stations of Dayr and Shrash, the cause of changes is due to the nature of the climate of Iraq. This results agreements with [19] who compared the same range in the region.
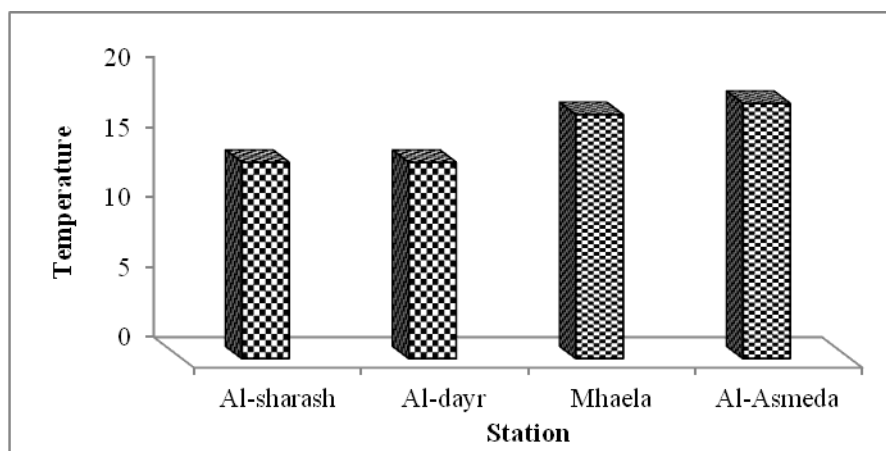
Figure 1: Show the average of temperature in different stations

2- Potential of hydrogen ions (pH)

The pH is an important parameter that determines the suitability of water for different purposes [20]. The pH values were close to the alkaline side at all the studied stations and at all the studied periods, the values ranged between 7.85-8.89 (figure 2). The WHO and Iraqi standards set the permissible pH limit of 6.5-8.5. The current study recorded the highest value in the area of Mhaela (8.89) and the lowest value in the area of Al-Shrash (7.85).
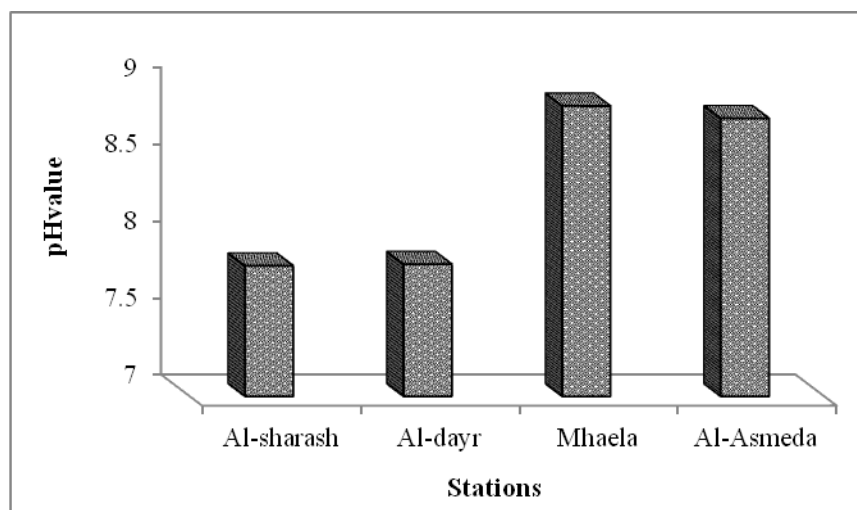

Figure 2: The mean PH values in different stations

The relatively high values in pH are due to increase discharges to the Shatt al-Arab river from wastewater [21; 22]. [23] Showed the pH values of all tested sites fall within the acceptable

range, where the water quality of the river tends to be slightly alkaline, pH is closely related to water solubility and chemical form, and has a significant impact on aquatic life activities.

3-Electrical conductivity and salinity

Electrical Conductivity values ranged between (2.84-3.920) ms / cm in stations of North and South of Shatt al-Arab (figure 3and 4). The highest value was recorded in Al-asmeda area (3.920) ms / cm and the lowest value in Al-dayr station, (2.84)ms/cm, either salinity had different values between the North and South of the river. The variation was in small values which ranged between (1.81-2.5) PPT. Al-asmeda area was recorded the highest value at (2.5) PPT and the lowest value in the Al-dayr area (1.81) PPT. The results of the present study showed clear changes in the values of electrical conductivity, the highest value recorded in the southern part. The high value of salinity was due to the income water from the Arabian Gulf, while the lowest value in the Al-dayr station because of its low impact on the saline tongue as well as source From the Shatt Al-Arab when the confluence of the Tigris and Euphrates rivers [19].
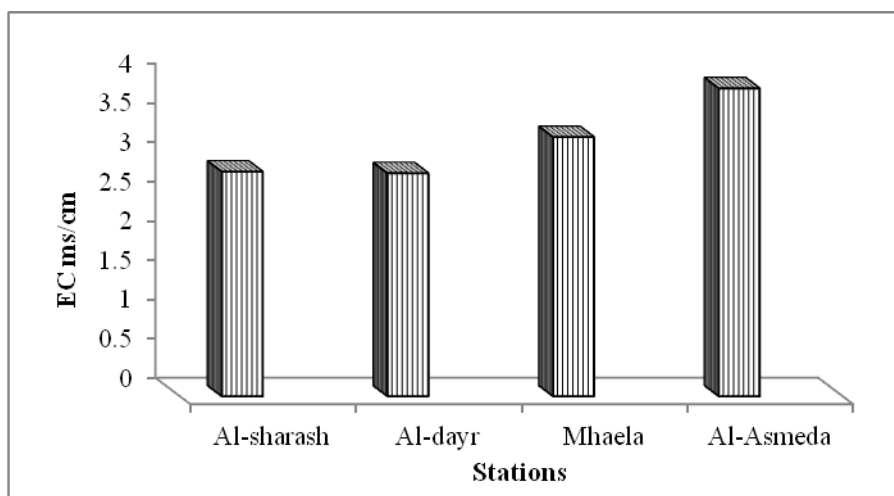

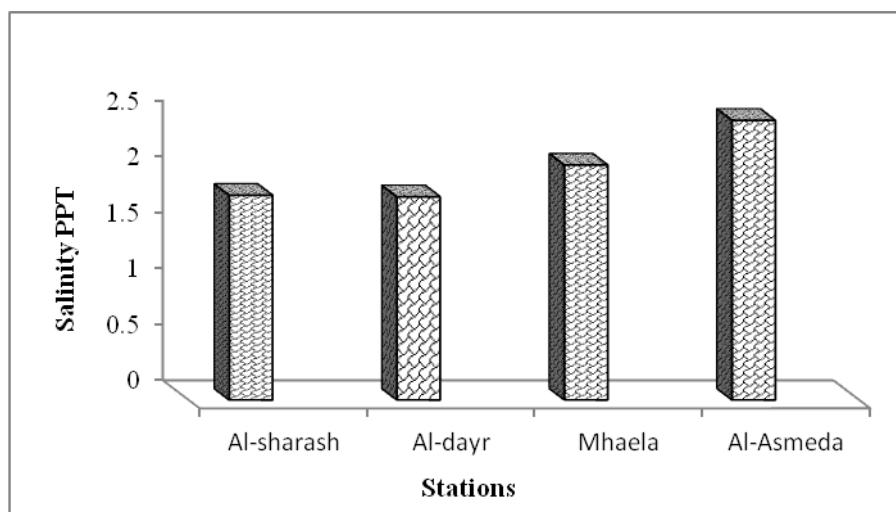Figure 3: Show the average EC values in different stations

Figure 4: Show the average salinity values in different stations

4- Dissolved Oxygen (DO) and Biological Oxygen Demand (BOD5):

We can notice from (figure 5) that Dissolved oxygen values (DO) were different between the Northern stations and the Southern stations, dissolved oxygen values ranged between (6-9.22) mg/l. In the current study Al-sharash and Al- dayr stations recorded highest values of dissolved oxygen, while decrease in temperature compared the two stations with fertilizers in the southern part of the Shatt Al-Arab, this is causes healthier aquatic environment in Al- dayr area showed the highest value was recorded at (9.22) mg/l and the lowest level in the Mhaela area as (6) mg/l, due to the degradation of organic waste lead to increase [24; 25]. The biological oxygen demand is good values ranged between (1-5) mg/l (figure 6). The highest value was recorded in the Al-asmeda area, (5) mg/ l, While the lowest values recorded in Al-Sharash station at (1) mg/l. With obvious differences between the stations came at the lowest value in the station Alsharash. This may be because it is less exposed to organic pollution compared to the fertilizer plant, which was close to dense population and the arrival of large amounts of sewage waste and these results were consistent with the ranges recorded in the same areas previously and the biological requirement of oxygen directly with the temperature increase [26]. Different stations showed different values of biological oxygen demand.
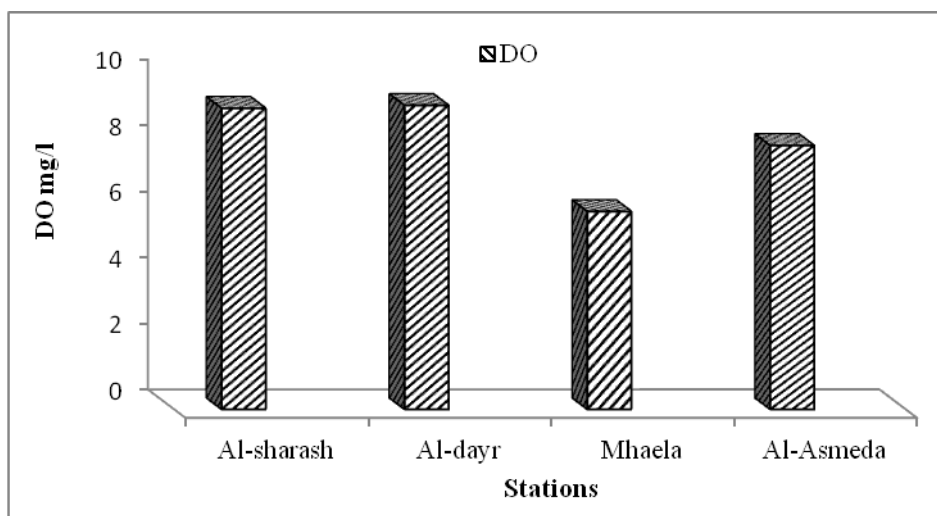
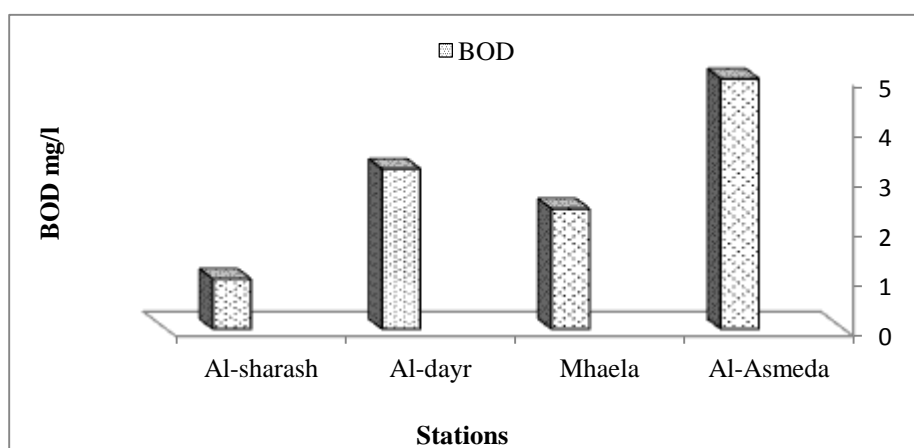Figure 5: Show the average DO values in different stations

Figure 6: Show the average BOD$_5$ values in different stations

5- Heavy metals measurement in different stations

a- Heavy metals in water

Heavy metals in water was affected of by many conditions such as pH, conductance and mutual interaction between sediment with water because it was represented as an important reservoir for many heavy metals through accumulation operations in various conditions [27]. The table 1 refers to the trace metals concentration in the studied area in the environment through their formation of the ground crust and some metals are important for the growth of living within the limits allowed. Dissolved and suspended particles trace elements are toxic generally contain in the industrial effluent at high quantities, this causes deleterious effects on vegetation and the freshwater sediments when discharged into water bodies [13]. Some minerals are toxic, although

with a few concentrations our study focused on heavy metals in water, fish and plants. The metal of iron is a natural metal in the geological structure of the soil and there are many oxidative forms. It is affected by the increase and decrease of the hydrolysis where iron is not deposited in the acid medium [19]. We note the increase in iron in the area Al-dayr (13.928) mg/l and area Alasmeda (14.966) mg/l (Tab.1), because it is residential areas and the use of chemical fertilizers in them as well as affected in navigation. The permissible limits are 0.3mg / l. Copper naturally is appeared as mineral in rocks and soil. Its concentration is about 50ppm of ground crust; it is a naturally occurring metal in living organisms, it is a vital metal of growth [28]. However, if it exceeds the permissible limits, it becomes a harmful metal that affects every side of environment.

Table 1: The average of concentrations of total heavy metals in water at the studied stations

Location	Cd mg/kg ±SD	Pb mg/kg ±SD	**Cu mg/l** ±SD	**Zn mg/l** ±SD	**Fe mg/l** ±SD
Al-sharash	ND	ND	0.515± 1	1.113± 0.9	9.52±1.5
Al-dayr	ND	ND	0.848±0.3	1.036± 0.7	13.928± 2.2
Mhaela	ND	ND	0.309±0.9	1.116±0.5	10.501± 1.2
Al-asmeda	ND	ND	0.275±0.1	0.481±0.3	14.966±2

The limits measured in drinking water are about 0.3mg /l [29]. Where in the present study the highest value was in Al- dayr (0.848) mg/l and the lowest value was in the Al-asmeda (0.275) mg/l. All these metals can reach water from many industries and may have complex structures within the environment and become toxic to the living organisms. The highest value of zn recorded in the current study was in the area of   Mhaela (1.116) mg/l and the lowest value in the Al-asmeda (0.481) mg/l that may be due to the erosion and may be transmitted with the wind or rain and causing this increasing. Lead and Cadmium were measured and their concentrations were not detected.

3.2 Heavy metals in fish

Table 2 shows that iron metal recorded the highest concentration in Al-asmeda (15.833) mg/kg of the *tilapia* species and the second type of fish (15.596) mg/kg recorded (11.188)

mg/kg. The concentration of certain metal in the fish tissue is the accumulation due to the concentrations increased in the fish tissues; they can be transmitted to humans through the food chain and affect human health. Some disease related with hemoglobin of the human body and causes a risk to the human [30; 19]. The zinc component recorded the highest concentration in the area of alsharash (74.25) mg/kg and the lowest value in the alasmeda area. (17.306)mg/kg in two kinds of fish, While in the second type of fish area of alasmeda (69.56) mg / kg Where it moves into the environment by means of nautical navigation, natural processes, and normal irrigation and drainage processes [31]. The copper recorded the highest value in the alsharash (43) mg/kg and the lowest value in the alasmeda (11.454) mg/kg area and depends on the pollutants that reach the water environment. The accumulation of the metals in the fish tissues can reflect the amount of pollution in the aquatic environment [32]. Including contaminants of wastewater and other contaminants that reach the environment through natural and anthropogenic processes [29].

Table 2: The average of concentrations of heavy metals in fish's body at the studied stations

Fish species and its location	Cd mg/kg ±SD	Pb mg/kg ±SD	Cu mg/kg ±SD	Zn mg/kg ±SD	Fe mg/kg ±SD
Liza abu (Alshrash)	ND	ND	43±4	74.25±4.3	11.188±1.6
Mugil cephalus (Alasmeda)	ND	ND	11.503±1.1	17.306±2.2	15.596±1.3
Tilapia *sp.* (Alasmeda)	ND	ND	11.454±0.9	69.56±3.2	15.833±1

3.3 Heavy metals in plants

Table 3 shows that copper was recorded in *Ceratophyllum demersum* plant (65.875) mg/kg and in *Potamogeton crispus*   (94.5) mg/kg, where the plants recorded *C. demersum* has copper) less than *P. crispus* and compared with previous results [33; 16]. The current study recorded higher concentrations; this is due to the increase of industrial pollutants and domestic access to the water environment without treatment and the low level of water at Shatt al-Arab. The ability of these plants to accumulate and eliminate trace metals in relation to their concentrations in ambient led to the observed variations in metal concentrations in plants. The results showed higher concentration of trace metals in sediment than in plants [34].

Table 3: The mean concentrations of heavy metals in plants at the studied stations

plant	Cd mg/kg ±SD	Pb mg/kg ±SD	Cu mg/kg ±SD	Zn mg/kg ±SD	Fe mg/kg ±SD
Ceratophyllum demersum (alsharsh)	0.00	0.00	65.875±3.5	22.55±1.6	42.125±3.3
Potamogeton crispus (Al-dayr)	0.00	0.00	94.5± 2.8	142± 5.6	16.126±1.6

This leads to accumulation within the plant tissues and we conclude that the *p. crispus* plant is more to the copper metal while the *C. demersum* plant more for the iron element. In the current study, *C. demersum* was recordeding higher 42.125mg/kg and in *p. crispus* 16.166mg/kg recorded concentrations less than previous studies As recorded in the previous studies in the plant *ceratoohyllum* 1880ug/kg either *p. crispus* plant recorded 820 ug / kg In the zinc component, the higher values than the current study [4]. The current study was the highest concentration 142mg/kg and the increase of the elements of the root cause is geological region, and different areas, and the type of pollutants that reach the environment, whether agricultural or industrial, etc. [35].

4. Conclusions

The study showed a few differences in some qualitative variables between the sites north and south of the Shatt al-Arab. The study showed different concentrations for metals (Zn, Cu, Ni, Cd, Pb) in the environment of the Shatt al - Arab with clear differences in the distribution of heavy metals between water, fish and plants .The study showed that concentrations of heavy metals in plant and fish tissues were higher than concentrations in water and that these concentrations make them a good life evidence of heavy metal pollution .The current study showed difference of heavy metals concentration between the two sites with the difference of elements, some of which did not record any occurrence and not detected values for lead and cadmium.

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بعض العناصر الثقيلة في المياه والأسماك وانواع النباتات من شط العرب
في محافظة البصرة ـ العراق

المستخلص

المعادن الثقيلة تحتوي على تأثير سام بشكل خاص على البيئات المائية. تمت الدراسة في نوفمبر 2018. في أربع محطات تشمل محطتين في الجنوب ومحطتين أخريين في شمال شط العرب في العراق. تراوحت قيم الأس الهيدروجيني بين (7.85-8.89) وكذلك الموصلية الكهربائية من (2.84-3.92) مللي / سم بينما تراوحت الملوحة من (1.81-2.5) PPT (وتم تسجيل هذه القيم عند درجات حرارة تتراوح بين (14-18.2) درجة مئوية ، كان الأكسجين المذاب (9.22-6) ملغم / لتر. تراوحت كمية الأكسجين البيولوجي الذي تم تطهيره بين (1-5) ملغم / لتر. أظهر إجمالي العناصر الثقيلة المذابة اختلافات معنوية في عينات المياه والأسماك والنباتات. في عينات الماء تراوحت قيم الحديد من (9.52-14.97) ملغم / لتر. تراوحت قيم عنصر الخارصين بين (0.48-1.11) ملغم / لتر ، وتراوحت قيم عنصر النحاس بين (0.275- 0.848) ملغم / لتر. في جميع عينات أسماك الجسم ، أظهر عنصر الحديد أن القيم تراوحت بين (11.18-15.83) ملغم / كغم من الوزن الجاف بينما أظهر عنصر الخارصين قيم تتراوح بين (17.306-74.25) ملغم / كغم من الوزن الجاف ، وسجلت قيمة عنصر النحاس مابين (11.45 - 34) ملغم / كغم من الوزن الجاف. كما هو موضح في العينات النباتية، تراوحت قيم عنصر الحديد بين (16.12- 42.12) ملغم / كغم من الوزن الجاف بينما تراوحت قيم عنصر الحارصين بين (22.55-142) ملغم / كغم من الوزن الجاف بينما سجل عنصر النحاس قيم تتراوح من (65.875) -94.5) ملغم / كغم من الوزن الجاف. لم يتم اكتشاف الكادميوم والرصاص في جميع أنواع النباتات. تهدف الدراسة الحالية إلى المقارنة بين نوعية المياه في شمال وجنوب شط العرب ، وتحديداً لبعض المتغيرات الفيزيائية والكيميائية في مناطق معينة ، وكذلك تقدير العناصر الثقيلة في العينات المحددة.

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