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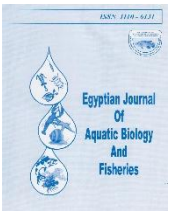

Assessment of metals contents, petroleum hydrocarbons and physico-chemical parameters in Shat Al-Arab River

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ABSTRACT

The waters of Shatt Al-Arab River were examined by determining the content of heavy elements (Ferrous, copper, Bromine, Chromium and zinc) and the petroleum hydrocarbons. In addition, 7 parameters were evaluated, including the chloride, phosphate (PO4), sulphate (SO4), nitrate (NO3), total suspended solids (TSS), temperature (°C) and the concentration of hydrogen ions (pH). The atomic absorption spectrometry was used to analyze the targeted heavy metals, whereas the infrared (IR) spectroscopy was used to measure petroleum hydrocarbons. The five heavy metals' values were recorded during 2021, and a slight fluctuation in the concentrations of petroleum hydrocarbons was detected. Their values were under the acceptable environmental limits. The levels of TSS (68 mg/l), the highest concentration of Cl (888 mg/l) and SO4 (677 mg/l) were higher than the acceptable environmental limits.

INTRODUCTION

The river of Shatt al-Arab is an important major river that is formed at the confluence of the Tigris and the Euphrates Rivers in the city of Qurna, north of Basra, Iraq, and then extends for about 200 km to flow into the northwest of the Arabian Gulf, south of the city of Al-Fao. The average width of the river is 500 meters, and its depth ranges from 7 to 22 meters. It is characterized by low current speed. It has great economic importance as a result of its many uses in industry and agriculture, in addition to the use of its water for the human consumption.

Shatt Al-Arab River is affected by tides that allow the penetration of the marine waters originated from the Arabian Gulf; it is characterized by the prevailing mixed-semi diurnal tide **(Al-Taei *et al*., 2014)**. This River is exposed to many pollutants, the most important of which are heavy metals and petroleum hydrocarbons, resulting from the economic activities adjacent to it, which throw domestic sewage and agricultural wastes into the river, in addition to the wastes discharged from the activities of fishing and transport boats.

Heavy metals have a high density of more than 5 grams/ cm^3; these metals are divided into essential and non- essential elements. The former has a basic function in the action of enzymes, viz. Zn^{+2} and Mg^{+2}. These elements are essential for cell metabolism, and they act as ionic cofactors. Whereas, the non-essential elements are toxic to cells and organs, and even low concentrations can damage the cell components. Cadmium (Cd) and lead (Pb) are two elements of the latter group. Heavy metals are distributed in the ecosystem and their prevalence has increased due to the industrial sources of acid rain, in addition to the pollution resulting from residues emitted in particular from fuels.

Heavy elements have the ability to accumulate in the organs tissues of fish and the aquatic organisms, and thus these elements are considered among the most dangerous types of pollution **(Shah, *et al*., 2020; Jaber *et al*., 2021)**. Because of their non biodegradability, they have acute and chronic effects on aquatic organisms **(Jantawongsri, *et al*., 2021)**. Industrial pollutants are released into environments, such as Cu, Cr, Cd, Ni, and Fe which are essentially colorless and odorless, therefore, these elements have become a source of threat to the aquatic organisms **(Singare *et al*., 2011)**.

Shatt Al-Arab River suffers from many problems related to pollution discharged from industrial activities and domestic wastes, in addition to the effect of the salt tide originated from the Iraqi marine waters. Consequently, this study aimed to determine the pollution level of heavy metals contents (Fe, Cu, Br, Cr, and Zn), the total petroleum hydrocarbons (TPHC) and the basic physico-chemical parameters (potential of hydrogen (pH) & temperature (Temp.)), the total suspended solids (TSS), chloride (Cl^{+1}), sulphate (SO_4^{+2}), phosphate (PO_4^{+2}) and nitrate (NO_3^{+2})) in Shat Al-Arab River.

MATERIALS AND METHODS

Study Location

The study area of Shatt Al-Arab River is located in the nearby area, where this river connects to the Garmat Ali River (Fig. 1). For the industrial activity, this area has a distiguished location, being near the electrical power plant and the activity of small boats. The current experiment extended from January – December 2021. Water samples monthly collected from the study site were carried out in three replicates.

Analysis of heavy metals

The water samples were digested according to method of **Islam *et al*. (2015)** to examine the toxic heavy metals (Fe, Cu, Br, Cr and Zn). The elements were analyzed using a Shimadzu 1800 PC, (Japan) atomic absorption spectrometer and the metal concentration was calculated based on the standard curve method.

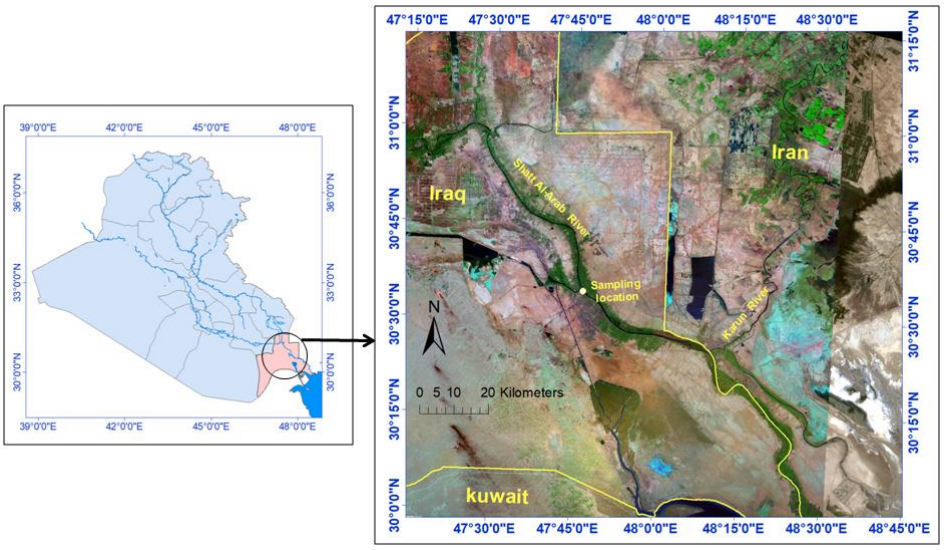

Fig. 1. A map showing the sampling sites of water

Extraction and analysis of petroleum hydrocarbon

The total petroleum hydrocarbons (PHCs) were extracted thrice using the method of EPA 3510 liquid-liquid extraction **(Adeniji *et al.*, 2017)**. The EPA 418.1 method was carried out using infrared (IR) spectroscopy. Basra oil was used as a standard with wavelengths of excitation and emission, which were (310 and 360 nm), respectively.

Water Physicochemical Parameters

Water samples were collected in glass bottles and transferred to the laboratories of the Marine Science Center. The samples were filtered using filter paper (Whitman 541), the samples were acidified by adding drops of nitric acid and stored at a temperature of 4°C, and then the physico-chemical measurements (Cl, PO_4, SO_4, NO_3 and TSS) were analyzed using the standard procedures method of **APHA (1998)**. The hydrogen ion concentration (pH) and temperature (°C) were tested via multimedia checker (YASI) model 556 MPS.

RESULTS AND DISCUSSION

The current study showed the presence of heavy metals in the studied part of Shatt Al-Arab River, where iron recorded the highest concentration, and copper showed the lowest concentration (Fig. 2 & Table 1).

The arrangement of heavy elements in the waters of this river was sequenced as follows: Fe> Br > Zn > Cr > Cu. The iron element recorded the highest concentrations at a significant level (<0.05) compared to the other elements, particularly in the cold months. Generally, most of the elements recorded higher concentrations in the hot

months; from June to September 2021. The iron element recorded the highest values, especially in the hot months (1.3 mg/l) that were less than the permissible limit (<2 mg/l).

The study of **Singh *et al*. (2019)** on fish *Labeo rohita* mentioned that the essential physiological functions of many organisms are positively affected by the iron metals; However, if an increase was detected in their concentrations, they would turn poisoning. It is worth mentioning that, the high iron content in the water bodies leads to lower productivity in the aquaculture systems. The previous authors noticed changes in the blood and the oxidative stress represented by the changes in the activity of the antioxidant enzyme in addition to the changes recorded in the histological parameters.

The copper element recorded close concentrations during the months of the year within 0.02 – 0.05 mg/l, which were within the permissible limits (< 0.2 mg/l). Copper is one of the essential elements that humans need. Nevertheless, if its concentration in water increases, it becomes toxic to aquatic organisms as well as to humans. Copper is an essential element for human life. This mineral is involved in multiple cellular processes; on the other hand, residues from industrial processes of copper can lead to serious environmental problems. Including physiological effects and environmental damage that directly or indirectly affect human health (Latorre *et al*., 2019).

As for the Br element, it was recorded within (0.02 mg/l) in May month and (1.08 mg/l) in November, which was within the permissible concentration (<1 mg/l). The reason for its existence was from the industrial activity of the electric power plant near the sampling area. Chromium element (Cr) showed the lowest value (0.02 mg/l) for March and the highest value was (0.37) for August. Air deposits resulting from gaseous emissions from the oil industry, in addition to electrical generators, lead to the pollution of the river with minerals such as chromium and bromine. The low level of its concentration in river water attributed to its solubility, in addition to the fact that heavy metals bind to suspended colloids easily over the adsorption progress. (Mimba *et al*. 2017).

Zinc element is one of the essential elements recorded the highest value was (0.7 mg/l) for April, where it was within the permissible measurements (< 2 mg/l) Zinc element has an effect on the hepatic enzymatic activity of live fish at a concentration level (1.2 mg/l) (Aldoghachi *et al*., 2019), as well as, when its concentration rises, it leads to toxic effects on aquatic organisms.

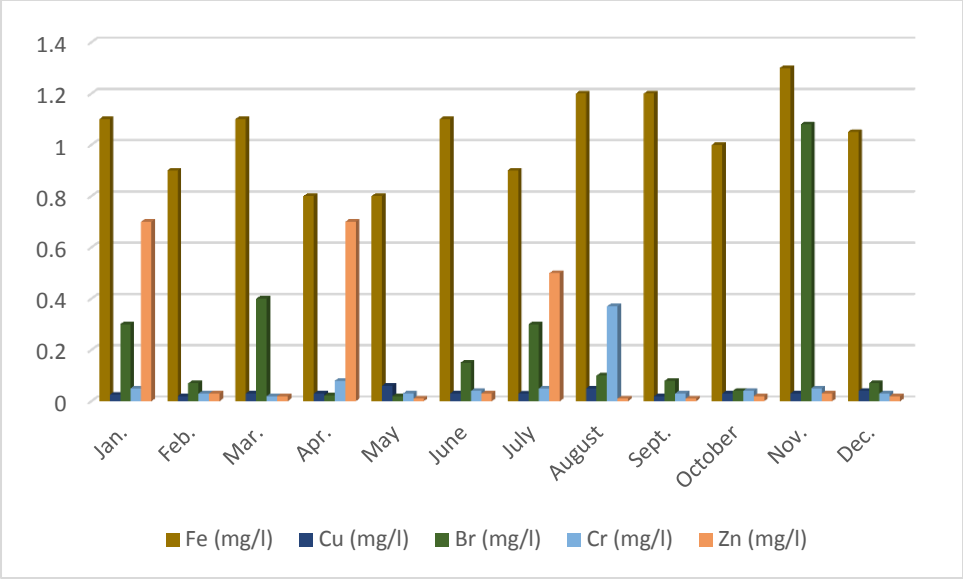

Fig. 2. Heavy metals concentrations (mg/l) of water samples collected from Shatt Al-Arab River during months of 2021

Table 1. Monthly variations of metals concentration in Shat Al-Arab River 2021

Month	**Fe (mg/l)**	**Cu (mg/l)**	**Br (mg/l)**	**Cr (mg/l)**	**Zn (mg/l)**
Jan.	1.1	0.025	0.3	0.05	0.7
Feb.	0.9	0.02	0.07	0.03	0.03
Mar.	1.1	0.03	0.4	0.02	0.02
Apr.	0.8	0.03	0.022	0.08	0.7
May	0.8	0.06	0.02	0.03	0.01
June	1.1	0.03	0.15	0.04	0.03
July	0.9	0.029	0.3	0.05	0.5
August	1.2	0.05	0.1	0.37	0.01
Sept.	1.2	0.02	0.08	0.03	0.01
October	1	0.03	0.04	0.04	0.02
Nov.	1.3	0.03	1.08	0.05	0.03
Dec.	1.05	0.04	0.07	0.03	0.02
Permission limit	<2	< 0.2	<1	0.1	<2

As for the total petroleum hydrocarbons (PHCs), the current results showed a slight fluctuation during the months of 2021 and the highest value was in July (5.36 µg/l) (Fig. 3), all of which were with the acceptable level for environment (<10 µg/l).

In general, there are many factors that completely affected this River water, the most significant factor is the tide coming from Arabian Gulf water which has distinctive activity in the transport of crude oil and therefore the oil hydrocarbons enter with the tidal movement into the Shatt al-Arab waters, especially the hot months when the water level of the Tigris and Euphrates decreases, and the discharge decrease with it. Previous research in the waters of the Arabian Gulf and Shatt al-Arab River recorded that the presence of petroleum hydrocarbons, A review of the northern Arabian Gulf by Al-Imarah *et al*. (2007) for water and sediment, where they recorded levels ranged between (2.5-47 µg/l) in the dissolved water phases and (1.62-31.1 µg/g) in the particulate phase. Thus, it affected the level of oil hydrocarbon concentrations in sewage waters, inland waters, and they attributed this to the waterways in southern Iraq were affected by the illegal transportation of oil derivatives. Furthermore, the ballast water that is discharged from big ships, in addition to the effect of waterways by oil refineries (Abadan and Shuaiba refineries).

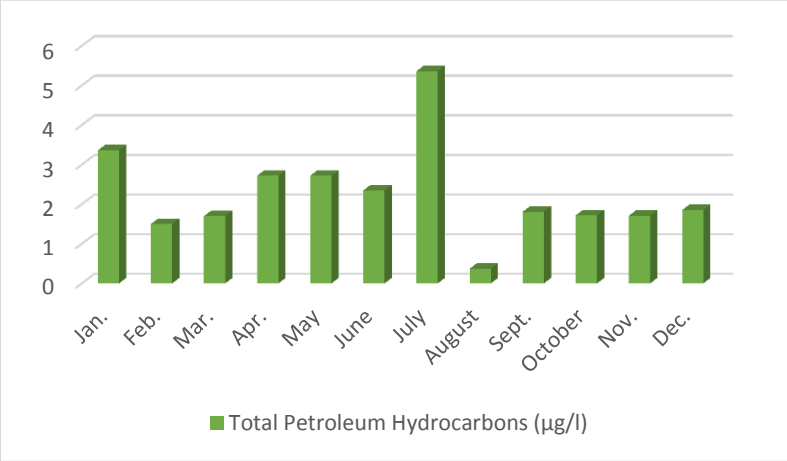

Fig. 3. Monthly differences of Total Petroleum hydrocarbons concentration (µg/l) in Shatt Al-Arab River. Permission limit (10µg/l).

Physico-chemical parameters

The current results showed that the pH was in the alkaline direction (7.3-7.9) constant for all month (Fig. 4). However, pH in water from Shatt Al-Arab River are with permissible level for aquatic organisms. When the pH is suitable for organisms, they will thrive, while the pH decreases, the solubility of metals in the water will increase, and then becoming more toxic to aquatic organisms (Mota *et al*., 2018). As for the water temperatures, they were within the guidelines for the acceptable level (<35 ºC), the values ranged from (16- 31 ºC) for January and July respectively (Figure 4).

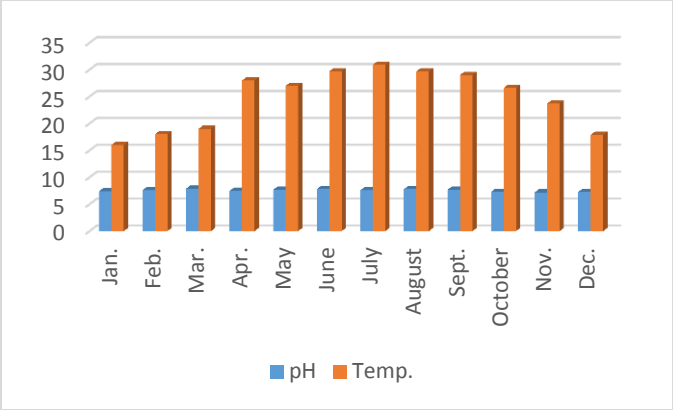

Fig. 4. Monthly differences of pH and Temperature (ºC) in Shatt Al-Arab River water. Acceptable level (6-9.5) and (<35 ºC) for pH and for temperature respectively.

The parameter mean of total suspended solids in current results for Months 2021 is shown in Figure (5). The data of this study indicated that TSS value were within the permissible levels for industrial uses (<60 mg/l), except for February and March, it reached concentrations (60 and 68 mg/l) respectively (fig. 5). Unusual high TSS concentrations results have negative effects on fish physiology and behavior and trans generational implications (Kjelland *et al*., 2015). Moreover, it might have respiratory impacts via thickening gill lamellae if its concentrations reached 100-500 mg/l for a duration of 21 days (Cavanagh *et al*., 2014)

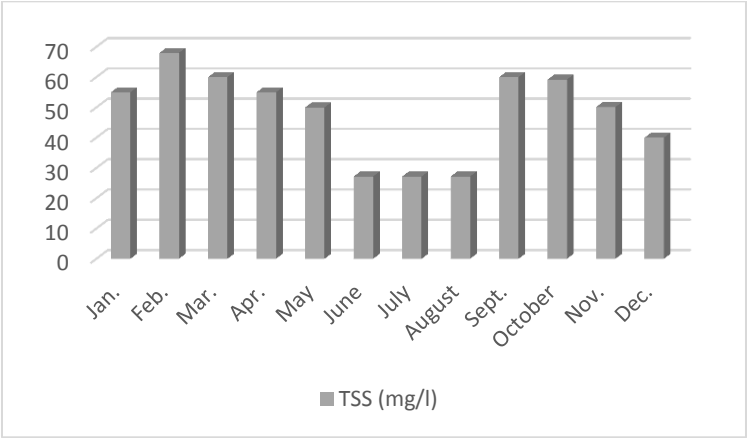

Fig. 5. Monthly variations of TSS values (mg/l) in Shatt Al-Arab River water. Permission limit (<60 mg/l)

Chloride recorded a high concentration level in Shat Al-Arab River during the months of 2021 showed in Figure (6), the higher value was (888 mg/l) for June which was higher than acceptable level for humans or industrial uses (< 250 and < 600) respectively (CCME 2008), while the lowest value was August (325) . Chloride is considered a toxic pollutant, and when its concentration in water increases, it causes endocrine disorders, in addition to being a mutagenic and carcinogenic substance for organisms that live in water (Granato *et al*., 2015). Many of the concentrations of this chloride in the waters of this studied river are from the source of the salty tides that came from the waters of the Arabian Gulf, especially in the hot season (Lateef et al., 2020).

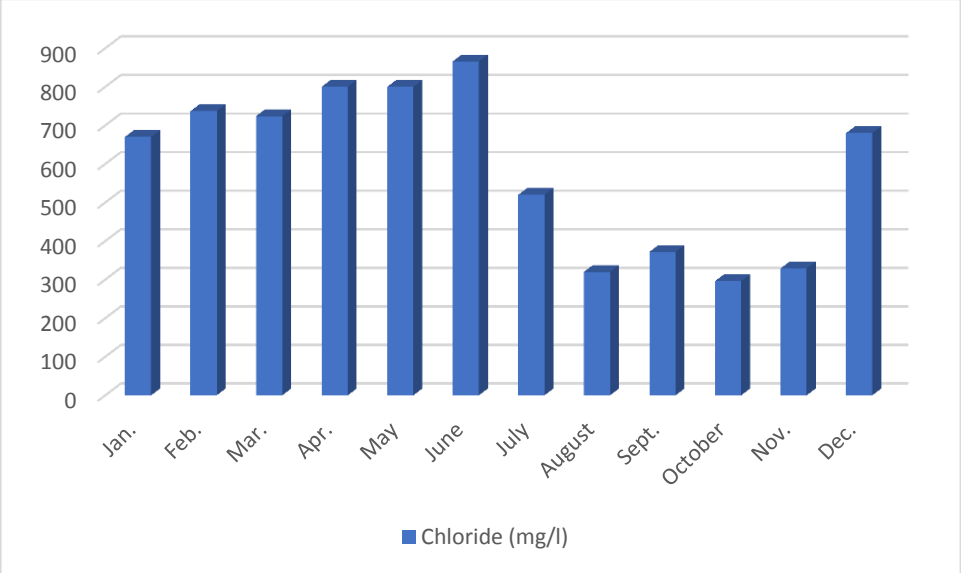

Fig. 6. Monthly variations of Chloride values (mg/l) in Shat Al-Arab River water. Permission limit (600 mg/l).

Concerning the concentrations of sulfates, phosphates and nitrates in river water, they were recorded in Table (2), Sulphate data average in most months during the year are exceeded than the permissible limit of CCME (2008) for humans or industrial uses where the highest value was recorded in March (677 mg/l). Water pollution with sulfates leads to an increase in sulfides and a rise in alkalinity in water that leads to hydrolysis Moreover, it causes eutrophication, and in addition to raising the level of sulfate reasons a substantial reduction in production of biomass, and thus, it causes a decrease in growth rates (Geurts *et al*., 2009).

The current data of PO4 concentrations during months 2021showed in Table (2). The high value of PO4 documented (2.1 mg/L) in May. Industrial raw materials, as well as agricultural waste water, are one of the main reasons for the presence of PO_4 ions (Grela *et al*., 2020). Al-Saadi *et al*. (2020) studied some of parameters in Shatt al-Arab River during the period 2017 to 2018, they reported that Cl was 225-22325mg/l, sulphate was 140-1600 mg/l, and PO4 was 0.22-0.97mg/l,

Regarding NO3, higher value in the current study was (1.5 mg/L) for April and December. High concentrations of nitrates in the aquatic medium affect the growth of fish and plants, as well as cause damage to their quality. Phosphate and nitrate concentrations recorded in the current study were within the standard limits that mentioned by Philminaq (2016) (< 3 mg/l for PO4 and <50 mg/L for NO3) for aquatic life.

Table 2. Monthly variations of SO_4, PO_4 and NO_3 concentrations (mg/L) in Shatt Al-Arab River during 2021.

Month	**SO4(mg/l)**	**PO4(mg/l)**	**NO3(mg/l)**
Jan.	578	1.5	1.4
Feb.	610	1.9	1.1
Mar.	677	1.6	1.1
Apr.	495	1.9	1.5
May	495	2.1	0.6
June	600	1.2	1.1
July	490	1.5	0.9
August	309	1.5	1.1
Sept.	367	1.65	1.1
October	363	1.6	1.1
Nov.	311	1.1	1.2
Dec.	610	1.3	1.5
Permission limit	<400	<3	<50

CONCLUSION

Heavy metals content and petroleum hydrocarbons in Shatt Al-Arab River were under acceptable environmental limits. The variation of physic-chemical parameters of Shat Al-Arab River prejudiced by the low water levels of the Tigris and Euphrates rivers and the chemical ions inflow from these rivers moreover the marine salts coming from Arabian Gulf. Levels of TSS, Cl and SO_4 were higher than the permissible environmental limits.

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REFERENCES

Adeniji, A.O.; Okoh; O. and Okoh, A. (2017a). Analytical methods for the determination of the distribution of total petroleum hydrocarbons in the water and sediment of aquatic systems: a review. Journal of Chemistry. 2017, Article ID 5178937, 13 pages. https:// doi.org/10.1155/2017/5178937

Adeniji, A.O.; Okoh; O. and Okoh, A. (2017b). Petroleum Hydrocarbon Proles of Water and Sediment of Algoa Bay, Eastern Cape, South Africa. Int. J. Environ. Res. Public Health. 14: 1263.http:// doi:10.3390/ijerph14101263

Al‑Asadi, S.A.; Al-Qurnawi, W.; Al Hawash, A.; Ghalib, H. and Alkhlifa, N. (2020). Water quality and impacting factors on heavy metals levels in Shatt Al‑Arab River, Basra, Iraq. Applied Water Science, 10:103. https://doi.org/10.1007/s13201-02001196-1

Aldoghachi, M.A.; Al-Zaidy, F. and AlKatrani, L. (2019). Effects of sublethal zinc ions and acute crude oil exposure on serum enzymes activity of Carassius gibelio. J Anim Behav Biometeorol, 7:155-159. doi.org/10.31893/2318-1265jabb.v7n4p155159.

Al-Imarah, F.J.; Hantoosh, A. and Nasir, A. (2007). Petroleum hydrocarbons in water and sediments of northwest Arabian Gulf 1980-2005. Aquatic Ecosystem Health & Management. 10 (3): 335 – 340.http:// dx.doi.org/10.1080/14634980701513200

Al-Taei, S.A.; Abdulla, S. and Lafta, A. (2014). Longitudinal intrusion pattern of salinity in Shatt Al Arab estuary and reasons. JKAU: Mar. Sci., 25 (2): 205-221. DOI :10.4197/Mar. 25-2.10

APHA (American Public Health Association), (1998). Standard method for the examination of water and waste water -20th edition. Washington, D C. (American Public Health Association pp 1136.

Cavanagh, J. E.; Hogsden, K. L. and Harding, J. S. (2014). Effects of suspended sediment on freshwater fish. Greymouth 7805. Retrieved from http://www.envirolink.govt.nz/PageFiles/1301/ 1445-WCRC129Effects of suspended sediment on freshwater fish.pdf

CCME Canadian Council of Minister of the Environment (2008). Canadian Water Quality Guidelines. https:/ /www.ccme.ca/files/Resources/supporting_ scientific_documents /cwqg _pn_1040.pdf

Geurts, J.J.; Sarneel, J.; Willers, B.; Roelofs, J.; Verhoeven, J. and Lamers, L. (2009). Interacting effects of sulphate pollution, sulphide toxicity and eutrophication. Environmental Pollution 157: 2072–2081. https://doi:10.1016/ j.envpol.2009.02.024

Grela, A.; Lach, M. and Mikula, J. (2020). An efficacy assessment of phosphate removal from drainage waters by modified reactive material. Materials, 13: 1190; doi:10.3390/ma13051190 Islam et al., 2015

Jaber, M.M.; Al-Jumaa, Z.; Al-Taee, S.; Nahi, H.; Al-Hamdany, M.; Al-Salh, M.; and Al-Mayahi, B., (2021). Bioaccumulation of heavy metals and histopathological changes in muscles of common carp (*Cyprinus carpio* L.) in the Iraqi rivers. *Iraqi Journal of Veterinary Sciences*, 35(2), 245-249. https://doi: 10.33899/ijvs.2020.126748.1368

Jantawongsri, K; Norregaard, R.; Bach, L.; Dietz, R; Sonne, C; Jorgensen, K.; Lierhagen, S.; Ciesielski, T.; Jenssen, B.; Haddy, J.; Eriksen, R. and Nowak, B. (2021). Histopathological effects of short-term aqueous exposure to environmentally relevant concentration of lead (Pb) in shorthorn sculpin (*Myoxocephalus scorpius*) under laboratory conditions. Environmental Science and Pollution Research, 28(43):61423-61440. https://doi.org/10.1007/s11356-021-14972-6

Lateef, Z.Q.; Al-Madhhachi, A. and Sachit, D. (2020). Evaluation of Water Quality Parameters in Shatt AL-Arab, Southern Iraq, Using Spatial Analysis. Hydrology, 7(4) 79; https:// doi:10.3390 / hydrology 7040079

Latorre, M.; Troncoso, R.; Uauy, R., (2019). Chapter 4 - Biological Aspects of Copper, Editor(s): Nanda Kerkar, Eve A. Roberts, Clinical and Translational Perspectives on WILSON DISEASE, Academic Press, 2019, pp. 25-31, ISBN 9780128105320, https://doi.org/10.1016/B978-0-12-810532-0.00004-5.

Mimba, M.E.; Ohba, T.; Nguemhe Fils, S.C.; Wirmvem, M.J.; Numanami, N.; and Aka, F.T. (2017). Seasonal hydrological inputs of major ions and trace metal composition in streams draining the mineralized Lom Basin East Cameroon: Basis for Environmental Studies. Earth Syst Environ. 1(22) : 1–9. https://doi.org/ 10.1007/s4174 8-017-0026-6

Mota, V.C.; Hop, J.; Sampaio, L.A.; Heinsbroek, L.; Verdegem, M.; Eding, Ep. and Verreth, J. (2018).The effect of low pH on physiology, stress status and

growth performance of turbot (*Psetta maxima* L.) cultured in recirculating aquaculture systems. Aquac Res., 49:3456–3467 .https://doi.org/10.1111/are.13812.

PHILMINAQ, Mitigating Impact from Aquaculture in Philippines, (2016). Water quality criteria and standards for freshwater and marine aquaculture. The Water Network, Marine Conservation Areas. https://thewaternetwork.com/_/marine-conservation-areas/library-Nuo/document-XAs/list

Shah, N.; Khisroon, M. and Shah, S.S.A. (2020). Metals Distribution, Histopathological Alterations, and Health Risk Assessment in Different Tissues of Fish (*Ctenopharyngodon idella*). Biol Trace Elem Res (2020). https://doi.org/10.1007/s12011-020-02373-8

Singare, P.U.; Jagtap, A. and Lokhande, R. (2011). Water pollution by discharge effluents from Gove industrial area of Maharashtra, India: dispersion of heavy metals and their toxic effects. International Journal of Global Environmental Issues, 11(1): 28-36. DOI: 10.1504/IJGENVI.2011.040249

Singha, M.; Barmana, A.; Devia, A.; Devib, A. and Pandey, P. (2019). Iron mediated hematological, oxidative and histological alterations in freshwater fish *Labeo rohita*. Ecotoxicology and Environmental Safety, 170: 87-97. andhttps://doi.org/10.1016/j.ecoenv.2018.11.129