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Seasonal variation for Some Heavy Metals in selected stations at Shatt Al-Arab River

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Abstract

Shatt al-Arab River is one of the most critical inland streams in Iraq because of its different monetary and social significance, the essential wellspring of surface water in Basrah Governorate. Heavy metals are the main sources of pollution in Shatt al-Arab. In this work, standard methods were adopted to collect, transport, and preserve samples as described in (APAH 2005) to get the best result. The samples were collected from Al-Qurna, Al-Ashar, and Abo Al-Khatib from Autumn 2019 to summer 2020. The samples were collected to measure the following parameters (temperature, PH, Cl^-, SO_4^{-2}, HCO_3^- and some heavy metals in water, namely, Pb, Cd, Cu, Mn, and Ni). Minitab version 19 for statics analysis was used. The results showed in range: temperature (16.7 – 31.8) ^oC, pH (7.78 – 7.99), EC (2.81 – 4.05) ms/cm, Cl^- (592.9 – 1211) mg/l and SO_4^{-2} (199.2 - 451.2) mg/l. Heavy metals in water were Pb (34.8 – 102.4) µg/l, Cd (2.18 – 5.77) µg/l, Cu (43.9 – 87.1) µg/l and µg/l, Ni (25.6 – 59.7) µg/l. The heavy metals Cu, Cd, Pb, and Ni were recorded to have an observed anthropogenic origin, mainly from manufacturing activities. However, the primary sources are industrial discharges, chemical weathering of minerals, domestic sewage and waste, atmospheric precipitation, and traffic sources that increase their concentration in water.

Keywords: Shatt Al-Arab River, Water pollution, heavy metals, poison

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Introduction

The aquatic system became contaminated with heavy metals. Heavy metals are natural metallic elements of the Earth's crust, unable to degrade or destroy a small material. It refers to elements whose density is higher than 5 g/cm^3 and toxic at low concentrations (Al-Juboury, 2009). many sources can supply the aquatic environment with heavy elements with different concentrations: these sources, either natural sources and anthropogenic or non-natural sources. The natural sources include erosion and weathering operations of natural elements, rocks, forest fires, vegetable crops, and storms. However, the anthropogenic sources represent all human activities, such as industrial waste such as fertilizers, textiles, batteries, leather, dyes, and refineries' outputs. In addition to household waste, it plays a significant role in adding quantities of heavy elements to the water (Brown *et al*., 2000; Dukes *et al.*, 2020; Koster *et al*., 2020; Liu *et al*., 2020). Pollution of heavy metals is a threat to the environment due to their toxicity, persistence, and bioaccumulation in nature. Heavy metals affected the water system; countless toxins become bound to the sediment due to the joining among streams and seawater, which can influence healthy aquatic life and humans through bioaccumulation enhancement in the natural food chain. The concentrations of heavy metals in the living condition of oceanic life forms is the essential factor influencing the amassing of substantial metals in living beings and biomass (Ali *et al*., 2016; Eeshwarasinghe *et al*., 2019; Fan *et al*., 2020). Cu (Copper), Pb (Lead), and Cd (Cadmium) have been reported to be the most dangerous heavy metals. In general, it is accepted that numerous harmful metals apply their awful impacts by troubling the compound frameworks of living beings. Vast numbers tie to explicit chemicals, and proteins vital for cell capacity and along these lines contend with other substances fundamental for support. They proceeded with the ability of cells. (Pandey & Madhuri, 2014).

Also, heavy metals in drinking water are connected regularly to human harming; however, the body requires them in limited quantities. Therefore, They constitute a critical group of environmentally hazardous substances (Duruibe *et al.*, 2007; Järup, 2003). Pb is one of the commonly present heavy metals in drinking water. So, in general, the metabolism of toxic substances and compound inhibitors to Pb can supplant Ca (calcium) in bone issues for long-term substitutes. (Järup, 2003; Mohod & Dhote, 2013). While Cd is very lethal even in low concentrations and will bioaccumulate in living beings and environments, it also has a natural half-life in the human body, extending from 10 to 33 years and long-term exposures to Cd, likewise initiating renal harm. So, Cd is one of the needed toxins structures observed in many nations and universal associations. The contamination of water is straightforwardly identified with water pollution. As a result, there is have to consistently survey the nature of ground and surface water sources (Duruibe *et al.*, 2007; Mohod & Dhote, 2013).

Shatt al-Arab river is one of the most critical inland streams in Iraq because of its different monetary and social significance and the essential wellspring of surface water in Basra Governorate. It also utilized various purposes, including providing drinking water, water system, farming, angling, and modern employments. This stream has a crucial significant area: the water entrance connecting Iraq with the Arab Gulf locale. Regardless of the signs above, it experiences a section of different poisons. It is put legitimately with no treatment frequently stacked with toxins that establish health hazards, negatively affecting this stream's beneficial uses. (Moyel & Hussain, 2015). In general, the temperature has a significant role in incrementing heavy metals toxicity. High temperatures get dangerous synthetic compounds are dissolved and increase the poisonous of numerous substantial metals, prompting expanded affectability of the organisms for toxic substances (Al-Helaly, 2010). On the other hand, pH plays a vital role in dissolving heavy metals and influencing their development. Also, chemical parameter anions such as Cl- and SO4-2 can react to heavy metals and precipitation sediment.

Shatt Al-Arab river suffered from pollution by heavy metals; many studies showed that like, Abdullah (2013) studied heavy metals in the Shatt Al-Arab River (Iraq). Six heavy metals: Fe, Zn, Cu, Pb, Cd, and Ni. The circumstance is a matter of worry as Fe, Zn, Cu, Cd, Pb, and Ni were anthropogenic inception and mostly originated from industrial activities, through municipal sewage, domestic wastes, traffic sources, atmospheric depositions, and Chemical weathering of minerals.

Akesh (2017) studied the concentration of two heavy metals, Pb and Hg, in rivers and sediments soil at different Basrah sites. The result showed that the level of these elements on-trend Pb>Hg because of combined heavy metal concentration and heavy metal assessment indicates that industrial activities and traffic emission represent Hg and Pb's essential sources.

This study counted the total heavy metals' concentration, namely, Pb, Cd, Ni, and Cu, and studied the effect of locals' change by collecting samples from three different stations, Alqurna, Alashar, and Abu Alkhasib. The impact of seasons changes by collecting samples at four seasons: autumn, Winter, Spring, and summer.

Materials and Methods

Study area

Shatt Al-Arab River is the primary source of surface water in Basrah, which stretches out from the North of Basrah toward the South, where it streams into the Gulf. Shatt Al-Arab River originates from the Tigris and the Euphrates Rivers, which stream inside Iraq and Karkheh and Karon's waterways inside Iranian terrains. Since the water shortage, the Euphrates River was cut as a feeder for Shatt Al-Arab and the water utilized to take care of Al-Hammar march, just as Iran removed the waters of Karkheh and Karon Rivers to reach Shatt Al-Arab. In this way, the Tigris River turns into the primary source of water to feed Shatt Al-Arab (Al-Hejuje, 2014; Al-Janabi *et al*., 2019; Hamdan, 2020)

Water samples were collected from three stations along the Shatt Al-Arab River. The first station is Al-Qurna (31.004361 N and 47.442989 E) in North of Basra, the second is AL-Ashar (30.522385 N and 47.841856 E), and the third station is Abo AL-Khasib (30.469512 N and 47.918127 E). See figure (1).

Figure 1: The study stations

Water samples were collected from the above study stations from October 2019 to September 2020 at three replications per station to obtain accurate results

Standard methods were adopted to collect, transport, and preserve samples as described in (APHA 2005) to get the best result. Plastic bottles were used to gather water samples from 10-30 cm subsurface of water; they were washed with the station water and filled entirely, and then placed in the icebox,

pH and temperature were measured in the field directly by WTW portable German-made model (pH 3110 set 2 & Cond 3110 set 1). Laboratory tests were performed as according (APHA, 2005) and measured anions such as chloride and sulfates

According to Bhuyan et al. (2017), Heavy metals have been extracted. Water sample 100 mL was taken in a Teflon beaker, and 5 mL HNO3 was added after that by hot plate was heated, and concentrated for two hours at 105̊C to 25 mL and transferred into 100 mL volumetric flask. Distilled water was added to supplement the mark then measured by the Atomic absorption spectroscopy model ASC-7000 Japan in the marine center at Basrah university. Statistical analysis has been used the program Minitab ver 19.2020.1, ANOVA analysis test to analyze the results under the probability level 0.05.

Results and Discussion

Temperature is one of the most significant factors in the aquatic environment (Darwall *et al.*, 2018; van Rees *et al.*, 2020). In this study, the result of the temperature of water shown in Al-Qurna station ranged between (16.25^{o}C - 32.3^{o}C), Al-Ashar station ranged between (16.75^{o}C - 32.5^{o}C), and Abo Al-Khasib station went between (16.35^{o}C - 32.5^{o}C). ANOVA showed that the maximum mean degree was 31.8^{o}C in summer. In contrast, the minimum mean degree was 16.7^{o}C in winter; there is a difference in temperature between the seasons ($p<0.05$) See figure 2.

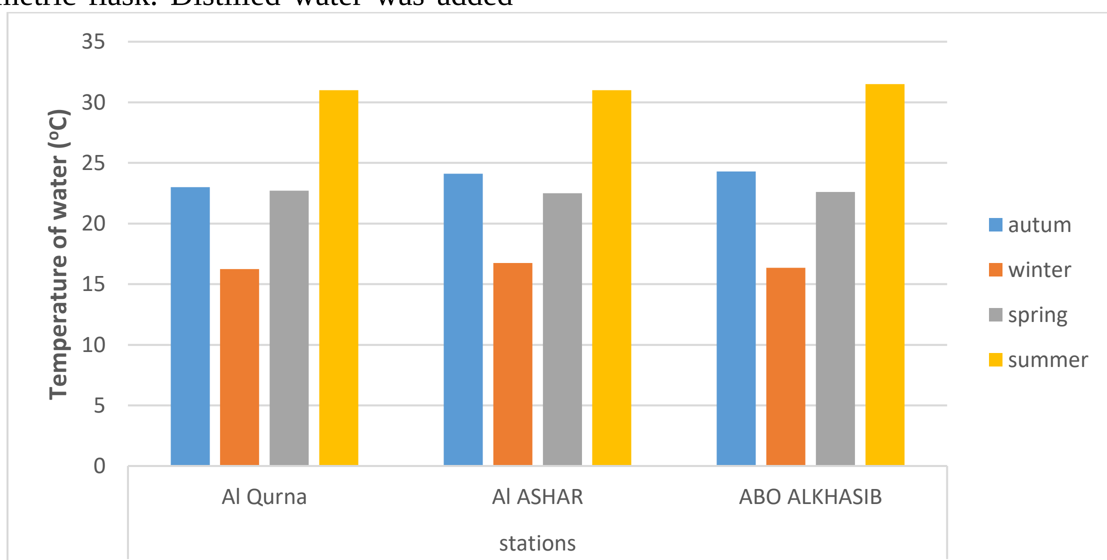

Figure 2: Water temperature (^{o}C) during the study

These results are the variation in the Iraqi climate, which is characterized by being hot, dry in summer and rainy, and humid in winter. It is possible that the intensity of radiation in solar and the length of the day, especially in summer. These results agree with the results reported by Al-Hejuje, (2014) and Abd al-Rasuil, (2019).

pH values were on the alkaline side at three stations in the current study, the highest recorded pH value 8.15 in summer at Al-Ashar station. In contrast, the lowest recorded pH value of 7.6 in spring at Al-Qurna station. ANOVA Analytics, the results have been shown a difference between seasons ($P<0.05$), the highest mean value was 7.99 in summer, and the lowest mean value found 7.78 in spring (Figure 3).

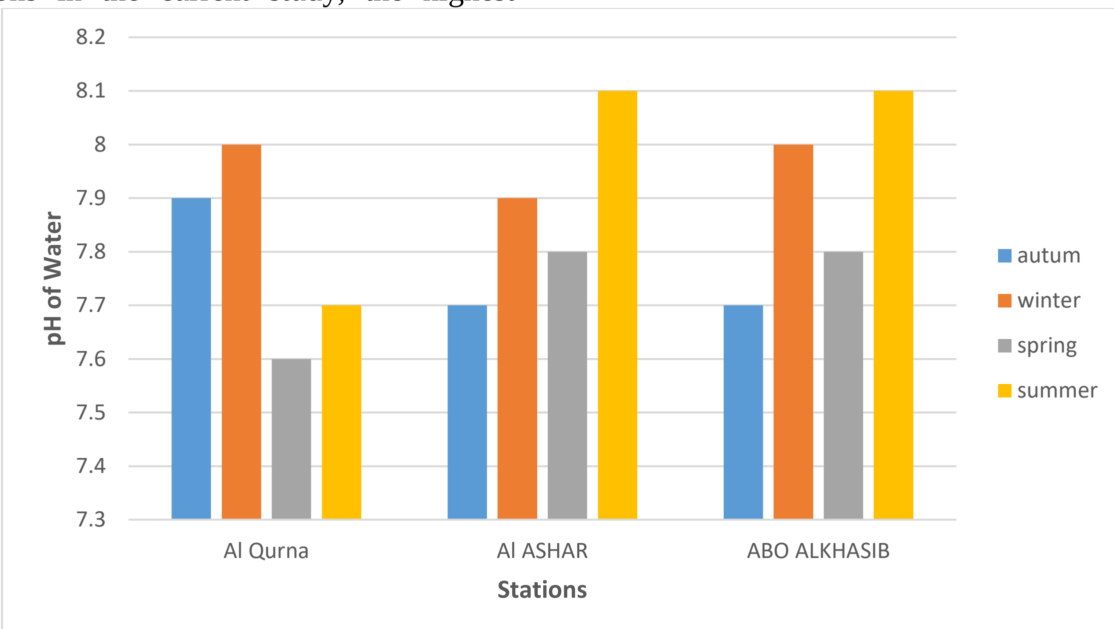

Figure 3: Potential of Hydrogen ions (pH) value during the study

The results found that increased pH value in the aquatic ecosystem during precipitation may be caused by the runoff of alkaline materials and the precipitation. Also, the decreasing pH value could be due to the decomposition of organic matter from wastewater release, which causes acidification, and eventually shrinks the pH value (Rubio-Arias *et al.*, 2013; Varol, 2011). However, pH is directed to influence other physicochemical properties of the water, which affect the biotic composition of the systems. The noticed values in the current study of the pH could be partly attributed to the industrial-wastes disposal, the existence of chemical detergent, domestic wastewater pollution, production of bicarbonate and carbonate ions and are often because of limestone (Balasime *et al.*, 2013; Chougule *et al.*, 2009; van Rees *et al.*, 2020). These attributes are in agreement with Abd al-Rasuil (2019), Al-Hejuje (2014), Moyel & Hussain (2015).

Sulfate anion is found in the most natural water bond with cations at a few milligrams concentrations to thousands of mg/l. $SO4^{-2}$ is considered one of the least toxic anions where WHO did not recommend any value as a guideline for drinking water (Bielmyer-Fraser *et al.*, 2020; WHO, 2011). The highest value was measured 560 mg/l in spring at Al-Ashar station, and the lowest value was 108mg/l in autumn at Al-Qurna station. ANOVA analysis showed that the lowest mean value was 199.2 mg/l in autumn, while the highest mean value was 451.2 mg/l in spring. This analysis revealed a different season ($P<0.05$). See figure 4

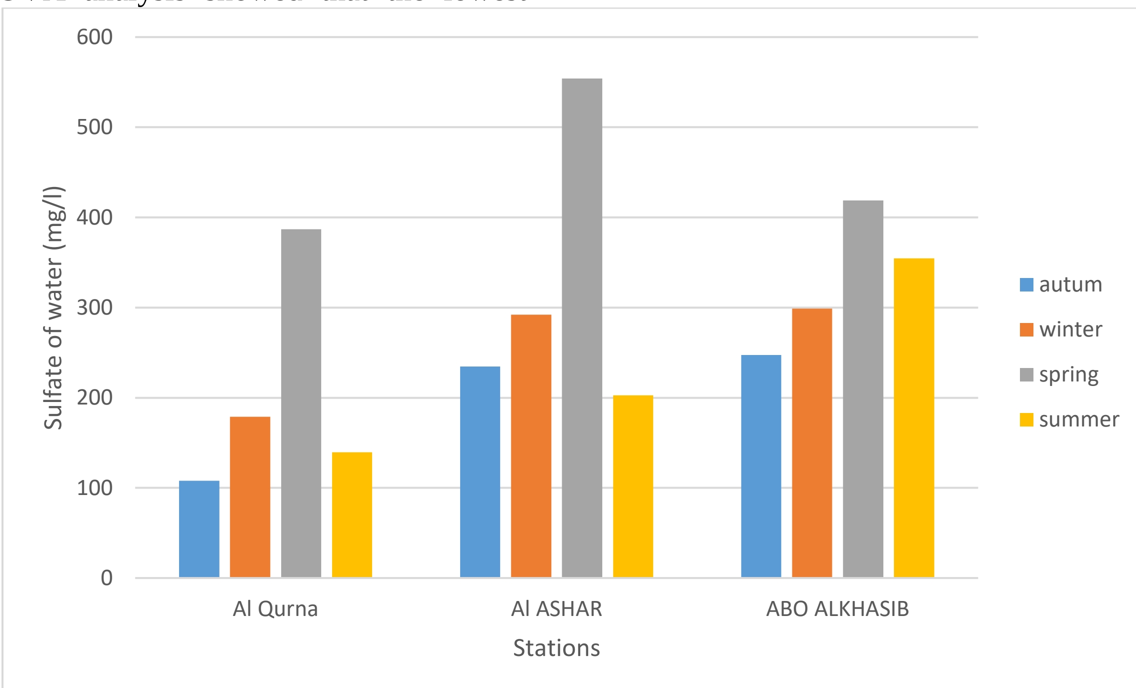

Figure 4: Sulfate ($SO4^{-2}$) concentrations(mg/l) during the study

The results showed a difference in sulfate anion values due to the saltwater wave from the Arabian Gulf. Agricultural activities also have a part in the increasing sulfate compounds and the high petroleum mixtures used for fuel released sulfate compounds to the aquatic system (Al-Hejuje, 2014; Al-Maliky *et al.*, 2015; Varol, 2020). The sulfate levels in surface water are related to emissions of sulfur dioxide from anthropogenic sources. Nevertheless, SO_4^{-2} is one of the anions that cause dominant hardness in water; also, it causes unpleasant taste if it exceeds 200 mg/l (Keller *et al.*, 1986). These results agree with the results reported by Al-Asadi *et al.* (2020)

The chloride anion result showed that Cl concentrations in the highest value were 1480 mg/l in spring at Abo Al-Khasib station. In contrast, the lowest value was 390 mg/l in autumn at Al-Qurna station. The highest mean value was 1211 mg/l in autumn, and the lowest mean value was 592 mg/l in summer. The analysis found significant differences in seasons and stations at $P<0.05$. (figure 5)

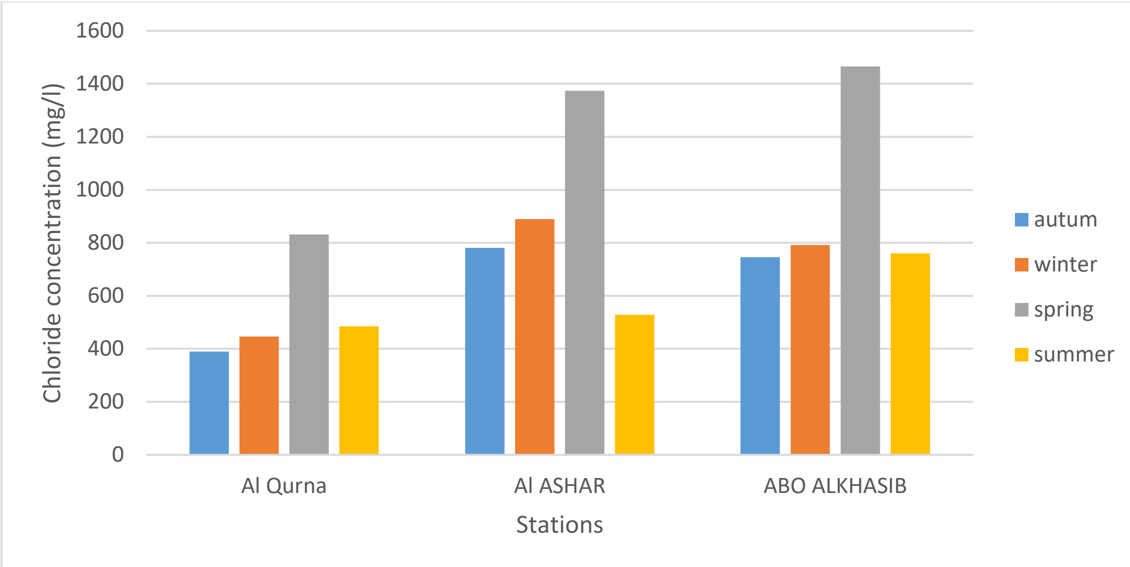

Figure 5: Chloride (Cl^-) concentrations(mg/l) during the study

The results revealed that the highest concentration of Cl^- maybe because Shatt al-Arab polluted sewage water and some industrial waste. As well as it could be caused by the geological components which contain chloride. Also, it may be because of tide sea or any saline water which have a noticeable effect on agriculture and factories (Ji *et al.*, 2020; Wu *et al.*, 2020)

Lead (Pb) is a natural component of the Earth's crust and is generally found in trace amounts in soils, plants, and water (Cheng & Hu, 2010). Lead concentration showed that the lowest value was 23.4 µg/l in spring at Al-Qurna station, while the highest value was 112.25 µg/l in summer at Al-Ashar station. ANOVA analysis showed that the highest mean value recorded was 102.42 µg/l in summer. In comparison, the lowest value was 34.84 µg/l in spring. The analysis found a significant difference in seasons ($P<0.05$). See figure 6

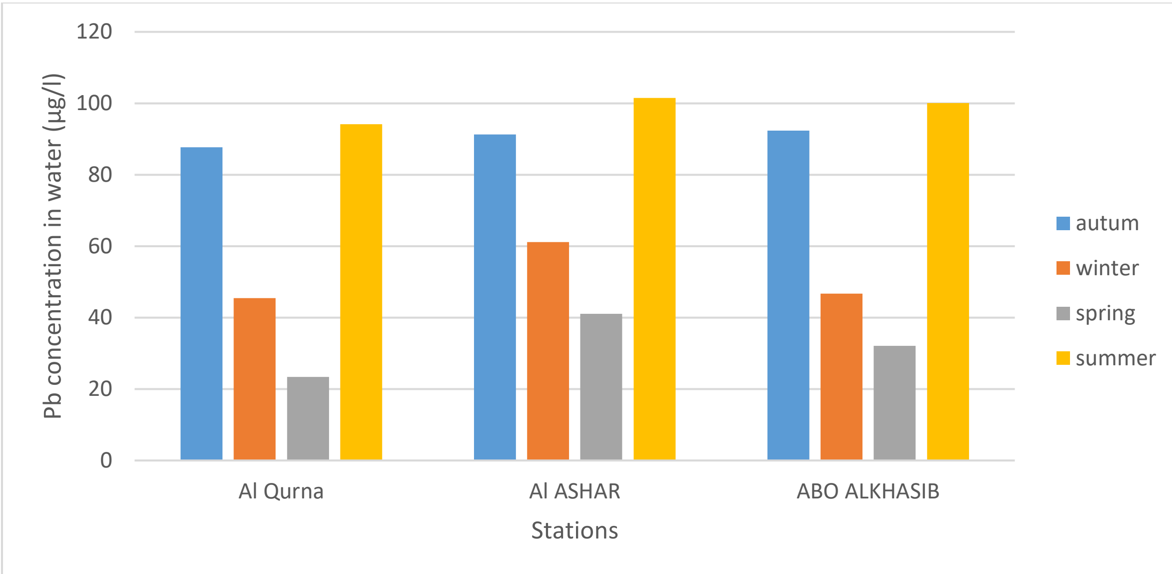

Figure 6: Lead (Pb) concentration in water (µg/l) during the study

The main reason for these results is that the quarantine might cause low concentration in spring for the COVID-19, which reduces the emission of vehicles that is one of the main parts of Pb sources as reported by Al-Hejuje, 2014 (Al-Hejuje, 2014). Anthropogenic activities, including the paint, manufacture of batteries, cement, smelting, and smelting mining, increase Pb concentrations (Cheng & Hu, 2010).

On the other hand, high concentration in summer at Al-Ashar station might cause by an oil spilling accident in Shatt al-Arab and affected all the sites along to the third station Abo Al-Khasib. Also, the temperature has a significant role in incrementing Pb due to dissolved compounds' high temperatures (Al-Helaly, 2010). The statistical analysis showed a significant positive correlation between Pb and temperature ($P<0.05$, $r = 0.704$). This, confirmed what was reported by Al-Helaly, 2010. As well as a significant positive correlation between Pb and some heavy metals, namely, Cu ($P<0.05$, $r = 0.541$), Ni ($P<0.05$, $r = 0.637$), and Cd ($P<0.05$, $r = 0.529$). That could be due to these elements coming from the same sources, such as sewage water, agriculture, and industrial waste. The statical analysis showed a significant negative correlation between Pb and some anions, namely, SO_4^{-2} at ($P<0.05$, $r = -0.537$) and Cl^- at ($P<0.05$, $r = -0.452$), which mean these anions react with Pb and precipitate to the sediment to form salts, such as $PbCl_2$ and $PbSO_4$.

Cadmium (Cd) is one of the most public environmental pollutants produced naturally or anthropogenic. Waterborne cadmium is too toxic for aquatic life (Järup, 2003; Silva *et al.*, 2019). In the present study, the results appeared that the highest value recorded was 8.95 µg/l in summer at Al-Ashar station, and the lowest value was ND in spring at Al-Qurna station. ANOVA analysis showed that the highest mean value was 5.77 µg/l in summer. In contrast, the lowest mean value was 2.183 µg/l in spring; a difference was found in the seasons ($P<0.05$). See figure 7

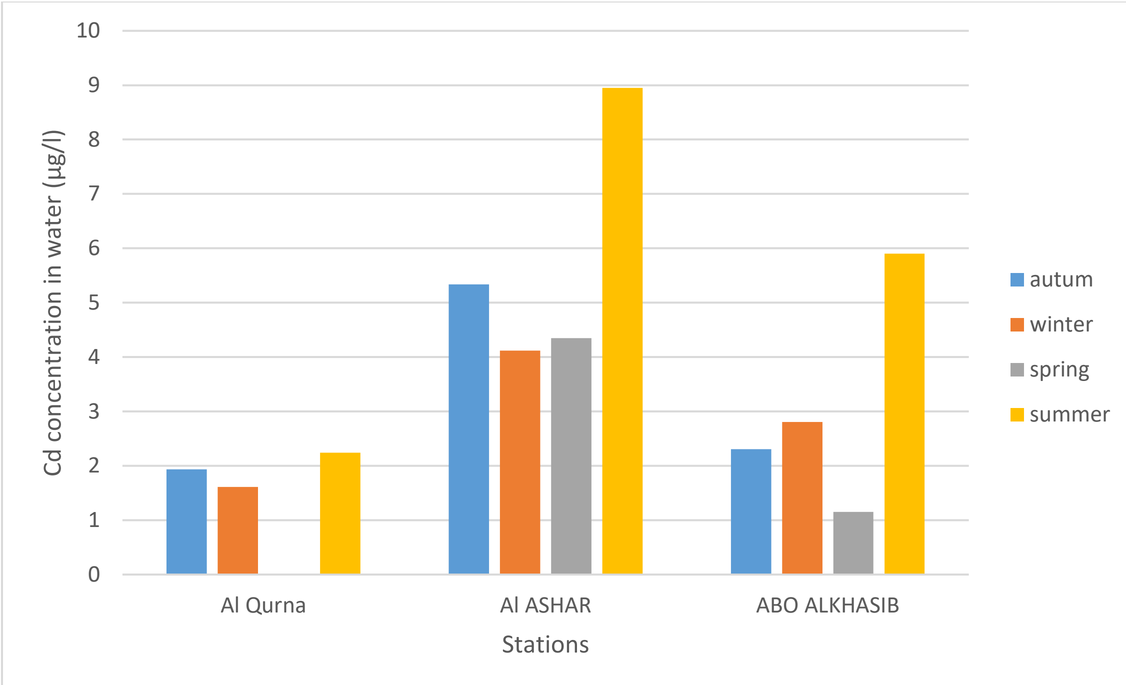

Figure 7: Cadmium (Cd) concentration in water (µg/l) during the study

The reasons for these results that the quarantine might cause a low level in concentration in spring for the COVID-19 lead to reducing the emission of traffic sources that is one of Cd's primary sources, which reported by Al-Hejuje, 2014.

However, the high concentration recorded may be related to the oil spilling accident or temperature rise (Al-Hejuje, 2014). There is a significant positive correlation between Cd and temperature ($P<0.05$, $r=0.510$). This may be because the high temperature dissolved the chemical compounds, as Al-Hejuje (2014) reported. Also, the sources of Cd include human activities and natural sources. The most important ones are human activities such as agricultural areas related to agrochemicals; some fertilizers present Cd as impurities, especially phosphate fertilizers (da Silva *et al.*, 2020; Dukes *et al.*, 2020). Cd is also used in the electric and electronic industry and pigment. Metal mining is another possible source of active and abandoned mines and tailings (Bhuyan *et al.*, 2017; Silva *et al.*, 2019).

Copper (Cu) is a crucial metal for some metabolic activities in organisms (Duruibe *et al.*, 2007). This study showed the highest recorded value was 128.3 µg/l in autumn at Al-Ashar station, and the lowest was 27.90 µg/l in autumn at Al-Qurna stations. ANOVA analysis appeared the highest mean value was 87.1µg/l in summer. In contrast, the lowest mean value was 43.92 µg/l in spring; there is a non-significant difference in seasons ($P>0.05$). See Figure 8

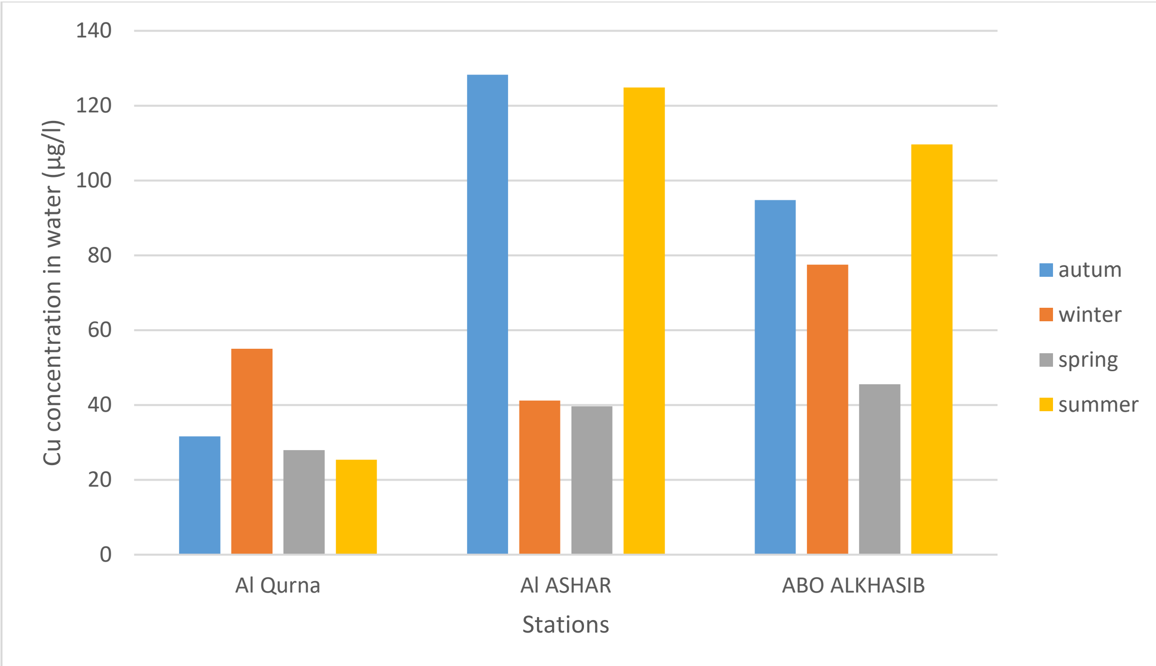

Figure 8: Copper (Cu) concentration in water (µg/l) during the study

These results could be due to Cu found in the environment as a mineral in rocks, soil, and low levels in natural water. Also, it is an essential element required to maintain good health. Low levels of Cu can be found naturally in all aquatic system sources (Liu *et al.*, 2020). A high concentration of Cu gets into the river through mining, farming, manufacturing operations, and municipal or industrial wastewater releases. As well as, Cu can get into water directly through corrosion of Cu pipes (Alam *et al.*, 2020; Kumar *et al.*, 2020). The decrease in Cu value may be because of the low density of most aquatic creatures during winter, which collected this metal in their bodies as essential components for growth (Al-Hejuje, 2014).

A significant positive correlation between Cu and pH ($P<0.05$, $r=0.432$) related that in low pH, the Cu became more soluble in water (Silva *et al.*, 2019; Tao *et al.*, 2012). Also, the analysis found a significant positive correlation between Cu and Cd ($P<0.05$, $r=0.780$). High concentrations of Cu and Cd in the water suggest providing a pathway for metal transport through the food web (Smith *et al.*, 1996).

Nickel (Ni) is the most fundable metal that performs from oil pollution; fossil fuel emission is the primary source of Ni (90%) (Duruibe *et al.*, 2007; Järup, 2003). The highest value was 72.14 µg/l in summer at Al-Ashar station, and the lowest value was 24.5 µg/l in autumn at the same station. ANOVA analysis showed that the highest mean value was 59.77 µg/l while the lowest mean value was 25.62 µg/l in winter, a significant difference found between seasons ($P<0.05$). See Figure 9

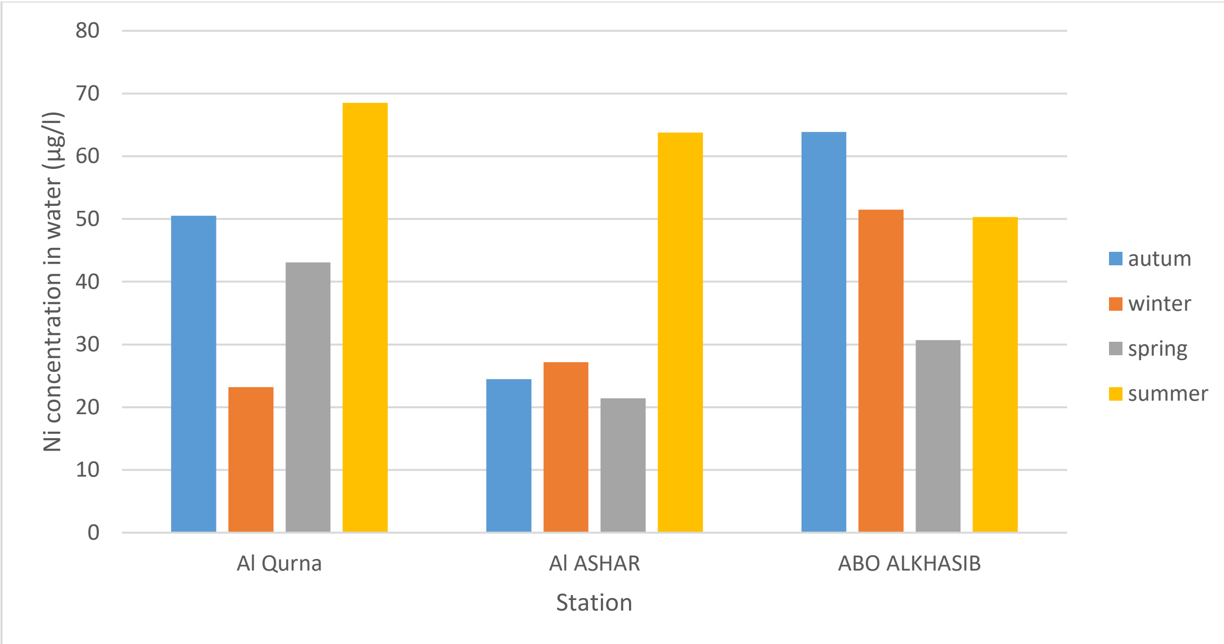

Figure 9: Nickel (Ni) concentration in water (µg/l) during the study

The levels of Ni were significantly higher because of the increased atmospheric precipitation oil pollutants and the excess from the agricultural areas and roads beside the river in rainy time can donate to the considerable quantity of Ni put in the river. In summer, high concentration recorded may be related to the oil spilling accident in Al-Ashar and Abo Al-Khasib station; there was a lot of boat leakage fuel directly to the river or related the temperature rises (Al-Hejuje, 2014).

There is a significant positive correlation between Ni and temperature ($P<0.05$, $r=0.504$). This confirmed what was reported by Al-Healy, 2010. A significant negative correlation between Ni and some anions, namely, SO_4^{-2} at ($P<0.05$, $r =-0.468$) and Cl^- at ($P<0.05$, $r =-0.395$), which mean these anions react with Ni to form salts and precipitate to the sediment.

It can be concluded that anthropogenic origins of Cu, Cd, Pb, and Ni were observed, mainly from manufacturing activities. The primary sources are industrial discharges, mineral weathering, domestic sewage and waste, atmospheric precipitation, and traffic sources.

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التباين الموسمي لبعض العناصر الثقيلة في محطات مختارة على شط العرب

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المستخلص

يعتبر شط العرب من أهم مجاري المياه العذبة في العراق بسبب أهميته النقدية والاجتماعية، كما أنه منبع أساسي للمياه السطحية في محافظة البصرة. تعتبر المعادن الثقيلة من أهم مصادر التلوث في شط العرب. في هذه الدراسة تم اعتماد طرق قياسية في عملية جمع ونقل وحفظ العينات كما هو موضح في (APAH) للحصول على أفضل نتيجة. جمعت العينات من ثلاث محطات وهي القرنة والعشار وأبو الخصيب خلال خريف 2019 إلى صيف 2020، وقيست المتغيرات التالية درجة الحرارة، الدالة الحامضية، وايونات الكلوريد والكبريتات وبعض المعادن الثقيلة في الماء وهي الرصاص والكادميوم والنحاس والنيكل واستخدم برنامج Minitab 19 لتحليل النتائج احصائيا. أظهرت النتائج في مديات: درجة الحرارة (16.7 - 31.8) درجة مئوية، درجة الحموضة (7.99 - 7.78)، ايون الكلوريد (1211 - 592.9) مجم / لتر ، ايون الكبريات (451.2 - 199.2) ملجم / لتر. المعادن الثقيلة في الماء كانت: الرصاص (34.8 - 102.4) ميكروغرام / لتر ، الكادميوم (2.18 - 5.77) ميكروغرام / لتر ، النحاس (43.9 - 87.1) ميكروغرام / لتر والنيكل (– 25.6 59.7) ميكروغرام / لتر توصلت الدراسة الى ان المعادن الثقيلة مثل النحاس والكادميوم والرصاص والنيكل من مصادر بشرية وجاءت بشكل رئيسي من الأنشطة الصناعية. ومع ذلك، فإن مياه الصرف الصحية والبلدية، والنفايات المنزلية، وتقاطعات المرور والترسبات الجوية، والتجوية الكيميائية للمعادن، والتصريفات الصناعية تزيد من تركيزها في المياه.

الكلمات المفتاحية: شط العرب، تلوث المياه، المعادن الثقيلة، سموم