MONITORING HEAVY METALS, CATIONS AND ANIONS LEVELS AND ITS POSSIBLE HEALTH RISKS IN TIGRIS RIVER AT BAGHDAD REGION

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Abstract

Various heavy metals, cations and anions of the Tigris River water in Baghdad region were studied during the winter, spring, summer and autumn of 2009, for 4 sampling sites. In the present investigation the levels of studied heavy metals, cations and anions were found in the range of (0.011-0.333 mg/L) for As, in the water samples (undetectable-0.0043 mg/L) for Sb,(0.011-0.080 mg/L) for Ti, (0.150-0.730 mg/L) for V, (0.01-1.06 mg/L) for Fe, (0.1-0.4 mg/L) for Zn, (0.011-0.15 mg/L) for Pb, (0.01-0.05 mg/L) for Cd, (0.01-0.04 mg/L) for Ni, (50-290 mg/L) for Ca, (97-270 mg/L) for Mg, (0.65-1.74 mg/L) for K, (11-38.33) for Na, (35-113 mg/L) for Cl, (150-256 mg/L) for HCO_3, (96-479 mg/L) for SO_4, (0.93-3.9 mg/L) for NO_3 and (undetectable - 0.360 mg/L) for PO_4. Some parameters like As, V, Fe, Pb, Cd, Mg and SO_4 are higher than the values recommended in international and Iraqi criteria for drinking water, while the rest ions were within the acceptable limits. In general, the results confirmed that Tigris River at study area is slightly contaminated with some hazardous heavy metals especially Pb and Cd which have ability to biological concentration in organisms bodies and that might affect human health as well as the health of the ecosystem.

مراقبة مستويات الفلزات الثقيلة والايونات الموجبة والسالبة وأخطارها الصحية المحتملة في مياه نهر دجلة في منطقة بغداد

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الخلاصة

تم دراسة مختلف الفلزات الثقيلة والايونات الموجبة والسالبة لمياه نهر دجلة في منطقة بغداد في أثناء الفصول الأربعة من العام ٢٠٠٩، وذلك باختيار أربعة مواقع لأخذ العينات. بينت الدراسة الحالية بأن مستويات الفلزات الثقيلة والايونات الموجبة والسالبة في مياه محطات الدراسة تراوحت ما بين ٠.٠١١ –٠.٣٣٣ ملغرام/لتر للزرنيخ وغير محسوس – ٠.٠٠٤٣ ملغرام/لتر للانتيمون و٠.٠١١ – ٠.٠٨٠ ملغرام/لتر للتيتانيوم و 0.150–0.730 ملغرام/لتر للفناديوم و٠.٠١–١.٠٦ ملغرام/لتر للحديد و ٠.١–٠.٤ ملغرام/لتر للزنك و0.011–٠.١٥ ملغرام/لتر للرصاص و٠.٠١–٠.٠٥ ملغرام/لتر للكادميوم و٠.٠١–٠.٠٤ ملغرام/لتر للنيكل و

٥٠-٢٩٠ ملغرام/لتر للكالسيوم و٩٧-٢٧٠ ملغرام/لتر للمغنيسيوم و ٠.٦٥-١.٧٤ ملغرام/لتـر للبوتاسـيوم و ١١-38.3٣ ملغرام/لتر للصوديوم و ٣٥-١١٣ ملغرام/لتر للكلوريد و١٥٠-٢٥٦ ملغرام/لتـر للبيكاربونـات و٩٦-٤٧٩ ملغرام/لتر للكبريتات و٠.٩٣-٣.٩ ملغرام/لتر للنترات وغير محسـوس - ٠.٣٦٠ ملغـرام/لتـر للفوسفات. أظهرت الدراسة أن بعض المؤشرات المدروسة مثـل الـزرنيخ والفنـاديوم والحديـد والرصـاص والكادميوم والمغنيسيوم والكبريتات كانت بتراكيز أعلى من القيم الموصى بها في المواصفات الدولية والعراقيـة للمياه الصالحة للشرب، بينما الايونات الاخرى كانت ضمن الحدود المقبولة. عموماً، أكدت نتائج الدراسة بأن نهر دجلة في منطقة الدراسةِ ملوث ببعض الفلزات الثقيلة الخطرة وخاصة الرصاص والكادميوم والتي لها قابلية كبيرة على التركيز الحياتي في اجسام الكائنات الحية و قد تؤدي الى تأثيرات عديدة على صحة الإنسان بالإضافة إلى صحة النظام البيئي.

Introduction

The concern for water resources containing contaminants, such as heavy metals, anions and cations that pose a threat to health, has increased worldwide [1]. Inorganic substances are present in the water at higher concentrations than the organic ones. Many of these substances are a result of natural conditions; the chemical composition for certain water is according to what type of rocks was in contact with [2]. A continuous monitoring of water quality is very essential to determine the state of pollution in our rivers. This information is important to be communicated to the general public and the Government in order to develop policies for the conservation of the precious fresh water resources [3]. In recent years there has been growing concern over increased contamination of aquatic system from a variety of anthropocentric sources. Heavy metals and most of ions are natural constitutes of natural waters; some are present at low concentrations and are biologically important in aquatic environment, but some are toxic. The toxicity of heavy metals has long been concerned since it is very important to the health of people and ecology [4,5]. Heavy metals are some of the main source of toxicity problems in the aquatic environment when they occur above the threshold concentrations [6]. In general, some trace metals such as, antimony, arsenic, vanadium and titanium has received less attention than those other heavy metals in environmental Iraqi studies due to the difficulty in measurement process. The objective of this study was to determine the seasonal of heavy metals, cations, and anions of the Tigris River in Baghdad of different seasons during 2009. As well as, comparison the results with standard values recommended by world health organization (WHO), United States environmental protection agency (U.S. EPA) and Iraqi standard limits for drinking water .

Experimental

Study sites

Four sites along that part of the Tigris River at Baghdad region were selected for samplcollection. These sites starting from upstream, site 1 (Al-Tarmiyah), site 2 (Al-Utafiah) , site 3 (AlJadiriah) and site 4 (Al-Rasheed) located downstream (figure 1).

Materials and methods

Water samples were collected seasonally in triplicates, from February 2009 to October 2009. Respective in winter (February), spring (May), summer (August) and autumn (October). Water samples were collected in containers, and transported to the laboratory ; then were filtered to remove particulate matter. Cadmium (Cd), Iron (Fe), Nickel (Ni), Zinc (Zn) and Lead (Pb) were determined by using an Atomic absorption Spectrophotometer (Perkin - Elemer model 5000). While other heavy metals; Arsenic (As), Antimony (Sb), Titanium (Ti), Vanadium (V) were estimated using colorimetric methods which described by Vogel [7] using (UV-VIS Spectrophotometer Varian-Cary model 100). Other studied parameters included cations (Na^+, K^+, $Mg^{2+,}$ Ca^{2+}) and anions (Cl^- , HCO_3^-, NO_3^-, SO_4^{-2} and PO_4^{-3}) were measured as indicated by American Public Health Association [8]. All these measurements were done in central laboratory in department of biology - college of science - university of Baghdad. As well as these parameters were compared with water quality standards to indicate probable pollution in river water. The obtained data were subjected to statistical analysis; the analysis of variance (ANOVA) and correlation coefficient among all the parameters using SPSS statistical package at significant probability (P<0.05) .

Results and discussion

- **Heavy metals**

The results of Arsenic (As) in present study showed variability in sampling season Table (1). Upon (Figure 2), it is evident the maximum concentration was detected in site 3 with 0.0333 mg/L. While, the lowest value of As was recorded in site 4 (0.011 mg/L). Furthermore, most As concentrations were below the permissible limits for Iraqi standard criteria (0.05 mg/L) [9] , while higher than the values recommended in WHO [10] for drinking water which reach to 0.01mg/L. It is important to point out that As level was found to be above the WHO standards in most samples. No known essential role for arsenic in human or animal diet, but is toxic. A cumulative poison that is slowly excreted. It could cause nasal ulcers, damage to the kidneys, liver, and intestinal walls and death. Recently suspected to be a carcinogen [11].

The concentrations of Antimony (Sb) range from undetectable to 0.00430 mg/L(Figure 3),Table(1) presented high values in summer season compared with other seasons. The maximum permissible concentration of Sb in drinking water is 0.006 mg/L, therefore this metal is found within the highest desirable or maximum permissible limit set by WHO. The low concentration of Antimony is found at very low levels in the environment, so low that we often cannot measure it [11]. The concentration of Sb that is dissolved in rivers and lakes is very low, usually less than 5 parts of antimony in 1 billion parts of water (ppb) [12] , and most of the antimony in the river; however, was not dissolved, but was attached to particles of dirt. Health effects of Sb include diarrhea, joint and/or muscle pain, vomiting, problems with the blood (anemia) and heart problems (altered electrocardiograms)[12].

The lowest Ti concentration was reported in spring with 0.011 mg/L, while the highest was noted in winter with 0.080 mg/L (Figure 4). These values are similar to those recorded in other regions. Titanium has been reported in all samples from 15 rivers in USA and Canada in concentrations ranging from 2 to 107 µg/L [13]. The average of titanium (Ti) concentration in some sites and seasons was higher than the limits for drinking water(0.5-15 µg/L) established in the EPA [11]. Titanium is not considered as an essential element for human and, in fact, is toxic, although titanium considered the ninth most abundant element in the earth's crust, is widely distributed. According to animal studies, titanium nitride, hydride, carbide, and boride may have fibrogenic effects. These compounds have also been observed to cause liver and kidney dystrophy, but there is no evidence of titanium being carcinogenic in man[14]. The highest concentrations of Ti observed in winter which may be due to a sudden rainfall followed by high river discharge from upstream environment. Vanadium(V), showing an average concentrations in a range of 0.150 to 0.756 mg/L in all sites (Figure 5). Vanadium is a naturally occurring trace element that is found ubiquitously in the earth's crust. While elemental vanadium does not occur in nature [13]. The levels of vanadium in fresh water in different parts of the world vary from undetectable to 0.220 mg/L [15], while concentrations in drinking water are generally must be less than 10 µg/L [11]. The analysis of variance showed significant difference ($P < 0.05$) between sites in winter and summer. The geographical differences in fresh water vanadium levels are due to differences in rainwater runoff from natural sources or in industrial effluent [15]. Vanadium was not known to be essential to human or animal nutrition, but believed to be beneficial in trace concentrations. It could be considered as an essential trace element for all green plants. Nevertheless, large concentrations may be toxic. According to animal studies, we can reasonably infer that low concentrations of absorbed vanadium can be apportioned to the kidney, bones, liver, and lungs of humans similarly exposed [16].

The Iron (Fe) concentration had a large variation in analyzed period, with a decrease from summer to winter in all studied sites Table(1),(Figure 6). In summer, the increasing of temperature lead to decrease the concentration of dissolved oxygen; therefore, the oxidation of soluble Fe(II) to insoluble Fe(III) compounds is slow and the concentration of soluble iron is higher[17]. Maximum iron concentration was determined in site 4 (1.06 mg/L) and minimum concentration in site 3 (0.01 mg/L) . The desirable concentration of dissolved Fe for surface water is 500 µg/L or less according to primary water quality criteria. The permissible concentration of iron in drinking water is 0.3 according to the WHO and Iraqi Standards[9]. Average value of Fe (total concentration) in water samples exceeded both of these standards. Iron considered objectionable for food and beverage processing and can promote growth of certain kinds of bacteria that clog pipes and well openings[11].

Zinc (Zn) in all seasons varies from 0.1 in summer to 0.40 in winter (Figure 7) The average values of Zn in all sites were below the permissible limits. The permissible concentration of Zn in drinking water according to Iraqi criteria is 1 mg/L. High levels of Zn may come from fertilizers, septic systems, animal feedlots, industrial waste, and food processing waste [1]. This metal is essential and beneficial in metabolism; its deficiency in young children or animals will retard growth and may decrease general body resistance to disease. It seems to have no ill effects even in fairly large concentrations (20,000-40,000 mg/L), but can impart a metallic taste or milky appearance to water [11].

Figure 1: Showing the sample locations on Tigris river in Baghdad region

Table 1: The range of Heavy metals, Cations and Anions in studied stations

Parameters	Al-Tarmiyah	Al-Utafiah	Al-Jadiriah	Al-Rasheed
As (mg/L)	0.0141 – 0.0330	0.0151 – 0.0290	0.0122-0.0333	0.0110-0.0280
Sb (mg/L)	0.0015 – 0.00400	0.0013 – 0.0026	0.0014 – 0.00301	ND – 0.00430
Ti (mg/L)	0.011 - 0.0405	0.002 – 0.0400	0.0103 – 0.0550	0.050 – 0.080
V (mg/L)	0. 230 – 0.730	0.200 – 0. 551	0.150 –522	0.460 -556
Fe (mg/L)	0.12 – 0.9	0.15 – 0.42	0.01 – 0.85	0.02 – 1.06
Zn (mg/L)	0.1 – 0.350	0.10 – 0.350	0. 100 – 0.210	0.080 - 0.400
Pb (mg/L)	0.110 – 0.150	0.120 – 0.125	0.110 – 0.120	0.01 – 0.130
Cd (mg/L)	0.0100 – 0.0500	0.0100 – 0.0300	0.0100 – 0.0300	0.0100 – 0.0400
Ni (mg/L)	0.012 – 0.031	0.011 – 0.0290	0.0122 – 0.040	0.0110 0.0280
Ca^{2+} (mg/L)	55 - 290	70 - 230	50 – 205	67 - 270
Mg^{+2}(mg/L)	97 – 185	110 – 235	135 - 270	120 – 245

K^+ (mg/L)	0. 65 – 1.30	0.87 – 1.30	0.87 – 1.74	0. 65 – 1. 52
Na^+ (mg/L)	11 – 33.33	11 – 33.33	11 – 38.80	20 - 38
Cl^-(mg/L)	40 - 99	35 - 99	48 - 113	44 - 113
HCO_3^-(mg/L)	164 – 256	155 - 212	154 - 248	150 - 228
SO_4^{-2}(mg/L)	108 - 331	113 – 335	96 – 365	107 - 479
NO_3^-(mg/L)	1.1 -3.08	0.95 – 3.9	0. 5 – 3.20	0.93 – 2.90
PO_4^{-3}(mg/L)	0.002 – 0.355	ND- 0.25	ND – 0.360	0.003 -0.035

ND = non detectable

The average values of Lead (Pb) concentration in all the samples were showed slightly local and seasonal variation. Lead concentrations vary from 0.011 to 0.150 mg/L (Figure 8) The maximum permissible concentrations of Pb in drinking water and freshwater are 0.05 and 0.65 mg/L, respectively [11]. Generally, this metal is a cumulative poison and toxic in small concentrations. It can cause lethargy, loss of appetite, constipation, anemia, abdominal pain, gradual paralysis in the muscles, and death [1]. . Cadmium(Cd) showed less variation, the maximum level of Cd was observed in spring with an average of 0.050 mg/L , while the concentration for the other months was quite homogeneous (Figure 9). The maximum permissible levels of Cd in drinking water and fresh water are 0.005 and 0.04 mg/L, respectively. It was found that average values of Cd in the samples of water are much higher than the permissible levels according to WHO and Iraqi criteria [9]. Cadmium is a highly toxic metal , not known to be either biologically essential or beneficial [18]. No statistical differences (P < 0.05) were noticed among sampling locations neither for the most seasonal variation Nickel (Ni) varied from 0.01 . in autumn to 0.0420 mg/L in winter (Figure 10) The acceptable values for Nickel reached to 0.470 mg/L in fresh water, while the average acceptable nickel concentration in drinking water is (0.2 mg/L) [10]. The atypical variation in site 2, in comparison with the other three sites, may be due to the greater influence of anthropogenic factor . Nickel (Ni) is only moderately toxic to fish and has little capacity for bioaccumulation. In humans, nickel can be carcinogenic and teratogenic [17]

- **Cations and anions**

Calcium ($Ca^{2+)}$ in the present study found at the range between 50 and 290 mg/L (Table1, (Figure 11). With respect to sampling date, it was noticed that maximum amount of Ca was observed in rainy months. These results are similar to that reported by Al-Lami [19]. Rivers generally contain 1 - 2 mg/L calcium, but in lime areas rivers may have calcium concentrations as high as 100 mg/L [20]. Calcium concentrations in present study(except winter) were lower than the values recommended in WHO and Iraqi criteria for drinking water which reached to 75 and 200 mg/L respectively[9]. Calcium, an essential element for living organisms, occurs in water naturally. But when it found at high concentrations may be lead to negative influencesfor aquatic organisms[20]. The Magnesium (Mg^{+2}) concentration was statistical different (P < 0.05) just for sampling seasons. The maximum level of Mg was obtained in winter with 270 mg /L in site 3, while the lower concentration persisted for the rest of the seasons (Figure 12) Magnesium, an essential nutrient for plants as well as for animals, is washed from rocks (dolomite, magnesite, etc.) and subsequently ends up in water, being also responsible for water hardness [21]. Rivers contain approximately 4 mg/L of magnesium and a concentration of 30 and 50 mg/L is recommended for drinking waters in Iraq [9] and EPA [11] respectively. There were no pronounced local variations in Ca and Mg values (according to analysis of variance) among the studied sites, Although its concentrations slightly increased toward south. Potassium (K^+) concentration was fluctuated between 0.65 to 1.54 mg/L Table (1),(Figure13), while Sodium (Na^+) concentrations varied between 11-38.88 mg/L (Figure 14) Al-Lami [19] reported that the concentration of potassium in Tigris river ranged 1 to 5 which was higher than the value of present investigation. There is very little variation in K concentration within the basin as well as between major rivers of the world. Potassium is released much more completely during weathering than many other dissolved ions [17]. The values of sodium recorded in this study were less than WHO standard limit for Drinking purpose which reached to 200mg/L. Highest value of Chloride ion (Cl^-) concentration was recorded in site 4 (113 mg/L) and lowest in site 2 (35 mg/L) in Tigris River (Figure15). The values recorded in this study were less than the preassemble values for drinking water (200mg/L) in Iraq [9]. Highest chloride concentrations being determined in winter, probably because the samples were collected during a period of raining. Large concentrations increase the corrosiveness of water and, in combination with sodium, give water a salty taste [11].

Bicarbonate (HCO_3^-) concentrations were fluctuated between 50 and 256 mg/L(Figure 16). Bicarbonates and carbonates can act as a storage area for surplus carbon dioxide, thus carbon dioxide will not be limited during

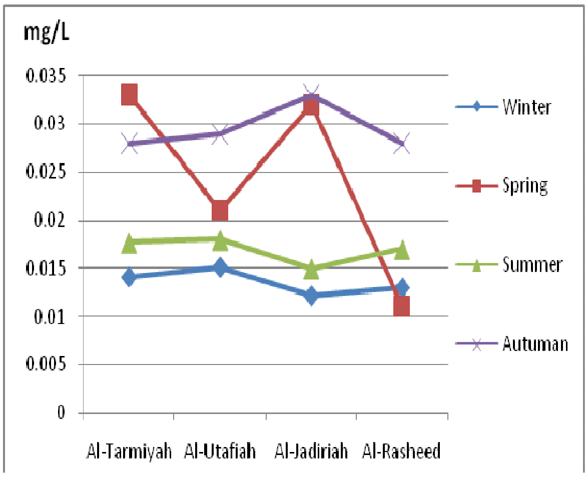

Figure 2:variation of arsenic in Tigris sites

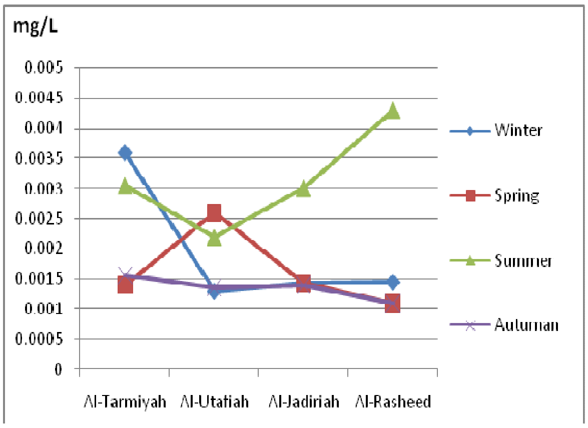

Figure 3:variation of Antimony in Tigris sites

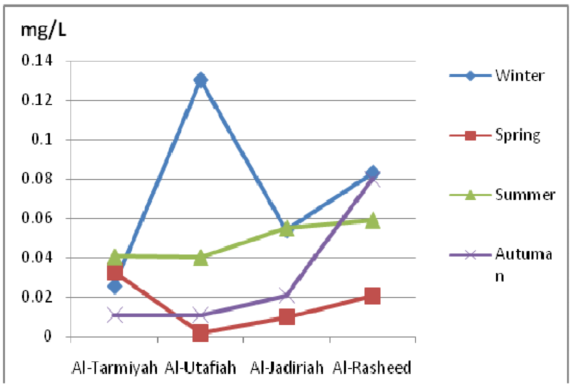

Figure 4:variations of Titanium in Tigris sites

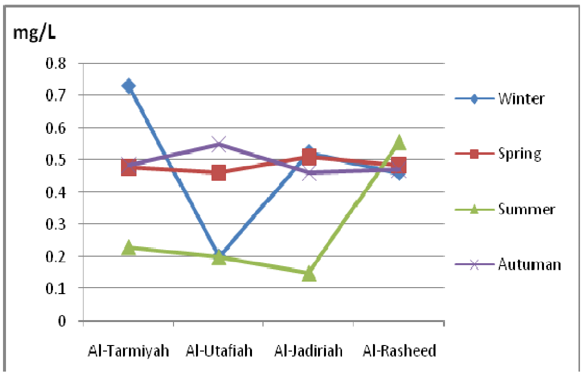

Figure 5:variation of Vanadium in Tigris sites

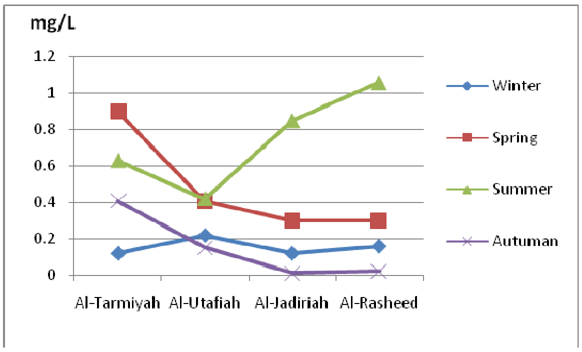

Figure 6: variation of Iron in Tigris sites

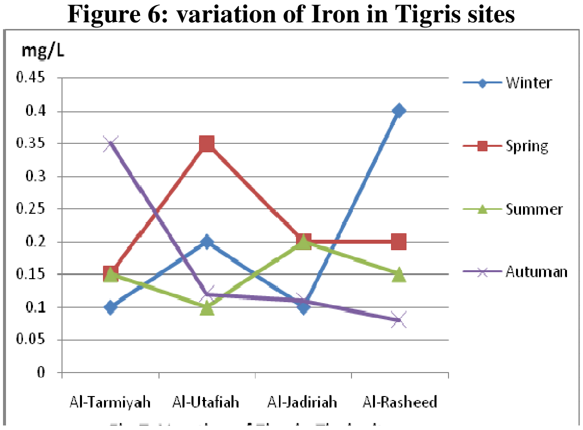

Figure 7: varaition of Zinc in Tigris sites

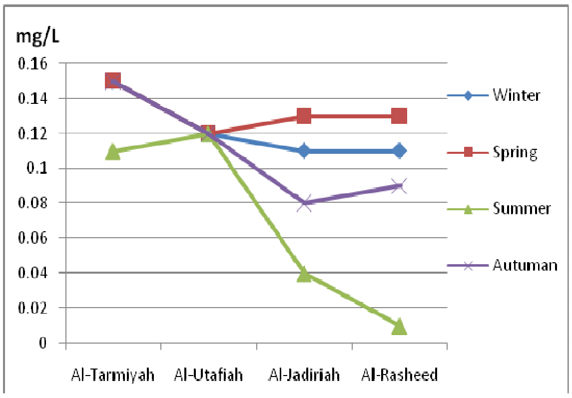

Figure 8:variation of Lead in Tigris sites

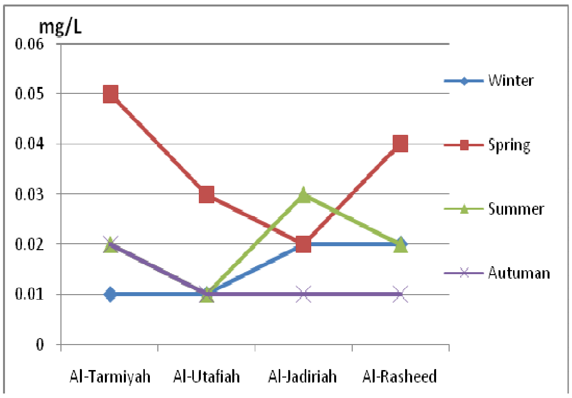

Figure 9: variation of Cadimum in Tigris sites

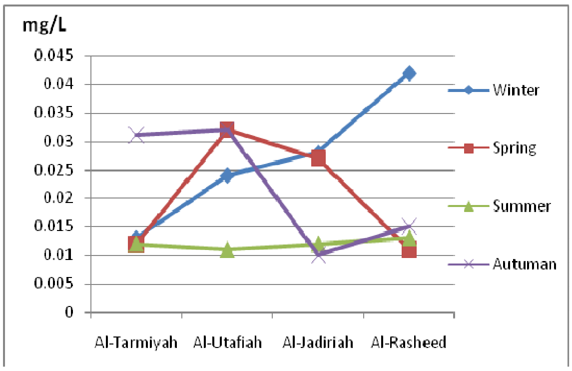

Figure 10:variation of Nickel in Tigris sites

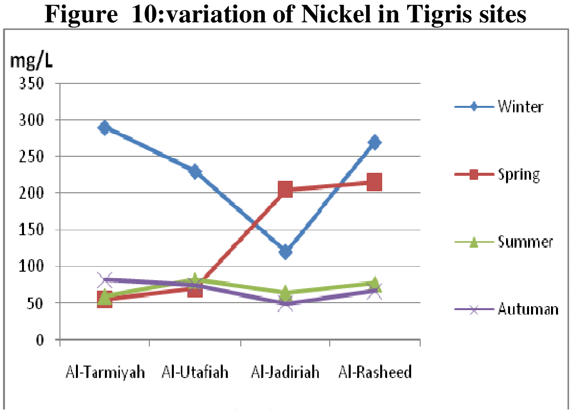

Figure 11:variation of Calcium in Tigris sites

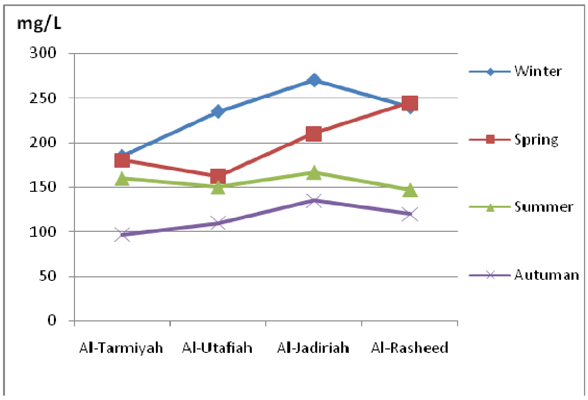

Figure 12:variation of magnesium in Tigris sites

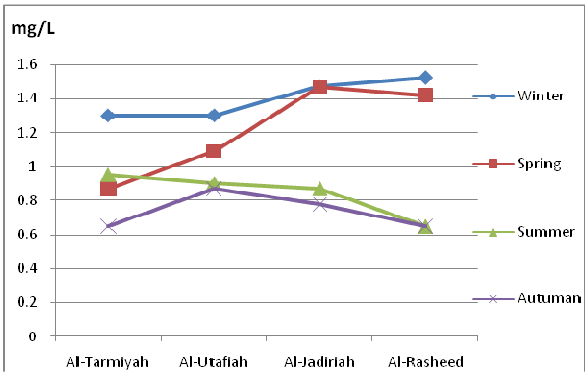

Figure 13: variation of potassium in Tigris sites

photosynthesis, and in combination with calcium and magnesium forms carbonate hardness. Total alkaline (Carbonates and bicarbonates) limit for natural fresh water ranged between 5- 500mg/L [22].

The concentrations of sulfate ions (SO_4^{-2}) fluctuated between 96 and 479 mg/L (Figure 17). The values in almost exceed the permissible concentration of sulfate in Iraqi drinking water which reached to 200 - 400 mg/L. Large concentrations of sulfate have a laxative effect on some people and, in combination with other ions, give water a bitter taste [23].

The concentrations of Nitrate ions (NO^-_3) varied between 0.93 - 3.9 mg/L (Figure 18). These values are within maximum permissible limit prescribed by WHO. The maximum permissible concentration of NO^-_3 in drinking water is 10 mg/L. The concentration above permissible values lead to illness in infants below the age of six months with symptoms include shortness of breath and blue baby syndrome [11]. The phosphate ions (PO_4^{-3}) concentration was different among sampling locations and seasons. The lowest phosphate concentration was obtained in site 2 (non detectable) in autumn, while the highest level was noted in site 1 (0.360 mg/L) in winter (Figure19). Compared with other nutrient, it is also the least toxic. However, high levels can affect osmoregulation, oxygen transport, eutrophication and algal bloom [22]. Acceptable levels of phosphate are 0.10 mg/L in fresh water[11]. Phosphates are not toxic to human or animals, unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphates [24]. The chemical composition of the Tigris River water shows HCO^{-}_{3} and SO_4^{-2} are the most abundant anion, and Ca^{2+} is the most abundant cation. High content of bicarbonate and calcium in Tigris sites confirms the fact that 98% of all river waters was of the calcium carbonate type [25]. Calcium, Magnesium and Bicarbonate are contributed to river water mostly by rock weathering and the pollution contribution is less significant [25]. As for the seasonal variation of bicarbonate , nitrate and phosphate, higher values were found during winter season corresponding with rainfall and high discharge. Similar results were obtained from other areas, since such case brings considerable quantities of nitrate, phosphate and bicarbonate along the river from nearby agricultural lands along the river [26, 27]. Nutrient like nitrogen and phosphate are necessary for healthy waters, but high levels of nutrients can cause several problems, ranging from nuisance algae blooms and cloudy water to threatening drinking water and harming aquatic life [28].

- **Correlation coefficient**

The correlation matrices were produced to examine the inter-relationships between the investigated substances concentrations showed high positive correlations of Fe/Zn and Fe/Pb with corresponding r values of 0.677, 0.570 respectively. The significant correlation co-efficient between these metals suggest a common source. As well as Cd has significant positive relationships with Pb and inverse associations(-0.409) exist between Sb and V. Also, high positive correlation were found between Cl / Ca (r = 0.845), Mg / SO_4 (r = 0.734), PO_4 / NO_3 (r = 0.701) and SO_4 / Cl (r = 0.948). As well as, nitrate showed high positive relation with bicarbonate (r = 0.860) , and positive relation with phosphate (r = 0.701). The combination of NO_3 with PO_4 and HCO_3 ions is an indication of the hydrogeochemical effect of runoff leakage on the water [23].

Conclusion

Overall, The presence of some heavy metals and other studied ions in the Tigris River in concentrations higher than normal values is a permanent problem. The high concentration of these substances may be correlated with the general trend in Tigris basin (industrial/or agricultural activities, etc.) The result of this work revealed that th mean level of some heavy metals discharged into the river have exceeded the maximum permissible limit set by Iraqi and WHO criteria. The resulting effect is the increase in background level of all the pollutants along the river. When the quality of the river is compared with the Iraq and WHO recommended limits for source of water supply, the river was found to contain some heavy metals above the recommended limits, indicating pollution. The consequence of this may result in water borne diseases affecting people in the area. Though some of the detected heavy metals are beneficial for human and plants up to a certain limit, it may be

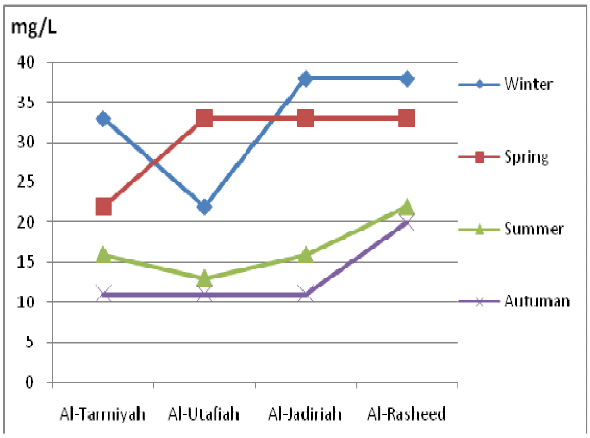

Figure 14:variation of sodium in Tigris sites

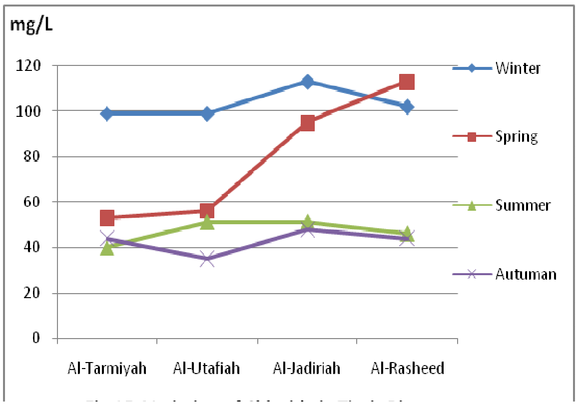

Figure 15:variation of Chloride in Tigris river

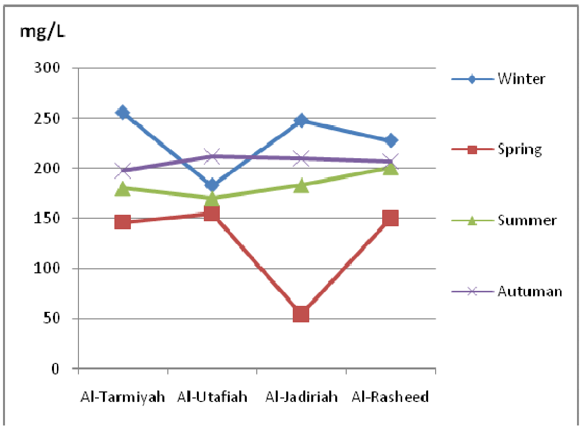

Figure 16:variation of Bicarbonate in Tigris sites

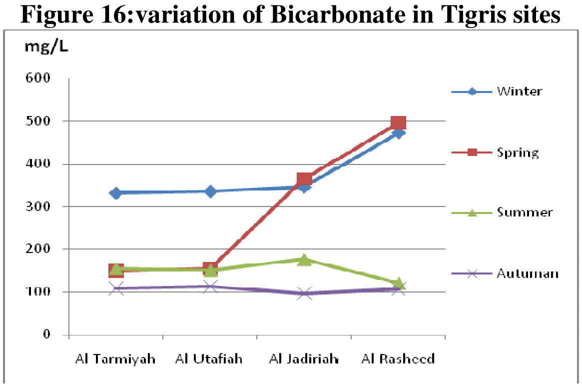

Figure 17:variation of Sulfate in Tigris sites

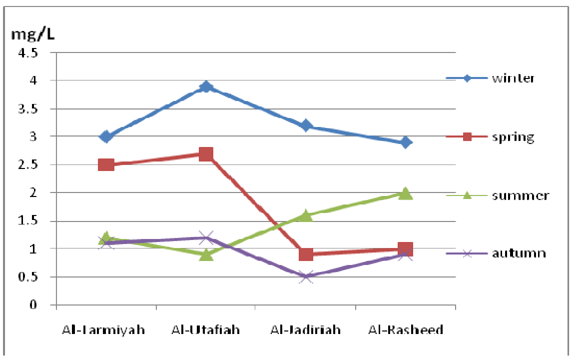

Figure 18:variation of Nitrate in Tigris sites

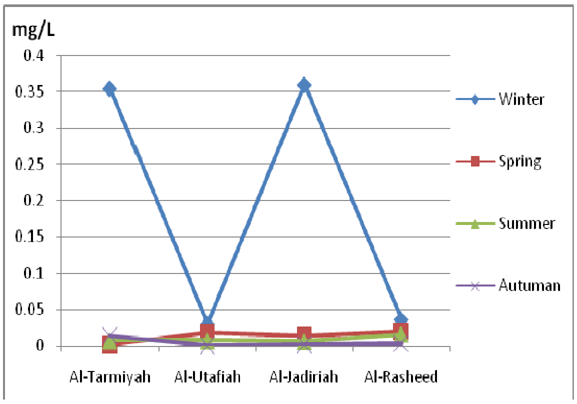

Figure 19:variation of phosphate in Tigris sites

harmful beyond that. Adoption of adequate measures to remove the heavy metal load from the industrial waste water and sewage water are suggested to avoid further deterioration of the river water quality. As well as, developed water treatment units by add advanced units to stations of supply drinking water to remove undesirable substances such as heavy metals, cations and anion

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