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Distribution of some heavy metals in the sediments of Tigris river from sewage of Thermal Electrical Station at Baiji City in Salah-aldin Governorate-Iraq

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ABSTRACT

This study was conducted to determine four heavy metals including copper, zinc, lead and cadmium in the sediments of the Tigris river for a distance of 3,500 km for the time period autumn2012 – summer 2013.This is the first time that such a study carried out by the river sediments so studies on the Tigris river about sequential extraction to compare them with the results of the research not available, total concentrations recorded of Cu (11.23-12.1)µg/g, Zn (39.6-41.03) µg/g, Pb (115.82-117.34) µg/g,Cd (4.1-4.34) µg/g dry weight, the distribution in the sediment layers, exchangeable metal ion recorded of Cu (0.42-0.44) µg/g, Zn (0.32-0.33) µg/g, Pb (0.22-0.25) µg/g, Cd (0.15-0.17) µg/g dry weight, and layer of carbonate bound of Cu(1.6-1.63) µg/g ,Zn (4.47-6.71) µg/g, Pb (0.2-0.22) µg/g , Cd (1.44-2.17) µg/g dry weight, and the metal layer of Cu (1.26-1.41) µg/g, Zn (15.84-17.07) µg/g, Pb (46.38-49.46) µg/g, Cd (1.9-2.17) µg/g dry weight, concentration of organic layer Cu (7.85-8.67) µg/g, Zn (17.63-17.96) µg/g, Pb (68.57-67.48) µg/g, Cd (0.58-0.86) µg/g dry weight. The arrangement of total concentration Pb>Zn>Cu>Cd (4,42-12,09-41,69-116,88) µg/g dry weight. Distribution of Cu organic layer> carbonate bound> metal layer> exchangeable metal ion (8,41-1,78-1.52-0.35) µg/g dry weight, Zn metal layer> organic layer> carbonate bound> exchangeable metal ion (18.99-17,58-5.52-0.29) µg/g dry weight, Pb organic layer>metal layer> exchangeable metal ion> carbonate bound (66.42-49.81-0.22-0.2) µg/g dry weight, Cd metal layer> carbonate bound> organic layer> exchangeable metal ion (2.02-1.87-0.91-0.18) µg/g dry weight .The high concentration recorded in four station, these results indicated that the possibility of using sequential extraction for the detection of the distribution of metals and determine the impact of diversity through release them to the aquatic environment, all concentration mentioned are rate they aren't single value.

Introduction

Water is a gift from God and consists of all living things [1]. The Tigris river is one of the natural sources of water for human use, Agricultural uses and industrial purposes, is exposed to various types of pollution during its raw and the importance of the subject of thermal pollution on the one hand and its effects on the other hand was selected Baiji power station to be a site for study It is located on the left side of the river in the province of Salah al-Din, about 20 km northeast of the city of Baiji at the area of alfatha near the river Tigris, bordered by a mountain from the east is Hamrin and the mountains of Makhoul [2]. It is the largest power station in Iraq, consisting of six units with a design capacity of 1320 MW, and operates with types of liquid and gaseous fuels, as available from fuel at the North Refinery Company [3].Thermal pollution as a result of wastewater disposal in factories and electric power station for refrigeration, where hot water is thrown into rivers or lakes, which increases it is temperature, resulting in a change in the percentage of dissolved oxygen in the aquatic environment and harmful to aquatic life, and operations ,the cooling required to absorb the high heat produced from manufacturing processes and energy conversion uses more amounts of water for cooling purposes, so it will disburse cooling water with high temperatures of up to 40 °c and thermal effect to the condition where there isn't fish life [4]. Heavy metal is the element that density is more than of water density that 5 g/cm^3 [5], but trace elements whose concentration in the Earth's crust is equal to or less than 0.1% (equal to or less than 1000 Part by million) [6]. The toxic effect on the organisms due with the cumulative characteristic in organisms[7];[8]. The materials that used to paint water cooling pipes affected by environmental conditions [9],the flow of stations in the addition of quantities of trace used in Particulate air pollutants and acid rain can also be a significant source of environmental contamination with these metals [10]. Sediment layers are divided into the ion of the cross metal and include metals on the surface of the deposit and with a weak density of the metal on a hard surface due to the weakness of the electrical stability, and released during ion exchanges and lowering of the pH will allow its liberation [11]. The ion of the metal is an indicator and measure of the existence and potential of the environment, and in this layer reveals less than 2% of the total content of the metal. The component can be edited in exchange with weak positive ions[12]. The carbon bond layer, as carbonate tends to have the main capacity to absorb many minerals, when there is a shortage of iron oxides, manganese, fe-mn Oxide and organic matter , metals can be freed by lowering the pH and factors influencing the efficiency and speed of the process Extraction of the type and quantity of carbonate in the sample and the size of the solid particles and the metal layer are characterized as rich in metals and come from the secondary oxides of coating of metal surfaces or separate pieces falling from the paint [13]. The organic layer is the process of bioaccumulation and is considered the primary source and the president that we can get the metals associated with the organic matter within it such as organisms, the residues of aquatic biology and the tendency of metals to remain for a longer period of time within this layer but degrade by the processes of destruction [14] .Sediment is a potential source of contamination in the environment, as its role is a storage and vector of metals and may be used to record the history of contamination ([15];[16]). Sediment is a key indicator for different types of pollutants, especially those that settle more rapidly in slow-flux water[17].Refers the study [18] to estimate the industrial pollutants resulting from the two power stations aldurah and south of Baghdad, Dumped into the river and compared the concentrations of these pollutants with the standard specifications allowed by the approval of the monthly readings of these two stations, the readings of aldurah station Within allowed limits, the station south of Baghdad has found some irregularities in the concentrations of the allowed limits.

In a study [19] to review the sequential extraction stages some types of heavy soil and sediment metals and to determine the impact of activities concentrations of these minerals, metal of the most toxic environmental pollutant, The availability and easy of accumulation in plant and the continuity of its existence is due to the increase in population, growth and development in the industries, loading and unloading of goods, maintenance of ships and engines, agricultural activities and dumping of some waste directly to the aquatic body as well as accumulation in its sediments, when contaminated The aquatic environment with these pollutants will be absorbed by the organisms to enter the food chain in aquatic organisms**.**

Study area description : Includes four station on an area 3.5 Km: 1- First station: It farther 300 m north of baiji power station electricity in alfathah, include sediment of raw water, outside of power station. The qir eye lied on the lift side farther 2 Km and sulfuric eye on the lift side farther 3 Km

2-Second st.: The sidement basin of desilter farther 507 m of first st.,lied inside of power staon ,it concrete basin the long 40 m and contain of 2 part every one width 5m,depth 4.8m, have a mechanical deposition, when water passed in this basin the muds sedimentation because of heavy weight ,the sediment took from this muds.

3-Third st.:The sediment drainage basin, farther 38 m of second st.,lied inside of power station, It's rectangular shape the long 15m,width 10m,depth 4.8,the sediment pump from tank to this basin depending on the separation process, all 2 hour in winter and all 8hour in summer.

4- Fourth st.: the sediment of the river after mixing water river with hot water from power station, farther 3.113 Km outside power station, located at the village shwesh.

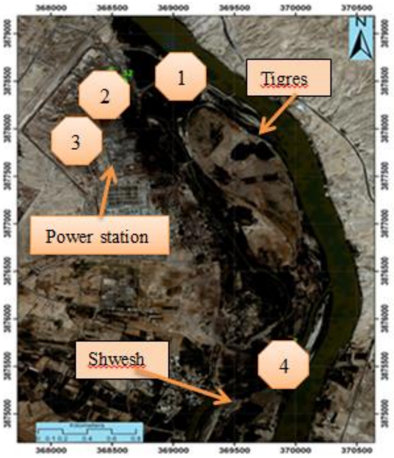

Fig. (1): Study Stations.

Materials and methods

Sediment samples were collected by a slightly covered river shelf with water,after the surface layer using grap sampler, it was stored in plastic bags marked, after drying in oven at 60°c until dehydration, grinding with ceramic mortar and cleared sieve 2mm until the extraction process[20]. method pre-dry phase cools and nominates the Whatman type of the ashless 541 and completes the water described in [21] take 1g of the sediment in a volumetric flask, add 10 ml HNO_3 close with watch class, digested in sandy bath until the Sequential extraction of metals from sediment layers followed from [22] as follows**:**

1-Exchangeable metal ion: Add (1m) $MgCI_2$ at room temperature, pH = 7, mixing for 1 hour and constant speed using the magnetic motor and separating the centrifuge at 3000 cycles/minute for 30 minutes, the separated pipe is operated in closed tubes after completing the volume to 10 ml with ion-free water to measure ions of metals**.**

2-Surface oxide and carbonate bound metal ion: taking the previous step, adding (1m) $NaCOOCH_3$, the pH is lowered to 5 by adding (1-2) ml CH_3COOH and mixing for two hours and at constant speed using the magnetic motor and separated by the same previous step with the opening of the pipe lid with great caution as a result of bubbles becoming larger when opening lid, the pipe is operated in closed tubes after completing the volume to 10 ml in ion free water.

3- Metal ions bound to Fe-Mn oxide: Extraction deposit by adding (0.04 M) NH_2OH. HCl dissolved in 25% (V/V) CH_3COOH and the models were placed in a water bath at 96 ±3°c until the volume less than 6 ml, completes the resin to 10 ml**.**

4-The organic matter: Bring 30% of H_2O_2 and add 0.02 (M) HNO_3, Add the prepared solution for the suit and heat for 5 hours at 85 ± 2 °c in the water bath, The mixture is extracted with (2.3 m) NH_4COOCH_3 minutes at 20% HNO_3, using Centrifuge and at speeds of 3000 round/minutes for half an hour, the filtrate to measure.

Technique of atomic absorption spectroscopy was used to determine the concentrations of metals in the sediment and sequential extraction method to Detected within the chemical layers of sediments**.**

Result and discussion:

Total concentrations of heavy metals in sediment:

cupper (Cu): The river sediment record values from (8.05-14.6) µg/g both in the first st., and the increase was in winter and these values are lower than (2.9 - 19) mg/kg for the sediment of lake Gorecki in Poland in a study [23]for total concentration and distribution of metals in chemical layer and less than the values of the Tigris deposits (17.4-28.9) µg/g in a study [24]. The first st. (8.05-14.6) µg/g was recorded more than the fourth st. recorded (10.53-13.5) µg/g, the increase in concentration due to pesticides in the agricultural areas, phosphate fertilizers and industrial waste and correlation between increase temperature of water and increase of concentration [25]. Inside the power station, sediment basin (9.48-16.25) µg/g higher than drainage basin due to don't use water treatment only sedimentation. The total concentration of Cu gradually in station was second> third >fourth> first(figure2).The results of the statistical analysis showed no significant differences Spatial and differences significant temporal at level $p \le 0.05$**.**

Zinc (Zn): The sediment record (25.3-77.78) µg/g both in the first st. in autumn and the rainy season due to the high water level and the dredging of the fertilizer adjacent to the riverbed where the Iraqi fertilizer contains 406 ppm. When comparing these values, they were lower than the values (13-110) mg/Kg [23] and higher values (8.3-47.1) µg/g for the Tigris river sediments in a study [24]. Inside the power station sediment (30.00-66.5) µg/g below was recorded at the second st. and above at the third station, the raw water record (25.3-77.78) µg/g is higher than in hot water (25.85-68.5) µg/g,the concentration of the zinc in the sediment of first st. is higher than sediment of fourth st. due to population density, household residues and factories. The total concentration of Zn gradually in station was third> second> first >fourth figure (2). Zn not exceed [(26);(27);(28)] and exceed [26],the results of the statistical analysis showed no significant differences spatial and differences significant temporal at the level $p \le 0.05$**.**

Lead (Pb): The sediment record (101.5-130.5) µg/g both in the fourth st. different from values (11-74) mg/kg in a study [23] and higher than values (17.9-30.6) µg/g for Tigris river sediments in [24]. The raw water record (106.25-126.25) µg/g, and the increase in autumn and summer due to increased levels and flow water and throw the Refineries Baiji station materials quadruple ethylate lead that used for Improve the quality of gasoline. Fourth st. has recorded (101.5-130.5) µg/g and the increase was in autumn and summer, the highest concentration in fourth st.,inside power station second st. (105-135) µg/g below at the third st. and above at the second st., the total concentration of Pb gradually in station was second >fourth> first >third figure (2).Pb don't exceed the limit of ([26];[27]) and exceed (28) table (1). Statistical analysis results no significant differences spatial and temporal at the level $p \le 0.05$.

Cadmium (Cd): The concentrations of Tigris sediment (2-10.5) µg/g in the first and fourth st., highest at the first and the high concentrations agreed with a study [29] and don't agreed with [23] that record 1.2-5.2) mg/kg .The study record (0.1-1.7) µg/g higher than [24].Sediment raw water (2-10.5) µg/g in summer and autumn ,hot water (2-8.25) µg/g, inside power station, the third st. register higher and lower values (2.5-8.8) µg/g increase in summer and autumn due to decreased water causes increased concentration of metals. the total concentration of Cd gradually in station was third >second >fourth >first figure (2).Cd not exceed limit [(26);(28)] table (1).

Statistical analysis results no significant differences spatial and found of temporal at the level $p \leq 0.05$ .most of the dissolved metals will accumulate in sediments through the sludge or sedimentation on the surface of the sediment with increased pH [13]. most of station alkalinity that agreed with [30,31,32].

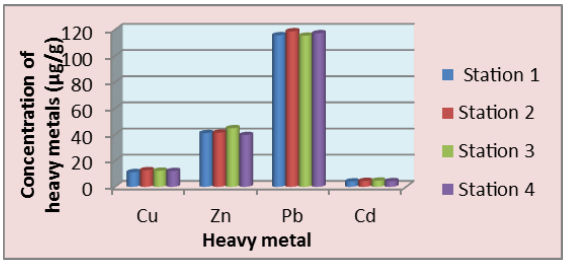

Fig. 2: Distribution total concentrations of the metals in sediment stations.

Distribution ions of heavy metals in sediment layers:**1**-Exchangeable metal ion: The lowest value of Cu was 0.263 µg/g in sediments of second st. and the highest 0.443 µg/g in fourth st. Zn recorded the lowest value of 0.23 µg/g at the second st. And highst 0.329 µg/g in first st. The lowest value of Pb ions was 0.191 µg/g in the sediments of third st .and the highest 0.245 µg/g in first st., the lowest Cd ions 0.146 µg/g at the first st. and the highest 0.2 µg/g at the second and third st. ,the increase Cu,Zn due to The use of agricultural pesticides and the effect of sulfuric and qir eyes before the thermal station several meters figure[3].The following arrangement of the ionic presence was Cu> Zn> Pb> Cd for Tigris river (st. 1) and sediment basin (st. 2) and the sediment of the river after mixing with water (st.4) different from the study [33]of the Delele channel in France was Zn> Cd >Cu >Pb,while sediment drainage basin (st. 3) record Zn>Cu> Cd>Pb.These metals don't pose a real risk if they are in the form available (active). The ion will be free, easy to obtain and exchange, and the increase in concentrations of some heavy metals in the mutual part of the sediment is due to the presence of human resources such as industrial, agricultural and domestic activities[34].

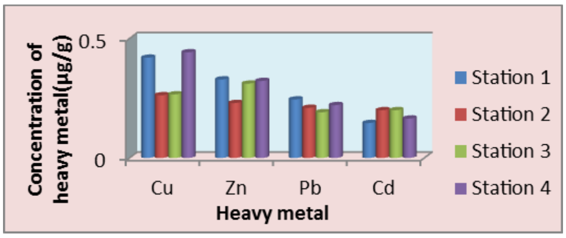

Fig. 3: Distribution of metals ions in the mutual ion layer in the sediments.

2- Layer of carbonate bound metal ion**:** The lowest concentration value of Cu was 1.602 µg/g at the first st .associated with the carbonate bond and the highest value of Cu 2.131 µ g/g in the second st. , the lowest value of Zn 4,688 µg/g at the fourth st. and the highest value 6.708 µg/g at the first st The lowest Pb value was 0.188 µg/g at the second st., the highest value was 0.23 µg/g at the fourth st.,Cd recorded the lowest of 1.063 µg/g at the second st. and the highest of 2.166 µg/g at the fourth st. .Zn recorded high concentration more other due to correlated with carbon bond .The following arrangement of the metal associated with carbonate bond in first st. Zn>Cd>Cu>Pb, second st. Zn>Cu>Pb>Cd, third and fourth st. Zn>Cu>Cd>Pb, figure (4). Water treatment processes within the power station affect the different of metals concentration. In the carbon bond, the metal will be ready to be free and interchangeable when environmental conditions have changed [23].

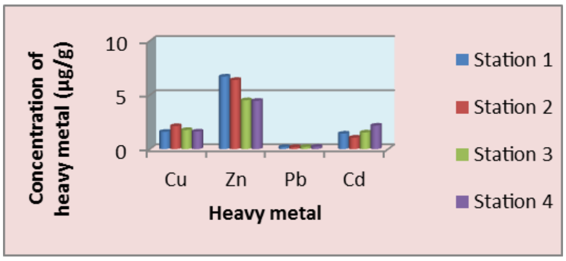

Fig. 4 : Distribution of metals in carbon bonding layer in sediments

3- Layer of Mineral bound to bonding metal ion: It has been found that the lowest value of copper associated with mineral layer was 1.263 µg/g in the first st. and the highest value was 1.758 µg / g at the second st., the lowest Zn was 15.836 µg/g in the first st. and the highest was 21.873 µg/g in the second st., while Pb 46.373 µg / g as the lowest value at the first st. and highest 52.488 µg/g in the second st.,The lowest cadmium 1.904 µg / g was recorded at the first st. and the highest 2.166 µg/g at the fourth st. .The following arrangement of metals associated with mineral bound in all st. record Cu>Zn>Pb>Cd , figure (5),high concentration due to the waste of factories and villages and their accumulation in this layer. Metals in this layer related with Fe-Mn oxide and will be more related than another layers, possibility of being freed also depending on environmental conditions [23].

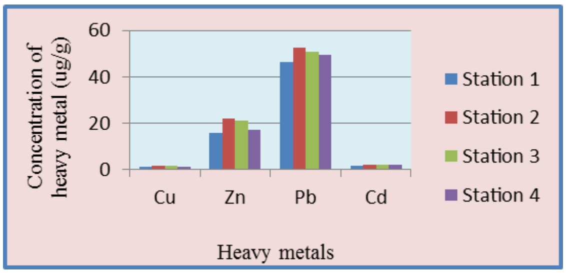

Fig. 5: Distribution of metals in mineral layer in sediments

4-Layer of Metal ion bound to organic matter: Cu was recorded the lowest value 7.851 µg/g in the first st. and the highest value 8.666 µg/g at the fourth st. and Zn record the lowest value 16,098 µg/g in the second st. and the highest was 18.615 µg / g at the third st. , Pb was the lowest 63.675 µg/g at the third st. and the highest 68.571 µg / g at the first st., Cd recorded the lowest 0.575 µg / g at the first st. and the highest 1.263 µg/g at the second st , the following arrangement of the metals associated with organic matter that Pb>Zn>Cu>Cd in all station of this study figure (6). In organic layer will be stable and not easy to release into the water environment, and its presence in this layer is a high reservoir of metal in the deposits of that environmental site but it does not pose a real danger if it is active (available), the presence of the metal in the mineral layer and organic is not from Easy to be biologically available. The sedimentation rate depends on the particle size and the presence of organic matter in the sediments [33].

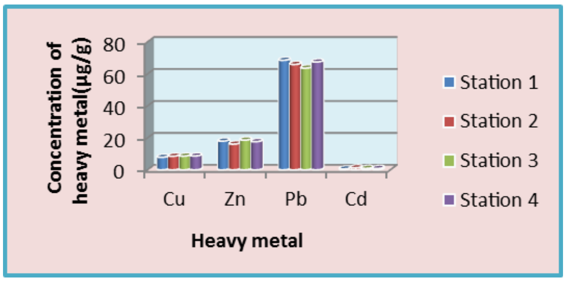

Fig. 6: Distribution of metals in the organic layer in sediments.

In this study Pb,Zn,Cu have more concentration means high stock in this layer agree with [33] that high concentration of Pb and Cu associated with organic matter and don't agree with [23] that high concentration of Pb and Cu associated with mineral layers.

This study record more concentration of Zn Cd associated with mineral layer that agree with [23],Which means that it is a higher risk of Cu and Pb to the existence of the majority in the metal layer and the possibility of freeing them by changing environmental conditions, which creates greater opportunity for environmental availability and don't agree with [33] that the biggest content of Cd in organic matter. The difference back to presence of the sulfuric and qir eyes north of first St. Materials used in water treatment.

Table (1) Standard determinants unit µg / g.

Limited Metal	[26]	[27]	[28]
Zn	150.00-410.00	410.00	123.00-315.00
Pb	46.70-218.00	450.00	35.00-91.30
Cd	9.60-110.00		0.60-3.50

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توزيع بعض العناصر الثقيلة في رواسب نهر دجلة من مطروحات محطة الطاقة الحرارية عند مدينة بيجي ضمن محافظة صلاح الدين–العراق

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[2] قسم النباتات والعقاقير الطبية ، كلية الصيدلة ، جامعة تكريت ، تكريت ، العراق

الملخص

اجريت الدراسة لتحديد اربع من العناصر الثقيلة النحاس، الخارصين، الرصاص والكادميوم في رواسب نهر دجلة لمسافة 3500 كم للفترة الزمنية من خريف 2012–صيف 2013.هذه المرة الاولى التي تجرى فيها هكذا دراسة على رواسب النهر اذ لا توجد دراسات على نهر دجلة عن الاستخلاص المتسلسل من اجل المقارنة بها مع نتائج البحث، سجل التركيز الكلي للنحاس (11.23-12.1) µg/g ،الخارصين (39.6−14.03) µg/g ، الرصاص (117.34− 115.82) µg/g والكادميوم (4.34−4.34) µg/g وزن جاف. سجل التوزيع في طبقات الرواسب ،طبقة الايون المتبادل للنحاس (0.44−0.42) µg/g ،الخارصين (0.33−0.32) µg/g، الرصاص (0.25−0.22) µg/g والكادميوم (0.17−0.15) µg/g وزن جاف، وطبقة الرابطة الكربونية للنحاس (1.63−1.6) µg/g ،الخارصين (6.71−4.47) µg/g،الرصاص (0.22−0.2) µg/g والكادميوم (2.17−1.44) µg/g وزن جاف، والطبقة المعدنية كان النحاس فيها (1.41−1.26) µg/g، الخارصين (17.07−15.84) µg/g، الرصاص (49.46−46.38) µg/g والكادميوم (2.17−1.9) µg/g وزن جاف، اما التركيز في الطبقة العضوية للنحاس (8.67−7.85) µg/g،الخارصين (17.96−17.63) µg/g، الرصاص(68.57− 67.48) µg/g والكادميوم (0.86−0.58) µg/g. ترتيب التراكيز الكلية رصاص > خارصين > نحاس > كادميوم (116.88−41.69−12.09−4.42) µg/g وزن جاف. كان توزيع النحاس الطبقة العضوية >الطبقة الكربونية >الطبقة المعدنية > طبقة ايون العنصر المتبادل (0.35-1.52-1.78-8.41) µg/g وزن جاف، سجل الخارصين في الطبقة المعدنية >العضوية >الكربونية >الأيون المتبادل (0.29−5.52−17.58−18.99) µg/g وزن جاف، الرصاص في الطبقة العضوية > المعدنية > ايون العنصر المتبادل>الكربونية (0.2-0.22-49.81-66.42) µg/g وزن جاف اما الكادميوم المعدنية > الكربونية > العضوية > الايون المتبادل (2.02−1.87-0.91-0.18) µg/g وزن جاف. هذه النتائج هي مؤشر لأمكانية استخدام طريقة الاستخلاص المتسلسل للكشف عن توزيع المعادن وتحديد تأثيراتها من خلال تحررها للبيئة المائية، جميع التراكيز المذكورة هي معدلات وليست قيم مفرده .