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Temporal and spatial variation of total cyanide levels and using the pollution indices in Sediment of Shatt Al-Arab River and Marine environment of Iraq

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Abstract Fifteen stations were selected from surfaces sediment of Basra governorate in southern of Iraq . The samples were distributed among seven stations in Shatt Al-Arab river and eight stations in marine regions. All samples were collected from sediment surfaces at depth 10-15cm . Concentration of total cyanide in sediment was measured by using colorimetric method through complex formation with pyridine-barbituric acid at wavelength (578nm). The results for all the measurements showed the highest concentration of total cyanide in stations S_1(61.583±4.31 µg/g) and S_5 (71.627±1.95 µg/g) and lowest concentration at station S_3 (13.559±1.83 µg/g) and S_7 (16.711±1.90 µg/g) at spring season (2015and 2016) respectively, while the highest concentration of total cyanide in marine regions were recorded in station S_{15} (55.893±1.70 µg/g) . Standard deviation of all sites (n=3) for total cyanide of river and marine regions was calculated , it shows the range (1.837 - 6.092) , (1.702 - 3.125) respectively . The pollution indices such as geo accumulation index (I-geo) and pollution index (PI) were calculated for all selected stations .

Keywords : *Colorimetric method, Total cyanide , Standard deviation , pollution indices*

Introduction

Cyanide compounds go into environment by several industrial sources such as electroplating industry, blast furnaces, coke-producing plants , combustion of coal , oil plastic and synthetic fibers [1,2] , they are transferred into aquatic system under different natural and anthropogenic conditions such as pH , temperature ,weathering of rocks, mining , movement of wind, irrigation , drainage operations, wastewater and industrial wastes it depends on interactions between water and sediments , all of these parameters lead to precipitation cyanide compounds into sediment where sediments are considered as important reservoir for various pollutants [2,3,4]. Total cyanide indicates to all the CN groups in cyanide compounds that can be determined as the cyanide ion [4,5] . The chemical composition of cyanide in environmental samples is affected by different factors such as pH, temperature, trace metal content, and the exist of sulfur or sulfur compounds [2,6] .

Cyanide compounds are present in aquatic system by different chemical forms as organic and inorganic compounds such as simple compounds such as sodium and potassium cyanide these compounds are readily dissociate and hydrolysis in water Which leads to releasing the hydrogen cyanide gas [2] , furthermore, inorganic compounds for cyanide have different ability for dissociating in water and iron cyanide complex for example , weakly dissociates in water , while copper and zinc complexes represent relative insolubility in water [2,7] .

All the cyanide compounds have high toxic properties and especially the free cyanide species [4,8] . Moreover , increasing of anthropogenic activities lead to increasing of cyanide concentration in aquatic system and may causes many risks which threads a huge number of organisms and plants in water environment . Thus it harms the human health because the cyanide concentration will increase in tissues of fish by bioaccumulation operation and rapidly transferred to human via the food chain and it causes many diseases as goiters, hypothyroidism and some neuromuscular diseases [2,9] .

The current study aims to evaluate of total cyanide concentration in sediment for aquatic system in southern of Iraq in order to be a sensor of healthy risks on human , animals and plants .

Experimental Part

Description of the Study Area

Sediment samples were collected from different stations on river and marine environment of Iraq in Basra governorate which are shown in figure1 . The river sites represent various locations along Shatt Al-Arab river and were distributed as the following: one station(S_1) on Euphrates river before its confluence with Tigris river and Shatt Al-Arab river formation and existing of several activities in this station such as river navigation , fishing , population and agriculture , moreover this area is nearby from west Qurna field oil . The six stations (S_2 - S_7) were selected on Shatt Al-Arab river from Qurna city towards Fao city in southern of Basra governorate and it regions are important areas .They contain many activities such as population, agriculture, river navigation , industry (especially oil extraction industry like Nahr Bin Omar oil field , Basra paper factory and Abu Al-Khaseeb Fertilizer Factory) and commerce [10,11,12] . While marine sites were distributed as the following: three stations(S_8-S_{10}) in southern of Fao city towards Khor Abdullah and five stations were chosen from Um Qasr region S_{11} towards Khor alZubair region S_{14} and the last station Z_{15} was selected from the nearby region from the confluence point with the Basra canal . The selected marine sites are important areas since they contains several activities such as industry and marine navigation because the existing oil and commercial ports[11,12] . The marine samples were collected in winter season (December 2014) while Shatt Al-Arab river samples were collected in spring season (March 2015 and March 2016) . All samples were collected by grab sampler from surface sediment in low tide time and it kept in plastic bags and preserved in a cold box , then they transferred to the laboratory for carrying out different operations such as drying , grinding ,digestion and analysis [11,12] .

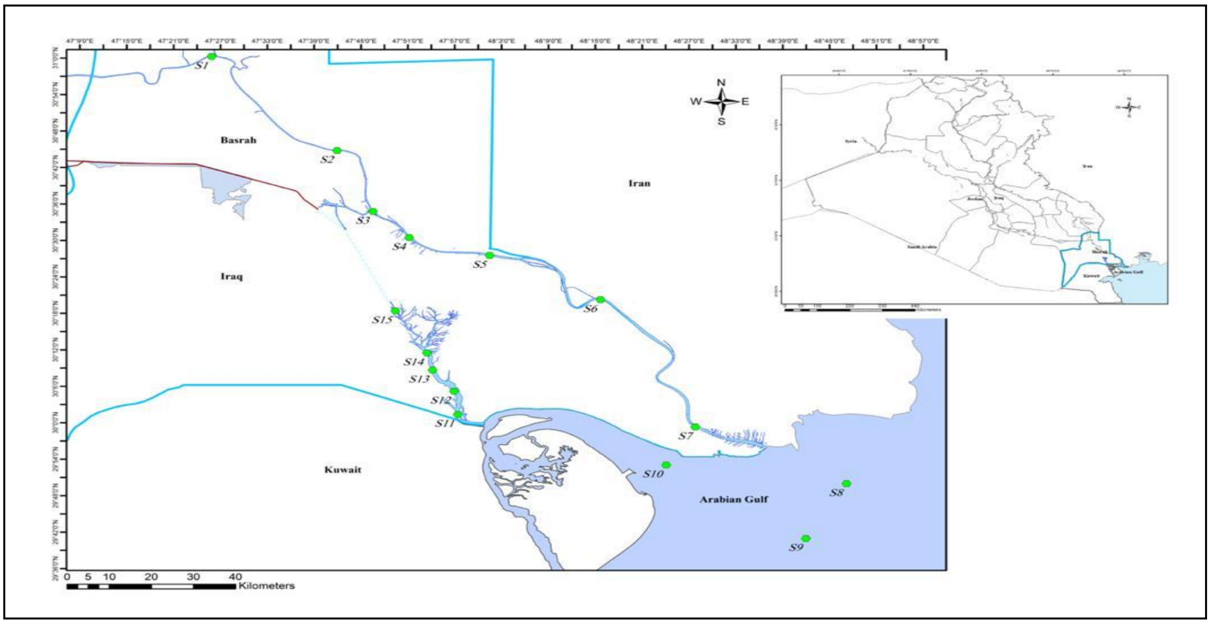

Figure 1 : Locations of the sample selected in Southern of Iraq

Material and methods

Several chemical materials were used in the procedure like Sodium acetate trihydrate , pyridine and sulfuric acid(97%) were obtained from J.T.Baker , glacial acetic acid and hydrochloric acid (37%) were supplied by Scharlau , chloroamine-T was obtained from PubChem , barbituric acid was obtained from Himeda , slphamic acid and lead carbonat were supplied by B.D.H , $MgCl_2.6H_2O$ was supplied by Merck . The sample is ready to carry out of analysis at 578nm by UV-Vis instrument from type : Shimadzu double- beam UV-Vis spectrophotometer (model 1800 PC , Japan) with 1.0 cm quartz cell was used for all spectral measurements for total cyanide . The procedures for analysis of total cyanide in sediment by distillation method are the same method described previously [4,6] .

Determination of Pollution indexes

The Cyanide groups (CN^{-1}) don't exist in nature but the increasing of cyanide concentration in sediment attributed to the different industrial activities such as the electroplating industry, blast furnaces, coke-producing plants , combustion of coal and oil , plastic and synthetic fibers [1,7,13] .

Determination of geo accumulation index (I-geo)

The geo accumulation index was calculated for cyanide concentration in various stations by using Muller equation [12,14] as follows :

$$\text{I-geo} = \log_2 (C / 1.5\ B)$$

Where : C is the measured value to the concentration of cyanide in the sediment , while B represents the background value to the concentration of cyanide in the sediment (CN^{-1} 2 µg/g) [15] . The values of I-geo were classified according to Muller classification [16] .

Type of class	I-geo	Sediments pollution case
Class 1	<0	practically unpolluted- Background sample
Class 2	1-2	unpolluted to moderately polluted
Class 3	2-3	moderately polluted to polluted
Class 4	3-4	strongly polluted
Class 5	4-5	strongly to extremely polluted
Class 6	>5	extremely polluted

Determination of pollution index (PI)

The pollution index was calculated of total cyanide concentration for all selected study stations by following equation :

$$PI = C_n / B_n$$

Where : PI is pollution index , C_n is the measured value and B_n is the background value to the concentration of cyanide in the sediment . The degree of pollution are depends on PI value and classified into : PI < 1 refers to low pollution , 1 ≤ PI < 3 refers to moderately pollution and PI > 3 refers to extremely pollution [17]

Results and Discussion

The term of total cyanide in sediment refers to the existing different cyanide compounds and these compounds have toxic properties and readily convert into high toxic species such as free cyanide by the decreasing of pH value towards the low acidic medium about 5-6.5[4,7] . Hence , it lead to increasing the ability of releasing the hydrocyanic acid in the aquatic system . The increasing of cyanide levels in the aquatic system causes several risks on the health of the water environment . Consequently, it will affect directly on human health throughout the food chain because it has ability to accumulate in different organisms, especially in fish [4]. Total cyanide in sediments was measured by colorimetric method at 578nm by complex formation with pyridine-barbituric acid . All measurements of total cyanide for Shatt Al-Arab sediments are shown in Table 1 and Figure 2 .

Table 1: Total cyanide concentration of Shatt Al-Arab stations selected from surface sediment at March 2015 &March 2016

Sampling locations		Mean(n=3) of Total cyanide concentration µg/g	Standard Deviation (SD)	geo accumulation index		Pollution index	
				I-geo	Class	PI	Class
Marsh 2015	S_1	61.583	4.3122	4.359	5	30.791	H*
	S_2	27.029	3.240	3.171	4	13.514	H
	S_3	13.559	1.838	2.176	3	6.779	H
	S_4	25.353	1.845	3.079	4	12.676	H
	S_5	39.451	4.850	3.717	4	19.725	H
	S_6	16.155	1.837	2.428	3	8.077	H

	S_7	38.034	4.257	3.664	4	19.017	H
Average		31.595	3.168	-		-	
Marsh 2016	S_1	45.945	6.092	3.936	4	22.972	H
	S_2	41.880	1.884	3.803	4	20.940	H
	S_3	41.496	6.036	3.789	4	20.748	H
	S_4	62.333	4.208	4.376	5	31.166	H
	S_5	71.627	1.955	4.577	5	35.813	H
	S_6	24.465	1.938	3.027	4	12.232	H
	S_7	16.711	1.900	2.477	3	8.355	H
Average		43.494	3.431	-		-	

*Where H is High pollution

The measurements of total cyanide in sediments are showed the highest value which is recorded in station S_1 while the lowest value was recorded in station S_3 in March 2015; on other hand, when we had compared the results of total cyanid measurements in March 2016 , they showed the highest value in station S_5 while the lowest value in station S_7 . The results of measurements of total cyanide were compared among the stations and noted the highest value was recorded at range (61.583±4.312 µg/g) in Qurna city (S_1) because this area undergoes to many activities such as river navigation , population and agriculture [11,12] . The concentration of total cyanide decreased recording a value at (27.029±3.240 µg/g) in station S_2 and noted continuous of decreasing in concentration recording the lowest level in station S_3 . Therefore the total cyanide concentration increases again in the station S_4 , S_5 and S_7 because these areas are important region to exist the commercial ports , as well as included of several activities such as river navigation . Moreover , domestic and industrial wastes are frequently drained into the river without treatment [4,10,11,12]. Once again, samples from the same stations were collected in March 2016 and analysed . The results were compared among different stations and the highest value was recorded in station S_5 and S_4 (71.627±1.955 and 62.333±4.208 µg/g) respectively. the increasing of total cyanide concentration might due to increasing of several activities such as increasing of population , hence , it leads to increasing the drain of domestic wastes , industrial activities as well as the river navigation, this is because of the existing of the commercial ports. Station S_1 recorded the high value when compression to the same group but it records a low value compression to the same station in 2015 while the station S_2 and S_3 recorded the highest concentration (41.880±1.884 and 41.496±6.036 µg/g) respectively when compared with the same station in 2015 . These increasings may be attributed to oil spills from alnajebia electric station (when collected samples) and these spills were spreaded in widely areas from Shatt Al-Arab especially in nearby zone from S3 station , while the increasing in station S_2 may due to industrial activities especially oil extraction station (Nahr Bin Omer station) . The pollution indexes for all study stations along Shatt Al Arab River were calculated and they showed the data for high pollution in sediments of all stations at period 2015 and 2016 according for Pollution index (PI) data , while the geo accumulation index data showed all stations are within class 4 (strongly polluted) excepte the station S_1 is within class 5 (strongly to extremely polluted) and the stations S_3 , S_6 are within class 3 (moderately polluted to polluted) for samples collected in 2015 , while the stations S_4 , S_5 are within class 5 and class 3 for S_7 station for samples collected in 2016 .

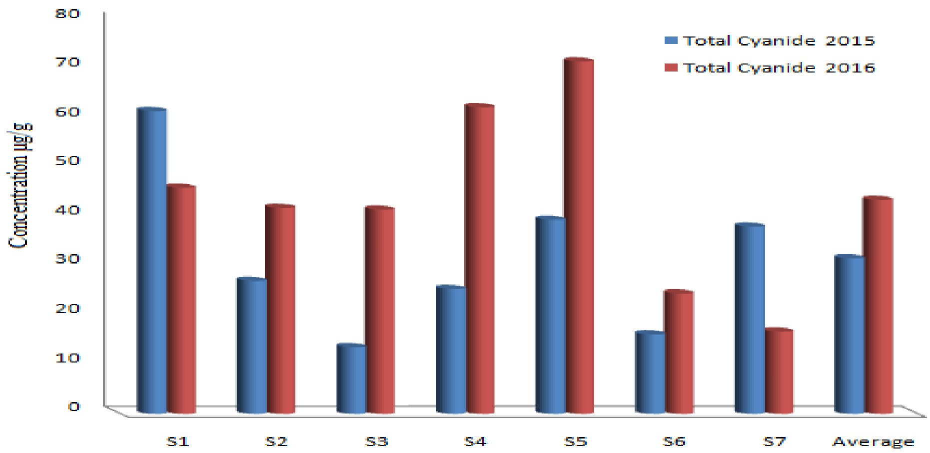

Figure 2 . Total cyanide concentration of Shatt Al-Arab sediment at March 2015 & 2016

The marine stations were selected along the Iraqi marine water and all the measurements of total cyanide are shown in Table 2 and figure 3 . The highest value was recorded in station S_{15} because the region is consider the confluence zone between Shatt Albasra and Khor Al-Zuber canal[18] . Shatt Albasra canal is considered as drainage canal of several pollutant towards Khor Al-Zuber canal where the domestic and indusrial waste are released into canal without treatment , While the lowest value was recorded in station S_9 because this area undergoes for continuous marine navigation as well as it can be described as gathering station for different loads of commercial and oil ships [11,12] , moreover the remaining of the sites in all study regions have not recorded any data and may be attributed to many reasons such as the type ,pH and components of the sediment in these regions [19,20] .

Table 2: Total cyanide concentration of marine stations selected from surface sediment at December 2014

Sampling locations	December 2014		geo accumulation index		Pollution index	
	Mean(n=3) of Total cyanide concentration µg/g	Standard Deviation (SD)	I-geo	Class	PI	Class
S_8	N.D	-	0	1	0	L*
S_9	14.588	3.125	2.281	3	7.294	H
S_{10}	N.D	-	0	1	0	L
S_{11}	N.D	-	0	1	0	L
S_{12}	N.D	-	0	1	0	L
S_{13}	N.D	-	0	1	0	L
S_{14}	N.D	-	0	1	0	L
S_{15}	55.893	1.702	4.219	5	27.946	H

Average	8.810	0.603	-	-	-	-

*Where L is Low pollution

The contamination indexes were calculated for all marine stations such as geo accumulation index (I-geo) and pollution index (PI) ,the geo accumulation index showed the all stations are within the class1(practically unpolluted) according to Muller classification except the station S_9 is within class 3 (moderately polluted to polluted) and station S_{15} is within class 5 (strongly to extremely polluted) , while the pollution index data for all marine stations were showed the low pollution except the stations S_9 and S_{15} were showed the high pollution .

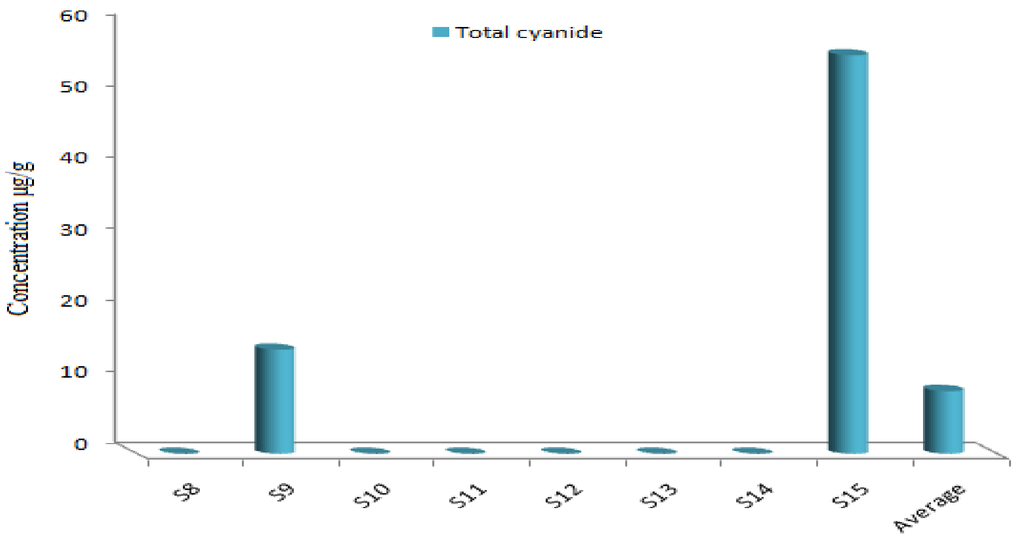

Figure 3 . Total cyanide concentration of marine sediment

Conclusion

This study has shown that total cyanide concentration that found in sediment of Shatt Alarab River and Iraqi marine region as resulting of several anthropogenic activities , which causes of many harms on human , plants and animal's health . the cyanide ions may be transferred from sediments towards water in aquatic system through mutual interaction between them.The results of total cyanide concentration in sediments of Shatt Alarab River have been compared for two periods time at 2015 and 2016 , where it revealed all stations have high pollution as accordingly to calculation pollution index whereas , the calculation of geo accumulation index in all stations have appeared as gradually values from moderately pollution to extremely pollution . Furthermore , all the marine sites have described as unpolluted except the sites S_9 and S_{15} are appeared high pollution in calculation of pollution index (PI) and geo accumulation index (I-geo) ..

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تقدير التباين الزماني والمكاني لمستويات السيانيد الكلي في رواسب مياه شط العرب والمنطقة الأقليمية البحرية بأستعمال دليلي التراكم الجيولوجي I-geo ومؤشر التلوث PI

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المستخلص : جمعت الرواسب من خمسة عشر محطة على طول نهر شط العرب والمنطقة البحرية العراقية في مدينة البصرة - جنوبي العراق , حددت سبع محطات نهرية على شط العرب وثمان محطات في المنطقة البحرية الأقليمية العراقية . جمعت الرواسب السطحية في جميع المحطات على عمق 10-15 سم من السطح . أستخدمت الطريقة اللونية لقياس تركيز السيانيد الكلي في الرواسب لجميع المحطات من خلال تشكيل معقد مع البردين – حامض الباربيوتريك عند طول موجي 578 نانوميتر. سجلت النتائج لقياس تراكيز السيانيد الكلي في جميع المحطات حيث اضهرت أعلى تركيز في محطة S_1 و S_5 بينما سجلت تراكيز منخفضة في محطتين S_3 و S_7 في فصل الربيع للسنوات 2015 و 2016 على التوالي , بينما في النماذج التي جمعت من المنطقة البحرية العراقية سجلت أعلى تركيز في محطة S_{15} . حسب الأنحراف المعياري في جميع المحطات وبواقع ثلاث مكررات لكل محطة حيث

بلغ بمدى (1,8377 – 6,0928) و (1,7024 – 3,1259) للمحطات الواقعة على نهر شط العرب و المنطقة البحرية العراقية على التوالي . أستخدمت دلائل التلوث حيث حسب مؤشر التراكم الجيولوجي I-geo و مؤشر التلوث PI في جميع المحطات المختارة .