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Assessing the Contamination of Coastal Mudflats in Iraq by Trace Elements

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Abstract - Iraq's mudflats are spread around Southern Coasts of Iraq which recently suffered from pollution by petroleum hydrocarbons and trace elements. Those pollutants affect the biological lives such as fishes, crabs, and algae's in this area which is reflected upon human being as a consumer. Within this study, nine sites of Iraqi coastal mudflats were chosen to collect water and certain trace elements Cd, Cr, Cu, Pb, and Zn were estimated by Atomic Absorption Spectrophotometry. Levels of trace elements estimated in mg/g were: (0.0015-0.0044) Cadmium, (0.6532 0.3299) Chromium, (0.2146-0.3773) Cupper, (0.2365-0.4682) lead and (0.0861-0.1822) Zinc. The detected levels of elements were more than the allowed values nationally and globally. Finally, the physical and chemical quantities of marine waters were measured.

تقييم التلوث بالعناصر النزرة في المسطحات الطينية العراقية

زينب جودت موسى و زهير علي عبد النبي و فارس جاسم الامارة ولمى جاسم العنبر
قسم الكيمياء وتلوث البيئة البحرية، مركز علوم البحار- جامعة البصرة

المستخلص - تنتشر المسطحات الطينية حول السواحل الجنوبية العراقية والتي عانت مؤخرا من التلوث الناجم عن النشاطات النفطية والصناعية وما وما يطرح منه من الهيدروكربونات النفطية والعناصر النزرة. وتؤثر تلك الملوثات على الحياة البيولوجية المستوطنة للمنطقة مثل الأسماك والسرطانات البحرية والطحالب الذي ينعكس على الإنسان كمستهلك غذائي. وفي الدراسة الحالية، اختيرت تسعة مواقع منطقة المسطحات الطينية الساحلية العراقية لجمع الرواسب، وقدُرت بعض العناصر النزرة Cd و Cr وCu وPb وZn من خلال القياس بجهاز طيف للامتصاص الذري. وكانت مستويات العناصر النزرة المقدرة mg/ g هي:0.0015 – 0.0044 الكادميوم، 0.6532 - 0.3299 كروميوم، 0.2146 – 0.3773 النحاس، 0.2365 – 0.4682 الرصاص، 0.0861 – 0.1822 الزنك . وكانت مستويات العناصر المكتشفة أكثر من القيم المسموح بها محليا وعالمياً. كذلك تم قياس المتغيرات الفيزيائية والكيميائية للمياه البحرية.

الكلمات المفتاحية: المسطحات الطينية، العناصر النزرة، مياه بحرية، السمية، مطياف الامتصاص الذري، الدليل الجيولوجي البيئي.

Introduction

All environments, such as freshwater or marine ecosystem. have low concentration of most of the heavy metals that naturally occurred in the Earth's crust or come from dust storm. (Adam *et .al*., 2007) addition to different pollutant come from many sources of area and reached to human body , (AI-Hejuje,1999). Sediment act as a sink for heavy metals that makes it a possible source for water pollution in case of any changes in environmental conditions (Al-Edresy *et.al*.,2019;

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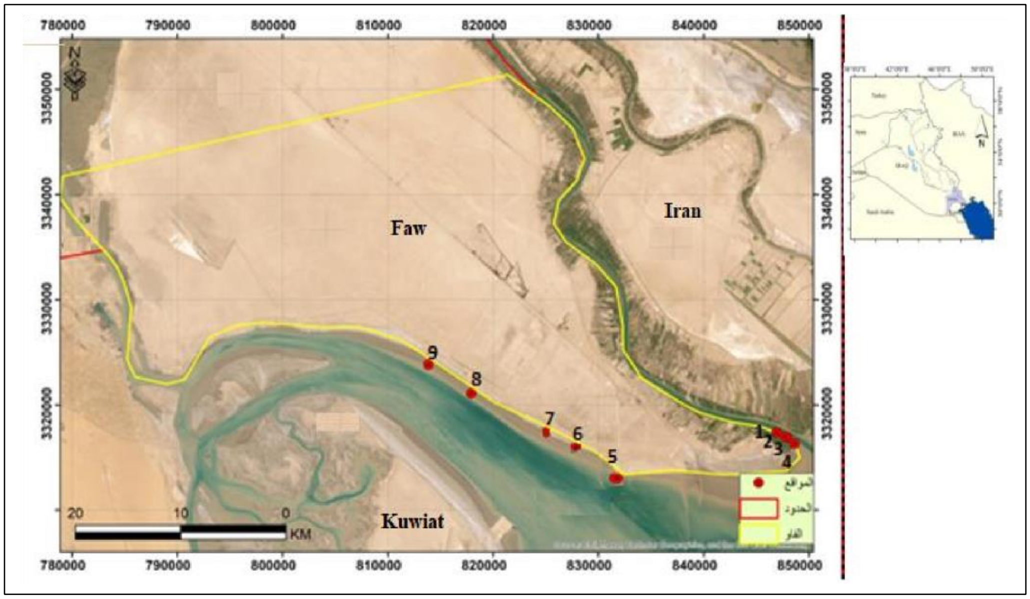
Ali *et al.*,2019). Trace metals occur in the aquatic environment both. Particles deposited as silt or suspended loads in water. However, measuring their concentrations in water for a short period does not give accurate results on the extent of pollution due to heterogeneity in water discharges, as well as the irregularity of topical releases of these pollutants. Hence, there were a focus on the sediment as it act as a recipient of all kinds of pollutants and organic matter that falls from the water column above because they reflect more stable indicator about the degree of heavy element pollution of water environment (Al-Qarooni, 2011). Sediment is also a good indicator for pollution due to its ability of archiving many types of pollutants in the aquatic ecosystem (Al-Ubaidi *et.al*., 2011). Trace elements, especially the heavy ones, are not soluble for long periods of time in water as they appear in the form of suspended or stabilized particles by plankton (Azeez and Madhi, 2019). The heavy metals are easy to be attracted and captured by clay minerals, organic compounds, iron or manganese hydroxides and other metals or carbonates (Cai *et al.*,2019). They are accumulated on surface sediment or are adsorbed by aquatic organisms (Christou *et.al*., 2017). Therefore, their concentration in surface sediment or in plants is evidence of water pollution with these elements. So, the percentage of pollutants and concentrations of minerals increases in the sediment more than in water (Cui *et.al*.,2019). Thus, sediment act as a potential source of pollution in aquatic environment and is used to record the history of pollution (Hassan,2007). In recent years, the rapid growth of population is associated with the expansion of industrial sector, which increases the trace metal concentration in the environment. Many studies have been conducted to assess heavy element pollution in water bodies south of Iraq. Trace metal like cadmium (Cd), arsenic(As), lead (Pb), mercury (Hg), and chromium are often deemed toxicants due to their lack of a physiological role in the body (Issa,*et.al*.2020). The presence of cadmium in the environment as a result of numerous human activities has led to numerous documented cases of exposure to the metal during the past century (Jassim *et.al*., 2021). Cadmium is used as a corrosive reagent in industry and as a stabilizer in PVC products, color pigments, and Ni-Cd batteries (Li *et.al*., 2008), all of which are ongoing sources of pollution. House dust can be a source of cadmium exposure in locations with polluted soils (Li *et.al*., 2009; Ciadamidaro, 2023). Copper and nickel smelting and refining, fossil fuel combustion, and the usage of phosphate fertilizers are all human made activities that release cadmium into the environment. Pollution from cadmium can also be found in the processing of non-ferrous metals and the reuse of electronic trash. The release of this metal into the atmosphere from zinc, lead, and copper mines contributes to soil contamination (Lin *et.al*.,2016), and other factors such as volcanic activity, the gradual process of erosion and abrasion of rocks and soil, and forest fires also play a role.

Experimental Section Description of Study Area

Nine stations were randomly selected from the Iraqi coasts in southern Basra city, these area is almost life - free except of some species of fish like Mudskipper. The mud zone was formed by the accumulation of river sediment as shown in (Figure 1).

The sediment samples were collected by Van ven grab sampler device during low tide, the samples kept in special dark container and preserved in cooling box, finally it transferred to the laboratory of Marine Science Centre / University of Basrah for further treatments as drying, crushing, sieving, digestion and analysis.



(Figure 1) The studied area in southern part of Basrah city (mudflat area)

(Table 1) The location of study

Stations No.	Locations
1	29.987921N,48.463892E
2	29.980445N,48.475929E
3	29.976616N,48.482765E
4	29.974339N,48.486865E
5	29.927617N,48.398069E
6	29.932675N,48.388535E
7	29.972695N,48.355878E
8	29.993848N,48.282863E
9	30.022389N,48.222398E

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Instrumentation

The physico-chemical properties were measured directly at the field such as pH, conductance, salinity and total dissolved solid using Multimeter device WTW (Multi 3410 Set C, Germany). Heavy metals after completing digestion of sediment samples were determined using atomic absorption spectrophotometer (AA7000 Atomic Absorption spectrophotometer, Shimadzu, Japan).

Digestion Process

Surface samples were taken in the summer of 2021. The sediments were packed in plastic bags and transferred to the laboratory, where they were exposed to air; dried in a laboratory before being reduced to a fine powder and sieved using 106 μm stainless steel mesh. The specimens were then placed in a plastic container in preparation for use digestion and analysis. The dried sediments were broken down by a combination of HF, HClO4, and HNO3 and then brought into 0.5M HCl solution (50 ml). Four total concentrations Heavy metals (Cr, Cu, Cd, pb and Zn) in samples were investigated by AAS (Kastaonvic and Jacimovic , 2020) .

Atomic Absorption Spectrometry

FAAS is one of the most conventional techniques for the determination of trace metal ions because of the relative simplicity and inexpensiveness of equipment. (Sultan *et al.*,2013) Liquid–liquid extraction transferring analyzed from the aqueous sample to a water immiscible solvent is widely used for samples' preparation. Cloud point extraction (CPE), similar to liquid–liquid extraction, transferring analyze from the aqueous sample to a water immiscible solvent, is widely used for samples' preparation and coupled with AAS technique. CPE is based on the property of surfactants to form micelles, which under certain conditions (temperature and concentration) separate into two phases: a surfactant-rich phase of a small volume and a large aqueous phase. Hydrophobic complexes of metallic elements present in such media are trapped in the hydrophobic micellar core and extracted in the surfactant-rich phase, which is directed to AAS detector. The small volume of the surfactant-rich phase obtained after the CPE methodology seems to be ideal for coupling with electrothermal AAS, even though there are applications of CPE coupled with FAAS (UNEP,2010), statistical analysis was done by (SPSS) program.

Determination of Geo Accumulation Index

The calculation of I-geo accumulation index in different metals through using Muller equation (Müller, 1969) is as follows: I-geo $\log_2$ (C / 1.5 B)

Where: the C refers to the measured value to the absorption of metals by the sediment, whereas B represents the remaining concentration of metals in the sediment (Cr 126mg/g , Cu 25 mg/g, Zn 52 mg/g,Cd 0.1 mg/g and Pb 15 mg/g) (Kabata-Pendias , 2011). The values of I-geo were classified by Muller classification (Ong,2013).

(Table 2) Shows the acceptable concentration of I-geo

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

Results and discussion

Metal fractionation is an important factor affecting the potential toxicity of trace elements. Total concentrations of trace elements can provide fundamental information of the sediments contamination levels, of the pollution indexes and of the quality guidelines for the sediments environmental risk assessment (Cai *et al.*,2019).

The value of cadmium in the samples analyzed was relatively excessive and ranged from 0.027 to 0.0044 mg/g. The value of cadmium in more than the soils was above the limit of 0.6 mg/g determined by the second grade. The highest Cd analysis values were nine times higher. Cadmium compounds bioaccumulate in fish muscles, then reach humans by seafood, and the human body disposes of cadmium by coronation, causing kidney damage similar results, recorded by (Abdulnabi *et al*., 2019).

The Cu value in the study samples ranged between (0.2146 to 0.3773 mg/g) the same values for copper in the mudflat sediments of Basra city were found by (Al-Khuzie, 2017). This is due to the fact that there has been an increase in oil and mining activities as well as sewage and industrial discharge; the value is higher than the concentration of copper in the earth's crust (mg/g 0.26) (Qazar *et al*.,2019; Raaheem,2009).

Zinc values in the muds vary between 0.0961to 0.1822mg/g. The highest concentration of Zn analyzed in the soils was more than five times higher than the natural background value. similar result was recorded by (Hassan, 2016) where find the Iraqi mudflat was contaminated with (Zn) in the sediments. There's a correlation between zinc and iron oxides and manganese, various organic compounds, these compounds are soluble in sediment, only a few of them are not soluble, zinc concentration is affected in sediment by pH and the oxidizing environment (Kastaonvic and Jacimovic, 2020).

The concentrations of Cr and Pb were (0.6532-0.3294 mg/g), (02365-0.4692 mg/g), quite low and did not exceed the limits of the national standards. The concentrations of the main risk elements (Cd and Cu) from our study and similar results from other worldwide Cu smelting and mining localities with comparable soil properties are compared below. Cai, *et al.,* 2019) pH is slightly acidic to slightly alkaline (6.5–7.5). Their results show a higher value of cadmium (0.0044mg/g) but consider higher copper values (0.2983mg/g). In accordance with the study by (Christou *et al.*, 2017; Njinga *et al*., 2011). Results of a close approach recorded by Hassan (2016) and Abdulnabi (2020).

The results of monitored variables are listed in Table (3). The highest values of Cu, Cd, Pb, and Zn found Increased concentrations of these risk elements. There are no significant industrial sources of pollution in this part of the area. Here, the major source of Cd is probably intensive agricultural activity. As stated by (Luo *et al*., 2016), Cd is considered to be an element typical for agricultural activities because Cd is often found as an impurity in phosphate fertilizers. Phosphate fertilizers can also be the source of As contamination (Hassan ,2016).

(Table 3) Values in mg/g of trace elements in mudflats area at Southern Iraqi Coasts

Station No.	Cr		Cu		Cd		Pb		Zn	
	Conc.	I-geo	Conc.	I-geo	Conc.	I-geo	Conc.	I-geo	Conc.	I-geo
1	0.4426	1.2276	0.2983	2.991801	0.0044	4.874469	0.4614	4.3580	0.1443	0.8875
2	0.3294	0.8014	0.2304	2.619178	0.0021	3.807355	0.2997	3.7355	0.0961	0.3010
3	0.5036	1.4138	0.3773	3.33075	0.0015	3.321928	0.2672	3.5699	0.1462	0.9063
4	0.4426	1.2276	0.2983	2.991801	0.0044	4.874469	0.4692	4.3822	0.1327	0.7666
5	0.5915	1.6459	0.2493	2.73292	0.0036	4.584963	0.3648	4.0191	0.0861	0.1425
6	03945	14.349	0.3641	3.279372	0.0026	4.115477	0.4269	4.2459	0.1367	0.8094
7	0.6571	1.7977	0.2964	2.982583	0.0043	4.841302	0.2478	3.4611	0.1822	1.2239
8	0.5684	1.5885	0.2146	2.516688	0.0029	4.273018	0.2365	3.3938	0.1164	0.5775
9	0.6532	1.7891	0.2652	2.822118	0.0027	4.169925	0.4213	4.2268	0.1548	0.9888
L.S.D.	0.00161		0.00068		0.00016		0.0001838		0.0317	
*Standard Specification										

The pH values of the samples vary between 8.19 to 8.44 and its mean was 8.75 which indicates the moderate alkalinity in nearly all samples. This is probably caused by a higher content of calcite and dolomite in the bedrocks, such as calcareous slates or dolomites, Table (4) shows the value of physical and chemical parameters in study stations. Salinity in study areas is very high near the tidal area ranged between (46.1-31.1) ppt, TDS and EC are also recorded between (26400-39500) mg/g (65.8-43.1) mS cm-1. Table (3) shows that Cr concentrations were in the second class and were considered unpolluted or low-polluted. Cu was also in the second class, while Pb and Cd was in the fourth class and considered to be strong and harmful pollutants to the marine environment, thus affecting the food basket. Finally, Zn was in the second class, and these results are similar to those of researchers who had been in the same area for previous years (Abdulnabi,2019).

(Table 4) The physical and chemical parameters for the sediments in different station

Station No.	pH	Salinity (ppt)	TDS (mg/l)	EC (mS cm-1)
1	8.27	34.5	38000	63.3
2	8.19	34.4	39500	65.8
3	8.31	31.1	36900	61.6
4	8.57	42.2	38200	63.6
5	8.75	44.3	34300	57.1
6	8.66	46.1	31900	53.1
7	8.67	40.8	33200	55.5
8	8.29	40.7	26400	43.1
9	8.44	42.5	38000	63.3

(Table 5) The correlation coefficient factor among the value of trace element concentration and the physical and chemical parameters in study station

Parameters NO.	**Cr**	**Cu**	**Cd**	**Pb**	**Zn**
Cr	0	-	-	-	-
Cu	0.511427	0	-	-	-
Cd	-0.19989	0.401418	0	-	-
pb	0.287647	0.215516	0.401418	0	-
Zn	0.048888	0.50321689	0.23183738	-0.0002584	0
pH	0.36125	0.217865	0.423886	0.219375	0.115471
Salanity(ppt)	0.477066	-0.13646	0.339369	0.323289	-0.05878
EC (cm/l)	-0.28154	0.18691	0.002894	0.460587	0.048459

Table 5 shows the correlation coefficient factor values for the pH in the study stations and the trace elements as follows: (Zn<Cu<Pb<Cr<Cd) have been recorded, and we note the increase in Cd values with the increase in acidity., cadmium coming from a variety of sources because of its water solubility, which increases acidity relatively. same thing for Cr, Cu, Pb and Zn. For the salinity there is increase of correlation coefficient with Cr concentration) 0.477066 (but decrease in correlation coefficient with (Cu and Zn), EC recorded negative value with Cr (-0.28154) and increase value with Cu, Pb and Zn (0.18691 , 0.002894, 0.460587 and 0.048459) .

Conclusion

Trace elements are harmful contaminants in Iraq's marine environment. The current study showed the Pb and Cd were hazard but Cr, Cu, Zn were in the acceptable limited according to geo accumulation index. The accumulation of elements in the mud layer of the southern Iraqi mudflats and their possible transmission in the food chain.

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